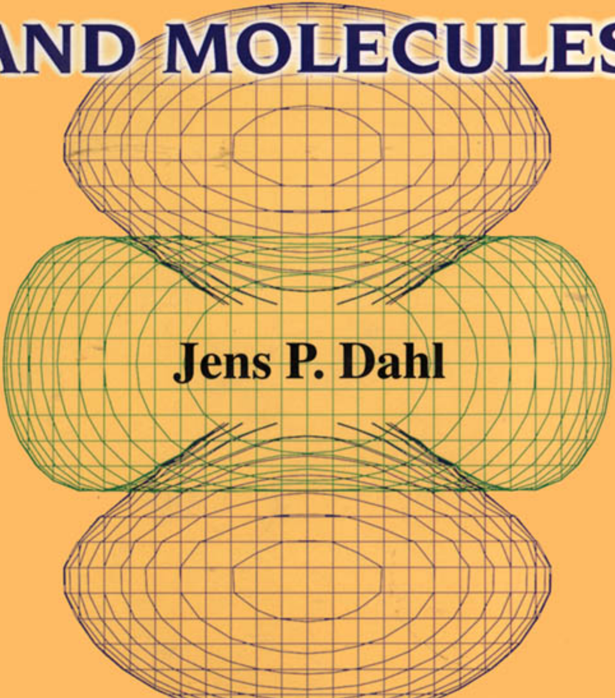
INTRODUCTION TO

THE QUANTUM WORLD OF ATOMS AND MOLECULES



Jens P. Dahl

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Preface

The present book is based on lectures given for the past several years at the Technical University of Denmark. The lectures have primarily been attended by students wanting to specialize in advanced fundamental chemistry (including quantum chemistry) or solid-state physics. They have also been attended by Ph.D. students.

Quantum mechanics is one of the greatest intellectual achievements of the twentieth century. It constitutes the firm foundation of modern physics and chemistry, and has to a large extent led to a synthesis of these sciences. Accordingly, every modern physicist and chemist must familiarize him/herself with the laws of quantum mechanics, in order to understand the basis of the enormous scientific and technological progress that the application of these laws has brought about.

The present treatise is an introduction to the quantum-mechanical laws with a molecular angle of approach. It should, however, be useful for most students of ordinary matter. I have chosen to make the presentation exact, but at the same time pedagogically obliging.

I value the historic tradition. I have, therefore, in the first two chapters tried to draw a picture of the way quantum mechanics emerged at the beginning of the twentieth century, in reply to efforts spent by chemists and physicists throughout the nineteenth century to make atoms real.

It took a quarter of a century to develop the proper basis of quantum mechanics. The highlights of the process are included in the second chapter. The Schrödinger equation is presented in Chapter 3. It is this equation that governs the behavior of electrons and atomic nuclei and thus supplies the basis for our understanding of atomic and molecular structure and molecular processes. The Schrödinger equation is solved for some simple, yet illustrative examples in Chapter 4. On this background the quantum-mechanical formalism is cultivated in Chapter 5. Emphasis is put on the properties of operators, quantum theory and measurements, and matrix algebra.

In Chapters 6–9 we discuss some exactly solvable systems in detail, namely, the free particle, the harmonic oscillator, and the hydrogen atom. In addition to solving these problems analytically, we also become familiar with wave packets, ladder operators, angular-momentum theory, and the general central-field problem.

A very fundamental concept in the theory of atoms and molecules is the electron spin. The magnetic moment that accompanies the spin gives rise to important effects. But the conceptual importance of spin is greatest in the interplay between spin and the antisymmetry requirement that is laid on many-electron wavefunctions. It is, for instance, in this interplay that one finds the origin of the periodic table and directed valence. Chapter 10 is devoted to a detailed description of the electron spin and its interaction with external fields. The interplay with the antisymmetry requirement is discussed in Chapter 11, which also gives a description of the many-electron atom on the basis of electron configurations and introduces determinantal wavefunctions.

The Schrödinger equation is exactly solvable only for the simplest systems, but very effective methods have been developed by means of which good approximate solutions may be determined even for quite complicated systems. The most frequently applied method is the variational method. Chapter 12 gives an introduction to this method.

In Chapters 13 and 14 we give the general principles for the quantum-mechanical description of molecules in terms of molecular electronic structure, molecular vibrations, and rotation. The discussion is concretized for diatomic molecules. The description of the electronic structure is based on exact wavefunctions for the single-electron molecule, and on electron configurations for many-electron molecules.

The remaining five chapters of the book are devoted to a deeper study of many-electron atoms and molecules. The concepts of terms and multiplets are discussed in Chapter 15, after a thorough discussion of the theory of angular-momentum coupling. In Chapters 16 and 17, we construct proper many-electron wavefunctions for selected atoms and molecules. We also derive expressions for the term energies of these systems by exploiting expressions for matrix elements between determinantal wavefunctions.

In Chapters 18 and 19, we discuss the determination of atomic and molecular orbitals by self-consistent field methods. The Hartree–Fock method is discussed in Chapter 18, by the author's own pedagogical approach, in which the so-called Lagrangian multipliers play a less dominant role than in most standard presentations. The multipliers are usually introduced in a fairly mechanical way that causes difficulties for many students.

The alternative self-consistent field method, the Kohn–Sham method, is discussed in Chapter 19. The method is based on the premises of density-functional theory, according to which all ground-state properties of an atom or a molecule are functionals of the electron density. We discuss density functional theory by imbedding it in the theory of reduced density matrices. This makes the energy expressions more transparent, and also demonstrates that the gap between Hartree–Fock theory and density-functional theory is smaller than one might otherwise suspect.

I believe that the present book gives the student a good understanding of the basic structures and the basic concepts of atomic and molecular quantum mechanics, although the coverage is far from complete. As to applications of atomic and molecular quantum mechanics, they are extensive and very successful. Some applications are included in the text and in the end-of-chapter problems, but the number is naturally quite limited. Fortunately, more and more textbooks now appear that do in fact focus on the various applications of atomic and molecular quantum mechanics. Those books are the ones that should be consulted for detailed information about each application.

The end-of-chapter problems have been carefully designed to support the main text. Solutions to the problems will be available on the World Wide Web from the fall, 2001. For further information, contact jpd@kemi.dtu.dk

During the preparation of the lecture notes behind this book, I have received many valuable comments from both students and colleagues, for which I am very grateful. My particular thanks are due to Dr. Helge Johansen for many years' fruitful collaboration in teaching quantum chemistry, and to Dr. Bjarne Amstrup for his enthusiasm and his expert assistance with the initial typesetting of the emanuscript with LaTeX.

Finally, and most importantly, I am grateful to my wife Asta for her patience and constant encouragement.

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March, 2001

Fundamental Physical Constants
1998-values

Speed of light in vacuum	$c = 299\,792\,458\ \mathrm{m\,s^{-1}}$
Planck constant	$h = 6.62607 \times 10^{-34}\ \mathrm{J\,s}$
	$\hbar = 1.05457 \times 10^{-34}\ \mathrm{J\,s}$
Permittivity of vacuum	$\epsilon_0 = 8.85419 \times 10^{-12}\ \mathrm{F\,m^{-1}}$
	$4\pi\epsilon_0 = 1.11265 \times 10^{-10}\ \mathrm{F\,m^{-1}}$
Elementary charge	$e = 1.60218 \times 10^{-19}\ \mathrm{C}$

Electron mass	$m_e = 9.10938 \times 10^{-31}\ \mathrm{kg}$
Proton mass	$m_p = 1.67262 \times 10^{-27}\ \mathrm{kg}$
Neutron mass	$m_n = 1.67493 \times 10^{-27}\ \mathrm{kg}$
Deuteron mass	$m_d = 3.34358 \times 10^{-27}\ \mathrm{kg}$
Atomic mass constant, $m(^{12}\mathrm{C})/12$	$m_u = 1\,\mathrm{u} = 1.66054 \times 10^{-27}\ \mathrm{kg}$

Avogadro constant	$N_A = 6.02214 \times 10^{23}\ \mathrm{mol^{-1}}$
Faraday constant	$F = 96485\mathrm{C\ mol^{-1}}$
Boltzmann constant	$k = 1.38065 \times 10^{-23}\ \mathrm{J\,K^{-1}}$
Molar gas constant	$R = 8.31447\ \mathrm{J\,mol^{-1}\,K^{-1}}$

Bohr radius	$a_0 = 0.52918 \times 10^{-10}\ \mathrm{m}$
Hartree energy	$E_h = 4.35975 \times 10^{-18}\ \mathrm{J} = 27.2114\ \mathrm{eV}$
Bohr magneton, $e\hbar/2m_e$	$\mu_B = 9.27401 \times 10^{-24}\ \mathrm{J\,T^{-1}}$
Nuclear magneton, $e\hbar/2m_p$	$\mu_N = 5.05078 \times 10^{-27}\ \mathrm{J\,T^{-1}}$

$1\ \mathrm{eV} = 1.60218 \times 10^{-19}\ \mathrm{J} \equiv 96.4853\ \mathrm{kJ\ mol^{-1}} \equiv 8065.55\ \mathrm{cm^{-1}}$
$1\ \mathrm{\AA} = 10^{-10}\ \mathrm{m}$

For additional significant figures and more constants, consult one of the following sources:
Reviews of Modern Physics **72**, No. 2, 2000.
Journal of Physical and Chemical Reference Data **28**, No. 6, 1999.
http://physics.nist.gov/cuu/Constants

Contents

Chapter 1

The Rise of Atomic Theory

Contents

Our present understanding of the chemistry and physics of matter rests firmly on the idea of atomism and the theories of quantum mechanics and statistical mechanics. The idea of atomism is very old and has assumed different forms throughout the centuries. The theory of statistical mechanics was founded in the nineteenth century. Quantum mechanics is, however, a product of the twentieth century. It was born in the year 1900 and emerged as a result of the efforts spent by chemists and physicists throughout the previous century to make atoms real. The first chapter describes these efforts and the way they connect to our modern view of matter.

1.1 Early Atomic Theories

The idea of atomism, which states that matter is composed of ultimate and indivisible particles (atoms) that move with respect to each other in empty space, can be traced back to the Greek philosopher Leukippos and his pupil Demokritos, in the fifth century B.C. The idea met considerable resistance from the Platonists and the Aristotelians who dominated the philosophical scene for many centuries. Still, it was accepted and further developed by Epicurus (about 300 B.C.), and it was highly praised by the Roman poet Lucretius (about 65 B.C.) in the didactic poem *De rerum natura.* This extensive work is an important source to the understanding of the atomic theories of the classical antiquity.

It is likely that the antique idea of atomism has been familiar to most educated men since the days of Leukippos and Demokritos. The idea was, however, purely philosophical. It was a stimulation to the intellect, but lacked any documented connection with the real world outside the minds of the philosophers. Hence its impact remained very small.

It doesn't seem that the atomic idea played any noticeable role in the Middle Ages, but it was revived during the scientific revolution of the sixteenth and seventeenth centuries, in particular by René Descartes and Pierre Gassendi in France, and by Robert Boyle and Isaac Newton in England. A detailed and interesting contribution was made by the influential Croatian Jesuit scholar Ruder Bošković in his *Philosophiae naturalis theoria* published in 1758.[1] What Bošković tried in his treatise was, *inter alia*, to create a general theory of matter based on the idea of atoms and Newton's concept of force. Unlike the Greeks he assumed the atoms to be point-like, and he also assumed that Newton's law of attraction became a law of repulsion at small distances. This implies that two atoms are pulled toward each other by an attractive force until the distance between them reaches the point where the force starts to become repulsive. At this distance we must have stability of matter because the force is now neither attractive nor repulsive. Bošković even assumed that the force might change sign more than once as the distance between atoms varied, and in this way he

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[1] Until 1757 the Roman Catholic Church did not allow the publication of books that supported views implying the motion of the Earth. Between 1616 and 1757, such books were entered in the Index of Forbidden Books (*Index Librorum Prohibitorum*).

could account for the existence of more than one stable form of the same kind of matter in a qualitative way. Thus, the theory proposed by Bošković had some intuitively appealing features, but it was still a purely speculative theory and a theory devoted to generalities. Like its predecessors, it was of little help in the solution of specific problems.

1.2 The Chemical Atom

The first practical atomic theory was put forward by the English chemist and physicist John Dalton during the years 1803 to 1808. The background for this theory was the *law of conservation of mass* and the *law of constant proportions.* The first of these laws had been formulated by the French chemist Antoine Laurent Lavoisier in 1785. It was based on the exact process of weighing and states that there is no measurable change in mass during a chemical reaction. The second law was enunciated by the French chemist Joseph Louis Proust in 1799. It states that different samples of a substance contain its elements in the same proportions.

An element had been defined by Lavoisier as being a substance that cannot be decomposed (by chemical means), and he had given a list of 33 substances that he considered to be elements (among them light and caloric, or heat). Dalton's hypothesis was then that all elements consist of atoms, and that all atoms of the same element have the same weight, but the weights of atoms of different elements are different. Dalton also formulated the *law of simple multiple proportions.* This law states that when two elements combine to form more than one chemical compound, the weights of one element that combine with the same weight of the other are in the ratio of small integers. The meaning that Dalton gave to this law was that a chemical compound consists of units of a characteristic number of atoms.

The radically new in Dalton's atomic theory, as compared to earlier atomic theories, was its quantitative element. It was based on the process of weighing. This made it a practical theory that could grow and expand over the years to come.

The first addition to the theory was proposed in 1811 by the Italian physicist Amadeo Avogadro, and independently in 1814 by the French physicist André Marie Ampère. It is known as *Avogadro's hypothesis.* It gives independent existence to the smallest units of a compound by referring to them as molecules and states that any two gases, taken under the same conditions of temperature and pressure, contain in the same volume the same number of molecules. The hypothesis was, however, relatively unnoticed for many years. Its implication for the determination of a rational table of atomic weights was in fact not fully appreciated until 1858, when the Italian chemist Stanislao Cannizzaro published his *Sketch of a Course of Chemical Philosophy*, and it was only after then that the concept of free molecules gained its immense importance.

But in the meantime, a large number of new elements were discovered, and the atomic theory was enriched with the concept of valency, by the contributions of many chemists. The elements were grouped according to their valencies and general properties, and this allowed the Russian chemist Dmitri Ivanovich Mendeleev to construct his *periodic table of the elements*, in 1869.

Next, the chemical formulae were extended into space. The molecules became three-dimensional. It was in 1874 that the Dutch chemist Jacobus Henricus van't Hoff and the French chemist Joseph Achille le Bel independently documented that the valencies of the carbon atom are directed toward the corners of a tetrahedron of which the carbon atom itself occupies the center.

With the three-dimensional structure of molecules understood, the valence concept became too narrow to account for the binding capacity of all atoms, especially transition metal atoms. It was accordingly supplemented with the concept of coordination number, by the German chemist Alfred Werner, in 1893. This was the last major addition to Dalton's atomic theory in the nineteenth century. The theory of *the chemical atom* had now reached a high level of development and had shown its ability to rationalize a huge amount of chemical data.

But how big were atoms and molecules, and how should they be visualized?

1.3 The Kinetic Molecule

The first serious estimate of the size of atoms and molecules was made by the Austrian physicist Joseph Loschmidt in 1865. It was based on the results of a new science, the *kinetic theory of gases*, which had been initiated by the physicists Rudolf Clausius in Germany and James Clerk Maxwell in England.

Together with the English physicist William Thomson (Lord Kelvin), Rudolf Clausius was the founder of thermodynamics as an exact phenomenological science of energetics. He was the first to formulate the second law of thermodynamics, and the father of the concept of entropy. But he also wanted to understand the mechanical (microscopic) basis of the thermodynamic laws, and he realized that this basis must be statistical.

Thus, the kinetic theory of gases is a statistical theory which deals with the average behavior of an immense number of particles. It operates with concepts like mean free path and collision time, and it allows the derivation of theoretical expressions for coefficients of diffusion, coefficients of thermal conductivity, coefficients of viscosity, etc. Maxwell had shown that the mean free path of a gas could be calculated from measured values of the coefficient of viscosity, and Loschmidt was now able to derive a simple expression for the diameter, s, of a molecule, viz.

$$s = 8\varepsilon l, \tag{1.1}$$

in which l = mean free path, and ε is a *condensation coefficient*, expressing the ratio of the actual volume of condensed gas molecules to the volume they take up in the gas phase. Using the values $l = 1.40 \times 10^{-7}\,\mathrm{m}$ and $\varepsilon = 0.000866$, he obtained $s = 10^{-9}\,\mathrm{m} = 1\,\mathrm{nm}$ as his estimate for the diameter of a molecule of air. This result compares reasonably well with the currently accepted value of about 0.3 nm for the diameter of O_2 and N_2 molecules.

The mean free path is the average distance which a molecule traverses between two collisions, so by combining l with s it is possible to derive the number of atoms or molecules in the volume of $1\,\mathrm{cm}^3$ at standard conditions. This number is referred to as *Loschmidt's constant.* Equivalently, one may calculate the number of atoms or molecules in a molar mass. This number is *Avogadro's constant*, whose value is[2]

$$N_A = 6.02214 \times 10^{23}\,\mathrm{mole}^{-1}. \tag{1.2}$$

The estimate one obtains from Loschmidt's data is $0.4 \times 10^{23}\,\mathrm{mole}^{-1}$.

The kinetic molecule of the nineteenth century was essentially the kind of entity we have just implied, i. e., an impenetrable, perhaps spherical particle without internal structure which moves according to the laws of Newtonian mechanics and undergoes collisions with other particles. This was a simple picture, and it did not distinguish between atoms and molecules, but in the hands of some of the great scientists of the time it was a very fruitful one. The foremost of these scientists was the Austrian physicist Ludwig Boltzmann.

Boltzmann studied the mechanics of collisions between the particles of a gas in great detail, and as a result he succeeded in constructing a statistical function that he could identify with the entropy of the gas. Entropy, he stated, is a measure of the disorder of a physical system, and he showed (1877) that

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[2] An abbreviated list of the values of the fundamental constants of physics and chemistry is given in the back of this book.

if the physical system is left to itself its statistical entropy will always either increase in time or remain constant, rather than decrease. Thus, he had given the second law of thermodynamics an intuitively clear formulation.

Boltzmann's definition of entropy is contained in the equation

$$S = k \ln W \tag{1.3}$$

where S is the entropy and W the so-called thermodynamic probability, i. e., the number of microstates which are compatible with the same macroscopic properties. k is *Boltzmann's constant*, with the value

$$k = 1.38065 \times 10^{-23}\,\mathrm{J\,K^{-1}}. \tag{1.4}$$

Actually, Boltzmann never specified the constant k, nor did his analysis allow him to, for his counting of microstates was necessarily relative rather than absolute. It was the German physicist Max Planck who first wrote Eq. (1.3) in this explicit form and obtained the numerical value of k, in his important work on the black-body radiation that we shall discuss in the next chapter.

Eq. (1.3) is not only a central equation in the kinetic theory of gases. It is also a fundamental equation in the broader theory of *statistical mechanics* which deals with a general macroscopic system. The remarkable development of this science during the second half of the nineteenth century was also to a large extent due to Boltzmann. The other great contributor was the American physicist Josiah Willard Gibbs.

Boltzmann arrived at his definition of entropy and his interpretation of the second law of thermodynamics through his studies of the kinetic theory of gases, and it was the simplistic assumption of kinetic molecules without internal structure that allowed him to carry his analysis so far. This did not imply, however, that molecules were actually believed to be devoid of internal structure. Rather, motion of a particle was imagined to mean motion of its center of mass.

Both Maxwell and Boltzmann, as well as several others, considered a molecule to be a rotating and vibrating cluster of atoms, and they tried to estimate the heat capacity of molecules from this picture, by using the general relations of statistical mechanics. For a diatomic molecule, for instance, this resulted in the value $C_V = 3.5\,R$ for the molar heat capacity of a gas at constant volume, where R is the general gas constant, with the value

$$R = 8.31447\,\mathrm{J\,K^{-1}mole^{-1}} = kN_A. \tag{1.5}$$

The value $3.5\,R$ is made up of separate contributions from the various *degrees of freedom*. There are three degrees of freedom which correspond to the motion of the center of mass along the three coordinate axes, and each of these contribute $0.5\,RT$ to the molar internal energy at absolute temperature T, according to the kinetic theory of gases, and hence $0.5\,R$ to C_V. In addition, there are two rotational degrees of freedom according to the two angles that describe the direction of the internuclear axis in space, and by a general assumption about equipartition of energy each of these also contribute $0.5\,R$ to C_V. Finally, there is one vibrational degree of freedom corresponding to the variation of the internuclear distance. By the equipartition theorem this gives a contribution of $1.0\,R$ because kinetic and potential energy contribute separately to C_V. Adding up the various contributions, we arrive at the value $C_V = 3.5\,R$. This value for C_V is, however, only observed at very high temperatures (several thousand degrees), whereas at normal temperatures the molar heat capacity of diatomic gases is only about $2.5\,R$.

The failure of statistical mechanics to describe the temperature dependence of C_V was, of course, a serious shortcoming. It remained a riddle until the advent of quantum mechanics.

1.4 The Spectroscopic Atom

The nineteenth-century attempts to determine the heat capacity of molecular gases from first principles were, as we have seen, only modestly successful. The situation was, however, even worse when it came to the understanding of the optical spectra of atoms and molecules.

Optical spectroscopy became a well-developed subject during the nineteenth century. It was realized early that elements liberated from a chemical compound in a flame or an electric arc would emit light at discrete and characteristic wavelengths, and in 1859 the German chemist Robert Wilhelm Bunsen and his colleague, the physicist Gustav Robert Kirchhoff founded the method of spectral analysis based on this fact. The presence of many elements could now be verified by their line spectra. The elements rubidium, cesium, indium, and thallium were, in fact, discovered spectroscopically, and helium was detected by observation of the sun (1868) long before it was found on the earth (1895).

The line spectrum of an element has in general a very complex structure, but with marked constellations of lines. The simplest line spectrum is that of atomic hydrogen. It consists of three lines in the visible part of the spectrum, a red line called H_α, a blue-green line called H_β , and a violet line called H_γ. On the photographic plate it is found that the spectrum continues in the ultraviolet region with a large number of close-lying lines which form a *spectral series* that converges to a limiting wavelength of 364.6 nm. It was of course a challenge to try to represent the series by some simple arithmetic law, and in 1885 the Swiss school teacher Johann Jacob Balmer succeeded in showing that the following formula would reproduce the series,

$$\lambda = 364.6 \frac{m^2}{m^2 - 2^2}\,\mathrm{nm}, \tag{1.6}$$

where λ is the wavelength and m is an integer parameter that runs from 3 to ∞. The visible lines are reproduced by putting m equal to 3, 4, and 5. If, instead of λ, we introduce the *wavenumber*, $\tilde{\nu} = 1/\lambda$, the formula becomes

$$\tilde{\nu} = R_H \left(\frac{1}{2^2} - \frac{1}{m^2} \right) \tag{1.7}$$

where R_H is the so-called *Rydberg constant*, with the numerical value

$$R_H = 1.097 \times 10^7\,\mathrm{m}^{-1}. \tag{1.8}$$

The constant is named after the Swedish physicist Johannes Robert Rydberg who generalized Eq. (1.7) to other series and other simple atoms. For the hydrogen atom, the set of all spectral series may be represented by the general formula

$$\tilde{\nu} = R_H \left(\frac{1}{n^2} - \frac{1}{m^2} \right). \tag{1.9}$$

For $n = 2$ we get the above *Balmer series*. $n = 1$ gives the *Lyman series* with wavelengths in the ultraviolet part of the spectrum, $n = 3$ gives the *Paschen series* with wavelengths in the infrared region, etc.

Light is electromagnetic radiation, and this was fully understood by the end of the nineteenth century. Maxwell had succeeded in combining all theoretical knowledge about electric and magnetic phenomena into a set of four differential equations (1873). The equations are expressed in terms of electric charges, electric currents, and electric and magnetic fields, and they allow the calculation of the fields once the charges and the currents are specified. The equations show, in particular, that an accelerated charge, for instance an oscillating charge, will generate electromagnetic waves that spread in space with the speed of light. Such waves were first produced and studied by the German physicist Heinrich Rudolf Hertz in 1886.

It was accordingly natural to assume that the emission of light from agitated atoms and molecules was caused by oscillations of electric charge. It was well known from electrochemistry that electric charge was intimately connected with the forces of chemical combination, and chemical affinity had often been ascribed to the attraction between opposite charges. This led, in turn, to the suggestion that both positive and negative electric charge existed in discrete units. But nothing definite was known about the way electric charge operated in the atomic and molecular world, and it was consequently completely impossible to calculate the nature of the light that an atom or a molecule might emit.

It was obvious, however, that the atomic emission of light must reflect some internal structure of the atom, and speculative suggestions as to what this structure might possibly be were certainly made, also prior to the appearance of Maxwell's equations, and independent of the assumption of charges. Thus proposed William Thomson, in 1867, that atoms should be thought of as being vortex rings in the omnipresent ether. The motion and mutual interactions of such vortices, he contended, could account for the kinetic behavior of atoms. They could be linked together to form molecules, and their fundamental vibrations could supposedly account for the spectral lines of an atomic gas.

The vortex atom was an intelligent construction, and it was highly regarded by several scientists. But it had to be abandoned as a working model, because it was unable to give a quantitative description of the real world after all. No other model could do better either.

1.5 Antiatomism

As we have discussed it in the previous sections, chemistry, experimental spectroscopy, and statistical mechanics were highly developed sciences at the end of the last century. But nobody had been able to unite the various aspects of atomic behavior met in these sciences into a single and coherent picture of the atom. As a result, there were several scientists who did not believe in the physical reality of atoms and molecules, and some of them were very influential indeed, like the German chemists Hermann Kolbe and Friedrich Wilhelm Ostwald, and the Austrian physicist Ernst Mach.

The criticism by these scientists was both deep and varied. The cardinal point was their objection to the metaphysical aspect of atomic theories. These theories, they said, work with forces whose existence we cannot prove between atoms that we cannot observe. So it is better to consider atoms and molecules as purely formal, albeit useful entities and concentrate on what we can in fact measure, and on the pure energetics of processes.

The strong opposition of the antiatomists led to many fierce debates and much bitterness. And their attitude survived long into the twentieth century, but quite unwarranted, for soon new experimental results provided unambiguous proofs of the reality of atoms.

1.6 The Discovery of the Electron. The Planetary Atom

The experimental study of the interaction of an electric current with chemical substances in a melt or a solution played a considerable role for the development of chemistry and chemical ideas during the nineteenth century. The process of decomposing a chemical compound by an electric current is known as *electrolysis*, and the first quantitative laws concerning this process were formulated in 1834 by the English scientist Michael Faraday who also introduced the notion of ions for the carriers of the current. The laws state that the amount of matter decomposed by an electric current is proportional to the amount of electricity which passes, and that the weights of different substances produced by the same quantity of electricity are proportional to the equivalent weights of the substances. (The equivalent weights of different substances are defined in chemistry as the weights than can combine with each other or a same third substance, to saturate a single unit of valence.)

It is, of course, tempting to speculate from Faraday's laws, that if chemical compunds are composed of atoms, then electricity too, positive as well as negative, is divided into discrete units which attach themselves to the atoms and thus behave like atoms of electricity. This possibility was suggested by the English scientist George Johnstone Stoney in 1874 and, with great strength, by the German scientist Hermann von Helmholtz in 1881. The postulated unit of electricity was given the name *electron* by Stoney in 1891. By hypothesis, an ion will either accept or deliver an integer number of elementary electric units at an electrode during electrolysis. Hence, we may refer to N_A electrons as one mole of electrons and conclude, from the quantitative measurements by Faraday and other scientists, that the electric charge of one mole of electrons is 96485 C. This gives us *Faraday's constant*,

$$F = 96485\,\mathrm{C\,mole^{-1}}. \tag{1.10}$$

We also conclude, that if the charge of the electron is denoted by e and the mass of a hydrogen atom by M, then e/M is approximately equal to F (since the atomic weight of hydrogen is almost exactly equal to 1).

Toward the end of the century, several studies were performed on electrical discharges in gases and on the conductivity of gases subjected to radiation. The experiments were carried out in glass tubes fitted with electrodes and at different gas pressure. It was then found that when a tube was evacuated, rays were observed to cross the tube from a negative electrode (the cathode) to the positive electrode (the anode). These rays were given the name cathode rays. There was much discussion as to the nature of the rays, but in 1897 the physicists Emil Wiechert in Germany and Joseph John Thomson in England demonstrated that they were in fact negatively charged particles. By a very careful study, which involved deflections of the rays by both electric and magnetic fields, J. J. Thomson succeeded in determining the ratio of the electric charge (e) to mass (m) for cathode rays, showing that e/m was at least 1000 times as great as the value for hydrogen mentioned above. Later, the value was corrected to become almost twice as large.

This experiment is considered to mark the discovery of the electron.

The study of cathode rays only allowed the determination of the e/m ratio and not the values of e and m separately. Approximate values for e and m were estimated, but exact values were not determined until 1909. In that year the American physicist Robert Andrews Millikan succeeded in determining the value of e to within 1%, by measuring the velocity in an electric field, of falling oil drops charged with electrons that had been produced by irradiating the air with a beam of X-rays. With the value of e thus determined, the value of m could of course be found from the e/m ratio.[3]

X-rays had been discovered already in 1895, by the German physicist Wilhelm Konrad Röntgen, and the next year the French physicist Henri Becquerel had discovered the phenomenon of radioactivity. During the following years it was found that radioactivity involved no less than three distinct types of radiation. They were called α (alpha) radiation, β (beta) radiation, and γ (gamma) radiation respectively. It was also found that beta rays consist of electrons, wheras gamma rays and X-rays are electromagnetic waves like visible light, but with much shorter wavelengths. Alpha rays were shown, by the British physicist Ernest Rutherford, to be the dipositive ions of helium atoms, moving at high speed. He showed this, partly by measuring the deflection of the rays in electric and magnetic fields, partly by shooting the rays through a thin metal foil into a chamber and demonstrating the presence of helium in the chamber.

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[3] Millikan's determination of the electronic charge became also the first truly direct determination of Avogadro's constant, by comparison of e with the known charge of the Faraday.

Much work was done on the scattering of the newly discovered rays by matter. J. J. Thomson derived a formula which showed that the scattering of X-rays should be proportional to the number of electrons in the target, and this led to the experimental finding that the number of electrons in an atom equals its atomic number, Z. Studies of radioactive decay, by Rutherford and others, pointed in the same direction. But if an atom contains Z electrons each of charge $-e$, then by charge neutrality it must also contain a positive charge Ze. And because the mass of Z electrons is only a tiny part of the atomic mass, the positive charge and the majority of the atom's mass must belong together. But how is this positive charge and remaining mass distributed within the atom?

J. J. Thomson, who incidentally had been working on Kelvin's theory of vortex atoms several years earlier, made the simplest possible assumption. He suggested that the mass and the positive charge was uniformly distributed within a sphere with an approximate radius of 10^{-10} m, a value supported by the kinetic theory of gases and other evidence. The electrons were then supposed to form an electrostatically stable constellation inside the sphere. This model of the atom is referred to as Thomson's model, and thus its name also does justice to Kelvin who earlier had presented some ideas of a similar type.

Thomson's atomic model was of course unable to account for the large number of spectral lines and laws like those hidden in Balmer's and Rydberg's formulae. It was again a new model based on speculation and incomplete knowledge.

The final step toward a correct picture of the atom was taken by Rutherford in 1911. It was based on experimental results on the scattering of alpha rays, obtained in 1909 by his collaborators Hans Geiger and Ernest Marsden. Geiger and Marsden had allowed a beam of alpha particles to pass through a thin gold foil and observed that most of the particles showed very slight deviations from a straight path. However, a small fraction of the particles showed deflections through very large angles. Rutherford went carefully through the dynamics of possible collision processes and showed that such large deflections could come only from a collision of a heavy particle with another particle of comparable mass, and at such a small distance that the electric force of interaction was extremely great.

On the basis of his analysis, Rutherford introduced his model of the *planetary atom*, or *solar atom*, according to which the positive charge and the majority of the atomic mass is concentrated in a tiny *nucleus* at the center of the atom. The electrons, on the other hand, are distributed throughout a sphere of atomic dimensions.

Rutherford's analysis marked the end of a long search for an objective model of the atom, a search in which both chemists and physicists had taken part, and a search during which several false models had emerged and led the way for some time. The new atom became the principle of unification for chemistry and physics, but so far only its constitution was known. To understand its internal dynamics it became necessary to enter a whole new world, the world of quantum mechanics, in which the classical laws of motion lose their validity. Thus, the end of a long development also became the beginning of a new epoch for science.

It is this epoch that the present exposition is about. But before we enter the discussion of quantum mechanics, let us update the description and give a brief sketch of our present picture of the constitution of atoms and molecules and their interactions.

1.7 The Constituents of Atoms and Molecules. The Modern View

The constituents of atoms and molecules are electrons and atomic nuclei. The present section specifies the basic physical parameters of these particles.

Modern physics considers the electron to be a *true* elementary particle, i. e., it is believed that the electron cannot be divided into smaller constituents. Its mass is

$$m_e = 9.10938 \times 10^{-31}\,\mathrm{kg}. \tag{1.11}$$

The electron is a carrier of the negative elementary electric charge $-e$, where

$$e = 1.60218 \times 10^{-19}\,\mathrm{C}. \tag{1.12}$$

As to the spatial extension of the electron, its radius is known to be less than 10^{-18} m. There is in fact nothing in our present knowledge that conflicts the assumption that the electron is contracted into a point.

However, it is incorrect to consider the electron to be merely a charged mass point. The contraction into a point is such that it produces an anisotropy which, in a certain sense, allows us to talk about the orientation of an electron. This orientation is defined by the so-called *spin* of the electron and the magnetic dipole accompanying this spin. The spin, which we shall consider in much more detail later, is the intrinsic angular momentum of the electron. It has the magnitude $\hbar/2$ where

$$\hbar = h/2\pi \tag{1.13}$$

and h is *Planck's constant* (the quantum of action), with the numerical value

$$h = 6.62607 \times 10^{-34}\,\mathrm{J\,s}. \tag{1.14}$$

The introduction of this natural constant will be the first thing to be discussed in the following chapter.

The magnetic dipole accompanying the spin has a magnetic moment whose magnitude is almost exactly given by

$$\mu_B = e\hbar/2m_e = 9.27401 \times 10^{-24}\,\mathrm{J\,T^{-1}}. \tag{1.15}$$

This quantity is called the *Bohr magneton.*

Unlike the electron, atomic nuclei are composite particles, the constituents being protons and neutrons. The masses of the proton and the neutron are

$$m_p = 1.67262 \times 10^{-27}\,\mathrm{kg} = 1836.15\,m_e \tag{1.16}$$

and

$$m_n = 1.67493 \times 10^{-27}\,\mathrm{kg} = 1838.67\,m_e, \tag{1.17}$$

respectively. The proton carries the positive electric charge e, whereas the charge of the neutron is zero. Protons and neutrons are collectively referred to as nucleons. The number of nucleons in a nucleus consisting of Z protons and N neutrons is therefore

$$A = Z + N. \tag{1.18}$$

A is called the mass number and Z the atomic number.

Protons and neutrons are each composed of three so-called quarks and are not point-like. They both have a radius of approximately $10^{-15}\,\mathrm{m}$. The volume of a nucleus increases essentially linearly with its mass number A, and in accordance with this it is found that the approximate radius of a nucleus may be represented by the formula

$$R = 1.1 \times 10^{-15} A^{1/3}\,\mathrm{m}. \tag{1.19}$$

The nuclear surface is, however, often deformed from the spherical shape and, in addition, it should be considered as diffuse rather than sharp.

Just like the electron, a nucleon has a spin and a magnetic dipole associated with it. The spin is the same as for the electron, but the magnetic moment is three orders of magnitude smaller than that of the electron. It is expressed in terms of the so-called *nuclear magneton*

$$\mu_N = e\hbar/2m_p = 5.05078 \times 10^{-27}\,\mathrm{J\,T^{-1}}. \tag{1.20}$$

Both the spin and the magnetic dipole are vector quantities, and when the nucleus is formed, these quantities add like vectors. This implies that the resulting spin and magnetic dipole of the nucleus may be zero or only a few times larger than the spin and magnetic dipole of a free nucleon.

Electric charge is, however, a scalar quantity, and the total electric charge of a nucleus with atomic number Z is consequently Ze. Such a nucleus may bind Z electrons to form a neutral atom.

The radius of a neutral atom is of the order of 10^{-10} m. This is five orders of magnitude larger than the radius of the nucleus. In discussing the properties of the electronic cloud, it is accordingly an extremely good first approximation to consider the nucleus as point-like.

An atom, X, with only $Z - n$ electrons is referred to as the positive ion X^{n+}, and an atom, X, with $Z + n$ electrons is referred to as the negative ion X^{n-}. For a positive ion, n may take any value between 1 and Z. On the other hand, no free negative ion is known for which n is larger than one.

An atomic nucleus consists of *nucleons in interaction*. The nuclear forces that govern this interaction will not be discussed in the present text. Such a discussion belongs in the realm of nuclear physics. Hence, we shall always express nuclear properties in terms of parameters like charge, magnetic moment, and electric moments describing the shape of nuclei.

As a result of this simplification, we may now treat an atom or a molecule as a *collection of nuclei and electrons in interaction*. The forces responsible for this interaction are the electromagnetic forces between the particles.

In spite of the complexity of the problem, we shall see that quantum mechanics allows us to obtain a clear and exact description of atoms and molecules in their various internal states, on the basis of the above picture of nucleons and electrons in interaction. This description moves naturally from the smaller systems toward the larger ones. Thus, we obtain the so-called shell structure of atoms, and the picture of molecules as assemblies of atoms. But we also learn that shells in atoms, and atoms in molecules, are soft concepts that must be used with care.

1.8 External Interactions. Photons

Experimentally, one studies the structure and properties of atoms and molecules by letting them interact with each other in a vessel or a beam, and letting them interact with external media. An external medium may, for instance, be a static electric or magnetic field, or it may be a beam of free particles like electrons and neutrons. But the most widely applied external medium is electromagnetic radiation.

Electromagnetic radiation is, for instance, produced in light bulbs, electric arcs, lasers, X-ray generators, and synchrotrons. As we shall discuss it in the following chapter, it consists of *photons* of distinct energy.

Like the electron, the photon is a true elementary particle. It has a spin of magnitude $\hbar$, but its mass is zero and it has no intrinsic magnetic moment. It may have any energy, but it always moves with the speed of light which, in vacuum, is defined as

$$c = 299\,792\,458\,\mathrm{m\,s^{-1}}. \tag{1.21}$$

A photon of energy ε carries a linear momentum whose direction is the direction of propagation, and whose magnitude is

$$p = \varepsilon / c. \tag{1.22}$$

When a photon interacts with an atom or molecule, there may be three different outcomes. Thus, the photon may leave the region of interaction with its energy unchanged, but with a different direction of its momentum. Such a process is called elastic scattering. Or the energy, and hence also the magnitude of the photon's momentum, may be changed. This is the process of inelastic scattering. Finally, the photon may be destroyed as a result of the interaction. Its energy and momentum are absorbed by the atom or molecule affected. We call this an absorption process.

The reverse of the process of absorption is the process of emission, during which an atom or a molecule emits a photon and loses corresponding quanta of energy and momentum.

Although electromagnetic rays are composed of photons, and although interaction processes are elementary events that only involve one or a few photons at a time, it is usually possible to represent a ray composed of many photons by an electromagnetic wave. This is certainly the case for all situations studied in the nineteenth century. All such situations are, as we know, governed by Maxwell's equations which predict electromagnetic radiation to be true wave motion. For a ray consisting of photons with energy ε, the frequency ν that characterizes the wave is given by the relation

$$\varepsilon = h\nu. \tag{1.23}$$

The corresponding wavelength is related to the frequency through the general equation

$$\nu\lambda = c \tag{1.24}$$

which simply states that an electromagnetic wave propagates with the speed of light.

Eqs. (1.23) and (1.24) allow us to write Eq. (1.22) as

$$p = h/\lambda. \tag{1.25}$$

The remarkable *dualism* between particle properties (ε and p) and wave properties (ν and λ), expressed by Eqs.(1.23) and (1.25), is a genuine and general feature of quantum mechanics. It also plays a most fundamental role in the description of electrons and nucleons and will be properly discussed in the following chapters.

The elastic scattering of photons is observed as Rayleigh scattering and Thomson scattering, the inelastic scattering as Compton scattering and Raman scattering. The measurements of photon absorption and photon emission are called absorption and emission spectroscopy, respectively. Depending on the energy of the photons, and the nature of the atomic or molecular changes brought about through the interaction with the photons, different experimental techniques are used, and thus many different branches of spectroscopy have developed. This has, in turn, led to a natural division of the so-called *electromagnetic spectrum* into subregions.

The *spectrum* of a physical quantity is the set of values that the quantity may take. This set may be discrete or continuous, or it may have both a discrete and a continuous part. The energy of a photon may take any value between zero and infinity (in arbitrary units). The energy spectrum is accordingly continuous. It is this energy spectrum that is called the electromagnetic spectrum. It may, of course, equally well be characterized by the possible values of ν, or the possible values of λ, for the associated wave, and this is common practice. The range of values is again from zero to infinity, and so is the range for the so-called wavenumber

$$\tilde{\nu} = 1/\lambda = \varepsilon/hc \tag{1.26}$$

Table 1.1: The Electromagnetic Spectrum

λ	Spectral region
$< 10\,\text{pm}$	γ-ray
$10\,\text{pm} - 10\,\text{nm}$	X-ray
$10 - 180\,\text{nm}$	Vacuum ultraviolet
$180 - 400\,\text{nm}$	Quartz ultraviolet
$400 - 760\,\text{nm}$	Visible region
$760 - 1000\,\text{nm}$	Photographic infrared
$1 - 5\,\mu\text{m}$	Near infrared
$5 - 40\,\mu\text{m}$	Medium infrared
$40 - 400\,\mu\text{m}$	Far infrared
$> 400\,\mu\text{m}$	Micro- and radiowaves

which we already introduced in Section 1.4. It is a frequently used quantity in spectroscopy.

A coarse division of the electromagnetic spectrum into subregions is shown in Table 1.1. Each subregion may, of course, be further divided. The visible region may, for instance, be divided into subregions according to the various colors.

We shall now return to our historical approach and discuss how the study of electromagnetic radiation in equilibrium with matter led to quantum mechanics, and hence to the discovery of the photon and the dynamics that governs the behavior of the particles in the atomic and molecular world.

Supplementary Reading

The bibliography, entries [1], [2] and [3].

Problems

1.1. From your favorite physics textbook, repeat the classical description of the harmonic oscillator, i. e., a particle with mass m and position coordinate x, bound to the origin ($x = 0$) by the elastic force $F = -kx$. Set up Newton's second law and determine x as a function of time. Express the frequency of oscillation in terms of k and m.

1.2. In the atomic model suggested by J. J. Thomson (page 12), the hydrogen atom is imagined to consist of a positive charge e, uniformly distributed inside a sphere with radius R, and an electron with the negative charge $-e$, originally placed at the center of the sphere, O.

a. Write down the expression for the force acting on the electron if it is pulled out to a distance $r < R$ from O. (According to the laws of electrostatics, one may calculate this force by assuming that the positive charge inside the sphere of radius r is concentrated at O, while the positive charge outside this sphere is neglected.)

b. Show that the force just calculated is a harmonic force (Problem 1), and write down the expression for the frequency of the oscillations that the electron may execute under the influence of this force.

c. Assume that $R = 0.53 \times 10^{-10}$ m, corresponding to the radius of the first Bohr orbit defined in the following chapter. Determine the numerical value of the frequency of oscillation under this assumption. Calculate also the corresponding wavenumber $\tilde{\nu}$ and relate it to the Rydberg constant defined by Eq. (1.8).

The Thomson model has a quantum-mechanical parallel in the so-called *jellium model* which is sometimes used as a first description of large systems, for instance a crystal or a cluster of atoms. The sum of nuclear charges is uniformly distributed over the region of the crystal or the cluster. The motion of the electrons is then modelled by solving the Schrödinger equation with the electrostatic potential arising from the positive "jellium".

Chapter 2

The Birth of Quantum Mechanics

Contents

In this chapter we cover the first twenty-five years of quantum mechanics. Those were the years of the so-called *early quantum mechanics*, which was the precursor of the modern theory. As far as solving problems were concerned, the idea behind the early quantum theory was to first write down all possible classical motions of a system and then pick out 'the quantum-mechanically allowed motions' by means of a set of cleverly devised quantization conditions. This method of attack was successful for simple systems like the harmonic oscillator and the hydrogen atom, but it failed for more complex systems. It was not the true theory.

We devote a full chapter to early quantum mechanics for three reasons. Firstly, there is the obvious historical reason. Secondly, the period of the early quantum theory produced a number of concepts that are of lasting value. The third reason for still studying the methods of early quantum mechanics is that the so-called semiclassical mechanics—which is a proper and frequently used limit form of modern quantum mechanics—has many similarities with it and hence uses much of its language.

We begin with Max Planck's important discovery of the quantum of action, the Planck constant.

2.1 Black-Body Radiation and Planck's Discovery

The official birthday of quantum mechanics is the 14th of December, year 1900, the day when Max Planck, in der *Deutschen Physikalischen Gesellschaft*, presented his final analysis of the energy distribution in what he called the normal spectrum.[1] This is the part of the electromagnetic spectrum seen in the radiation from a so-called black body at a definite temperature.

A black body is an object which absorbs all radiant energy incident upon it, without discriminating between wavelengths. A good candidate is a perfectly insulated electric oven with only a tiny hole in it. For even if the walls of the oven are not ideal absorbers practically all radiation shone upon the opening of the oven will be absorbed, for it would have to bounce back and forth many times within the oven before it would have any chance of hitting the opening again and escape.

When the oven is heated, electromagnetic radiation will build up in the *cavity* of the oven, and the intensity and spectral composition of this *black-body radiation* may be observed and measured through the hole of the oven. It is a thermodynamic system just as well as a gas or piece of matter is, and we may also describe it in the same way, by means of the usual thermodynamic functions. In particular, the radiation may be characterized by the same temperature, T, as the walls with which it is in thermodynamic equilibrium. The internal energy of the radiation is proportional to the volume of the cavity, and so is the entropy. We shall therefore let u and s denote energy and entropy *densities* respectively, i. e., energy and entropy per unit volume.

The first quantitative information about these densities was derived by the Austrian physicists Josef Stefan (1879) and Ludwig Boltzmann (1884). Stefan

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[1] M. Planck, Ann. Physik **4**, 553 (1901).

found experimentally that the intensity, J, of emission from a black body has the form

$$J = \sigma T^4 \tag{2.1}$$

where σ is a constant whose value is the same for all black bodies and is called the *Stefan–Boltzmann constant*. The intensity of emission is defined as the total energy radiated per unit area per unit time, and elementary though somewhat lengthy considerations show that it is connected to u through the relation $u = 4J/c$. Hence, we also have that

$$u = \frac{4\sigma}{c} T^4 = \alpha T^4 \tag{2.2}$$

where $\alpha = 4\sigma/c$.

It was Boltzmann's achievement that he was able to derive the form of this expression theoretically,[2] on the basis of thermodynamic arguments and Maxwell's theory of electromagnetic radiation, to which we alluded in Section 1.4. He also derived the following form for the entropy density:

$$s = \tfrac{4}{3}\alpha T^3 + const. \tag{2.3}$$

Eqs. (2.2) and (2.3) give the energy and entropy densities of the black-body radiation, but the expressions say nothing about the spectral composition of the radiation. In order to describe this composition we need universal functions $\rho(\nu, T)$ and $\sigma(\nu, T)$ such that $\rho(\nu, T)d\nu$ gives the partial energy density corresponding to the frequencies between ν and $\nu + d\nu$, while $\sigma(\nu, T)d\nu$ gives the corresponding partial entropy density. $\rho(\nu, T)$ and $\sigma(\nu, T)$ are called *spectral distributions*, or just distributions. They must satisfy the *normalization conditions*:

$$\int_0^\infty \rho(\nu, T)d\nu = u(T), \qquad \int_0^\infty \sigma(\nu, T)d\nu = s(T), \tag{2.4}$$

with the T dependence of $u(T)$ and $s(T)$ as given by Eqs. (2.2) and (2.3), respectively.

Instead of $\rho(\nu, T)$, much of the original work used a function $E(\lambda, T)$ showing how the energy density is distributed with respect to the wavelength λ. Since $\nu\lambda = c$, we have that $d\nu = -(c/\lambda^2)d\lambda$. $E(\lambda, T)$ must be normalized with respect to λ. Hence, we get

$$E(\lambda, T) = (c/\lambda^2)\rho(\nu, T). \tag{2.5}$$

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[2] L.Boltzmann, Ann. Physik **22**, 291 (1884).

We may, of course, also introduce the wavenumber $\tilde{\nu} = 1/\lambda = \nu/c$ and define the corresponding distribution function

$$\tilde{\rho}(\tilde{\nu}, T) = c\rho(\nu, T). \tag{2.6}$$

The actual form of the function $E(\lambda, T)$ was much discussed during the 1890s. For a given T, it has a maximum at some definite value, Λ. In Berlin, Wilhelm Wien found the remarkable result that the product of T and Λ is a universal constant, today called b:

$$T\Lambda = b. \tag{2.7}$$

This relation is known as *Wien's displacement law.* Wien also found an expression for the function $E(\lambda, T)$ which was correct for higher frequencies. For lower frequencies, an independent expression was found by the English physicist Lord Rayleigh. For the actual form of these expressions, see the introduction to the next section.

In Berlin, in 1899, Otto Lummer and Ernst Pringsheim produced experimental graphs of $E(\lambda, T)$ for different values of T and hence derived the value of b. The value of the constant σ in Eq. (2.1) had been accurately determined in 1898 by Ferdinand Kurlbaum. On the basis of these results and Wien's and Rayleigh's expressions, Max Planck found the analytic form of $E(\lambda, T)$, in the pioneering contribution mentioned at the beginning of this section.

From the very outset of his analysis, Planck looked not only for the form of the function $E(\lambda, T)$, or $\rho(\nu, T)$, but also for the form of the entropy function $\sigma(\nu, T)$. To determine the form of these functions, he introduced a collection of harmonic oscillators (resonators) with which the radiation was supposed to be in thermal equilibrium. He then used Newton's and Maxwell's equations to find relations between the energy and entropy of the oscillator system on the one hand, and the energy and entropy functions, $\rho(\nu, T)$ and $\sigma(\nu, T)$, for the radiation on the other. In this way, he reduced the problem to that of determining the energy and the entropy of the oscillator system from first principles.

To this end, he wrote the entropy of the oscillator system in the form (1.3), with k as a parameter, and set out to evaluate the thermodynamic probability, W. He then arrived at the remarkable conclusion that in order to obtain a qualitative agreement with the form of Lummer and Pringsheim's curves, it was necessary to limit the possible energy values of an oscillator with frequency ν to a discrete set and write

$$\varepsilon_n = nh\nu, \quad n = 0, 1, 2, \dots \tag{2.8}$$

where h is a constant. A quantitative agreement was obtained by treating h and k as adjustable parameters with values to be determined from the values of the constants σ and b that we mentioned above. k is Boltzmann's constant, and h is Planck's constant. Their numerical values have already been given, in Eqs. (1.4) and (1.14) respectively.

> Thus, Planck's struggle to understand the energy and entropy relations for electromagnetic radiation simultaneously crowned the science of statistical mechanics with Boltzmann's constant, and gave birth to quantum mechanics with the introduction of the constant h.

We shall not attempt to reproduce Planck's analysis here. It is quite an exercise in classical mechanics, electrodynamics, and statistical mechanics. So, we shall pass on to a direct presentation of the fundamental function $\rho(\nu, T)$. Its analytic expression is

$$\rho(\nu, T) = (8\pi h\nu^3/c^3)\frac{1}{\exp(h\nu/kT) - 1}\,. \tag{2.9}$$

The corresponding function $E(\lambda, T)$, defined by Eq. (2.5) becomes

$$E(\lambda, T) = (8\pi hc/\lambda^5)\frac{1}{\exp(hc/\lambda kT) - 1}\,. \tag{2.10}$$

By integrating $\rho(\nu, T)$ over ν, as in Eq. (2.4), we obtain the energy density $u(T)$. The integration is readily performed by utilizing that[3]

$$\int_0^\infty \frac{x^3}{\mathrm{e}^x - 1}dx = \frac{\pi^4}{15}\,. \tag{2.11}$$

The result is

$$u(T) = \frac{8\pi^5 k^4}{15h^3c^3}T^4 = 7.56598 \times 10^{-16}\,T^4\,\mathrm{K}^{-4}\,\mathrm{J\,m}^{-3}. \tag{2.12}$$

Hence we find, by comparison with Eq. (2.2), that the Stefan–Boltzmann constant has the value

$$\sigma = \frac{8\pi^5 k^4}{60h^3c^2} = 5.67051 \times 10^{-8}\,\mathrm{W\,m}^{-2}\mathrm{K}^{-4}. \tag{2.13}$$

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[3] See, for example, I. S. Gradshteyn and I. M. Ryshik, *Table of Integrals, Series and Products*, Academic Press, New York, 1965, Sec. 3.411.

We also find, by standard methods, that $\rho(\nu, T)$ and $E(\lambda, T)$ attain their maximum values when

$$h\nu/kT = 2.821440 \quad \text{and} \quad hc/\lambda kT = 4.965114, \tag{2.14}$$

respectively. That these values correspond to different wavelengths (and frequencies) is a consequence of the relation (2.5), according to which the functions $\rho(\nu, T)$ and $E(\lambda, T)$ differ by the factor c/λ^2.

By Eq. (2.14), the constant b in Wien's displacement law, Eq. (2.7), attains the value

$$b = \frac{hc}{4.965114\,k} = 2.89776 \times 10^{-3}\,\mathrm{m\,K}. \tag{2.15}$$

Eqs. (2.13) and (2.15) provide theoretical expressions for σ and b. On the other hand, they also allow a determination of h and k from experimentally determined values of σ and b, and as we mentioned above, this was the route that Planck had to follow.

It is instructive to write Eq. (2.9) in the form

$$\rho(\nu, T) = \frac{hu(T)}{kT} f(x), \qquad x = \frac{h\nu}{kT}, \tag{2.16}$$

where $u(T)$ is given by Eq. (2.12), and x is a dimensionless variable, while $f(x)$ is given by

$$f(x) = \frac{15}{\pi^4} \frac{x^3}{\mathrm{e}^x - 1}, \qquad \int_0^\infty f(x)dx = 1. \tag{2.17}$$

Since $f(x)$ is normalized to unity, we may interpret $f(x)dx$ as the fraction of the radiation that corresponds to values of $h\nu/kT$ between x and $x + dx$. We see that this fraction is the same for all black bodies.

The function $f(x)$ is shown in Fig. 2.1 and, with logarithmic axes, in Fig. 2.2.

We close this section by evaluating a few Λ values from Eqs. (2.7) and (2.15). The results are presented in Table 2.1. In the table, $T = 300\,\mathrm{K}$ corresponds to room temperature, $T = 1808\,\mathrm{K}$ to the melting point of iron, $T = 5800\,\mathrm{K}$ to the temperature of the solar surface, $T = 10^7\,\mathrm{K}$ to the temperature in a nuclear explosion and $T = 2.9\,\mathrm{K}$ to the temperature of the cosmic background radiation (*which was created approximately 300 000 years after the big bang*, at a temperature around 3000 K). We note that the cosmic background radiation falls in the microwave region (see Table 1.1). The Λ values corresponding to room temperature and the temperature of molten iron fall in the infrared

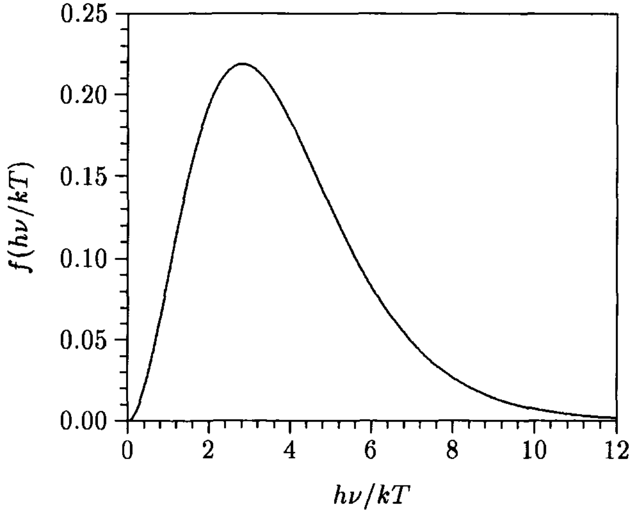

Figure 2.1: Universal Planck distribution.

region. However, a large part of the radiation from the surface of the sun falls in what we call the visible region. This coincidence may, of course, be considered to be a result of evolution which has adapted our eyes so that we may take maximum advantage of the light from the sun. Finally, we note that the radiation from an atomic explosion has its highest intensity in the X-ray region.

The last column in Table 2.1 gives the photon density, i. e., the number of photons per unit volume, as calculated from Eq. (2.27) below.

Table 2.1: Properties of the black-body radiation as function of temperature, T. Λ: Characteristic wavelength (Wien's displacement law). $N(T)$: Number of photons per unit volume.

T	Λ	$N(T)$
2.9 K	1 mm	$495\,\mathrm{cm}^{-3}$
300 K	9659 nm	$5.48 \times 10^{8}\,\mathrm{cm}^{-3}$
1808 K	1603 nm	$1.20 \times 10^{11}\,\mathrm{cm}^{-3}$
5800 K	500 nm	$3.96 \times 10^{12}\,\mathrm{cm}^{-3}$
10^7 K	290 pm	$2.03 \times 10^{22}\,\mathrm{cm}^{-3}$

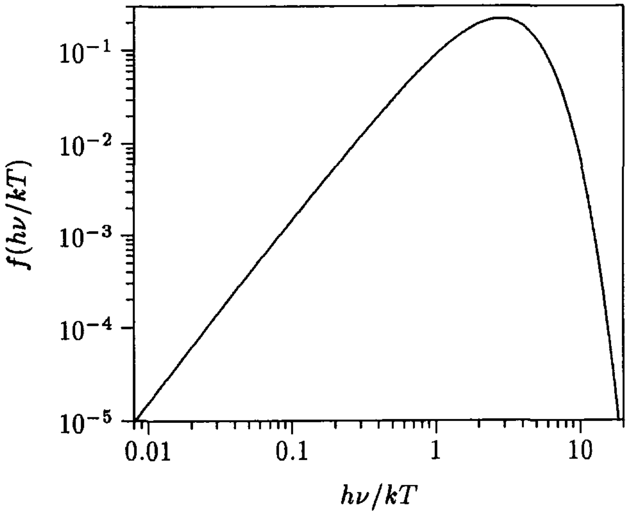

Figure 2.2: Universal Planck distribution. Logarithmic axes.

2.2 Photons and the Photoelectric Effect

In Eq. (2.9) we presented the analytic expression for the distribution function $\rho(\nu, T)$. We shall now consider the limits of low and high frequencies. Hereby, we arrive at expressions whose qualitative forms were already known to Planck and used by him in his derivation of Eq. (2.9)—as mentioned on page 23 above.

In the low-frequency limit we replace $\exp(h\nu/kT)$ by $1 + h\nu/kT$ and get:

$$\rho(\nu, T) \simeq (8\pi\nu^2/c^3)kT. \tag{2.18}$$

This expression is known as the *Rayleigh–Jeans formula.*[4] It was suggested by Lord Rayleigh on the basis of the equipartition theorem for energy and a simple counting of standing waves in a cavity. The number of possible standing waves per unit volume, with frequencies between ν and $\nu + d\nu$, is shown to be $(8\pi\nu^2/c^3)d\nu$, and by assigning to each standing wave an energy of kT one arrives directly at Eq. (2.18). We note that this expression does not involve the Planck constant. It is the so-called *classical limit* of Eq. (2.9). Working from the classical limit we may, with some hindsight, replace the kT in Eq. (2.18) with the average energy of a quantized harmonic oscillator. The expression for that energy is derived in Sec. 2.4 and is given by Eq. (2.36). When it is

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[4] Lord Rayleigh, Phil. Mag. **49**, 539 (1900). J. H. Jeans, Phil. Mag. **10**, 91 (1905).

inserted in Eq. (2.18), it correctly gives Planck's distribution function (2.9). This was pointed out by the Dutch physicist Petrus Debye in 1910.[5]

The high-frequency limit of Eq. (2.9) is obtained by neglecting the number 1 against $\exp(h\nu/kT)$. Thus we get:

$$\rho(\nu,T) \simeq (8\pi h\nu^3/c^3)\exp(-h\nu/kT). \tag{2.19}$$

This expression is known as the *Wien formula*, because it is similar to the formula suggested by Wien a few years prior to Planck's work—with arbitrary constants instead of $8\pi h/c^3$ and h/k.[6] The background for the formula was a statistical analysis of the interaction between radiation and the molecules of a gas.

We recall that Planck's *quantum condition* (2.8) is a condition on the oscillators representing the matter with which the blackbody radiation is supposed to be in equilibrium. It implies that energy is exchanged with the radiation in multiples of $h\nu$. But Planck did not suggest that the radiation itself consist of energy quanta. This suggestion was made in 1905 by the German (later American) physicist Albert Einstein,[7] on the basis of an analysis of the entropy of the radiation, in the high-frequency limit. He derived an expression for the entropy of the radiation from general considerations and Wien's formula, and he demonstrated that the volume dependence of the entropy thus derived was the same as for an ideal gas. This convinced him that radiation should be conceived of as consisting of particles, with energy $h\nu$. These particles are, of course, the photons which we described in Section 1.8.[8]

To give an experimental proof of the existence of photons, Einstein merely had to refer to a large series of measurements by the German physicist Philipp Lenard on the so-called *photoelectric effect*. The photoelectric effect amounts to the observation that free electrons may be emitted from a metal surface when it is illuminated by ultraviolet light. Such *photoelectrons* had already been detected by J. J. Thomson in 1898 as cathode rays. Lenard had found that the velocity of the liberated electrons was independent of the intensity of the incident light, and Einstein took this as a proof that the liberation of an electron was an elementary process that only involved a single photon. The photon would transfer its energy, $h\nu$, to an electron which would then come out of the metal with a kinetic energy, $\frac{1}{2}m_e v^2$, which equals the difference

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[5] P. Debye, Ann. Physik **33**, 1427 (1910).

[6] W. Wien, Ann. Physik **58**, 662 (1896).

[7] A. Einstein, Ann. Physik **17**, 132 (1905).

[8] Einstein merely referred to the particles as energy quanta. The name photon was designed much later by G. N. Lewis, Nature **118**, 874 (1926).

between the received energy, $h\nu$, and the so-called *work function*, W, of the metal. The work function is simply the minimum energy required to liberate an electron. Thus, we get Einstein's equation

$$\boxed{\tfrac{1}{2}m_e v^2 = h\nu - W} \tag{2.20}$$

v is, of course, the velocity of the electron.[9]

Since the left-hand side of Eq. (2.20) is invariably non-negative, a *threshold value* of ν must exist, below which no electrons are ejected at all, because the photon energy is too small. This threshold value, ν_0, is obviously determined by the condition

$$h\nu_0 = W. \tag{2.21}$$

The existence of the threshold is amply borne out by experiment.

In practice, one measures the number of photoelectrons by registering the charge transferred from the photoelectrode to a metallic plate placed at some distance from it. The velocity of the photoelectrons is measured by applying a negative voltage to the plate, just big enough to stop the flow of electrons. Let the necessary potential difference between the photoelectrode and the plate be $\mathcal{E}$. Then the electron must have been emitted with an initial kinetic energy of $e\mathcal{E}$, i. e.,

$$\tfrac{1}{2}m_e v^2 = e\mathcal{E}. \tag{2.22}$$

The kinetic energy which an electron acquires (or loses) by traversing an electric potential difference of 1 Volt is denoted 1 eV (1 *electron Volt*). Thus we get, by inserting the value of e from Eq. (1.12):

$$\boxed{1\,\mathrm{eV} = (1.60218 \times 10^{-19}\,\mathrm{C})(1\,\mathrm{V}) = 1.60218 \times 10^{-19}\,\mathrm{J}} \tag{2.23}$$

This is a practical unit of energy which we shall often use in the following.

The value of the work function, W, varies for pure metals from 1.9 eV (for cesium) to several eV.

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[9] Actually, v is the maximum velocity of an outgoing electron. One sees a distribution of velocities, corresponding to the fact that the photon energy is transferred to the solid as a whole. So a single electron will, in general, only receive part of the photon energy.

In Fig. 2.3 we show a graphic representation of Eq. (2.20) with the metal of barium as an example. The work function for barium is 2.5 eV. This gives the threshold frequency

$$\begin{aligned}\nu_0 = W/h &= (2.5 \times 1.60218 \times 10^{-19}\,\mathrm{J})/(6.62608 \times 10^{-34}\,\mathrm{J\,s}) \\ &= 6.0 \times 10^{14}\,\mathrm{Hz}\end{aligned}$$

or, if we prefer to measure the frequency in wavenumbers,

$$\begin{aligned}\tilde{\nu}_0 = \nu_0/c &= (6.0 \times 10^{14}\,\mathrm{s}^{-1})/(2.99792 \times 10^{8}\,\mathrm{m\,s}^{-1}) \\ &= 2.0 \times 10^{6}\,\mathrm{m}^{-1} = 20000\,\mathrm{cm}^{-1}.\end{aligned}$$

This corresponds to a wavelength of 500 nm, and hence to light in the visible region.

Now that we have convinced ourselves of the reality of photons, let us calculate the density of photons in the black-body radiation. We recall that $\rho(\nu,T)d\nu$, with $\rho(\nu,T)$ given by Planck's formula (2.9), is the contribution to the energy density from frequencies between ν and $\nu + d\nu$. Hence the number of photons (per unit volume) in the same frequency interval is $n(\nu,T)d\nu$, where

$$n(\nu,T) = \frac{\rho(\nu,T)}{h\nu} = (8\pi\nu^2/c^3)\frac{1}{\exp(h\nu/kT) - 1}. \tag{2.24}$$

The total number of photons per unit volume is

$$N(T) = \int_0^\infty n(\nu,T)d\nu. \tag{2.25}$$

We evaluate this integral by utilizing that[10]

$$\int_0^\infty \frac{x^2}{e^x - 1}dx = 2\zeta(3) = 2.40411 \tag{2.26}$$

where $\zeta(n)$ is the Riemann zeta function.[11] The result is

$$N(T) = 60.422\left(\frac{kT}{hc}\right)^3 = 2.0287 \times 10^7\,T^3\,\mathrm{K}^{-3}\,\mathrm{m}^{-3}. \tag{2.27}$$

A set of calculated $N(T)$-values have been included in Table (2.1).

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[10] See footnote 3.

[11] See, for example, M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions*, Dover, 1965, Chapter 23.

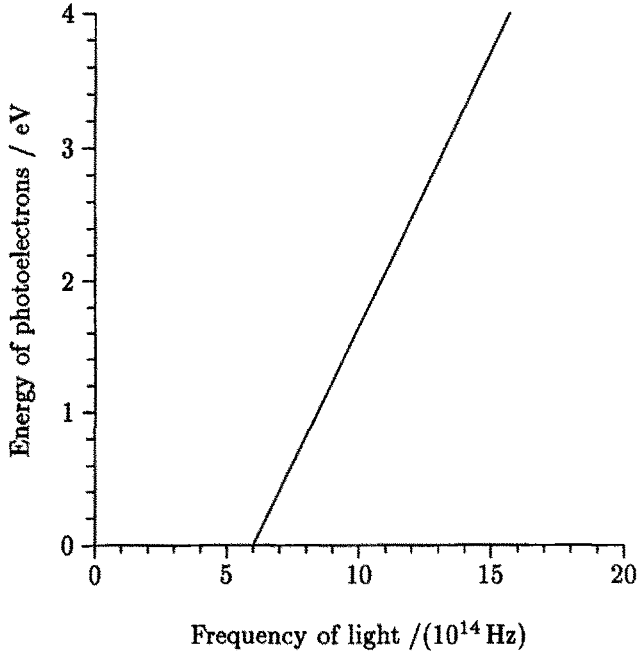

Figure 2.3: Kinetic energy of photoelectrons as a function of frequency of incident light, for the metal of barium.

After having proved the existence of photons, Einstein turned to the description of matter and, in particular, to the problem of correctly calculating the molar heat capacity of a gas or a solid. We shall return to this problem in Section 2.4, after the following brief section which teaches us more about the nature of the photon.

2.3 The Photon is a Relativistic Particle

1905 was also the year when Einstein presented his *special theory of relativity*, according to which c, the speed of light, is the same in all inertial systems.[12] An important concept in the theory of relativity is that of the 4-vector. This is a quantity with four components that transform into linear combinations of each other under a Lorentz transformation, i. e., a transformation from one inertial

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[12] An inertial system is a coordinate system in which any free particle moves along a straight line with constant velocity.

system to another. The three position coordinates of a free particle, together with ct where t is the time coordinate, form one such 4-vector. Another is formed by the three components of the linear momentum p, together with E/c where E is the energy, and one shows the following relation:

$$E = \sqrt{c^2p^2 + m^2c^4} \tag{2.28}$$

where m is the mass of the particle.

For a free particle at rest the linear momentum is zero, and hence

$$E_0 = mc^2 \tag{2.29}$$

where E_0 is the *rest energy* of the particle. This is the famous equation that introduces the equivalence of mass and energy.

If p is small as compared with mc, we take a factor mc^2 outside the square-root sign and replace the new square root function with the two first terms in its Taylor expansion. This yields

$$E \simeq mc^2\left(1 + \frac{1}{2}\frac{c^2p^2}{m^2c^4}\right) = mc^2 + \frac{p^2}{2m}. \tag{2.30}$$

In the same approximation, we have that $p = mv$, where v is the velocity of the particle. Hence we see that the relativistic energy is the sum of the rest energy and the non-relativistic kinetic energy, T, where

$$T = \frac{p^2}{2m} = \tfrac{1}{2}mv^2. \tag{2.31}$$

For a particle whose velocity is small as compared with c, the non-relativistic description is a good one.

But the photon is a truly relativistic particle, for it moves with the speed of light. Moreover, its mass is zero, and Eq. (2.28) gives:

$$\varepsilon = cp \tag{2.32}$$

where ε is the photon energy. This is Eq. (1.22) again. The momentum of a photon is a vector whose direction is the direction of propagation, and whose magnitude is ε/c.

If we go from one inertial system to another the energy and the momentum of the photon will change, and hence also the wavelength and the frequency of an associated electromagnetic wave. Light emitted by a body moving away from us will reach us with a smaller frequency than similar light emitted from a body at rest. This is the reason for the *red shift* of the light from stars moving away from us.

2.4 The Heat-Capacity Problem

In Section 1.3 we described how classical statistical mechanics led to the value $C_V = 3.5R$ for the molar heat capacity of a diatomic gas. In particular, the vibrational motion was claimed to contribute RT to the molar internal energy at absolute temperature T, and hence R to C_V. We also mentioned that these results only match the experimental findings for high values of T.

For a monatomic crystal, the molar heat capacity has the value $3R$ at high temperatures. This is the *law of Dulong and Petit* (1819). But the heat capacity decreases with the temperature and goes to zero when the temperature does. Again, it is easy to account for the high temperature value, for each atom in the crystal can vibrate about its equilibrium position in three different directions. It has, therefore, three vibrational degrees of freedom, and with N_A atoms in the crystal this leads to a contribution of $3RT$ to the internal molar energy, and hence to a contribution of $3R$ to the molar heat capacity. But again a statistical description based on classical mechanics is unable to account for the observed temperature dependence of C_V.

In a classical harmonic oscillator, the position coordinate executes sinusoidal oscillations around a fixed value with a definite frequency, ν, and the energy is a continuous function of the maximum amplitude. Thus, the oscillator has a continuous energy spectrum. In his study of the black-body radiation, Planck replaced this continuous energy spectrum with a discrete one: The only allowed energy values are $nh\nu$, as in Eq. (2.8), with $n = 0, 1, 2, \ldots$

In an important paper from 1907,[13] Einstein made the suggestion that if the energy of the black-body oscillators should be treated as quantized, then one might expect the same to hold for the energy of any other oscillator. He therefore went on to calculate C_V for a monatomic crystal under this assumption. Let us take the opportunity to be more specific about the statistical method.

Assume that the only possible energies of an oscillator are ε_0, ε_1, $\varepsilon_2, \ldots$ and that we have a large collection of oscillators as we do in a gas or a crystal, and assume also that all these oscillators correspond to the same frequency, ν. Each oscillator may exchange energy with the other oscillators, and as a result of this it only makes sense to talk about the *mean energy*, $\bar{\varepsilon}$, of an oscillator. This mean energy must be a function of the temperature, and each allowed

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[13] A. Einstein, Ann. Physik **22**, 180 (1907).

energy value will contribute to it with a definite *weight*:

$$\bar{\varepsilon}(T) = \sum_{n=0}^{\infty} w_n(T)\varepsilon_n \tag{2.33}$$

where w_n is the weight corresponding to the energy ε_n. The sum of all weights must equal 1,

$$\sum_{n=0}^{\infty} w_n(T) = 1, \tag{2.34}$$

and we may therefore also refer to the weights as probabilities.

The way to determine the weights is by finding the maximium contribution to the entropy function (1.3). This is a fundamental problem in statistical mechanics,[14] and the result is that

$$w_n(T) = \frac{\exp(-\varepsilon_n/kT)}{\sum_{i=0}^{\infty} \exp(-\varepsilon_i/kT)}. \tag{2.35}$$

These weights define the so-called *Boltzmann distribution*. When we put $\varepsilon_n = nh\nu$ in the above expressions, the sum in Eq. (2.33) may be evaluated explicitly, to give

$$\bar{\varepsilon}(T) = \frac{h\nu}{\exp(h\nu/kT) - 1}. \tag{2.36}$$

For a monatomic crystal with $3N_A$ vibrational degrees of freedom we must multiply $\bar{\varepsilon}$ by $3N_A$ to get the internal molar energy, $U(T)$. The result may be written

$$U(T) = 3RT \frac{h\nu/kT}{\exp(h\nu/kT) - 1}. \tag{2.37}$$

C_V is the derivative of $U(T)$ with respect to T, and becomes

$$C_V = 3R(\Theta/T)^2 \frac{\exp(\Theta/T)}{(\exp(\Theta/T) - 1)^2} \tag{2.38}$$

where

$$\Theta = h\nu/k. \tag{2.39}$$

Θ is called the Einstein temperature. It is readily seen that the expression for C_V approaches the classical one, $C_V \simeq 3R$, for T sufficiently large.

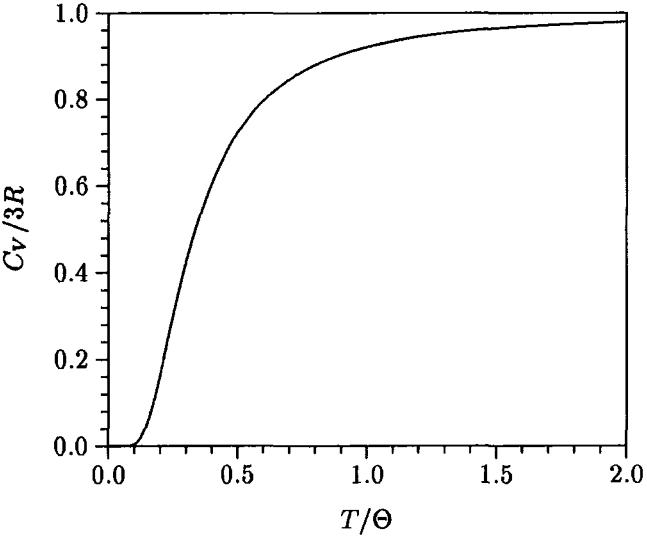

Figure 2.4: Einstein's heat-capacity curve.

Eq. (2.38) gives a reasonable agreement with experimental C_V versus T curves for monatomic crystals when proper values are assigned to Θ. These values lie largely between 100 and 2000 K. The agreement with experiment is, however, not exact. But this was to be expected, for it is obviously a very crude approximation to treat the oscillators on different atomic centers as being dynamically independent. When this approximation is removed, at the expense of a more complex analysis, a perfect agreement between theory and experiment is obtained.

Figure 2.4 shows a graph of Einstein's C_v curve, as defined by Eq. (2.38). With $3R$ replaced by R, the curve also represents the vibrational contribution to the molar heat capacity of a diatomic gas.

Thus the problem of explaining the temperature dependence of the molar heat capacity had been solved, and it became obvious that the discrete energy spectrum of an oscillator was a very real thing.

It should be noted that the expression for C_v remains unchanged if one introduces a so-called *zero-point energy* ε_0 by replacing Planck's original ex-

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[14] See any standard textbook on statistical thermodynamics.

pression (2.8) for the energy spectrum by an expression of the form

$$\varepsilon_n = \varepsilon_0 + nh\nu, \quad n = 0, 1, 2, \ldots \tag{2.40}$$

For Eqs. (2.33) and (2.34) show that $\bar{\varepsilon}(T)$ is merely modified by ε_0 and hence becomes

$$\bar{\varepsilon}(T) = \varepsilon_0 + \frac{h\nu}{\exp(h\nu/kT) - 1}. \tag{2.41}$$

Similarly, the expression (2.37) is modified by $3N_A\varepsilon_0$. This temperature-independent term does not contribute to C_V which therefore remains unchanged, as claimed.

In this context it is interesting to rewrite the expression (2.41) as ε_0 plus kT times a Taylor series in $h\nu/kT$. In this way we get:

$$\bar{\varepsilon}(T) = \varepsilon_0 + kT - \frac{1}{2}h\nu + \frac{1}{12}\frac{(h\nu)^2}{kT} - \frac{1}{720}\frac{(h\nu)^4}{(kT)^3} + \ldots \tag{2.42}$$

For large values of T this approaches $kT + (\varepsilon_0 - \frac{1}{2}h\nu)$. Thus, a pure approach to kT is obtained with $\varepsilon_0 = \frac{1}{2}h\nu$.

The concept of zero-point energy was suggested by Max Planck in a second discussion of the black-body problem[15], in which he was led to the expression

$$\bar{\varepsilon}(T) = \frac{1}{2}h\nu\frac{\exp(h\nu/kT) + 1}{\exp(h\nu/kT) - 1}. \tag{2.43}$$

It is readily seen that this expression may be written in the form (2.41), with $\varepsilon_0 = \frac{1}{2}h\nu$. Subsequently, Einstein and Stern[16] discussed an expansion similar to (2.42) and presented some independent arguments for the existence of a zero-point energy equal to $\frac{1}{2}h\nu$. These arguments were based on a comparison between the rotational and vibrational contributions to C_V for diatomic molecules. Today, these arguments can hardly be considered conclusive,[17] but they stirred some interest at the time.

In modern quantum mechanics, a zero-point energy of $\frac{1}{2}h\nu$ shows up automatically (See Chapter 7). The correct expression for the energy spectrum of the harmonic oscillator is accordingly

$$\varepsilon_n = \tfrac{1}{2}h\nu + nh\nu, \quad n = 0, 1, 2, \ldots \tag{2.44}$$

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[15] M. Planck, Ann. Physik **37**, 642 (1912).

[16] A. Einstein and O. Stern, Ann. Physik **40**, 551 (1913).

[17] J. P. Dahl, J. Chem. Phys. **109**, 10688 (1998).

But if the energy spectrum of an oscillator is always discrete, should we not expect the energy spectra of other physical systems to be discrete as well? The first explicit answer to this question was given by Niels Bohr.

2.5 Bohr's Theory of the Hydrogen Atom

In Section 1.6 we described Rutherford's picture of the atom as a solar system, with the light electrons circling the heavy, positively charged nucleus at the center of the atom. This is an intuitively simple picture. But as it was realized at the time, it is a picture of an unstable mechanical system if the laws of classical mechanics hold. For while the electrons move, they must be continuously changing their directions in order to stay within the atomic region. But an electron changing its direction is an accelerated electron, and as a charged particle it should therefore emit electromagnetic radiation, as mentioned in Section 1.4. And because of the energy loss associated with such an emission, the electron should spiral toward the nucleus. The atom would collapse, and during the collapse it would emit radiation of all possible wavelengths. Nothing like the well-known line spectra could possibly emerge in this way.

Also, it would not help to assume that the electrons form some fixed electrostatic configuration around the nucleus For it may be shown that no electrostatic configuration of point charges can be stable (Earnshaw's theorem).

It was obvious that drastic modifications of the classical description of moving particles would be required to account for the stability of the planetary atom and the observation of spectral lines. This was where the Danish physicist Niels Bohr entered the scene, in 1913.[18]

With reference to Planck's and Einstein's work, Bohr made the suggestion that we hinted at in the previous section, namely, that also the energy of an atom should be quantized. Thus, he simply postulated that an atom possesses a series of discrete *stationary states* just as a harmonic oscillator does, and in each of these states the atom has a definite energy. (We may denote the energies of these stationary states by E_1, E_2, $E_3, \ldots$ and assume an energy ordering such that $E_1 < E_2 < E_3 < \ldots$)

Next, Bohr suggested that the atom may pass from one stationary state to another under emission or absorption of a light quantum with an energy equal to the energy difference, ΔE, between the two states. This leads to the

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[18] N. Bohr, Phil. Mag. **26**, 1 (1913).

fundamental energy-frequency condition:

$$\boxed{\Delta E = h\nu} \tag{2.45}$$

where ν is the frequency characterizing the absorbed or emitted photon. Thus, Bohr treated the absorption and emission of radiation as an elementary process that merely involves a single atom and a single photon.

It is obvious that such a model leads to the appearance of line spectra, for the values of ν that are in accordance with Eq. (2.45) form a discrete set. But so far, the model is an entirely qualitative one. To turn it into a quantitative model, Bohr suggested that the allowed energies could be calculated, and he devised a method of doing so for the one-electron atom. He contended that in a stationary state of a one-electron atom the electron moves around the nucleus in a *stationary circular orbit*, subject to the laws of classical mechanics. The stationary orbits and hence the allowed energies, he postulated, would then be determined from the condition that the angular momentum, l, be a multiple of $\hbar = h/2\pi$:

$$l = n\hbar, \qquad n = 1, 2, 3, \ldots \tag{2.46}$$

This *quantum condition* was ad hoc, i. e., it was exclusively introduced because it worked. But so was, of course, Planck's quantum condition (2.8). Let us, without further ado, accept Bohr's quantum condition and calculate the allowed energies of the one-electron atom.

To this end we introduce a Cartesian coordinate system centered on the atomic nucleus which, for the time being, we consider to be at rest. The electron, whose position vector we denote by $\boldsymbol{r}$, is then subject to an attractive electrostatic force, $\boldsymbol{F}$, from the nucleus. According to the well-known Coulomb law, $\boldsymbol{F}$ has the form:

$$\boldsymbol{F} = -\frac{Ze^2}{4\pi\varepsilon_0}\frac{\boldsymbol{r}}{r^3} \tag{2.47}$$

where Z is the nuclear charge ($Z = 1$ for hydrogen) and ε_0, which is the so-called permittivity of vacuum, has the value

$$\varepsilon_0 = 8.85419 \times 10^{-12}\,\mathrm{F\,m^{-1}}. \tag{2.48}$$

r is the electron's distance form the nucleus. For the magnitude of the force, we get:

$$F = \frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{r^2}\,. \tag{2.49}$$

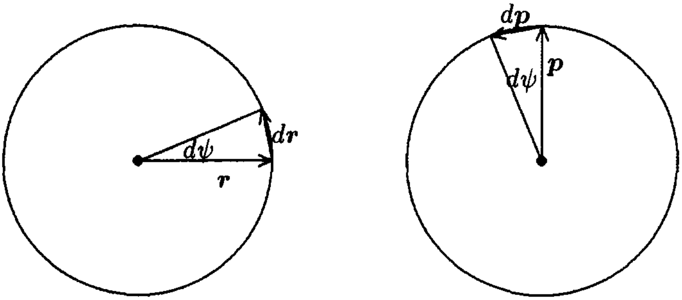

Figure 2.5: Circular motion as viewed in *position space* (left) and *momentum space* (right). The origin of position space is the atomic nucleus, and $\boldsymbol{r}$ is the instantaneous position vector of the electron. The origin of momentum space corresponds to an electron at rest. $\boldsymbol{p}$ is the instantaneous linear momentum of the electron. For circular motion, corresponding values of $\boldsymbol{r}$ and $\boldsymbol{p}$ are mutually perpendicular.

The linear momentum of the electron is

$$\boldsymbol{p} = m_e \boldsymbol{v} \tag{2.50}$$

where $\boldsymbol{v}$ is the velocity.

The angular momentum of the electron is defined as

$$\boldsymbol{l} = \boldsymbol{r} \times \boldsymbol{p}. \tag{2.51}$$

Its magnitude is

$$l = rp|\sin u| \tag{2.52}$$

where u is the angle between $\boldsymbol{r}$ and $\boldsymbol{p}$. For a circular orbit, r and p are constant, u equals $\pi/2$, and $l = rp$.

Bohr's quantum condition (2.46) may now be written

$$rp = n\hbar, \qquad n = 1, 2, 3, \ldots \tag{2.53}$$

To proceed, we introduce Fig. 2.5 which shows the increments of the vectors $\boldsymbol{r}$ and $\boldsymbol{p}$, corresponding to the infinitesimally small time interval dt during which both vectors traverse the angle element $d\psi$. From the left part of the figure, we see that $|d\boldsymbol{r}| = r d\psi$ and hence

$$v = \left|\frac{d\boldsymbol{r}}{dt}\right| = r\frac{d\psi}{dt}. \tag{2.54}$$

From the right part of the figure, we get that $|dp| = pd\psi$ and thus

$$\left|\frac{dp}{dt}\right| = p\frac{d\psi}{dt}. \tag{2.55}$$

From Eq. (2.54) we see that $d\psi/dt = v/r$, and by inserting this in Eq. (2.55) while using Eq. (2.50), we get:

$$\left|\frac{dp}{dt}\right| = \frac{p^2}{m_e r}. \tag{2.56}$$

Newton's second law states that

$$\frac{d\boldsymbol{p}}{dt} = \boldsymbol{F}. \tag{2.57}$$

Hence we get, from Eqs. (2.49) and (2.56):

$$\frac{p^2}{2m_e} = \frac{1}{2}\frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{r}. \tag{2.58}$$

This equation must be satisfied for any circular orbit.

The orbits that satisfy the quantum condition (2.53) may now be found by utilizing that the n'th orbit for which the quantum condition is satisfied has its r-value, r_n, and its p-value, p_n, correlated by the condition $r_n p_n = n\hbar$. The value of p_n is found from this condition and Eq. (2.58) divided by p. We get

$$\boxed{p_n = \frac{Ze^2}{4\pi\varepsilon_0}\frac{m_e}{n\hbar} = \frac{Z\hbar}{na_0}} \tag{2.59}$$

where

$$\boxed{a_0 = \frac{\hbar^2}{m_e}\frac{4\pi\varepsilon_0}{e^2}} \tag{2.60}$$

Inserting the value of p_n on the left-hand side of Eq. (2.58) gives subsequently:

$$\boxed{r_n = \frac{n^2}{Z}a_0} \tag{2.61}$$

a_0 is the so-called *Bohr radius.* It is the radius of the first allowed orbit for hydrogen ($n = 1$ and $Z = 1$). It has the numerical value

$$a_0 = 0.52918 \times 10^{-10}\,\text{m}. \tag{2.62}$$

For the energy we write:

$$E = T + V \tag{2.63}$$

where T is the kinetic energy,

$$T = \frac{p^2}{2m_e}, \tag{2.64}$$

and V is the potential energy,

$$V = -\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)\frac{1}{r}. \tag{2.65}$$

Eq. (2.58) tells us that

$$\boxed{T = -\tfrac{1}{2}V} \tag{2.66}$$

This relation is called the *virial theorem.* It implies that $E = V/2$. Hence, we get that

$$E_n = -\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)\frac{1}{2r_n}. \tag{2.67}$$

Substituting the expression for r_n from Eq. (2.61) gives finally:

$$\boxed{E_n = -\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \frac{Z^2 m_e}{2\hbar^2 n^2}} \tag{2.68}$$

This is Bohr's expression for the allowed energies of the one-electron atom.

We now turn to Eq. (2.45) which gives the possible spectral lines. We rewrite the equation in the form

$$\tilde{\nu} = \nu/c = (E_m - E_n)/hc \qquad n < m, \tag{2.69}$$

and insert the values for E_m and E_n from the above equation. This gives

$$\tilde{\nu} = Z^2 R_\infty \left(\frac{1}{n^2} - \frac{1}{m^2}\right) \tag{2.70}$$

where

$$\boxed{R_\infty = \left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \frac{m_e}{4\pi c\hbar^3} = 1.09737 \times 10^7\,\mathrm{m}^{-1}} \tag{2.71}$$

Eq. (2.70) has exactly the same form as the experimentally derived Rydberg formula (1.9). We even see that R_∞ and R_H are identical to within the accuracy with which the latter is quoted in Eq. (1.8). Thus, Bohr's theory is in fact capable of reproducing the actual spectrum of hydrogen, and the quantum condition (2.46) must conceal something essential about the internal dynamics of the one-electron atom.

A more exact value for R_H is, however

$$R_H = 1.09679 \times 10^7\,\mathrm{m}^{-1} \tag{2.72}$$

which deviates 0.05% from R_∞. But this discrepancy is readily accounted for by relaxing the condition that the atomic nucleus be at rest. As we shall discuss it later (Sec. 8.1), the effect of taking the motion of the nucleus into account simply amounts to replacing m_e in Eq. (2.71) by the *reduced mass*

$$\mu = \frac{m_e m_n}{m_e + m_n} \tag{2.73}$$

where m_n is the mass of the nucleus. Thus, R_∞ really corresponds to an infinitely heavy nucleus. With m_n equal to the proton mass m_p as given by Eq. (1.16) we get

$$\mu = 0.99946\,m_e. \tag{2.74}$$

The replacement of m_e by μ yields $R_H = 1.09677 \times 10^7\,\mathrm{m}^{-1}$. Thus, the agreement with Bohr's theory is restored.

Still, the position of spectral lines may be measured with an accuracy that corresponds to three more digits in R_H and R_∞ than given above. Such accurate measurements reveal that what was so far treated as single lines are in fact groups of two or more lines that lie very close together. The spectrum shows a so-called fine structure. This fine structure is further enhanced when the emitting or absorbing atoms are subjected to electric and magnetic fields.

In the years following 1913, great efforts were made to extend the Bohr theory so that the fine structure could be accounted for. These efforts were to a large extent successful. The German physicist Arnold Sommerfeld replaced

Bohr's circular orbits with elliptical orbits, and new quantum numbers were introduced in addition to the quantum number n above. Also, relativistic corrections were included and their effect accounted for.

But the extension to atoms with more than a single electron turned out to represent too big a challenge for Bohr-like theories. Some very important qualitative results were obtained, however, the most conspicuous being Bohr's explanation of the periodic table in terms of rings of electrons at various distances from the nucleus, in 1921.[19] This account was almost directly translatable to the proper quantum-mechanical language that finally came into being.

The quantum mechanical theories that we have considered in the present chapter constitute what we now call the *old quantum mechanics.* It developed over a period of 25 years and, in spite of all its incompleteness, it gave considerable insight in atomic structure, much less insight in molecular structure, however.

The old quantum mechanics was, as we have seen, really classical mechanics subjected to quantization conditions. A rich formalism was developed around the problem of quantization, but we shall not consider this formalism further here. It is, however, worth while emphasizing that it is still a very useful formalism. It includes, in particular, valuable formulations of quantum mechanics in the so-called semiclassical limit.

We complete this chapter on the birth of quantum mechanics with the introduction of *matter waves*, the so-called *de Broglie waves.*

2.6 De Broglie Waves

In the previous sections we have learned that electrodynamic radiation is composed of photons. A photon has zero mass and moves with the speed of light. It is defined by its energy, ε, and its linear momentum, $\boldsymbol{p}$, whose direction is the direction of propagation and whose magnitude is $p = \varepsilon/c$.

We have, however, also learned that we may associate an electromagnetic wave with the same photon. The frequency, ν, and the wavelength, λ, of this wave correspond to the relation

$$(\boldsymbol{p}, \frac{1}{c}\varepsilon) = (\frac{h}{\lambda}\boldsymbol{n}, \frac{1}{c}h\nu) \tag{2.75}$$

where $\boldsymbol{n}$ is a unit vector in $\boldsymbol{p}$'s direction.

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[19] N. Bohr, Dansk Fys. Tidsskr. **19**, 153 (1921), Z. Phys. **9**, 1 (1922).

In 1924, the French physicist Louis de Broglie made the suggestion that this relation is valid for all types of particles, whether or not they are carriers of mass, when ε is taken to be the relativistic energy as defined by Eq. (2.28), or Eq. (2.30) when v/c is small.[20] He was led to this suggestion by studying a parallelism between the description of wave propagation and the description of particle motion in an advanced formulation of classical mechanics due to the nineteenth century mathematical physicists William Rowan Hamilton in Ireland and Carl Gustav Jacobi in Germany. He was also governed by relativistic considerations, of which the simplest was that both sides of Eq. (2.75) represent 4-vectors. This has the consequence that the relation is invariant under Lorentz transformations. We must of course desist from reproducing de Broglie's analysis here.

For a particle with mass m (and v/c small) we have that $p = mv$, and hence that

$$\boxed{\lambda = \frac{h}{mv}} \tag{2.76}$$

λ is called the *de Broglie wavelength* of the particle. We see that heavy particles and particles moving at high speed have the shorter de Broglie wavelengths.

Let us calculate the de Broglie wavelength, λ_n, for an electron in the n'th Bohr orbit. The radius, r_n, of the orbit and the linear momentum, p_n, are related by the quantum condition (2.53), i. e.,

$$r_n p_n = n\hbar. \tag{2.77}$$

We get, accordingly:

$$\lambda_n = \frac{h}{p_n} = \frac{2\pi r_n}{n} \tag{2.78}$$

or,

$$2\pi r_n = n\lambda_n. \tag{2.79}$$

Thus, the circumference of the n'th Bohr orbit equals exactly n de Broglie wavelengths. If we view the amplitude of a wave as a succession of troughs and crests, then the wavelength is defined as the distance between neighboring

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[20] L. de Broglie, Ann. de Physique **3**, 22 (1925). The article is based on de Broglie's thesis from 1924, republished under the title *Recherches sur la théorie des quanta*, Masson, Paris, 1963.

crests (or troughs). That a de Broglie wave satisfies Eq. (2.79) implies, therefore, that the amplitude varies continuously and matches itself as we follow it all the way around a Bohr orbit. Such a way wave may be construed of as a stationary, or standing wave.

The fact that the stationary states of Bohr are exactly those that correspond to stationary waves associated with the atomic electron threw new light on the real meaning of the quantum condition (2.46). It was an important finding on the way toward the exact theory. But apart from that, the concept of de Broglie waves alone was unable to throw further light on the internal structure of atoms and molecules.

The concept has proven much more useful in the description of free particles and the center-of-mass motion of atoms and molecules. For electrons, the reality of matter waves was experimentally proven in 1927 by the American physicists Clinton Davisson and Lester Halbert Germer, and by the English physicist George Paget Thomson (the son of J. J. Thomson). Davisson and Germer obtained diffraction patterns of electrons reflected from a nickel surface, of a similar type as the diffraction patterns produced by x-rays. Thomson, on the other hand, observed diffraction rings upon the passage of electrons through thin metal sheets.

Precise studies of matter waves may be carried out by experiments based on the diffraction at single-, double- and multiple-slit assemblies. Consider, for instance, a planar plate with a narrow rectangular opening of width b—this is a *slit*, and imagine a wave with wavelength λ falling perpendicularly upon the plate. We may then observe a diffracted wave behind the slit and study it in a plane parallel to the plate. Let the distance between the plate and the plane of observation be L, and let z be the coordinate in the direction across the slit. The intensity in the plane of observation may for instance vary with z as shown by the upper graph in Fig. 2.6. Next, add another slit parallel to the first. The intensity we observe will now have a much richer structure, like the one shown by the lower graph (for which the distance between the centerlines of the two slits was chosen to be $5b$). This richer structure is due to *interference* between the elementary waves emerging from the two slits. The interference may be understood as follows, by drawing on the general rule that the intensity of a wave with amplitude φ is $|\varphi|^2 = \varphi^*\varphi$, where * means complex conjugation.

Let $\varphi_1(z)$ be the amplitude of the wave emerging from the first slit. With the second slit absent, we measure the intensity $|\varphi_1(z)|^2$ along z (upper graph in Fig. 2.6). Next, let $\varphi_2(z)$ be the amplitude of the wave emerging from the second slit. With the first slit absent, it gives rise to the intensity $|\varphi_2(z)|^2$ along z. If the two slits are exactly similar, and L is large, we have that

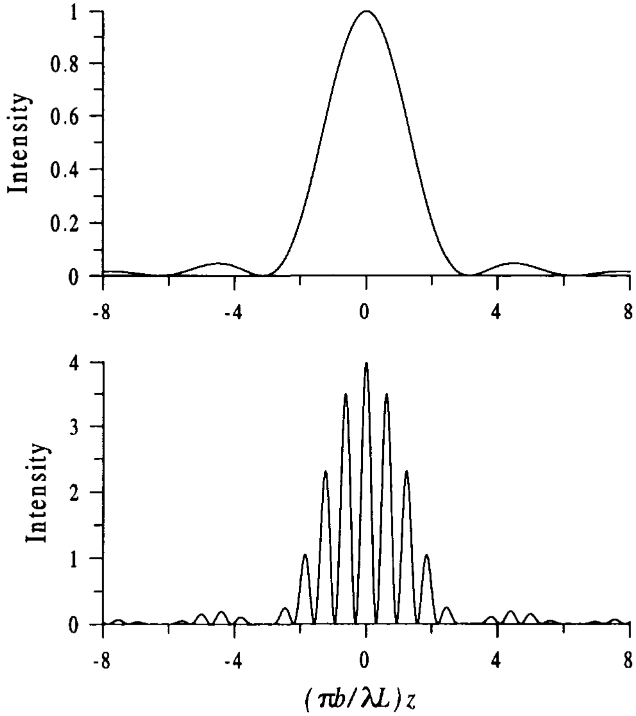

Figure 2.6: Single- and double-slit experiments. See the text for a detailed description.

$|\varphi_2(z)|^2 \approx |\varphi_1(z)|^2$. With both slits open, we might therefore expect to observe the intensity distribution $2|\varphi_1(z)|^2$. But this is not how waves behave. The *rule of superposition* for waves is that it is the amplitudes that should be added, not the intensities. With both slits open, we will therefore observe the *amplitude*

$$\varphi(z) = \varphi_1(z) + \varphi_2(z) \tag{2.80}$$

along z. The intensity will be

$$|\varphi(z)|^2 = |\varphi_1(z)|^2 + |\varphi_2(z)|^2 + \varphi_1^*(z)\varphi_2(z) + \varphi_1(z)\varphi_2^*(z). \tag{2.81}$$

It is the last two terms that represent the interference between the elementary de Broglie waves emerging from the two slits and gives rise to the oscillatory structure in the lower graph.

The graphs of Fig. 2.6 are theoretically calculated graphs, based on what is known as Kirchhoff diffraction theory[21] in the Fraunhofer region. This region corresponds to large values of L. For smaller values of L, one must work in the so-called Fresnel region. This results in qualitatively similar graphs. There are, however, quantitative differences, one being for instance that the intensity as a function of z no longer drops completely to zero at the displayed minima. The most precise experiments require the Fresnel description for their interpretation.

Thanks to great advances in beam- and laser-technology it is now possible to perform very accurate diffraction experiments over a large range of de Broglie wavelengths. Thus, accurate double- and multiple-slit experiments have been carried out for systems as different as neutrons,[22] Na atoms and Na_2 molecules,[23] and C_{60} molecules.[24] In every case, it has been possible to interpret the results as diffraction of the de Broglie waves associated with the center-of-mass motion of the particles.

It is essential to realize that the way graphs like those in Fig. 2.6 are verified experimentally is by directing a beam of particles toward the diffraction plate and then measure the arrival of each particle in the plane of observation. The beam is sufficiently dilute that the particles do not interact. Hence the particles pass through the slits one after another and arrive at the plane of observation independently. It appears that they arrive at mutually random positions. However, after the passage of a large number of particles a pattern begins to build up. There are positions where particles hit frequently and positions where only a few particles are observed. Eventually, when a sufficiently large number of particles have arrived, it becomes possible to draw a stable graph of the number of hits as a function of position. With a single slit open, this graph will reproduce the upper graph in Fig. 2.6. With two slits open, it will reproduce the lower graph.

Thus, the diffraction of a single de Broglie wave really reflects the cumulative result obtained by performing the same experiment a very large number of times on identical copies of a single particle. This is the essence of the wave-particle dualism.

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[21] See, for instance, M. Born and E. Wolf, *Principles of Optics*, Cambridge University Press, Cambridge, 1999.

[22] A. Zeilinger, R. Gähler, C. G. Shull, W. Treimer, and W. Mampe, Rev. Mod. Phys. **60**, 1067 (1988).

[23] M. S. Chapman, C. R. Ekstrom, T. D. Hammond, R. A. Rubenstein, J. Schmiedmayer, S. Wehinger, and D. E. Pritchard, Phys. Rev. Letters **74**, 4783 (1995).

[24] M. Arndt, O. Nairz, J. Vos-Andreae, C. Keller, G. van der Zouw, and A. Zeilinger, Nature **401**, 680 (1999).

The wave-particle dualism is of fundamental importance for our description of atoms and molecules, and the elementary particles of which they are composed. But how can we understand this dualism in a rational way, without the many ad hoc assumptions that we have so far had to accept. The answer to this question is given by the exact theory of modern quantum mechanics, to which we now turn. As far as de Broglie waves are concerned, we shall meet them again in Chapter 6, which deals with the exact quantum-mechanical description of free-particle motion.

Supplementary Reading

The bibliography, entries [4] and [5].

Problems

2.1. Calculate the intensity of emission ($\mathrm{W\,m^{-2}}$) from a 'black body' at 800 K (the temperature of dark-red iron).
Next, calculate the energy density ($\mathrm{J\,cm^{-3}}$) in the radiation field inside an oven with 'black walls' at 800 K.
Calculate the number of photons/cm^3 in the oven, again at 800 K.

2.2. When a lithium crystal is irradiated with light of wavelengths 300 nm and 400 nm photoelectrons are emitted with maximum kinetic energies 1.83 eV and 0.80 eV, respectively. From this information, calculate the Planck constant, the wavelength corresponding to the threshold frequency ν_0, and the work function W for lithium.

2.3. By means of lasers it has become possible to produce hydrogen-like atoms with n-values exceeding 300, and in interstellar space atoms with even higher n-values have been observed.
From the Bohr model calculate the 'diameter' of a hydrogen atom with $n = 732$. Also calculate the value of the wavenumber $\tilde{\nu}$ corresponding to to the transition from $n = 732$ to $n = 731$.

2.4. What is the value of v/c for an electron in the first Bohr orbit for hydrogen, and for a one-electron atom with $Z = 54$? (v is the velocity of the electron.)

2.5. Calculate the de Broglie wavelength of

a. An electron with the kinetic energy 10 eV.
b. A neutron with the velocity $220\,\mathrm{m\,s^{-1}}$.
c. A Na atom with the velocity $830\,\mathrm{m\,s^{-1}}$.

d. A Na_2 molecule with the velocity $830\,\mathrm{m\,s^{-1}}$.
e. A C_{60} molecule with the velocity $220\,\mathrm{m\,s^{-1}}$.

(The atomic masses of Na and C are 22.990 u and 12.000 u, respectively; $1\,\mathrm{u} = 1.66054 \times 10^{-27}\,\mathrm{kg}$.)

2.6. By directing a 589 nm laser beam toward a well-focused beam of Na atoms and Na_2 molecules, at right angles, it is possible to separate the Na atoms from the Na_2 molecules. The wavelength 589 nm corresponds to a strongly allowed electronic transition in the Na atom, and the atom is therefore most likely to absorb a photon from the laser beam. The momentum delivered by the photon is essentially big enough to remove the atom from the beam.
Calculate the magnitude of the momentum delivered by the photon, and the velocity component that the atom acquires in the direction of the laser beam as a result of the momentum transfer.

Chapter 3

Wave Mechanics

Contents

The exact foundation of modern quantum mechanics was laid within a few consecutive months of 1925–1926, by the German physicists Werner Heisenberg, Max Born and Pascual Jordan,[1] and by the Austrian physicist Erwin Schrödinger.[2] Important contributions were also made by the English physicist Paul Adrien Maurice Dirac.[3] The formulation by the first three men is usually referred to as Heisenberg's matrix mechanics, while Schrödinger's formulation is known as Schrödinger's wave mechanics.

At the outset, these two versions of quantum mechanics appeared very different, but it was soon realized that they were in fact equivalent, and that they

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[1] W. Heisenberg, Z. Phys. **33**, 879 (1925); M. Born and P. Jordan, Z. Phys. **34**, 858 (1925); M. Born, W. Heisenberg and P. Jordan, **35**, 557 (1926).

[2] E. Schrödinger, Ann. Physik **79**, 361 (1926); **79**, 489 (1926); **80**, 437 (1926); **81**, 109 (1926).

[3] P. A. M. Dirac, Proc. Roy. Soc. A **109**, 642 (1926); **110**, 561 (1926).

merely represented two different entrances to the same theory. Subsequently, other entrances were added, and the science of quantum mechanics may today be approached from several different angles. This diversity reflects the rich structure of the science. It also deepens the understanding and facilitates the applications. Schrödinger's approach is probably the most readily accessible, so it is the one we shall follow. But as we get deeper into the quantum mechanical world, we shall gradually enrich our language by looking out toward some of the other entrances. Heisenberg's formulation is, in particular, briefly discussed at the end of Section 5.10.

In this chapter, we introduce the basic elements of wave mechanics and set up the Schrödinger equation for a particle in a potential field. The Schrödinger equation is the proper equation of motion for particles that move with a moderate speed. For a particle that moves with velocities comparable to the speed of light, it must be replaced by its relativistic counterpart, the Dirac equation.[4]

3.1 The Time-Dependent Schrödinger Equation

In Section 2.6 we saw how de Broglie was able to associate a stationary wave with the stationary orbits in Bohr's atomic model. Apart from this, the de Broglie theory threw no new light on the structure of the atom. But it was an important stepping stone, and it inspired the Austrian physicist Erwin Schrödinger to look for a description of atomic structure in terms of functions, but note, functions defined *everywhere* within the atom, not merely on selected classical orbits. He set up a differential equation by means of which these functions could be determined and found the energies of the one-electron atom without any introduction of ad hoc assumptions. The new functions were called *wavefunctions*.

Schrödinger published the results of his analysis in a series of four papers (See footnote 2), and added a fifth[5] on the connection between his and Heisenberg's approach. In the set of four papers he determined the wavefunctions and energies for the stationary states of the one-electron atom, the harmonic oscillator, and the rigid and non-rigid rotators that model the rotation of a diatomic molecule. He also studied the influence of an external electric field on the hydrogenic spectrum (the so-called *Stark effect*), and to this end he introduced the approximate treatment now known as *Schrödinger perturbation theory*. The stationary states and their changes in the electric field were de-

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[4] P. A. M. Dirac, Proc. Roy. Soc. A **117**, 610 (1926).

[5] E. Schrödinger, Ann. Physik **79**, 734 (1926).

scribed by means of time-independent functions. The actual time dependence of the wavefunctions was introduced in the fourth paper, which therefore also opened for an exact description of non-stationary quantum states.

We shall include the time from the very beginning and thus begin by presenting the *time-dependent Schrödinger equation*. But let us first remind ourselves that elementary particles are carriers of spin (Section 1.7). The hypothesis of the spin had been forwarded by the Dutch physicists George Eugene Uhlenbeck and Samuel Abraham Goudsmit in 1925. It was known to Schrödinger, and the complications caused by the presence of spin were the reason why he excluded the treatment of the hydrogenic atom in a static magnetic field from his analysis. As long as we exclude magnetic fields and only treat single-particle problems it is a good approximation to neglect the spin. Like Schrödinger, we shall therefore postpone its incorporation into the theory. With these remarks, the time-dependent Schrödinger equation for a single particle with mass m reads

$$\boxed{i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} + \frac{\partial^2\Psi}{\partial z^2}\right) + V\Psi} \tag{3.1}$$

where i is the imaginary unit ($i^2 = -1$). $\Psi = \Psi(x,y,z,t) = \Psi(\boldsymbol{r},t)$ is the wavefunction and $V = V(x,y,z,t) = V(\boldsymbol{r},t)$ is the potential-energy function. This is the same function as in classical mechanics. It determines the force on the particle, as the *negative gradient* of V,

$$\boxed{\boldsymbol{F}(\boldsymbol{r},t) = -\nabla V(\boldsymbol{r},t) = -\left(\frac{\partial V}{\partial x}, \frac{\partial V}{\partial y}, \frac{\partial V}{\partial z}\right)} \tag{3.2}$$

Eq. (3.1) is an *equation of motion* for Ψ. For if we know the wavefunction $\Psi(\boldsymbol{r},t_0)$ at some initial time t_0, then the equation gives us the wavefunction at time $t_0 + \delta t$, where δt is infinitesimal. To see this, we write the unknown function $\Psi(\boldsymbol{r},t_0+\delta t)$ as $\Psi(\boldsymbol{r},t_0+\delta t) = \Psi(\boldsymbol{r},t_0) + \delta\Psi(\boldsymbol{r})$, and ask for the form of $\delta\Psi(\boldsymbol{r})$. Replacing $\partial\Psi/\partial t$ in Eq. (3.1) by $\delta\Psi/\delta t$ gives

$$\begin{aligned}\delta\Psi = \frac{\delta t}{i\hbar}\Bigg\{ &-\frac{\hbar^2}{2m}\left(\frac{\partial^2\Psi(\boldsymbol{r},t_0)}{\partial x^2} + \frac{\partial^2\Psi(\boldsymbol{r},t_0)}{\partial y^2} + \frac{\partial^2\Psi(\boldsymbol{r},t_0)}{\partial z^2}\right) \\ &+ V(\boldsymbol{r},t_0)\Psi(\boldsymbol{r},t_0)\Bigg\}.\end{aligned} \tag{3.3}$$

This equation determines $\delta\Psi(\boldsymbol{r})$ and hence $\Psi(\boldsymbol{r}, t_0 + \delta t)$ from the known function $\Psi(\boldsymbol{r}, t_0)$. Next, we can determine $\Psi(\boldsymbol{r}, t_0 + 2\delta t)$ from $\Psi(\boldsymbol{r}, t_0 + \delta t)$ in a similar way. Thus, by continued iteration, Eq. (3.1) determines $\Psi(\boldsymbol{r}, t)$ at any later time from $\Psi(\boldsymbol{r}, t_0)$ at time t_0. So, it is in fact an equation of motion.

As to the permissible form of $\Psi(\boldsymbol{r}, t_0)$, it is only restricted by the conditions of continuity and integrability to be discussed in Section 3.4. In practice, we fix $\Psi(\boldsymbol{r}, t_0)$ by the *preparation* of the system, i. e., through some controlled experimental situation at time t_0.

Let us now consider a so-called *conservative* system, i. e. a system for which the potential energy function V is independent of time,

$$V = V(x, y, z) = V(\boldsymbol{r}). \tag{3.4}$$

Eq. (3.1) will then have particular solutions of the form

$$\boxed{\Psi(\boldsymbol{r}, t) = \psi(\boldsymbol{r})e^{-iEt/\hbar}} \tag{3.5}$$

To verify this, one simply inserts the expression (3.5) in Eq. (3.1) and performs the differentiation with respect to t. This gives

$$\begin{aligned} i\hbar(-iE/\hbar)\psi(\boldsymbol{r})e^{-iEt/\hbar} = \Bigg\{ -\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi(\boldsymbol{r})}{\partial x^2} + \frac{\partial^2\psi(\boldsymbol{r})}{\partial y^2} + \frac{\partial^2\psi(\boldsymbol{r})}{\partial z^2}\right) \\ + V(\boldsymbol{r})\psi(\boldsymbol{r})\Bigg\}e^{-iEt/\hbar}. \end{aligned} \tag{3.6}$$

The exponentials on the two sides of the equation cancel out, and $i(-i) = 1$. Thus, Eq. (3.1) will be satisfied, provided $\psi(\boldsymbol{r})$ is a solution of the equation

$$\boxed{-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi(\boldsymbol{r})}{\partial x^2} + \frac{\partial^2\psi(\boldsymbol{r})}{\partial y^2} + \frac{\partial^2\psi(\boldsymbol{r})}{\partial z^2}\right) + V(\boldsymbol{r})\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r})} \tag{3.7}$$

A wavefunction of the particular form (3.5) is said to describe a stationary state with energy E. Wavefunctions describing stationary states play a fundamental role in the applications. They are the exact substitutes for the Bohr orbits of the old quantum mechanics. Eq. (3.7) is the *time-independent Schrödinger equation* which we shall now proceed to discuss. Later, we shall consider non-stationary states, for which the time dependence of the wavefunction is more complicated than in Eq. (3.5). We shall also consider non-conservative systems, for which the potential energy function depends on the time.

3.2 The Time-Independent Schrödinger Equation

Eq. (3.7) which determines the stationary states of a particle with mass m in the potential $V(\boldsymbol{r})$ is a second-order partial differential equation. It has solutions for every value of E, but only certain solutions are physically acceptable. Schrödinger put the restrictions on an acceptable ψ, that it should be singlevalued and finite everywhere, and that the second derivatives in Eq. (3.7) should exist and be continuous everywhere (except perhaps at isolated points). With these restrictions it is found that not all values of E lead to acceptable solutions. Those values that do are called the eigenvalues of the equation, and in accordance with this, Schrödinger called his set of four papers *Quantisierung als Eigenwertproblem* (Quantization as an eigenvalue problem).

The eigenvalues E determine the spectrum of the energy.[6] For the hydrogen-like atom, the spectrum is found to consist of a discrete part with negative values of E and a continuous part with positive values of E. For the harmonic oscillator, all allowed values of E are positive and the whole energy spectrum is discrete.

It is found that a wavefunction going with a value of E from the discrete part of an energy spectrum vanishes at infinity and moreover is *square integrable*, i. e., the integral of $|\psi|^2 = \psi^*\psi$ taken over all space is finite. For a wavefunction going with an energy value from a continuous spectrum, ψ stays non-zero at infinity and the integral of $\psi^*\psi$ does not exist. As in Sec. 2.6, the symbol * means complex conjugation. ψ^* is the complex conjugate of ψ, and hence different from ψ unless ψ is real. The quantity $\psi^*\psi$ is always real and non-negative (See also Appendix A).

A square-integrable wavefunction, ψ, may always be so chosen that it is *normalized to unity*, by which we mean that

$$\int \psi^*\psi dv = \int \psi^*\psi dx dy dz = 1, \tag{3.8}$$

where the integration is extended over all space. The possibility of imposing this *normalization condition* on ψ becomes obvious when we look at the form of the Schrödinger equation (3.7). For it is readily seen, by insertion, that if ψ is a solution then so is $c\psi$, where c is any real or complex number. We say that Eq. (3.7) is a *homogeneous* differential equation. All functions of the form $c\psi$,

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[6] The spectrum of a physical quantity was defined in Section 1.8 as the set of values that the quantity may take.

with c different from zero, are understood to define the same physical state, and hence we may choose to represent the state by a normalized wavefunction.

At this stage two questions present themselves:

1. How did Schrödinger arrive at the exact form of his equation?
2. What is the interpretation of the wavefunction?

We shall answer these questions in the following sections.

3.3 Schrödinger Operators

The answer to the first question above is that Schrödinger, like de Broglie before him, was well versed in the Hamilton–Jacobi formalism of classical mechanics, and that his intuition led him the one and decisive step beyond de Broglie. Schrödinger did not derive his equation from classical mechanics. For that is impossible since quantum mechanics is not a part of classical mechanics. But classical mechanics is, on the other hand, a certain limit form of quantum mechanics, and so it is in fact possible to derive classical mechanics from quantum mechanics. It is especially easy to pass from quantum mechanics to the Hamilton–Jacobi formulation of classical mechanics. There is no route the other way. Yet, Schrödinger saw how to make the jump.

Although the Schrödinger equation cannot be derived from classical mechanics it is found that we can, in fact, generate it from the expressions of classical mechanics in a purely formal way. Namely, one replaces the dynamical functions of classical mechanics (like position, linear momentum, energy, etc.) by *operators*. The remarkable recipe, which is also due to Schrödinger, is the following.

Turn the three Cartesian components of the linear momentum (p_x, p_y, p_z) into three operators $(\hat{p}_x, \hat{p}_y, \hat{p}_z)$ according to the rule

$$\boxed{(\hat{p}_x, \hat{p}_y, \hat{p}_z) = \left(-i\hbar\frac{\partial}{\partial x}, -i\hbar\frac{\partial}{\partial y}, -i\hbar\frac{\partial}{\partial z}\right)} \tag{3.9}$$

and let, for instance, $\hat{p}_x^2$ mean $\hat{p}_x$ applied twice, such that

$$\hat{p}_x^2 = \left(-i\hbar\frac{\partial}{\partial x}\right)\left(-i\hbar\frac{\partial}{\partial x}\right) = -\hbar^2\frac{\partial^2}{\partial x^2}. \tag{3.10}$$

Then the kinetic energy $T = p^2/2m$ is transformed into the operator

$$\widehat{T} = \frac{\hat{p}^2}{2m} = \frac{1}{2m}\left(\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2\right) = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right). \tag{3.11}$$

Next, turn the position coordinates (x, y, z) into operators according to the trivial rule

$$(\hat{x}, \hat{y}, \hat{z}) = (x, y, z) \tag{3.12}$$

Then the potential energy is trivially transformed into

$$\widehat{V}(\hat{x}, \hat{y}, \hat{z}) = V(x, y, z). \tag{3.13}$$

The so-called *Hamiltonian*,

$$H(p_x, p_y, p_z, x, y, z) = T(p_x, p_y, p_z) + V(x, y, z), \tag{3.14}$$

which gives the classical energy of a particle, if its kinetic energy is T and its position is (x, y, z), is transformed into the operator

$$\boxed{\widehat{H} = \widehat{T} + \widehat{V}} \tag{3.15}$$

i. e.,

$$\boxed{\widehat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(x, y, x)} \tag{3.16}$$

Having constructed our quantum-mechanical operators, we must introduce something for them to act upon. Otherwise they are devoid of meaning. This something is the wavefunction. We see that the Schrödinger equation (3.7) may in fact be written

$$\boxed{\widehat{H}\psi = E\psi} \tag{3.17}$$

In words: When the Hamiltonian (operator) acts on the wavefunction of a stationary state, we get the wavefunction back again, but multiplied by the energy of the state. We say that ψ is an *eigenfunction* of $\widehat{H}$, and that E is its *eigenvalue*.

Eq. (3.17) is a transparent way of writing the time-independent Schrödinger equation. The time-dependent Schrödinger equation, Eq. (3.1), may be written in the equally transparent way,

$$\boxed{i\hbar\frac{\partial\Psi}{\partial t}=\widehat{H}\Psi} \tag{3.18}$$

With reference to the discussion around Eq. (3.3), this equation says that the Hamiltonian $\widehat{H}$ is the *generator of the motion*: from the wavefunction at some time t_0, it generates the wavefunction at any later time t. This is a very fundamental way of interpreting $\widehat{H}$.

The process of *quantization* which we have carried through in the present section may be directly transferred to systems with more than a single particle. Thus, the Schrödinger equation for such systems is easily written down, and we shall of course give several examples of this in the following chapters. For now, we shall turn to the second of the questions posed at the end of the preceding section.

3.4 The Statistical Interpretation

Having introduced the wavefunction, Schrödinger worried a lot about its physical interpretation. At first, he believed that an atomic wavefunction in some way must describe a real oscillation within the atom and that $\Psi(\boldsymbol{r},t)^*\Psi(\boldsymbol{r},t)$ might represent the distribution of negative charge. It was, however, difficult to apply this picture to a many-electron atom, and it had to be abandoned.

It was Max Born who gave the wavefunction its present interpretation.[7] It is one that we will have to look at from different angles in order to understand its full implication, and we shall do so as we go along. But for the present, the simple statement will do, that provided the wavefunction $\Psi(\boldsymbol{r},t)$ is normalized to unity,

$$\int\Psi^*(\boldsymbol{r},t)\Psi(\boldsymbol{r},t)dv=1, \tag{3.19}$$

with the integration extended over all space, then

$$\boxed{|\Psi(\boldsymbol{r},t)|^2=\Psi^*(\boldsymbol{r},t)\Psi(\boldsymbol{r},t)\text{ is a \textit{probability density}}} \tag{3.20}$$

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[7] M. Born, Z. Phys. **37**, 863 (1926); Nature **119**, 354 (1927).

What this means is that the quantity

$$\Psi^* \Psi dv = \Psi^*(\boldsymbol{r},t)\Psi(\boldsymbol{r},t)dxdydz \tag{3.21}$$

is the probability of finding the electron (or whatever particle we are studying) around the point $\boldsymbol{r} = (x,y,z)$ in the volume element $dv = dxdydz$, at time t. This interpretation allows our particle to be observed around a definite point in space, but only with a certain probability. We can never say exactly where the particle is or claim that we can describe exactly how it moves. The only statements that may be made are entirely statistical.

With this interpretation of $\Psi(\boldsymbol{r},t)$, Eq. (3.19) simply states that the probability of finding the particle *somewhere* in space is unity. It is of course an absolute requirement that the particle must be somewhere, and hence we deduce that only square-integrable wavefunctions can represent physical states. For a stationary state with the wavefunction (3.5) we get, in particular

$$\Psi^*(\boldsymbol{r},t)\Psi(\boldsymbol{r},t) = \psi^*(\boldsymbol{r})e^{iEt/\hbar}\psi(\boldsymbol{r})e^{-iEt/\hbar} = \psi^*(\boldsymbol{r})\psi(\boldsymbol{r}). \tag{3.22}$$

Thus, we learn that the probability density associated with a stationary state is independent of time. This is, in fact, the reason for calling the state stationary.

In Section 3.2 we pointed out, that for a stationary-state wavefunction to be square integrable, it must go with a value of E from the discrete part of the energy spectrum. For a wavefunction going with an energy value from a continuous spectrum, ψ stays non-zero at infinity and the integral of $\psi^*\psi$ does not exist. Hence, wavefunctions of this type cannot represent physical states in a strict sense. This, however, does not imply that such wavefunctions are without physical significance. We shall come back to this point in Section 6.1.

The interpretation of $\Psi^*(\boldsymbol{r},t)\Psi(\boldsymbol{r},t)$ as a probability density might well lead us to believe that all information about the quantum mechanical state of a particle is contained in this quantity. This is, however, far from being so. We shall see that Ψ may carry substantial information beyond that of $\Psi^*\Psi$, and that this information allows us to make statistical predictions about other properties than the position of the particle. One such property is, for instance, the linear momentum.

We shall often use the word *probability amplitude* for Ψ. This notion reflects that Ψ is a quantity from which various probabilities *may be calculated* and used to predict the possible outcome of experiments. A quantity of this type is all that we can ever arrive at. Correspondingly, the outcome of an experiment involving an elementary particle like an electron must also be statistical. The fact that this is always found to be the case is the confirmation that our interpretation of Ψ is the correct one.

That the outcome of an experiment must be statistical, marks a fundamental difference between classical mechanics and quantum mechanics. As we have put it above: we can never say exactly where the particle is or claim that we can describe exactly how it moves. Yet, the wavefunction that describes the motion in the quantum mechanical sense is a well-defined quantity, and the time-dependent Schrödinger equation allows us to follow its detailed evolution in time.

Note that these considerations are similar to those we made in order to interpret the diffraction of a de Broglie wave at the end of the previous chapter. The de Broglie wave is a well-defined quantity that leads to a unique intensity distribution in the plane of observation. Yet, we cannot tell where a particular particle will hit the plane. What the said intensity distribution gives us is the probability with which the particle hits at the various points in the plane.

This is indeed a new world. It takes some time and effort to become familiar with it. So let us try to gain understanding by solving real problems, and let us actually begin by determining the form of the stationary-state wavefunctions in some simple cases. We shall enter into thorougher discussion of the statistical interpretation in Section 5.5.

Supplementary Reading

The bibliography, entries [6], [10], [7] and [11].

Problems

3.1. For a particle restricted to moving in a single dimension,which of the following functions are physically acceptable as wavefunctions according to the criteria set up in Sec. 3.2:

$$\psi(x) = x^2,\ e^{-x},\ e^{-x^2},\ \cos x,\ e^{ix}, \qquad -\infty < x < \infty$$

Which of the functions are square integrable?

3.2. Show that the function

$$\psi(x) = \sqrt{2}e^{-x}$$

is normalized to unity on the interval $0 \leq x < \infty$.
Determine the constants N_1 and N_2 such that the functions

$$\psi_1(\theta) = N_1 \cos\theta$$

and

$$\psi_2(\theta) = N_2 e^{i\theta}$$

are normalized to unity on the interval $0 \leq \theta < 2\pi$.
Plot the probability densities $\psi_1(\theta)^*\psi_1(\theta)$ and $\psi_2(\theta)^*\psi_2(\theta)$.

3.3. The function

$$\psi(x) = (\pi)^{-\frac{1}{4}} e^{-\frac{1}{2}x^2}$$

is normalized to unity on the interval $-\infty < x < \infty$. Evaluate

$$\hat{p}_x\psi(x),\ \hat{p}_x^2\psi(x),\ \hat{x}\hat{p}_x\psi(x),\ \hat{p}_x\hat{x}\psi(x)$$

and

$$\tfrac{1}{2}(\hat{x}\hat{p}_x + \hat{p}_x\hat{x})\psi(x), \qquad \tfrac{1}{2}(\hat{x}\hat{p}_x - \hat{p}_x\hat{x})\psi(x).$$

Note that $xp_x = p_x x$, whereas $\hat{x}\hat{p}_x \neq \hat{p}_x\hat{x}$. Hence, Schrödinger's prescription does not give a unique result for the operator corresponding to the classical quantity xp_x. The proper operator to use here is generally taken to be the symmetrized expression $\frac{1}{2}(\hat{x}\hat{p}_x + \hat{p}_x\hat{x})$.

Chapter 4

Particle in a Box

Contents

The time-independent Schrödinger equation for the one-electron atom is obtained from Eq. (3.7) by inserting the expression (2.65) for $V(\boldsymbol{r})$. The resulting differential equation is, however, too complicated to serve as our first example. We shall consider it later and study some easier problems first.

Much is learned by studying the simple problem called the particle in a box, which is the problem of free motion within a box, or cavity, of a specified shape. We shall consequently devote the present chapter to this problem. In particular, we shall consider a box of rectangular shape, as in Fig. 4.1.

We begin by noticing that the problem of solving the time-independent Schrödinger equation for the rectangular box may be reduced to that of solving the Schrödinger equation for the one-dimensional box, i. e., the motions in the x-, y- and z-directions may be treated separately. We shall therefore study the one-dimensional problem in detail, and subsequently construct the solution of the three-dimensional problem.

The wavefunctions for the particle in a box are analytically very simple, yet they have many qualitative properties in common with wavefunctions for more complicated systems. These properties, which include mutual orthogonality, nodal structure, symmetry, and degeneracy, are accordingly also illustrated and discussed in the present chapter.

Solving the Schrödinger equation for the particle in a box is, as already implied, not a big mathematical exercise. It is hence gratifying to note that the solutions of this problem may sometimes be used to crudely model the behavior of much more complex systems. As an example of this, we consider the electronic stucture of conjugated hydrocarbons in some detail.—We might equally well have considered an atomic nucleus, a molecular cluster or a simple metal.

The final section of the present chapter illustrates how the solutions of the time-independent Schrödinger equation allow us to construct wavefunctions for a general non-stationary state. It is also illustrated how the explicit time evolution of such a state may be easily determined from the time-dependent Schrödinger equation. Again, we use the solutions of a simple problem to display general behavior of quantum systems.

4.1 Introduction

To set up the Schrödinger equation for a particle enclosed in the rectangular box of Fig. 4.1, we must specify the potential energy function $V(\boldsymbol{r})$. Except for its confinement to the interior of the box, the particle is assumed to be free. Hence, we take the potential energy to be zero inside the box, so that the force defined by Eq. (3.2) vanishes. Outside the box, we let the potential energy tend to infinity. The wavefunction must therefore be zero outside the box, for otherwise $V\psi$ would be infinite there, and Eq. (3.7) could not be satisfied for a finite value of E. But if the wavefunction is zero outside the box, then it must also vanish on the walls of the box, by the requirement of continuity.

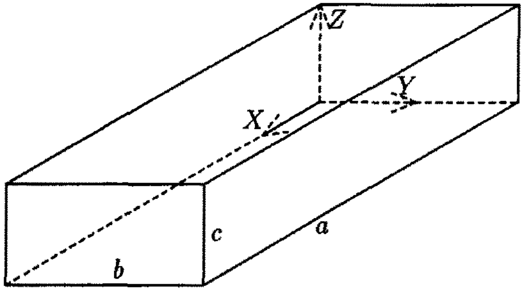

Figure 4.1: Three-dimensional rectangular box.

The acceptable solutions of Eq. (3.7) must accordingly satisfy the equation

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right)=E\psi \tag{4.1}$$

within the box and vanish on the walls of the box.

The requirement that ψ vanish on the walls of the box is called a *boundary condition.* Hence

> Our problem is to solve a partial differential equation with specified boundary conditions.

The problem of finding those solutions of a partial differential equation that satisfy a specified set of boundary conditions is a fundamental problem in mathematics, and it is frequently met in theoretical chemistry and physics. We meet it, for instance, in the study of sound, the study of electromagnetic fields, the study of heat conduction, and now in the study of quantum mechanics. The general theory is extensive, but specific methods have been developed to deal with large classes of special differential equations.[1]

Eq. (4.1) may be solved by the method called separation of variables, according to which one seeks solutions of the form

$$\psi(x,y,z)=X(x)Y(y)Z(z). \tag{4.2}$$

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[1] See, for example, P. Morse and H. Feshbach, *Methods of Theoretical Physics*, McGraw-Hill, New York, 1953, Chapter 5; or P. Dennery and A. Krzywicki, *Mathematics for Physicists*, Harper and Row, New York, 1967, Chapter 4.

That such a method may be applied here is due to the simplicity of the equation and the fact that the boundary conditions refer to planes of constant x, y, and z.

We begin by substituting the ansatz expression (4.2) into Eq. (4.1). This yields

$$-\frac{\hbar^2}{2m}\left\{Y(y)Z(z)\frac{d^2X}{dx^2}+X(x)Z(z)\frac{d^2Y}{dy^2}+X(x)Y(y)\frac{d^2Z}{dz^2}\right\}=EX(x)Y(y)Z(z). \tag{4.3}$$

We then divide on both sides of this equation by $X(x)Y(y)Z(z)$ and get

$$-\frac{\hbar^2}{2m}\left\{\frac{1}{X}\frac{d^2X}{dx^2}+\frac{1}{Y}\frac{d^2Y}{dy^2}+\frac{1}{Z}\frac{d^2Z}{dz^2}\right\}=E. \tag{4.4}$$

Next, we rewrite this equation in the form

$$-\frac{\hbar^2}{2m}\frac{1}{X(x)}\frac{d^2X}{dx^2}=\frac{\hbar^2}{2m}\left\{\frac{1}{Y(y)}\frac{d^2Y}{dy^2}+\frac{1}{Z(z)}\frac{d^2Z}{dz^2}\right\}+E. \tag{4.5}$$

The left-hand side of this equation, taken as a whole, is obviously a function of x, whereas the right-hand side is independent of x. Thus, the left-hand side is a function of x which does not depend upon x. The only such function is a constant Hence, the left-hand side must be a constant, E_x say. It follows that X must satisfy the differential equation

$$-\frac{\hbar^2}{2m}\frac{d^2X}{dx^2}=E_xX. \tag{4.6}$$

By a similar argument we find that Y and Z must satisfy the equations

$$-\frac{\hbar^2}{2m}\frac{d^2Y}{dy^2}=E_yY \tag{4.7}$$

and

$$-\frac{\hbar^2}{2m}\frac{d^2Z}{dz^2}=E_zZ. \tag{4.8}$$

Finally, a comparison with Eq. (4.4) shows that

$$E_x+E_y+E_z=E. \tag{4.9}$$

These four equations, Eqs. (4.6)–(4.9), are a direct consequence of the ansatz (4.2).

Thus, the problem of solving a differential equation of three variables has been reduced to that of solving three differential equations of a single variable. Moreover, the equations (4.6), (4.7), and (4.8) are all of the same form, so if we have solved one of them we have in fact solved them all. The boundary condition, that $\psi(x, y, z)$ vanish on the walls of the three-dimensional box, will be satisfied if

$$X(0) = X(a) = 0, \quad Y(0) = Y(b) = 0, \quad Z(0) = Z(c) = 0, \tag{4.10}$$

where a, b, and c are the lengths of the box edges, as in Fig. 4.1.

Let us now solve the first of the above equations, i. e., Eq. (4.6), with the boundary condition $X(0) = X(a) = 0$.

4.2 The One-Dimensional Box

Eq. (4.6), rewrittten here for convenience,

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2X}{dx^2} = E_x X} \tag{4.11}$$

may be interpreted as the Schrödinger equation for a particle restricted to move in a single dimension, the corresponding Hamiltonian being

$$\hat{H}_x = \frac{\hat{p}_x^2}{2m} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}. \tag{4.12}$$

In the following chapter, we shall see that Hamiltonians are so-called Hermitian operators, and that the eigenvalues of such operators are always real. Anticipating this result, we may assume E_x to be real in the ensuing analysis.

Now, we observe that not only is Eq. (4.11) a homogeneous differential equation (see Sec. 3.2), it is also a linear equation. By this we simply mean that it is linear in X and its derivatives (it contains no terms like X^2 or XdX/dx). Thus, Eq. (4.11) is a *homogeneous linear differential equation of second order*, and of a single variable, x.

The general theory of differential equations tells us that the complete solution of such an equation (for a given E_x) may be written in the form

$$X(x) = c_1 X_1(x) + c_2 X_2(x), \tag{4.13}$$

where X_1 and X_2 are two linearly independent solutions of the equation and c_1 and c_2 are arbitrary constants.

Eq. (4.11) has solutions of the type (4.13) for all real values of E_x. We must determine the values of E_x for which it is also possible to satisfy the boundary conditions $X(0) = 0$ and $X(a) = 0$.

Let us first consider negative values of E_x. It is then expedient to write:

$$E_x = -\frac{\hbar^2 \kappa^2}{2m}, \qquad \kappa > 0, \tag{4.14}$$

so that Eq. (4.11) assumes the simple form

$$\frac{d^2X}{dx^2} = \kappa^2 X. \tag{4.15}$$

It has the two independent solutions:

$$X_1(x) = e^{\kappa x}, \quad X_2(x) = e^{-\kappa x}, \tag{4.16}$$

and hence the complete solution

$$X(x) = c_1 e^{\kappa x} + c_2 e^{-\kappa x}. \tag{4.17}$$

This is the complete *mathematical solution.* To get the possible *physical solutions* we must observe the above-mentioned boundary conditions $X(0) = 0$ and $X(a) = 0$. Since $e^0 = 1$, the first of these becomes

$$c_1 + c_2 = 0. \tag{4.18}$$

It shows that $c_2 = -c_1$. Using this result, the second condition reads

$$c_1 \left(e^{\kappa a} - e^{-\kappa a}\right) = 0. \tag{4.19}$$

But this equation is only satisfied for $c_1 = 0$, and this does certainly not lead to an acceptable solution, because it defines nothing but a vanishing wavefunction.

Thus, Eq. (4.11) does not have acceptable solutions for negative values of E_x. But this is exactly what we would expect on physical grounds. For the energy of the particle in a box is purely kinetic and should therefore be non-negative.

Next, we consider positive values of E_x and write

$$E_x = \frac{\hbar^2 k_x^2}{2m}, \qquad k_x > 0, \tag{4.20}$$

so that Eq. (4.11) becomes

$$\frac{d^2X}{dx^2} = -k_x^2 X. \tag{4.21}$$

This equation has the two independent solutions:

$$X_1(x) = \sin(k_x x), \quad X_2(x) = \cos(k_x x), \tag{4.22}$$

and hence the complete solution

$$X(x) = c_1 \sin(k_x x) + c_2 \cos(k_x x). \tag{4.23}$$

Again, this is the complete mathematical solution. To get the physical solutions we must observe the boundary conditions $X(0) = 0$ and $X(a) = 0$. The first of these gives

$$c_1 \sin(0) + c_2 \cos(0) = 0. \tag{4.24}$$

It shows that c_2 must be zero. Using this result, the second condition reads

$$c_1 \sin(k_x a) = 0. \tag{4.25}$$

Here we cannot put c_1 equal to zero, for this would cause $X(x)$ to vanish. Hence, Eq. (4.25) is a condition on k_x. It is satisfied for the following set of values

$$k_x = n_x \pi / a, \qquad n_x = 1, 2, 3, \ldots \tag{4.26}$$

The corresponding allowed energies are then, by Eq. (4.20)

$$E_x = \frac{\pi^2 \hbar^2}{2ma^2} n_x^2, \qquad n_x = 1, 2, 3, \ldots \tag{4.27}$$

or, by writing E_{n_x} instead of E_x and remembering that $\hbar = h/2\pi$,

$$\boxed{E_{n_x} = \frac{h^2}{8ma^2} n_x^2, \qquad n_x = 1, 2, 3, \ldots} \tag{4.28}$$

Having considered both negative and positive values of E_x, we must finally examine what happens when $E_x = 0$. Eq. (4.11) becomes then

$$\frac{d^2 X}{dx^2} = 0. \tag{4.29}$$

It has the complete solution

$$X(x) = c_1 + c_2 x, \tag{4.30}$$

and it is readily seen that this solution cannot be made to satisfy the boundary conditions $X(0) = 0$ and $X(a) = 0$ for any values of c_1 and c_2.

Consequently, the quantum mechanical particle in a box cannot have zero energy, i.e., it cannot be at rest as it can in classical mechanics. The lowest possible energy is obtained by putting $n_x = 1$ in the expression (4.28). This energy is called the zero-point energy:

$$\boxed{\textit{Zero-point energy} = \frac{h^2}{8ma^2}} \tag{4.31}$$

The result of our analysis is, then, that the only allowed energies of the particle in a one-dimensional box are those of Eq. (4.28). The energy spectrum is accordingly discrete. This result is a consequence of the fact that the motion is bounded by the 'walls' at $x = 0$ and $x = a$. The wavefunction corresponding to the quantum number n_x is

$$X_{n_x}(x) = c_1 \sin(\pi n_x x/a) \tag{4.32}$$

where the value of c_1 is at our disposal. Let us determine it such that X is normalized to unity (see Eq. (3.8)). The condition is

$$\int_0^a X^*_{n_x}(x) X_{n_x}(x) dx = 1. \tag{4.33}$$

We have that

$$\int_0^a \sin^2(\pi n_x x/a) dx = a/2, \tag{4.34}$$

and thus Eq. (4.33) will be fulfilled if we choose c_1 to be

$$c_1 = e^{i\delta}\sqrt{2/a} \tag{4.35}$$

where δ is any real number. $e^{i\delta}$ is called a *phase factor.*[2]

The value of δ is left undefined by the normalization condition, since the product $c_1^* c_1 = (e^{-i\delta}\sqrt{2/a})(e^{i\delta}\sqrt{2/a}) = 2/a$, for any value of δ. We are therefore free to assign to δ any value that we want. Let us, by convention, *choose* $\delta = 0$. We get then the following normalized wavefunctions

$$\boxed{X_{n_x}(x) = \sqrt{2/a}\,\sin(\pi n_x x/a), \qquad n_x = 1, 2, 3, \ldots} \tag{4.36}$$

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[2] See Appendix A for a brief introduction to the complex exponential function.

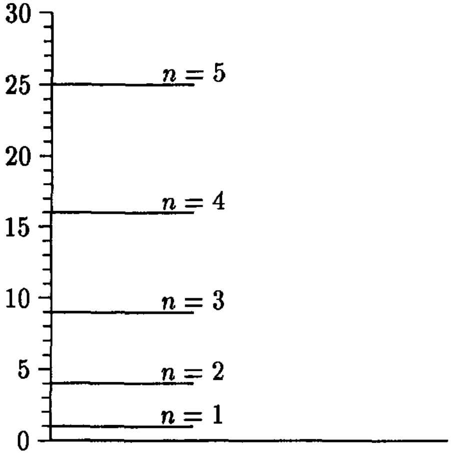

Figure 4.2: Energy level diagram for a particle in a one-dimensional box. Energies in units of $h^2/8ma^2$.

Thus, we have found both the energies and the wavefunctions for the stationary states of the particle in a one-dimensional box, by solving the Schrödinger equation (4.11) with the boundary conditions $X(0) = X(a) = 0$. The energy spectrum is defined by Eq. (4.28). Each energy value is said to define an *energy level.* There is one wavefunction per energy level, and its form is given by Eq. (4.36).

The energy spectrum is represented graphically in Fig. 4.2 which is called an *energy level diagram.* The wavefunctions and their squares are shown in Fig. 4.3, for some selected values of n_x. In this figure, we have discarded the subscript x on the quantum number n_x and written $\psi(x)$ instead of $X(x)$. We recall that $\psi(x)^2$ is a *probability density,* $\psi(x)^2 dx$ being the probability of finding the particle around the point x in the interval dx.

We proceed by emphasizing some very general properties of the set of wavefunctions given by Eq. (4.36).

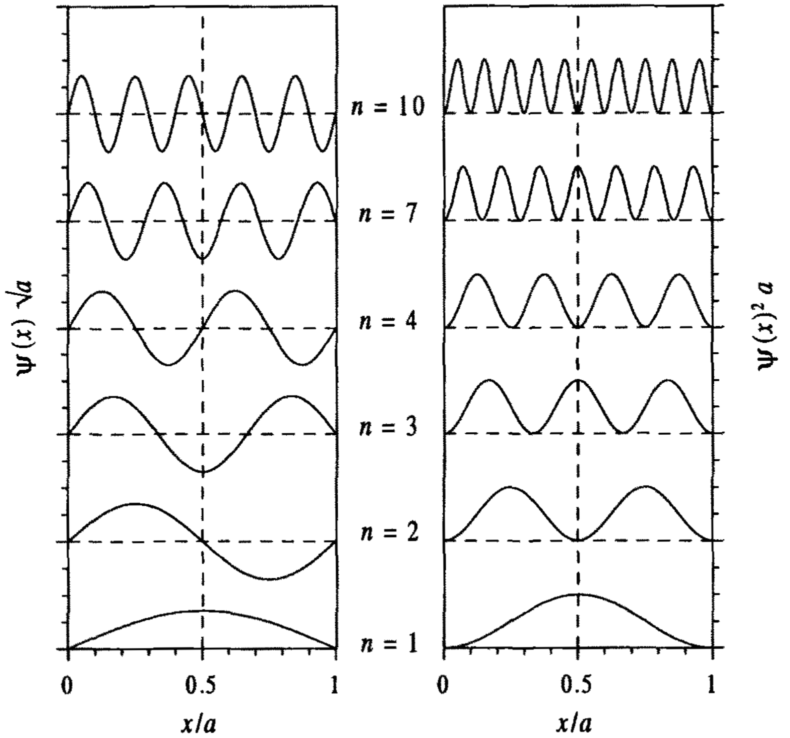

Figure 4.3: Wavefunctions, left, and probability densities, right, for particle in a one-dimensional box. $n = 1, 2, 3, 4, 7, 10$. The amplitudes are measured from the indicated base lines, the distance between two tick marks on the vertical axes being 1 dimensionless unit.

4.3 Orthogonality of Wavefunctions

Let us introduce the so-called *scalar product*, or *overlap integral*, between two functions, $f(x)$ and $g(x)$. We denote it by $\langle f|g\rangle$ and define it by the relation:

$$\langle f|g\rangle = \int f^*(x)g(x)dx \tag{4.37}$$

where the integration is extended over the range of x. Note that the first factor in the integrand is the complex conjugate of $f(x)$ rather than $f(x)$ itself. This is, of course, of no importance when we only deal with real functions, but when complex functions are used the complex conjugation is essential. Let us evaluate the integral $\langle f|g\rangle$ when f and g are two different functions taken from the set (4.36).

For simplicity, we drop the index x on the quantum number n_x (as in Fig. 4.2), and get:

$$\begin{aligned}\langle X_m | X_n \rangle &= \int_0^a X_m^*(x) X_n(x) dx = \frac{2}{a} \int_0^a \sin(m\pi x/a) \sin(n\pi x/a) dx \\ &= \frac{1}{a} \int_0^a \left\{ \cos\left(\frac{m-n}{a}\pi x\right) - \cos\left(\frac{m+n}{a}\pi x\right) \right\} dx,\end{aligned} \tag{4.38}$$

where we have used the general formula

$$2 \sin u \, \sin v = \cos(u-v) - \cos(u+v). \tag{4.39}$$

From a graph of the function $\cos(l\pi x/a)$, where l is a non-zero integer, or from a table of integrals, it is readily seen that

$$\int_0^a \cos(l\pi x/a) dx = 0, \qquad l \neq 0. \tag{4.40}$$

It is exactly this type of integral that occurs in Eq. (4.38), for both $m-n$ and $m+n$ are non-zero integers. Hence, we get:

$$\langle X_m | X_n \rangle = 0, \qquad m \neq n. \tag{4.41}$$

We express this result by saying that X_n and X_m are *orthogonal.*

Thus, our function set (4.36) fulfills the condition

$$\boxed{\langle X_m | X_n \rangle = \delta_{mn}} \tag{4.42}$$

where

$$\boxed{\delta_{mn} = \begin{cases} 1 & \text{if } m = n \\ 0 & \text{if } m \neq n \end{cases}} \tag{4.43}$$

The useful symbol δ_{mn} is called the *Kronecker delta.*

The condition (4.42) is called the *orthonormality condition*, and we say that our function set is an *orthonormal set.* We shall later be able to prove that any two solutions of a given Schrödinger equation are orthogonal, if they correspond to different energies (See Chapter 5). The relation (4.42) is therefore a specific example of a general relation.

4.4 Number of Nodes Versus Energy

A point in the interval $0 < x < a$ at which a wavefunction changes sign (becomes zero) is called a *node* of the wavefunction. It is obvious, both from Eq. (4.36) and Fig. 4.3, that the number of nodes equals $n_x - 1$, and hence that the number of nodes increases with the energy. This is a general result which may be transferred to more complicated systems. It is closely connected with the orthogonality theorem of the previous section, for the product $X_1^*(x)X_2(x)$ must necessarily change sign at least once in the interval $0 < x < a$ in order that $\langle X_1|X_2\rangle$ may become zero. A similar remark holds for $X_1^*(x)X_3(x)$, $X_2^*(x)X_3(x)$, etc.

4.5 Inversion Symmetry

The last, albeit rather lengthy remark concerning the wavefunctions for a particle in a one-dimensional box deals with their inversion symmetry. A glance at Fig. 4.3 shows that $X_1, X_3, X_5, \ldots$ are unchanged when reflected with respect to the midpoint of the box, whereas $X_2, X_4, X_6, \ldots$ change sign under such a reflection. We say that the functions are alternately *even* (or *gerade*) and *odd* (or *ungerade*).

Analytically, the inversion symmetry of the wavefunction is most clearly displayed, if we place the origin of the x-coordinate at the midpoint of the box rather than at one end. Such a shift of the origin corresponds to replacing x by $x + a/2$ in the analytical expression (4.36) for the wavefunctions. Thus we obtain, by using elementary properties of the trigonometric functions

$$X_{n_x}(x) = \begin{cases} (-1)^{(n_x-1)/2}\sqrt{2/a}\,\cos(\pi n_x x/a), & n_x = 1, 3, 5, \ldots \\ (-1)^{n_x/2}\sqrt{2/a}\,\sin(\pi n_x x/a), & n_x = 2, 4, 6, \ldots \end{cases} \tag{4.44}$$

where the range of x is $-\frac{a}{2} \leq x \leq \frac{a}{2}$. We would, of course have obtained these analytical expressions from the outset, if we had subjected the general solution (4.23) to the boundary conditions $X(-a/2) = X(a/2) = 0$ rather than $X(0) = X(a) = 0$. Had we done so, we would probably also have defined the functions (4.44) without the phase factors $(-1)^{(n_x-1)/2}$ and $(-1)^{n_x/2}$. As pointed out in connection with Eq. (4.35), the choice of a phase factor is always at our disposal.

A reflection with respect to the midpoint of the box is an inversion in the new origin and corresponds to replacing x by $-x$. The even/odd character of the wavefunctions is therefore easily read off the analytical expressions (4.44), by remembering the elementary relations

$$\begin{cases} \cos(-kx) = \cos(kx) \\ \sin(-kx) = -\sin(kx) \end{cases} . \tag{4.45}$$

So far we have done nothing but observe that the wavefunctions which we found by solving the Schrödinger equation (4.11) turned out to be either even or odd. We shall now show that this symmetry property can actually be derived by a simple formal consideration.

Let $X(x)$ be one of the above functions. It satisfies the Schrödinger equation (4.11) which we rewrite as

$$\widehat{H}_x X(x) = E_x X(x), \tag{4.46}$$

with $\widehat{H}_x$ as given by Eq. (4.12), i.e.,

$$\widehat{H}_x = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}. \tag{4.47}$$

Now it is obvious that an inversion in the point $x = 0$ (the new origin) leaves this Hamiltonian unchanged. In addition, it carries the "walls" at $x = -a/2$ and $x = a/2$ into each other. The whole physical setup is accordingly *invariant* under the inversion. But this does not imply that $X(x)$ must be invariant.

Let us introduce an operator, $\hat{I}$, which per definition carries a function $f(x)$ into its mirror image, $\hat{I}f(x)$, with respect to the origin. This new function, $\hat{I}f(x)$, is defined by

$$\hat{I}f(x) = f(-x). \tag{4.48}$$

Applying the inversion operator to both sides of Eq. (4.46) gives

$$\hat{I}\left(\widehat{H}_x X(x)\right) = \hat{I}\left(E_x X(x)\right). \tag{4.49}$$

But since the Hamiltonian is invariant under $\hat{I}$, and E_x is a constant, this becomes

$$\widehat{H}_x \hat{I} X(x) = E_x \hat{I} X(x). \tag{4.50}$$

What this equation tells us, is that the function $\hat{I}X(x)$ is an eigenfunction of $\widehat{H}_x$ with the eigenvalue E_x. But according to what we have found in Sec. 4.2, there is only a single eigenfunction per energy level. Hence, $\hat{I}X(x)$ can at most differ from $X(x)$ by a constant factor, c say. It follows that

$$\hat{I}X(x) = cX(x). \tag{4.51}$$

If we now apply the inversion operator to both sides of this equation we get

$$\hat{I}^2 X(x) = c\hat{I}X(x) \tag{4.52}$$

and hence, by using Eq. (4.51) again (on the right-hand side)

$$\hat{I}^2 X(x) = c^2 X(x). \tag{4.53}$$

But it is obvious that two inversions performed after each other restores the original, i.e,

$$\hat{I}^2 X(x) = X(x). \tag{4.54}$$

This follows also from the explicit definition (4.48). Comparing Eqs. (4.53) and (4.54) then shows that

$$c^2 = 1 \tag{4.55}$$

which obviously implies that

$$c = 1 \quad \text{or} \quad c = -1. \tag{4.56}$$

$c = 1$ defines an even function, $c = -1$ an odd function.

What we have obtained by this simple analysis is the important result that the presence of symmetry allows a classification of wavefunctions according to their symmetry properties. For more complicated symmetries this classification must be carried through by means of the mathematical discipline known as group theory. The group that characterizes the present problem is defined by the inversion operator $\hat{I}$ together with the identity operator $\hat{E}$. It is called C_i and is defined by a so-called group multiplication table of the form

C_i	$\hat{E}$	$\hat{I}$
$\hat{E}$	$\hat{E}$	$\hat{I}$
$\hat{I}$	$\hat{I}$	$\hat{E}$

The identity operator is the trivial operator which leaves everything unchanged. It appears in many formal considerations.

We have now given a rather thorough discussion of the one-dimensional problem and must return to the three-dimensional case.

4.6 The Three-Dimensional Box

As discussed in Sec. 4.1, the Schrödinger equation (4.1) for a particle in a three-dimensional box is solved once we have solved the three one-dimensional problems given by Eqs. (4.6)–(4.8). Each of the three problems is, however, equivalent to the problem of a particle in a one-dimensional box which we have solved above. We may accordingly write the solution of the three-dimensional problem down immediately. The possible energies are obtained from Eqs. (4.9) and (4.28), and become

$$\boxed{E = E_x + E_y + E_z = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right), \quad n_x, n_y, n_z = 1, 2, 3, \ldots} \tag{4.57}$$

The wavefunctions are obtained by inserting the analytical result (4.38) into the factorized expression (4.2). They are

$$\boxed{\begin{aligned}&\psi_{n_x n_y n_z}(x, y, z) = \sqrt{8/abc}\,\sin(\pi n_x x/a)\sin(\pi n_y y/b)\sin(\pi n_z z/c),\\ &\quad n_x, n_y, n_z = 1, 2, 3, \ldots\end{aligned}} \tag{4.58}$$

Thus, the solutions are characterized by three quantum numbers n_x, n_y, n_z which independently take the values $1, 2, 3, \ldots$ The wavefunctions form an orthonormal set, i.e.,

$$\boxed{\langle \psi_{n_x n_y n_z} | \psi_{n'_x n'_y n'_z} \rangle = \delta_{n_x n'_x} \delta_{n_y n'_y} \delta_{n_z n'_z}} \tag{4.59}$$

where the scalar product now is defined as

$$\langle \psi | \psi' \rangle = \int_0^a dx \int_0^b dy \int_0^c dz\ \psi^*(x, y, z)\psi'(x, y, z). \tag{4.60}$$

Eq. (4.59) follows immediately by noticing that the analytical form (4.58) causes the integral to factor into three, each of which satisfies an orthonormality condition of the type (4.42).

In Sec. 4.4 we discussed the nodal structure of the wavefunctions in a one-dimensional box and found that a wavefunction with quantum number n_x

possesses $n_x - 1$ nodes. The three-dimensional analog of a node is a *nodal surface* (and the two-dimensional analog a *nodal curve*). It is obvious that any node, say $x = x_0$, of a single-coordinate wavefunction of the type (4.36) produces a nodal plane ($x = x_0$) once it is a factor in the wavefunction (4.58). Thus, the nodal surfaces of the wavefunction (4.58) are planes parallel to one or the other of the coordinate planes. We don't count the walls of the box as nodal planes, so the wavefunction (4.58) possesses $n_x + n_y + n_z - 3$ nodal planes.

As to inversion symmetry, we note that the point $(a/2, b/2, c/2)$ is an *inversion center*, i.e., the whole physical setup is invariant under an inversion in this point. To study this symmetry analytically it is expedient to shift the origin of coordinates so that it coincides with the inversion center. We then obtain new analytical expressions for the wavefunctions, which may be obtained by inserting the alternative expressions (4.44) for the one-dimensional wavefunctions into the factorized expression (4.2). Under an inversion, which we denote by $\hat{I}$ as in the one-dimensional case, these functions are transformed according to the relation

$$\hat{I} f(x, y, z) = f(-x, -y, -z). \tag{4.61}$$

Drawing on the discussion of Sec. 4.5, we then see that the three factors in the wavefunction (4.58) are multiplied by $(-1)^{n_x-1}$, $(-1)^{n_y-1}$, and $(-1)^{n_z-1}$ respectively under the inversion. Thus, the total wavefunction is multiplied by the factor $(-1)^{n_x+n_y+n_z-3}$, and is therefore either even or odd. We call this factor the *parity* of the wavefunction, so

$$\boxed{\text{The parity of the wavefunction (4.58) is } (-1)^{n_x+n_y+n_z-3}} \tag{4.62}$$

The ground-state wavefunction ($n_x = n_y = n_z = 1$) is, in particular, a nodeless and even function.

4.7 The Concept of Degeneracy

An interesting situation occurs if two or all three of the box lengths a, b, c become equal, for in that case the same value of the energy may well be obtained for more than one set of the quantum numbers n_x, n_y, and n_z, and an energy level will have more than one wavefunction associated with it. This does not occur for one-dimensional bound states, but it is frequently met in

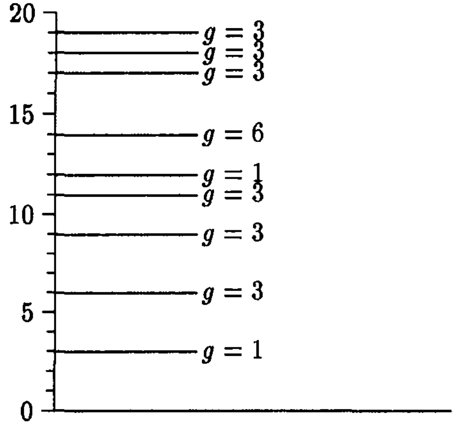

Figure 4.4: Energy level diagram and level-degeneracies, g, for a particle in a cubic box. Energies in units of $h^2/8ma^2$.

two- and three-dimensional systems. We say that the level is *degenerate* and call the number of linearly independent wavefunctions associated with the level for its *degeneracy*.

Assume that we have a *cubic box*, so that $a = b = c$. Then the energy expression (4.57) becomes

$$E_{\text{cubic}} = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right), \qquad n_x, n_y, n_z = 1, 2, 3, \ldots \tag{4.63}$$

The ground state is obtained by putting $n_x = n_y = n_z = 1$. It is *non-degenerate*. The first excited state corresponds to three sets of quantum numbers, namely (2,1,1), (1,2,1), and (1,1,2). Thus, the level is three-fold degenerate, and the wavefunctions ψ_{211}, ψ_{121} and ψ_{112} have the same energy. Continuing the counting procedure we obtain the energy level diagram shown in Fig. 4.4.

To fully appreciate the concept of degeneracy, let us consider a general level with degeneracy g. We have, then, g linearly independent wavefunctions, say $\psi_1, \psi_2, \ldots, \psi_g$. That these functions are linearly independent means that none of them can be expressed as a linear combination of the others. In other words, the only solution of the equation

$$c_1\psi_1 + c_2\psi_2 + \cdots + c_g\psi_g = 0 \tag{4.64}$$

is the trivial solution $c_1 = c_2 = \cdots = c_g = 0$.

The functions $\psi_1, \psi_2, \ldots, \psi_g$ are all eigenfunctions of the Hamiltonian $\widehat{H}$ with the same energy, E:

$$\begin{cases} \widehat{H}\psi_1 = E\psi_1 \\ \widehat{H}\psi_2 = E\psi_2 \\ \quad \ldots \\ \widehat{H}\psi_g = E\psi_g \end{cases} \tag{4.65}$$

Let us multiply the first of these equations by an arbitrary constant c_1, the second by an arbitrary constant c_2, etc., and add the resulting equations to get

$$\widehat{H}(c_1\psi_1 + c_2\psi_2 + \cdots + c_g\psi_g) = E(c_1\psi_1 + c_2\psi_2 + \cdots + c_g\psi_g). \tag{4.66}$$

What this equation says, is that any function of the form

$$\psi = \sum_{i=1}^{g} c_i\psi_i \tag{4.67}$$

is an eigenfunction of $\widehat{H}$ with energy E.

The set of all functions of the form (4.67) are said to form a linear function space, $\mathcal{V}$, of dimension g. Thus, we realize that

> A g-fold degenerate level is characterized by a linear function space, $\mathcal{V}$, of dimension g. Any function belonging to $\mathcal{V}$ is an eigenfunction of the Hamiltonian with the same energy. (4.68)

The set of the g linearly independent functions $\psi_1, \psi_2, \ldots, \psi_g$ is called a basis set, or simply a basis for $\mathcal{V}$, because any function in $\mathcal{V}$ may be represented in the form (4.67). It is obvious that any set of g linearly independent functions in $\mathcal{V}$ may serve as a basis, and that any such set therefore characterizes $\mathcal{V}$ just as well as the set $\psi_1, \psi_2, \ldots, \psi_g$ does.

A g-fold degenerate level is defined once a basis has been written down, but as just said, there are many equivalent ways of choosing a basis. In particular, it is always possible to choose an orthonormal basis,[3] i.e., a set of functions, $\psi_1, \psi_2, \ldots, \psi_g$, for which

$$\langle\psi_i|\psi_j\rangle = \delta_{ij}, \qquad i, j = 1, 2, \ldots, g. \tag{4.69}$$

---

[3] See Problem 4.

Any orthonormal set of g functions belonging to $\mathcal{V}$ may in fact serve as a basis. For we have the general theorem

$$\boxed{\text{Orthogonality implies linear independence, and any set of } m \text{ orthogonal functions is therefore a basis.}} \tag{4.70}$$

To prove this theorem, we assume that $\psi_1, \psi_2, \ldots, \psi_g$ is a set of g mutually orthogonal functions in $\mathcal{V}$ and look for values of the coefficients $c_1, c_2, \ldots, c_g$ for which Eq. (4.64) is satisfied. Scalar multiplication with ψ_1 gives

$$c_1\langle\psi_1|\psi_1\rangle + c_2\langle\psi_1|\psi_2\rangle + \cdots + c_g\langle\psi_1|\psi_g\rangle = 0 \tag{4.71}$$

and hence, by using the orthogonality relations (4.69)

$$c_1\langle\psi_1|\psi_1\rangle = 0, \tag{4.72}$$

i.e. $c_1 = 0$. Similarly, scalar multiplication with ψ_2 gives $c_2 = 0$, etc. Thus, Eq. (4.64) is only satisfied by $c_1 = c_2 = \ldots = c_g = 0$. Consequently, $\psi_1, \psi_2, \ldots, \psi_g$ is a linearly independent set, and hence a basis, which was to be proved.

The wavefunctions (4.58) define a natural orthonormal basis in the case of degeneracy, but other choices are equally valid. We shall not consider other choices here, but only mention that when we come to discuss the free particle and the hydrogen atom, we shall find it natural to set up two alternative basis sets for each degenerate level.

Apart from the null-function, any function belonging to the function space $\mathcal{V}$ defines a physical state (Sec. 3.2). But since all functions of the form $c\psi$, where c is a non-vanishing constant, define the same state, we may as usual (Sec. 3.4) restrict our attention to functions that are normalized to unity, i. e., functions for which

$$\langle\psi|\psi\rangle = 1. \tag{4.73}$$

In view of this, let us derive the condition that the coefficients in the linear combination (4.67) has to satisfy in order that the resulting function be normalized. We assume that the basis functions $\psi_1, \psi_2, \ldots, \psi_g$ form an orthonormal set (Eq. (4.69)), remember the definition (4.37) of the scalar product, and hence also of the normalization integral (4.73), and get

$$\begin{aligned}\langle\psi|\psi\rangle &= \sum_{i=1}^{g}\sum_{j=1}^{g}\langle c_i\psi_i|c_j\psi_j\rangle = \sum_{i=1}^{g}\sum_{j=1}^{g} c_i^* c_j \langle\psi_i|\psi_j\rangle \\ &= \sum_{i=1}^{g}\sum_{j=1}^{g} c_i^* c_j \delta_{ij} = \sum_{i=1}^{g} c_i^* c_i = \sum_{i=1}^{g} |c_i|^2.\end{aligned} \tag{4.74}$$

Hence, the normalization condition (4.73) requires that

$$\sum_{i=1}^{g} c_i^* c_i = \sum_{i=1}^{g} |c_i|^2 = 1. \tag{4.75}$$

This is a condition that we shall often have the opportunity to use. Note that nowhere in its derivation have we used that the basis functions $\psi_1, \psi_2, \ldots, \psi_g$ have the same energy. We have only used that they form an orthonormal set. The condition holds therefore for any expansion of a normalized function on an orthonormal set:

Let $\psi_1, \psi_2, \ldots, \psi_g$ be an orthonormal set of functions:

$$\langle \psi_i | \psi_j \rangle = \delta_{ij}, \qquad i, j = 1, 2, \ldots, g$$

and let ψ belong to the function space defined by this set, i. e., ψ may be written in the form:

$$\psi = \sum_{i=1}^{g} c_i \psi_i.$$

The condition for ψ to be normalized to unity,

$$\langle \psi | \psi \rangle = 1,$$

is then that

$$\sum_{i=1}^{g} c_i^* c_i = \sum_{i=1}^{g} |c_i|^2 = 1.$$

(4.76)

Let us now finally mention that degeneracy, just like parity, is closely associated with the symmetry of the problem. For a cubic box, there are 48 geometrical symmetry operations which leave the physical setup unchanged. They define the so-called *octahedral group* O_h. If ψ is an eigenfunction of $\widehat{H}$ with energy E, then so is $\hat{R}\psi$ where $\hat{R}$ represents one of the operations of O_h. This follows by an argument similar to the one used for the inversion operator in Sec. 4.5. Next, let $\hat{R}$ and $\hat{S}$ represent two different symmetry operations. The combinations $\hat{R}\hat{S}$ and $\hat{S}\hat{R}$ will then also represent symmetry operations. The functions $\hat{R}\hat{S}\psi$ and $\hat{S}\hat{R}\psi$ will accordingly also be eigenfunctions of $\widehat{H}$ with energy E. But if $\hat{R}\hat{S} \neq \hat{S}\hat{R}$, then $\hat{R}\hat{S}\psi$ and $\hat{S}\hat{R}\psi$ must in general be linearly independent functions. For this to be possible, the energy level must, of course, be degenerate.

A simple example of a symmetry related degeneracy is provided by the first excited state with wavefunctions ψ_{211}, ψ_{121} and ψ_{112}. These three functions are carried into each other under a rotation of magnitude $2\pi/3$ around the axis defined by the vector (1,1,1). This is readily verified from the analytical expressions for these functions when it is noted that the said rotation transforms x, y and z into each other.

In most cases, the degree of degeneracy of a level may be completely "understood" on the basis of symmetry. In some cases, however, additional degeneracy occurs which is then referred to as *accidental degeneracy.* Some of the degeneracies met in the present problem are in fact accidental, for it may be shown that the group O_h supports no higher degeneracy than three. This special situation is caused by the extremely simple form of the potential energy function: $V(\boldsymbol{r})$ is a constant (chosen to be zero). We shall, however, not discuss this problem further at present.[4]

With these remarks on symmetry and degeneracy, our analysis of the stationary states of the particle in a box has come to a natural end. The box problem is sufficiently simple that we have been able to solve it exactly without much effort. Yet, its solutions possess a number of important properties of a general nature, and we shall meet analogous properties over and over again in the following chapters.

The particle in a box is a useful first-model system for the description of "nearly free" particles in atomic nuclei, atomic clusters, molecules, and solids—especially when spherical and ellipsoidal box shapes are also allowed. We shall consider a simple application and then terminate the present chapter with a discussion of non-stationary states of the particle in a box.

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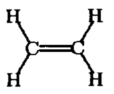
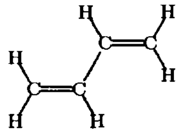
[4] For a discussion of the degeneracies in the square-box problem, see W.-K. Li, Am. J. Phys. **50**, 666 (1982); F. Leyvraz, A. Frank, R. Lemus, and M. V. Andrés, Am. J. Phys. **65**, 1087 (1997).

4.8 The Free-Electron Model

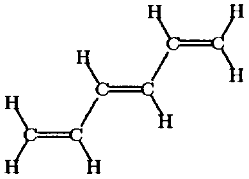
Consider the following planar hydrocarbon molecules:



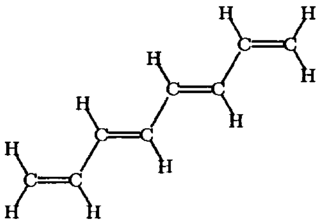
Ethylene



Butadiene



Hexatriene



Octatetraene

The displayed valence-bond structures show that ethylene contains a single double bond, and that the three other molecules contain respectively two, three and four double bonds "in conjugation". The two bonds in a double bond are, however, not considered to be equivalent. Much like a C-H single bond, one of them is formed by an electron pair that is fairly localized in the bond region. The two electrons that are responsible for the other part of a double bond are more delocalized. They are accordingly called mobile electrons. Ethylene, butadiene, hexatriene, and octatetraene contain respectively 2, 4, 6, and 8 mobile electrons, and one should in fact think of these electrons as being shared between all the carbon atoms in a chain rather than between separate atom pairs. Accordingly, the above valence formulae don't do full justice to the distribution of the mobile electrons.

In the usual quantum mechanical description of the mobile electrons they are placed in so-called molecular orbitals that extend over all the carbon atoms. We shall later discuss how molecular orbitals may be constructed from the atomic orbitals of the individual atoms. Here we shall show, however, that some general properties of the mobile electrons may already be gotten by the so-called *free-electron model*, which is constructed from the solutions of the particle in a box problem. The word *orbital* means one-electron wavefunction, and we shall therefore also, in the present context, refer to the box wavefunctions as orbitals.

Consider, then, a conjugated hydrocarbon, C_NH_{N+2}, with an even number of carbon atoms, N. The average length of a C-C bond in such a molecule is about $1.40\,\text{Å} = 1.40\times 10^{-10}\,\text{m}$, and by making the approximation of considering all C-atoms to lie on a straight line we may therefore fit the molecule into a rectangular box of length $a = 1.40(N+1)\,\text{Å}$. This gives a free distance of one bond length at each end of the chain.[5] We consider the box lengths b and c in Fig. 4.1 to be quite small, so that the lower energy levels defined by the energy expression (4.57) all correspond to $n_y = n_z = 1$ while n_x takes on the values $1, 2, 3, \ldots$

The number of mobile electrons in the molecule C_NH_{N+2} equals N. We neglect the electrostatic interaction between the electrons, and assign to each of them a stationary-state wavefunction of the form (4.58). But according to the so-called *Pauli principle*, whose origin we shall discuss later, we may associate no more than two electrons with the same orbital. The energetically lowest state of the N-electron system, i.e. its ground state, is therefore obtained by assigning two electrons to each of the orbitals defined by $n_x = 1, 2, \ldots, N/2$ while keeping n_y and n_z equal to 1. The condition $n_y = n_z = 1$ implies that the motion in the y- and z-directions is locked into a stiff pattern. The chemically interesting behavior of the mobile electrons is accordingly tied to their motion in the x-direction. The system is said to be *quasi one-dimensional.*

Let us therefore neglect the y- and z-motion altogether and simply work with the wavefunctions and energies of the one-dimensional box (Sec. 4.2). Let us also, in the same way as in Figs. 4.2 and 4.3, discard the subscript x on the quantum number n_x and write $\psi_n(x)$ instead of $X_{n_x}(x)$. The electron configurations of the above mentioned molecules are then

Ethylene: ψ_1^2, Butadiene: $\psi_1^2\psi_2^2$,
Hexatriene: $\psi_1^2\psi_2^2\psi_3^2$, Octatetraene: $\psi_1^2\psi_2^2\psi_3^2\psi_4^2$,

where, for instance, the symbol $\psi_1^2\psi_2^2\psi_3^2$ implies that each of the orbitals ψ_1, ψ_2 and ψ_3 are occupied by two electrons, and it is understood that corresponding orbitals for different molecules refer to different values of the box length a in the expression (4.36) for the box wavefunctions. It is important to realize that the designations given for the electron configurations are in fact nothing but symbols. They are *not* many-electron wavefunctions. Later, we shall learn how to construct proper many-electron wavefunctions for an N-electron system.

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[5] How much free space there should be allowed at each end of the chain is a matter of choice. After all, our description is only a model. Many authors allow only a free distance of half a bond length. This gives slightly better transition energies, but somewhat less realistic electron densities.

According to the statistical interpretation of quantum mechanics, the quantity $\psi_i^*(x)\psi_i(x)dx$ is the probability of observing an electron in the interval dx around the point x, when its wavefunction is known to be ψ_i. This makes us define the *electron density* for each of the above molecules by the expression

$$\boxed{n(x) = 2\sum_{i=1}^{N/2} \psi_i^*(x)\psi_i(x)} \tag{4.77}$$

The number of electrons that we are likely to find in the interval dx around x is then $n(x)dx$. Each ψ_i is normalized to unity, and we get therefore

$$\int_0^a n(x)dx = N, \tag{4.78}$$

showing that the electron density integrates to the total number of electrons, as it should.

Starting from the analytical expression (4.36) for the box wavefunctions and remembering that the box length a should be taken to be $1.40(N+1)$ Å for a particular molecule, it is straightforward to evaluate the electron density $n(x)$ for some chosen values of x and hence plot $n(x)$ as a function of x along the molecular axis. In this way we obtain the graphs shown in Fig. 4.5. The ethylene molecule is not included in the figure, but its electron density is simply $2X_1(x)^2$, with $X_1(x)^2$ as shown in Fig. 4.3.

The electron densities of Fig. 4.5 exhibit a characteristic oscillating behavior as functions of x. They show in fact a certain resemblance with the electron densities indicated by the valence-bond formulae shown at the beginning of this section, in the sense that they accumulate more electron density between carbon atoms connected by a double bond than between atoms connected by a single bond. A similar behavior is found by the molecular orbital method.

That such a simple model as the above is able to reproduce some qualitatively correct features of the charge oscillation in conjugated hydrocarbons is at first sight rather surprising, for the model entirely neglects the strong variation of the electron-nuclear attraction along the chain. The reason for the agreement must be sought in the fact that the free-electron orbitals and the true molecular orbitals have similar nodal structures with respect to the x-coordinate, i.e., the lowest orbital is nodeless, the second has a nodal plane at the middle of the molecule, etc. What we see, therefore, is that when we perform the summation (4.77) to get the electron density $n(x)$, then similar

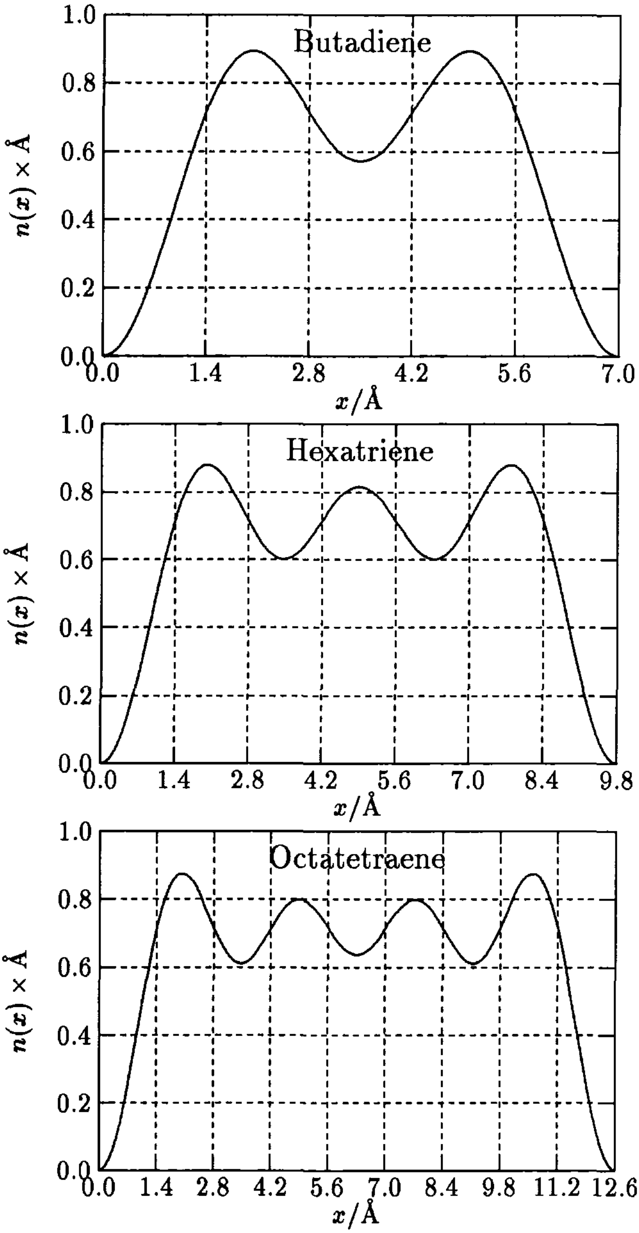

Figure 4.5: Electron densities in some conjugated hydrocarbons according to the free-electron model. The positions of the carbon atoms are indicated by the vertical grid lines.

nodal structures of the free-electron orbitals and the true molecular orbitals have similar effects on $n(x)$.

The calculation of electron densities is an important problem in quantum chemistry, but far from being the only one of course. Another important problem is, for instance, the calculation of transition energies. The first strong electronic absorption bands of the molecules ethylene, butadiene, hexatriene, and octatetraene have their maxima at the wavelengths 162, 217, 268, and 304 nm, respectively. These bands are known to be associated with the mobile electrons. We note that the absorption maxima are progressively displaced to longer wavelengths as the number of carbon atoms in the polyenes increases. We shall now show that this important trend can be understood on the basis of the free-electron model, whereas the positions of the absorption maxima cannot be calculated with any reasonable accuracy within the model.

The highest occupied orbital of a conjugated polyene with N electrons is $\psi_{N/2}$, as discussed earlier in this section. The first electronic absorption band may be assumed to originate when an electron is removed from this orbital and placed in the lowest unoccupied orbital which is $\psi_{N/2+1}$. The energy required to affect this transition is

$$\Delta E = E_{N/2+1} - E_{N/2}. \tag{4.79}$$

The orbital energies are given by Eq. (4.28), with the box length a being equal to $(N+1)d$, where $d = 1.40$ Å. Thus, we get:

$$\Delta E = \frac{h^2}{8md^2(N+1)^2}\left[\left(\frac{N}{2}+1\right)^2 - \left(\frac{N}{2}\right)^2\right] = \frac{h^2}{8md^2}\frac{1}{N+1}. \tag{4.80}$$

The transition may be effected by the absorption of a photon with frequency ν determined by the Bohr condition, $\Delta E = h\nu$. The corresponding wavelength is connected to ν by the usual relation, $\nu\lambda = c$. Hence, we get:

$$\lambda = \frac{hc}{\Delta E} = \frac{8mcd^2}{h}(N+1), \tag{4.81}$$

or, by inserting $d = 1.40 \times 10^{-10}$m together with the values of m, c and h:

$$\lambda = 64.6(N+1)\,\text{nm} = 646(N+1)\,\text{Å}. \tag{4.82}$$

For $N = 2$, 4, 6, and 8 this gives: $\lambda = 194$, 323, 452, 582 nm, respectively. These values are not in good agreement with the measured values, but they do show the experimentally observed trend, that λ increases with N. The effect, which is predicted to be linear by Eq. (4.82), is however highly overestimated. The red color of carrots is, for instance, due do the presence of carotenes which are hydrocarbons with about ten double bonds in conjugation. The carotenes absorb light in the blue-green region with $\lambda \approx 500\,\mathrm{nm}$; the above formula would predict a much longer wavelength. That carrots actually appear red is caused by the fact that the blue-green light is removed by the absorption, and hence the complementary color, which is red, will dominate in the light that reaches the eye.

This concludes our discussion of the free-electron model. It has shown us both the strengths and the weaknesses of a crude model. It is easy to apply and it does describe some important qualitative aspects correctly. But one may not hope to get anything like quantitatively correct predictions from the model. It is, of course, possible to improve on a model like the free-electron model, but it is usually more rewarding to adopt a more realistic description of the system under study.

4.9 Non-Stationary States

In the previous sections we have discussed the stationary states of the particle in a box. We shall now show how the acquired knowledge may be used to study more general time-dependent states. The procedure that will be used may be transferred to other systems with different Hamiltonians, so the idea is again to illustrate general principles by means of a simple model.

Let us restrict our attention to the one-dimensional box. Let us also, in the same way as in the previous section, denote the wavefunctions (4.36) by $\psi_n(x)$ instead of $X_{n_x}(x)$, and denote the energies of Eq. (4.28) by E_n. We have then:

$$\boxed{\psi_n(x) = \sqrt{2/a}\,\sin(n\pi x/a), \quad E_n = \frac{h^2}{8ma^2}n^2, \qquad n = 1,2,3,\ldots} \tag{4.83}$$

The time-dependent stationary-state wavefunctions are, according to Eq. (3.7)

$$\boxed{\Psi_n(x,t) = \psi_n(x)e^{-iE_nt/\hbar}} \tag{4.84}$$

The time evolution of any—stationary or non-stationary—state described by a wavefunction $\Psi(x,t)$ is given by the time-dependent Schrödinger equation

(3.18),

$$\boxed{i\hbar\frac{\partial\Psi(x,t)}{\partial t}=\widehat{H}\Psi(x,t)} \tag{4.85}$$

with the Hamiltonian (4.12), which we now simply denote by $\widehat{H}$:

$$\widehat{H}=-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}. \tag{4.86}$$

We have of course that

$$\widehat{H}\psi_n(x)=E_n\psi_n(x), \qquad n=1,2,3,\ldots \tag{4.87}$$

Assume, now, that we are given the form, $\Psi(x,0)$, of the wavefunction at some initial time $t=0$. We may then determine the time evolution of Ψ by continued iteration by the method indicated in Eq. (3.3). Such an iteration may, for instance, be performed numerically on a computer. There is, however, another useful way of representing the time dependence of Ψ.

As we emphasized in Sec. 3.1 and 3.4, there are no severe restrictions on the possible form of $\Psi(x,0)$, except that it must be smooth and square integrable, and of course satisfy the boundary conditions of the problem. But now it is known from the theory of Fourier series, that any well-behaved function which vanishes at $x=0$ and $x=a$ may be written as a linear combination of the functions $\sin(n\pi x/a)$, $n=1,2,3,\ldots$ These functions are, however, just the functions in (4.83). It is, consequently, possible to expand $\Psi(x,0)$ on the set $\{\psi_n(x)\}$ and write

$$\Psi(x,0)=\sum_{n=1}^{\infty}c_n\psi_n(x). \tag{4.88}$$

The wavefunction at any later time will then be

$$\Psi(x,t)=\sum_{n=1}^{\infty}c_n\Psi_n(x,t), \tag{4.89}$$

where $\Psi_n(x,t)$ is given by Eq. (4.84). For this function reduces to $\Psi(x,0)$ for $t=0$, and it also satisfies Eq. (4.85). To see this, note that Eq. (4.87) implies that

$$\widehat{H}\Psi(x,t)=\sum_{n=1}^{\infty}c_n\widehat{H}\Psi_n(x,t)=\sum_{n=1}^{\infty}c_nE_n\Psi_n(x,t), \tag{4.90}$$

while Eq. (4.84) yields

$$i\hbar\frac{\partial}{\partial t}\Psi(x,t) = i\hbar\sum_{n=1}^{\infty} c_n\frac{\partial}{\partial t}\Psi_n(x,t) = \sum_{n=1}^{\infty} c_n E_n \Psi_n(x,t). \tag{4.91}$$

The right-hand sides of these two equations are identical. Hence, Eq. (4.85) is satisfied, and this is the condition for the function (4.89) to be the correct time-dependent function.

It follows, from this exercise, that the wavefunction associated with any non-stationary state may be written in the form (4.89) with time-independent coefficients c_n. We have been able to prove this for the one-dimensional box by referring to the theory of Fourier series, but the result is generally valid and holds for any system. Thus we can state the important *principle of superposition*:

> For a given system, any time-dependent wavefunction can be written as a superposition of the system's time-dependent stationary-state wavefunctions, with coefficients that are independent of time. (4.92)

The coefficients are determined by the way the system is prepared at $t = 0$.

As an illustration, let us consider the simple initial function

$$\Psi(x,0) = \sqrt{1/2}\{\psi_1(x) + \psi_2(x)\} \tag{4.93}$$

where ψ_1 and ψ_2 are given by Eq. (4.83). This is a properly normalized function, for the expansion coefficients satisfy the condition spelled out in statement (4.76). We get then, by Eq. (4.89):

$$\Psi(x,t) = \sqrt{1/2}\{\psi_1(x)e^{-iE_1t/\hbar} + \psi_2(x)e^{-iE_2t/\hbar}\}, \tag{4.94}$$

and hence (See Appendix A):

$$\Psi^*(x,t)\Psi(x,t) = \frac{1}{2}\{\psi_1(x)^2 + \psi_2(x)^2 + 2\psi_1(x)\psi_2(x)\cos[(E_2 - E_1)t/\hbar]\}. \tag{4.95}$$

The probability density is $\frac{1}{2}$ times a sum of three terms: The first term is the probability density associated with the stationary state $\Psi_1(x,t)$. Similarly, the second term is the probability density associated with the stationary state $\Psi_2(x,t)$. The third term is said to describe the *interference* between the two

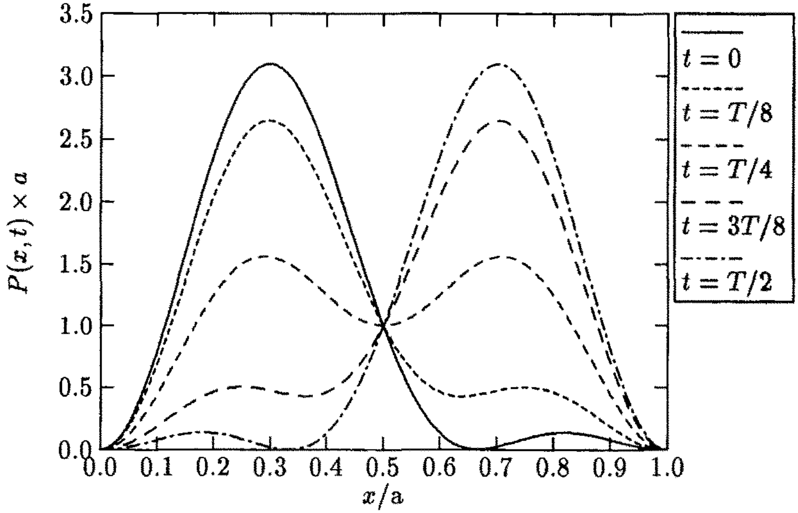

Figure 4.6: Probability density for a non-stationary state of the particle in a box. See text.

stationary states $\Psi_1(x,t)$ and $\Psi_2(x,t)$. Note that this contribution to the probability density oscillates in time.

The origin of the interference term is similar to the origin of the interference terms in Eq. (2.81) for the double-slit experiment. In both cases, the interference terms occur because the principle of superposition applies to amplitudes rather than probability densities.

We remind the reader that a function of the type $\cos(2\pi\nu t)$ is said to oscillate in time with *frequency* ν, *period* $T = 1/\nu$, and *angular frequency* $\omega = 2\pi\nu$. For the above oscillation, the angular frequency is seen to have the magnitude:

$$\omega = (E_2 - E_1)/\hbar. \tag{4.96}$$

We may also write

$$E_2 - E_1 = \hbar\omega = h\nu, \tag{4.97}$$

which reminds us of the Bohr frequency rule, Eq. (2.45), but the content is of course different.

In Fig. 4.6 we show graphs of the probability density (4.95), here denoted by $P(x,t)$:

$$P(x,t) = \Psi^*(x,t)\Psi(x,t). \tag{4.98}$$

The graphs are instant pictures of $P(x,t)$ corresponding to $t = 0$, $T/8$, $T/4$, $3T/8$, $T/2$, where

$$T = \frac{h}{E_2 - E_1} \tag{4.99}$$

is the period of the oscillation.

We have now studied the wavefunctions associated with both stationary and non-stationary states of a single particle, and we have plotted probability densities, $P(x,t)$, for both types of states. The probability densities give statistical information about the behavior of the particle. Important aspects of this behavior are reflected in the so-called expectation values and uncertainties. This will be discussed in some detail in the next chapter.

Supplementary Reading

The bibliography, entries [6], [11] and [9].

Problems

4.1. Imagine an electron confined to a cubic box with edge a. Determine the value of a for which the electron's zero-point energy equals its rest-mass energy, m_ec^2. Express the result in units of the so-called *Compton wavelength*, $\lambda_C = h/(m_ec)$, and in atomic units (Appendix B.2).

4.2. According to the kinetic theory of gases, the average speed of an atom in an atomic gas at the absolute temperature T is given by the expression

$$v = \sqrt{\frac{3kT}{m}}$$

where m is the mass of the atom and k is the Boltzmann constant.

a. Write down an expression for the de Broglie wavelength λ corresponding to v.

b. Calculate the value of λ for a Na atom in a Na gas at $T = 300\,\mathrm{K}$ and at $T = 100 \times 10^{-9}\,\mathrm{K}$. (The atomic mass of Na is $22.990\,\mathrm{u}$, with $1\,\mathrm{u} = 1.66054 \times 10^{-27}\,\mathrm{kg}$.)

c. Assume that a Na atom is enclosed in a cubic box with edge λ. Give an expression for the energy separation ΔE between the ground state and the first excited state of such an atom.

d. Determine the value of $kT/\Delta E$.

4.3. Write down the energy levels and the stationary-state wavefunctions for a particle in a two-dimensional box with edges a and b.
For $a = b$ (a square box), construct the energy level diagram corresponding to that of Fig. (4.4). Specify the sets of quantum numbers (n_x, n_y) corresponding to each level in the diagram.
Sketch the form of the ground-state wavefunction by means of contour curves in the x, y-plane, i. e., curves on which the wavefunction has a constant value.

4.4. At time $t = 0$, a particle in a one-dimensional box is known to be in a non-stationary state described by the wavefunction of Eq. (4.93). Calculate the quantity

$$\bar{x}(t) = \int_0^a x\Psi^*(x,t)\Psi(x,t)dx,$$

i. e., the mean position of the particle as a function of t. Specify the x-interval traversed by the possible values of $\bar{x}$.

Use, for instance, that

$$2\sin\alpha\sin\beta = \cos(\alpha - \beta) - \cos(\alpha + \beta)$$

and

$$\int_0^\pi u\cos(nu)du = \frac{1}{n^2}\left[(-1)^n - 1\right].$$

4.5. Consider a two-dimensional linear function space, $\mathcal{V}$, with basis (ψ_1, ψ_2) where ψ_1 and ψ_2 are linearly independent functions. ψ_1 and ψ_2 are assumed to be normalized to unity, but they are not orthogonal. Thus, we have.

$$\langle\psi_1|\psi_1\rangle = 1, \quad \langle\psi_2|\psi_2\rangle = 1, \quad \langle\psi_1|\psi_2\rangle = S,$$

where S is the overlap integral between ψ_1 and ψ_2 (cf. Eq. (4.37)).
In what follows, it may be assumed that S is real-valued.

a. Construct an orthonormal basis in $\mathcal{V}$ defined by the functions

$$\psi_1' = \psi_1, \quad \psi_2' = N(\psi_2 + a\psi_1).$$

First, determine a such that $\langle\psi_1'|\psi_2'\rangle = 0$. Next, determine the value of the normalization constant N.
(This method of orthogonalization is called *Gram–Schmidt orthogonalization*. It is readily extended to function spaces of higher dimensions.)

b. Construct another orthonormal basis, defined by the functions

$$\psi_1'' = N_1(\psi_1 + \psi_2), \quad \psi_2'' = N_2(\psi_1 + b\psi_2).$$

First, determine the value of b. Next, determine the normalization constants N_1 and N_2.

Chapter 5

Quantum-Mechanical Operators

Contents

We have now performed a rather detailed study of a concrete quantum-mechanical problem. On the way, we have made some important observations on the general behavior of quantum systems. It was possible to make these observations because of the simplicity of the problem. But for more complex problems, we may benefit considerably from a refinement of the formalism. Consequently, we shall devote the present chapter to a formal study of the properties of quantum-mechanical operators.

In Sec. (3.3) we discussed the process of quantization by means of which the dynamical functions of classical mechanics (like position, linear momentum, angular momentum, etc.) are replaced by operators in quantum mechanics. This process induces a fundamental algebraic difference between the dynamical quantities in classical mechanics and quantum mechanics: Two classical functions like x and p_x multiply together as xp_x and $p_x x$ with the same result, whereas the result of multiplying the two corresponding operators $\hat{x}$ and $\hat{p}_x$ depends on the order of multiplication. Thus, the operators $\hat{x}\hat{p}_x$ and $\hat{p}_x\hat{x}$ are different. The difference between the two operators is called a commutator. As may well be imagined, commutators play a fundamental role in quantum mechanics. We shall lay the basis for the understanding of that role in this chapter.

Operators like $\hat{x}$ and $\hat{p}_x$, and the Hamiltonian $\widehat{H}$, are all operators that represent quantities that can be measured. Such quantities are called observables. There are other interesting operators in quantum mechanics besides those that represent observables, but operators representing observables have special properties. They belong to the class of so-called Hermitian operators. We shall accordingly put much focus on Hermitian operators and their properties in what follows.

The commutator between two Hermitian operators is obviously an important quantity. We shall see that if it vanishes, then it is possible to construct quantum states for which both observables involved have so-called sharp values. But if the commutator between the two operators is different from zero, then it is impossible to construct such states in general. The famous uncertainty relation puts a well-defined limit on the accuracy with which the two observables may be measured simultaneously. This limit is determined by the commutator. The discussion in the present chapter is sufficiently precise that it enables us to derive the exact form of the uncertainty relation and we shall accordingly do so, before we close the chapter with a more general discussion of quantum theory and measurements, and a section on matrix mechanics.

5.1 The Bra-Ket Notation

In Chapter 3 we introduced the Schrödinger wave mechanics according to which the state of a physical system is determined by a wavefunction, Ψ. The wavefunction depends on the time and all the coordinates of the system. For the latter, we shall use the collective notation q in what follows and thus write $\Psi = \Psi(q,t)$. The time development of the wavefunction is governed by the system's Hamiltonian, $\widehat{H}$, through the time-dependent Schrödinger equation,

$$i\hbar\frac{\partial\Psi}{\partial t} = \widehat{H}\Psi. \tag{5.1}$$

The stationary states are described by wavefunctions of the particular form

$$\Psi_n(q,t) = \psi_n(q)e^{-iE_nt/\hbar}, \tag{5.2}$$

where E_n is the energy of the state, and $\psi_n(q)$ is a solution of the time-independent Schrödinger equation,

$$\widehat{H}\Psi = E\Psi. \tag{5.3}$$

In the preceding chapters we have considered this equation in some detail and found its solutions for the particle in a box, in a single dimension and in three dimensions.

It was pointed out in Sec. 3.2, that if ψ is a solution of Eq. (5.3) then so is $c\psi$, where c is any nonvanishing complex constant. In a similar way, $c\Psi$ satisfies Eq. (5.1) whenever Ψ does. Accordingly, all functions of the form $c\Psi$ are understood to define the same physical state. One sometimes says that the state is determined by the *ray* $c\Psi$.

For Ψ to represent a physical state it must be square integrable, i.e., the integral

$$\langle\Psi|\Psi\rangle = \int \Psi^*(q,t)\Psi(q,t)dq, \tag{5.4}$$

where dq denotes integration over all the coordinates of the system, must be finite. We may consequently choose the constant c such that the integral is unity, which is useful in most applications. $\Psi^*\Psi$ is then a probability density, and $\Psi^*(q,t)\Psi(q,t)dq$ is the probability of finding the system in the 'volume element' dq around the configuration q, at time t. But we *need not* normalize the wavefunction to unity. If we don't, then the quantity to be interpreted as a probability density is $\Psi^*(q,t)\Psi(q,t)/\langle\Psi|\Psi\rangle$.

We begin the next section with some basic definitions. They all refer to a given quantum system at some instant of time. Hence, we shall omit the argument t and write $\Psi(q)$ for a possible wavefunction of the system. We do not assume that $\Psi(q)$ is an eigenfunction of the Hamiltonian. On the contrary, we allow Ψ to be a very general function of the system coordinates q. The only requirements are that Ψ be a smooth function of the arguments, and that it be square integrable so that the integral

$$\langle\Psi|\Psi\rangle = \int \Psi^*(q)\Psi(q)dq \tag{5.5}$$

is finite.

For two square integrable functions, Ψ_r and Ψ_s, we introduce the *scalar product*, or *overlap integral*, by the definition

$$\langle\Psi_r|\Psi_s\rangle = \int \Psi_r^*(q)\Psi_s(q)dq, \tag{5.6}$$

in analogy with Eq. (4.39). As in Sec. 4.3, we underline that the first factor in the integrand is the complex conjugate of $\Psi_r(q)$ rather than $\Psi_r(q)$ itself. As a result of this, we have the general relation

$$\boxed{\langle\Psi_s|\Psi_r\rangle = \langle\Psi_r|\Psi_s\rangle^*} \tag{5.7}$$

Note, also, that Eq. (5.5) is but a special case of Eq. (5.6).

As we have stated, q is a collective notion for all coordinates of the system. When we need a more explicit notation and the number of coordinates is f, we may write

$$\{q\} = \{x_1, x_2, \ldots, x_f\}. \tag{5.8}$$

If, for instance, the system consists of N particles, then we might let x_1, x_2, x_3 represent the x, y, z coordinates of particle 1, x_4, x_5, x_6 the x, y, z coordinates of particle 2, etc. Thus, we would write

$$\{q\} = \{x_1, x_2, \ldots, x_{3N}\}. \tag{5.9}$$

The notation $\langle\Psi_r|\Psi_s\rangle$ which we have used above, and also in the previous chapter, is the so-called *bra-ket notation*. The terms bra and ket were coined by Dirac. They were extracted as the left and right parts of the word *bracket* and denote quantities of the type $\langle\Psi_r|$ and $|\Psi_s\rangle$, respectively. A ket $|\Psi\rangle$ was meant by Dirac to designate a vector in an abstract space. Hence it is written without reference to specific variables, except possibly the time. $\Psi(q)$ is the so-called *position-space representation* of $|\Psi\rangle$, and one writes

$$\Psi(q) = \langle q|\Psi\rangle \tag{5.10}$$

and

$$\Psi^*(q) = \langle\Psi|q\rangle. \tag{5.11}$$

But since we shall mainly work in position space, we may generally think of $|\Psi\rangle$ as being simply $\Psi(q)$, and of $\langle\Psi|$ as being simply $\Psi^*(q)$. Obviously, we obtain the symbol $\langle\Psi_r|\Psi_s\rangle$ for the scalar product (5.6) by a simple juxtaposition of the bra symbol $\langle\Psi_r|$ and the ket symbol $|\Psi_s\rangle$, the two vertical lines being contracted to one for brevity.

The bra-ket notation is both useful and elegant, and we shall extend its use in the following sections.

5.2 Linear Operators. The Commutator

An operator $\hat{\Omega}$ is called linear if the relation

$$\boxed{\hat{\Omega}(c_1\Psi_1 + c_2\Psi_2) = c_1\hat{\Omega}\Psi_1 + c_2\hat{\Omega}\Psi_2} \tag{5.12}$$

is satisfied for arbitrary complex coefficients, c_1 and c_2, and for arbitrary functions, Ψ_1 and Ψ_2. We shall only meet linear operators in the following.

Let us consider the successive application of two operators, $\hat{\Omega}_a$ and $\hat{\Omega}_b$, to a function Ψ. Applying $\hat{\Omega}_b$ first results in a new function $\hat{\Omega}_b\Psi$, and when $\hat{\Omega}_a$ is applied next we get the function $\hat{\Omega}_a\hat{\Omega}_b\Psi$. Applying $\hat{\Omega}_a$ before $\hat{\Omega}_b$ results, on the other hand, in the function $\hat{\Omega}_b\hat{\Omega}_a\Psi$. The difference between the two functions is

$$\hat{\Omega}_a\hat{\Omega}_b\Psi - \hat{\Omega}_b\hat{\Omega}_a\Psi = (\hat{\Omega}_a\hat{\Omega}_b - \hat{\Omega}_b\hat{\Omega}_a)\Psi. \tag{5.13}$$

If this function vanishes, it does not matter in which order we apply $\hat{\Omega}_a$ and $\hat{\Omega}_b$. And if this is found to be true for *any* Ψ, we say that $\hat{\Omega}_a$ and $\hat{\Omega}_b$ commute. However, quantum-mechanical operators do not commute in general, so an important quantity is the *commutator*:

$$\boxed{[\hat{\Omega}_a, \hat{\Omega}_b] = \hat{\Omega}_a\hat{\Omega}_b - \hat{\Omega}_b\hat{\Omega}_a} \tag{5.14}$$

It follows from the definition that this is an *antisymmetric* quantity, in the sense that

$$\boxed{[\hat{\Omega}_b, \hat{\Omega}_a] = -[\hat{\Omega}_a, \hat{\Omega}_b]} \tag{5.15}$$

Let us consider some important examples.

As the first example we take

$$\hat{\Omega}_a = \hat{\Omega}, \quad \hat{\Omega}_b = c, \tag{5.16}$$

where $\hat{\Omega}$ is an arbitrary operator and c an arbitrary complex constant. Since $\hat{\Omega}$ is assumed to be linear we get, for any function Ψ, that $\hat{\Omega} c\Psi = c\hat{\Omega}\Psi$, and hence that $(\hat{\Omega} c - c\hat{\Omega})\Psi = 0$. But this implies that

$$\boxed{[\hat{\Omega}, c] = 0} \tag{5.17}$$

In our second example we put

$$\hat{\Omega}_a = \frac{\partial}{\partial x_1}, \quad \hat{\Omega}_b = x_1, \tag{5.18}$$

in the notation of Eq. (5.9). We get

$$\frac{\partial}{\partial x_1} x_1 \Psi = x_1 \frac{\partial}{\partial x_1} \Psi + \Psi, \tag{5.19}$$

and hence

$$\left(\frac{\partial}{\partial x_1} x_1 - x_1 \frac{\partial}{\partial x_1} \right) \Psi = \Psi. \tag{5.20}$$

Since this holds for any Ψ, we have derived the following *commutation relation*

$$\left[\frac{\partial}{\partial x_1}, x_1 \right] = 1. \tag{5.21}$$

Provided that the coordinates involved are Cartesian, $\partial/\partial x_1$ defines the momentum operator $\hat{p}_1$ by the definition (3.11)

$$\hat{p}_1 = -i\hbar \frac{\partial}{\partial x_1}. \tag{5.22}$$

Hence we get, by multiplying Eq. (5.20) by $i\hbar$

$$\boxed{[x_1, \hat{p}_1] = i\hbar} \tag{5.23}$$

A similar relation holds, of course, for the commutator between $\hat{p}_2$ and x_2. To derive the commutator between $\hat{p}_1$ and x_2 we note that

$$\frac{\partial}{\partial x_1} x_2 \Psi = x_2 \frac{\partial}{\partial x_1} \Psi, \tag{5.24}$$

which shows that

$$[x_2, \hat{p}_1] = 0. \tag{5.25}$$

Extending these findings to all the Cartesian coordinates in a set of the type (5.9) allows us to write

$$\boxed{[x_i, \hat{p}_j] = i\hbar\delta_{ij}} \tag{5.26}$$

This is a very basic quantum-mechanical result.

In our last, and somewhat more complicated example we consider a single particle in three dimensions. Its Cartesian coordinates are called (x, y, z) as usual. We seek the commutation relations between the angular-momentum operators $(\hat{l}_x, \hat{l}_y, \hat{l}_z)$, which are defined as the Cartesian components of the angular-momentum vector operator

$$\hat{\boldsymbol{l}} = \hat{\boldsymbol{r}} \times \hat{\boldsymbol{p}}. \tag{5.27}$$

These components are

$$\begin{cases} \hat{l}_x = y\hat{p}_z - z\hat{p}_y = -i\hbar\left(y\dfrac{\partial}{\partial z} - z\dfrac{\partial}{\partial y}\right), \\ \hat{l}_y = z\hat{p}_x - x\hat{p}_z = -i\hbar\left(z\dfrac{\partial}{\partial x} - x\dfrac{\partial}{\partial z}\right), \\ \hat{l}_z = x\hat{p}_y - y\hat{p}_x = -i\hbar\left(x\dfrac{\partial}{\partial y} - y\dfrac{\partial}{\partial x}\right). \end{cases} \tag{5.28}$$

The square of the angular momentum is represented by the operator

$$\hat{l}^2 = \hat{l}_x^2 + \hat{l}_y^2 + \hat{l}_z^2. \tag{5.29}$$

Straightforward evaluation gives first

$$\begin{aligned} [\hat{l}_x, \hat{l}_y]\Psi &= \left(\hat{l}_x\hat{l}_y - \hat{l}_y\hat{l}_x\right)\Psi \\ &= -\hbar^2\left\{\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\left(z\frac{\partial\Psi}{\partial x} - x\frac{\partial\Psi}{\partial z}\right)\right. \\ &\qquad \left. - \left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\left(y\frac{\partial\Psi}{\partial z} - z\frac{\partial\Psi}{\partial y}\right)\right\}, \end{aligned} \tag{5.30}$$

and next,

$$\begin{aligned}[\hat{l}_x,\,\hat{l}_y]\Psi = -\hbar^2 \Big\{ & y\frac{\partial}{\partial z}z\frac{\partial\Psi}{\partial x} - y\frac{\partial}{\partial z}x\frac{\partial\Psi}{\partial z} - z\frac{\partial}{\partial y}z\frac{\partial\Psi}{\partial x} + z\frac{\partial}{\partial y}x\frac{\partial\Psi}{\partial z} \\ & -z\frac{\partial}{\partial x}y\frac{\partial\Psi}{\partial z} + z\frac{\partial}{\partial x}z\frac{\partial\Psi}{\partial y} + x\frac{\partial}{\partial z}y\frac{\partial\Psi}{\partial z} - x\frac{\partial}{\partial z}z\frac{\partial\Psi}{\partial y}\Big\} \\ = \hbar^2 & \left(x\frac{\partial\Psi}{\partial y} - y\frac{\partial\Psi}{\partial x}\right) = i\hbar(-i\hbar)\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\Psi = i\hbar\hat{l}_z\Psi.\end{aligned} \tag{5.31}$$

The result of the exercise is that

$$[\hat{l}_x,\,\hat{l}_y] = i\hbar\hat{l}_z. \tag{5.32}$$

Similar results are obtained for the commutators $[\hat{l}_y,\,\hat{l}_z]$ and $[\hat{l}_z,\,\hat{l}_x]$. Thus, we arrive at the fundamental commutation relations

$$\boxed{\begin{aligned}[\hat{l}_x,\,\hat{l}_y] &= i\hbar\hat{l}_z, \\ [\hat{l}_y,\,\hat{l}_z] &= i\hbar\hat{l}_x, \\ [\hat{l}_z,\,\hat{l}_x] &= i\hbar\hat{l}_y.\end{aligned}} \tag{5.33}$$

Note that these three commutation relations are transformed into each other under a cyclic shifting of the indices ($x \to y,\ y \to z,\ z \to x$). For the square of the angular momentum, as defined by Eq. (5.29), one finds

$$\boxed{[\hat{l}^2,\,\hat{l}_x] = [\hat{l}^2,\,\hat{l}_y] = [\hat{l}^2,\,\hat{l}_z] = 0} \tag{5.34}$$

so that $\hat{l}^2$ commutes with each of the components $\hat{l}_x, \hat{l}_y$, and $\hat{l}_z$.

In the derivation of more complicated commutation relations it is often helpful to take advantage of the following general relations, in which the $\hat{\Omega}'s$ are arbitrary operators and the c's arbitrary complex constants,

$$\boxed{\begin{aligned}[\hat{\Omega},\,c_1\hat{\Omega}_a + c_2\hat{\Omega}_b] &= c_1[\hat{\Omega},\,\hat{\Omega}_a] + c_2[\hat{\Omega},\,\hat{\Omega}_b] \\ [\hat{\Omega}_a\hat{\Omega}_b,\,\hat{\Omega}_c] &= \hat{\Omega}_a[\hat{\Omega}_b,\,\hat{\Omega}_c] + [\hat{\Omega}_a,\,\hat{\Omega}_c]\hat{\Omega}_b \\ [\hat{\Omega}_a,\,\hat{\Omega}_b\hat{\Omega}_c] &= \hat{\Omega}_b[\hat{\Omega}_a,\,\hat{\Omega}_c] + [\hat{\Omega}_a,\,\hat{\Omega}_b]\hat{\Omega}_c\end{aligned}} \tag{5.35}$$

Each of these relations is easily verified by evaluating the two sides of the relation separately and comparing the results. We get, for instance, for the second relation

$$[\hat{\Omega}_a\hat{\Omega}_b,\, \hat{\Omega}_c] = \hat{\Omega}_a\hat{\Omega}_b\hat{\Omega}_c - \hat{\Omega}_c\hat{\Omega}_a\hat{\Omega}_b, \tag{5.36}$$

and

$$\begin{aligned}\hat{\Omega}_a[\hat{\Omega}_b,\, \hat{\Omega}_c] + [\hat{\Omega}_a,\, \hat{\Omega}_c]\hat{\Omega}_b &= \hat{\Omega}_a\hat{\Omega}_b\hat{\Omega}_c - \hat{\Omega}_a\hat{\Omega}_c\hat{\Omega}_b + \hat{\Omega}_a\hat{\Omega}_c\hat{\Omega}_b - \hat{\Omega}_c\hat{\Omega}_a\hat{\Omega}_b\\ &= \hat{\Omega}_a\hat{\Omega}_b\hat{\Omega}_c - \hat{\Omega}_c\hat{\Omega}_a\hat{\Omega}_b \qquad (5.37)\end{aligned}$$

which verifies the relation.

As an example of using the relation just proven, let us evaluate the commutator $[\hat{l}^2,\, \hat{l}_x]$. We get

$$\begin{aligned}[\hat{l}^2,\, \hat{l}_x] &= [\hat{l}_x^2,\, \hat{l}_x] + [\hat{l}_y^2,\, \hat{l}_x] + [\hat{l}_z^2,\, \hat{l}_x]\\ &= 0 + \hat{l}_y[\hat{l}_y,\, \hat{l}_x] + [\hat{l}_y,\, \hat{l}_x]\hat{l}_y + \hat{l}_z[\hat{l}_z,\, \hat{l}_x] + [\hat{l}_z,\, \hat{l}_x]\hat{l}_z\\ &= \hat{l}_y(-i\hbar\hat{l}_z) + (-i\hbar\hat{l}_z)\hat{l}_y + \hat{l}_z(i\hbar\hat{l}_y) + (i\hbar\hat{l}_y)\hat{l}_z\\ &= 0. \qquad (5.38)\end{aligned}$$

This verifies the first part of the relation (5.34). The rest is verified in a similar manner.

In closing this section, let us note that we may also use the bra-ket notation freely when operators are involved. The effect of operating with an operator $\hat{\Omega}$ on the ket $|\Psi\rangle$ is written $\hat{\Omega}|\Psi\rangle$. It equals the ket $|\hat{\Omega}\Psi\rangle$, which we may think of as $\hat{\Omega}\Psi(q)$ as long as we stay in the position representation.

5.3 Hermitian Operators. Hermitian Conjugation

An important class of quantum-mechanical operators are the so-called *Hermitian operators*. The Hamiltonian is a Hermitian operator, and the same is true for any other operator that represents an observable. We shall show this in the following section. Here, we shall merely introduce the definition of Hermitian operators and make ourselves familiar with the definition through some simple, but important examples.

Let us consider an operator $\hat{\Omega}$, together with two functions, $\Psi_r(q)$ and $\Psi_s(q)$, which so far are completely arbitrary except for the condition that the integral

$$\boxed{\Omega_{rs} = \langle\Psi_r|\hat{\Omega}|\Psi_s\rangle = \langle\Psi_r|\hat{\Omega}\Psi_s\rangle = \int \Psi_r^*(q)\hat{\Omega}\Psi_s(q)dq} \tag{5.39}$$

must exist. Integrals of this type play an important role in quantum mechanics, and are often referred to as matrix elements, because any set of functions, $\Psi_1(q), \Psi_2(q), \ldots$, allows us to construct a matrix, namely, the matrix with elements $\Omega_{11}, \Omega_{12}, \Omega_{21}, \Omega_{22}$, etc. The notation $\langle\Psi_r|\hat{\Omega}|\Psi_s\rangle$ is a natural extension of the bra-ket notation. We recall again that whenever a function appears in a bra position, as Ψ_r does in the above expression, then it is the complex conjugate of the function that is involved. Remembering this, we may establish the following relation,

$$\langle\hat{\Omega}\Psi_r|\Psi_s\rangle = \langle\Psi_s|\hat{\Omega}|\Psi_r\rangle^*, \tag{5.40}$$

for when we specify the integrals involved, the relation becomes

$$\int(\hat{\Omega}\Psi_r)^*\Psi_s dq = \left(\int \Psi_s^*\hat{\Omega}\Psi_r dq\right)^* \tag{5.41}$$

which is a trivial identity.

With the definition of the matrix element $\langle\Psi_r|\hat{\Omega}|\Psi_s\rangle$ completely understood, let us recall the relation (5.7), which says that if we interchange the two functions Ψ_r and Ψ_s in the scalar product $\langle\Psi_r|\Psi_s\rangle$, then the value of the scalar product is merely replaced by its complex conjugate. This implies, in particular, that the absolute value $|\langle\Psi_r|\Psi_s\rangle|$ is unchanged. We cannot expect the relation between $\langle\Psi_r|\hat{\Omega}|\Psi_s\rangle$ and $\langle\Psi_s|\hat{\Omega}|\Psi_r\rangle$ to be equally simple. But for a certain class of operators it is. This is just the class of Hermitian operators. The proper definition of a Hermitian operator is

An operator $\hat{F}$ is said to be Hermitian if and only if
$\langle\Psi_r|\hat{F}|\Psi_s\rangle = \langle\Psi_s|\hat{F}|\Psi_r\rangle^*$
for arbitrary, well-behaved functions Ψ_r and Ψ_s.
The condition may also be written
$\langle\Psi_r|\hat{F}|\Psi_s\rangle = \langle\hat{F}\Psi_r|\Psi_s\rangle$. (5.42)

The latter form of the definition is readily obtained from the first by exploiting the relation (5.40). By *a well-behaved function* we understand a function that may, at least in principle, serve as a wavefunction for the system under study (in general a non-stationary wavefunction). This implies, as we know, that the function must be square integrable, and that it must honor the boundary conditions imposed on the system. A well-behaved wavefunction for the particle in a box must, for instance, vanish on the walls of the box. The importance of requiring the functions Ψ_r and Ψ_s to be well-behaved in the present context will become clear through the following examples. (See, in particular, the derivation of Eqs. (5.50) and (5.52).)

For a general operator $\hat{\Omega}$ we may introduce the so-called *Hermitian conjugate operator* $\hat{\Omega}^\dagger$ by the requirement that the matrix element $\langle\Psi_r|\hat{\Omega}^\dagger|\Psi_s\rangle$ equal $\langle\Psi_s|\hat{\Omega}|\Psi_r\rangle^*$ for arbitrary functions Ψ_r and Ψ_s. We may again exploit the relation (5.40) and turn the expression $\langle\Psi_s|\hat{\Omega}|\Psi_r\rangle^*$ into $\langle\hat{\Omega}\Psi_r|\Psi_s\rangle$. Thus, we have,

An operator $\hat{\Omega}^\dagger$ is said to be the Hermitian conjugate of the operator $\hat{\Omega}$ if and only if

$$\langle\Psi_r|\hat{\Omega}^\dagger|\Psi_s\rangle = \langle\Psi_s|\hat{\Omega}|\Psi_r\rangle^*$$

for arbitrary, well-behaved functions Ψ_r and Ψ_s. The condition may also be written

$$\langle\Psi_r|\hat{\Omega}^\dagger|\Psi_s\rangle = \langle\hat{\Omega}\Psi_r|\Psi_s\rangle.$$

This relation is known as the *turn-over rule*.. (5.43)

Hermitian conjugation is a symmetric relationship between the operators $\hat{\Omega}$ and $\hat{\Omega}^\dagger$, in the sense that $\hat{\Omega}$ is also the Hermitian conjugate of $\hat{\Omega}^\dagger$. The relation that certifies this is simply the complex conjugate of the first of the relations (5.43).

The condition for $\hat{F}$ to be a Hermitian operator may now be rephrased: The operators $\hat{F}$ and $\hat{F}^\dagger$ must be identical.

To proceed, let us determine the Hermitian conjugates of the operators studied in the previous section. In each case, the easiest route to follow is to write down the expression $\langle\hat{\Omega}\Psi_r|\Psi_s\rangle$, and then manipulate this expression such that it is brought on the form $\langle\Psi_r|\hat{\Omega}^\dagger|\Psi_s\rangle$, from which $\hat{\Omega}^\dagger$ may be identified by the turn-over rule.

First, we consider a complex constant c, and hence the expression $\langle c\Psi_r|\Psi_s\rangle$. We obviously have that

$$\int (c\Psi_r(q))^*\Psi_s(q)dq = \int \Psi_r^*(q)c^*\Psi_s(q)dq, \tag{5.44}$$

that is,

$$\langle c\Psi_r|\Psi_s\rangle = \langle\Psi_r|c^*|\Psi_s\rangle. \tag{5.45}$$

This shows that

$$\boxed{c^\dagger = c^*} \tag{5.46}$$

The steps just carried through may be repeated without modification for an arbitrary function of q, $V(q)$ say. Thus, we have that

$$\boxed{V^\dagger(q) = V(q)^*} \tag{5.47}$$

These simple examples might let us believe that Hermitian conjugation is the same thing as complex conjugation. That this is not so in general, is inherent in the following examples.

In the example to be taken up next, we want to determine the Hermitian conjugate of the operator $\partial/\partial x_1$, where x_1 belongs to a coordinate set of the type (5.9), i.e., we assume that we are dealing with a set of Cartesian coordinates $x_1, x_2, \ldots, x_{3N}$. We also assume that the functions involved satisfy the following boundary condition,

$$\Psi(a_1, x_2, \ldots, x_{3N}) = \Psi(b_1, x_2, \ldots, x_{3N}), \tag{5.48}$$

where a_1 and b_1 define the range of x_1. The condition is certainly satisfied if x_1 is defined on the interval $-\infty < x_1 < \infty$, for the integral $\langle\Psi|\Psi\rangle$ will only exist if Ψ tends to zero when $|x_1|$ tends to infinity. But the condition is, for instance, also satisfied for the particle in a box, where we require all physically acceptable wavefunctions to vanish on the walls of the box.

By observing Eq. (5.48), and introducing the notation dq' for the incomplete volume element $dx_2dx_3\ldots dx_{3N}$, we get:

$$\begin{aligned}
\left\langle \frac{\partial}{\partial x_1}\Psi_r|\Psi_s\right\rangle &= \int dq' \int_{a_1}^{b_1} \left(\frac{\partial}{\partial x_1}\Psi_r^*\right)\Psi_s dx_1 \\
&= \int dq' \left\{ \left[\Psi_r^*\Psi_s\right]_{a_1}^{b_1} - \int_{a_1}^{b_1} \Psi_r^* \frac{\partial}{\partial x_1}\Psi_s dx_1 \right\} \\
&= \int \Psi_r^* \left(-\frac{\partial}{\partial x_1}\right)\Psi_s dq \\
&= \left\langle \Psi_r \middle| -\frac{\partial}{\partial x_1} \middle| \Psi_s \right\rangle,
\end{aligned} \tag{5.49}$$

which shows that

$$\boxed{\left(\frac{\partial}{\partial x_1}\right)^\dagger = -\frac{\partial}{\partial x_1}} \tag{5.50}$$

Hence, $\partial/\partial x_1$ is not Hermitian. The operator is said to be *anti-Hermitian.*

If, however, we multiply all expressions in (5.49) by $i\hbar$, we get

$$\left\langle -i\hbar\frac{\partial}{\partial x_1}\Psi_r \middle| \Psi_s \right\rangle = \left\langle \Psi_r \middle| -i\hbar\frac{\partial}{\partial x_1} \middle| \Psi_s \right\rangle, \tag{5.51}$$

which shows that $-i\hbar\partial/\partial x_1$, is Hermitian. But this operator is nothing but the linear momentum operator $\hat{p}_1$. Hence $\hat{p}_1$ is Hermitian,

$$\boxed{\hat{p}_1^\dagger = \hat{p}_1} \tag{5.52}$$

A similar result holds, of course, for the operators $\hat{p}_2, \hat{p}_3, \ldots, \hat{p}_{3N}$, provided the functions involved also satisfy boundary conditions similar to (5.48) for the coordinates $x_1, x_2, \ldots, x_{3N}$.

The operators that represent the position variables $x_1, x_2, \ldots, x_{3N}$ are, as we know, just the functions $x_1, x_2, \ldots, x_{3N}$. These functions are all real-valued and therefore Hermitian operators, according to Eq. (5.47). We have thus learned that *Cartesian position and momentum variables are represented by Hermitian operators.*

In determining the Hermitian conjugates of more complicated operators, the following expression for the Hermitian conjugate of a product of operators is useful,

$$(\hat{\Omega}_a\hat{\Omega}_b\ldots\hat{\Omega}_p)^\dagger = \hat{\Omega}_p^\dagger\ldots\hat{\Omega}_b^\dagger\hat{\Omega}_a^\dagger. \tag{5.53}$$

To prove the relation, it is sufficient to consider the product of two operators. We use the turn-over rule, $\langle\hat{\Omega}\Psi_r|\Psi_s\rangle = \langle\Psi_r|\hat{\Omega}^\dagger|\Psi_s\rangle$, twice and get

$$\langle\hat{\Omega}_a\hat{\Omega}_b\Psi_r|\Psi_s\rangle = \langle\hat{\Omega}_b\Psi_r|\hat{\Omega}_a^\dagger|\Psi_s\rangle = \langle\Psi_r|\hat{\Omega}_b^\dagger\hat{\Omega}_a^\dagger|\Psi_s\rangle. \tag{5.54}$$

In the first step we have let $\hat{\Omega}_a$ play the role of the operator $\hat{\Omega}$ in the above reproduction of the turn-over rule, in the second step we have let $\hat{\Omega}_b$ play that role. A comparison of the first and the last expression in Eq. (5.54) shows that

$$(\hat{\Omega}_a\hat{\Omega}_b)^\dagger = \hat{\Omega}_b^\dagger\hat{\Omega}_a^\dagger. \tag{5.55}$$

An iteration of this result gives Eq. (5.53).

As an obvious deduction from the relations (5.55) and (5.46) we get that

$$(c_1\hat{\Omega}_a + c_2\hat{\Omega}_b)^\dagger = c_1^*\hat{\Omega}_a^\dagger + c_2^*\hat{\Omega}_b^\dagger. \tag{5.56}$$

For two Hermitian operators, $\hat{F}_a$ and $\hat{F}_b$, Eq. (5.55) reads

$$(\hat{F}_a\hat{F}_b)^\dagger = \hat{F}_b\hat{F}_a. \tag{5.57}$$

The right-hand side equals $\hat{F}_a\hat{F}_b$ if $\hat{F}_a$ and $\hat{F}_b$ commute. Hence the following theorem,

$$\boxed{\text{The product of two Hermitian operators is Hermitian if and only if the two operators commute.}} \tag{5.58}$$

This theorem guarantees, for instance, that the angular momentum operators (5.28) are Hermitian, as the following sequence of arguments shows: We have that $\hat{l}_x = y\hat{p}_z - z\hat{p}_y$, and we know that the Cartesian coordinates and momenta $y, \hat{p}_z, z$, and $\hat{p}_y$ are Hermitian. We also know that y and $\hat{p}_z$ commute, and so do z and $\hat{p}_y$, cf. Eq. (5.26). $y\hat{p}_z$ and $z\hat{p}_y$ are accordingly Hermitian, and the same must therefore hold for their difference, which equals $\hat{l}_x$. A similar series of arguments may be carried through for $\hat{l}_y$ and $\hat{l}_z$.

Thus, the theorem (5.58) causes $\hat{l}_x, \hat{l}_y$ and $\hat{l}_z$ to be Hermitian. It also guarantees that $\hat{l}^2$ is Hermitian (because $\hat{l}_x, \hat{l}_y$ and $\hat{l}_z$ are).

Finally, the theorem also guarantees that Hamiltonians are Hermitian operators. Thus, the Hamiltonian for a single particle in three dimensions reads

$$\hat{H} = \frac{1}{2m}\left(\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2\right) + V(\boldsymbol{r}). \tag{5.59}$$

This is a sum of Hermitian operators, for $\hat{p}_x^2$ is Hermitian because $\hat{p}_x$ is (the above theorem), and V is Hermitian because it is a real-valued function (Eq. (5.47)). Being a sum of Hermitian operators $\hat{H}$ is itself Hermitian, as claimed.

At the beginning of this section, we stated that quantum mechanical operators representing observables must be Hermitian. We have now demonstrated that this is in fact the case for a number of such operators. A general proof of the statement is contained in the following section.

In closing the present section we note that any non-Hermitian operator, $\hat{\Omega}$, determines two Hermitian operators, $\hat{\Omega}_1$ and $\hat{\Omega}_2$, by the definitions

$$\begin{aligned}\hat{\Omega}_1 &= \frac{1}{2}(\hat{\Omega} + \hat{\Omega}^\dagger),\\ \hat{\Omega}_2 &= \frac{1}{2i}(\hat{\Omega} - \hat{\Omega}^\dagger).\end{aligned} \tag{5.60}$$

Conversely, the operators

$$\begin{aligned}\hat{\Omega} &= \hat{\Omega}_1 + i\,\hat{\Omega}_2,\\ \hat{\Omega}^\dagger &= \hat{\Omega}_1 - i\,\hat{\Omega}_2,\end{aligned} \tag{5.61}$$

are each other's Hermitian conjugates whenever $\hat{\Omega}_1$ and $\hat{\Omega}_2$ are Hermitian. An example of such a pair of operators is, for instance, supplied by the angular-momentum operators $\hat{l}^+$ and $\hat{l}^-$ defined by the relations

$$\begin{aligned}\hat{l}^+ &= \hat{l}_x + i\,\hat{l}_y,\\ \hat{l}^- &= \hat{l}_x - i\,\hat{l}_y.\end{aligned} \tag{5.62}$$

5.4 Some Properties of Hermitian Operators

On the basis of the definition (5.42), we shall now derive some important results concerning the eigenvalues and eigenfunctions of Hermitian operators. First we prove that

$$\boxed{\text{The eigenvalues of a Hermitian operator are all real.}} \tag{5.63}$$

Let Ψ be eigenfunction of a Hermitian operator, $\hat{F}$, with eigenvalue f,

$$\hat{F}\Psi = f\Psi. \tag{5.64}$$

Scalar multiplication from the left with Ψ gives then:

$$\langle\Psi|\hat{F}|\Psi\rangle = f\langle\Psi|\Psi\rangle. \tag{5.65}$$

Now, it is obvious from the definition (5.5) that $\langle\Psi|\Psi\rangle$ is real. It also follows from the definition (5.42) that

$$\langle\Psi|\hat{F}|\Psi\rangle = \langle\Psi|\hat{F}|\Psi\rangle^*, \tag{5.66}$$

so $\langle\Psi|\hat{F}|\Psi\rangle$ is also real. Hence f must be real. This proves the theorem.

Next, we prove the theorem

$$\boxed{\begin{array}{c}\text{Eigenfunctions corresponding to different eigenvalues}\\ \text{of a Hermitian operator are orthogonal.}\end{array}} \tag{5.67}$$

Let the two eigenfunctions be Ψ_1 and Ψ_2, and let f_1 and f_2 be the corresponding eigenvalues, so that

$$\begin{aligned} \hat{F}\Psi_1 &= f_1\Psi_1, \\ \hat{F}\Psi_2 &= f_2\Psi_2. \end{aligned} \tag{5.68}$$

We shall evaluate the matrix element $\langle\Psi_1|\hat{F}|\Psi_2\rangle$ in two different ways. First, we use that Ψ_2 has the eigenvalue f_2 and get

$$\langle\Psi_1|\hat{F}|\Psi_2\rangle = \langle\Psi_1|f_2\Psi_2\rangle = f_2\langle\Psi_1|\Psi_2\rangle. \tag{5.69}$$

Secondly, we use that $\hat{F}$ is Hermitian, that Ψ_1 has the eigenvalue f_1, and that f_1 is real (Theorem (5.63)). This gives

$$\langle\Psi_1|\hat{F}|\Psi_2\rangle = \langle\hat{F}\Psi_1|\Psi_2\rangle = \langle f_1\Psi_1|\Psi_2\rangle = f_1^*\langle\Psi_1|\Psi_2\rangle = f_1\langle\Psi_1|\Psi_2\rangle. \tag{5.70}$$

Thus, we have derived the relations

$$\begin{aligned} \langle\Psi_1|\hat{F}|\Psi_2\rangle &= f_2\langle\Psi_1|\Psi_2\rangle, \\ \langle\Psi_1|\hat{F}|\Psi_2\rangle &= f_1\langle\Psi_1|\Psi_2\rangle. \end{aligned} \tag{5.71}$$

Subtracting these two relations from each other gives

$$(f_2 - f_1)\langle\Psi_1|\Psi_2\rangle = 0. \tag{5.72}$$

So, whenever $f_1 \neq f_2$ we must have that

$$\langle\Psi_1|\Psi_2\rangle = 0, \tag{5.73}$$

which proves the theorem.

In the previous section, we observed that the Hamiltonian is a Hermitian operator. Eigenfunctions corresponding to different energies must consequently be orthogonal. But this is exactly what we have found in the previous chapter, so the theorem (5.67) is the rationale for our earlier observation.

The theorem may be considered a special case ($\hat{G} = 1$) of the more general theorem:

When two functions, Ψ_1 and Ψ_2, are eigenfunctions of a Hermitian operator $\hat{F}$ with different eigenvalues, and $\hat{G}$ is any operator that commutes with $\hat{F}$, then $\langle\Psi_1|\hat{G}|\Psi_2\rangle = 0$. (5.74)

This theorem may be proved in a similar way as the previous one. We get first

$$\langle\Psi_1|\hat{G}\hat{F}|\Psi_2\rangle = \langle\Psi_1|\hat{G}|f_2\Psi_2\rangle = f_2\langle\Psi_1|\hat{G}|\Psi_2\rangle, \tag{5.75}$$

and then

$$\langle\Psi_1|\hat{F}\hat{G}|\Psi_2\rangle = \langle\hat{F}\Psi_1|\hat{G}|\Psi_2\rangle = \langle f_1\Psi_1|\hat{G}|\Psi_2\rangle = f_1\langle\Psi_1|\hat{G}|\Psi_2\rangle. \tag{5.76}$$

But because we have assumed that $\hat{F}\hat{G} = \hat{G}\hat{F}$, the results of the two calculations must be the same. Subtracting the results from each other gives therefore

$$(f_2 - f_1)\langle\Psi_1|\hat{G}|\Psi_2\rangle = 0. \tag{5.77}$$

We assume that $f_1 \neq f_2$. Hence,

$$\langle\Psi_1|\hat{G}|\Psi_2\rangle = 0, \tag{5.78}$$

which finishes the proof.

We have now made ourselves familiar with Hermitian operators and their properties, and it is time to prove the assertion made at the beginning of Sec. 5.3:

Observables must be represented by Hermitian operators.	(5.79)

Observables are physical quantities that can be measured, like position, linear momentum, energy etc. The problem of deriving the values of observables from a given wavefunction will be discussed in the following section. The basis of the discussion will be the postulate that the quantity

$$\langle\hat{F}\rangle = \frac{\langle\Psi|\hat{F}|\Psi\rangle}{\langle\Psi|\Psi\rangle} \tag{5.80}$$

is *the expectation value* of $\hat{F}$ in the quantum state Ψ. By this we mean that if we have a very large number of identical systems, each in a state described by the wavefunction Ψ, and if we measure the value of the physical quantity F for each of these systems, then the average value will be $\langle\hat{F}\rangle$. The wavefunction is not supposed to be an eigenfunction of $\hat{F}$. All that is required is that it should be well-behaved, in the sense discussed in connection with the definition (5.42) of Hermitian operators.

The important point is now, that the result of a measurement must be a real number. As a consequence, we must demand that the expectation value

$\langle \hat{F} \rangle$ be real, and this must hold no matter what the function Ψ looks like, as long as it is a well-behaved function. The quantity $\langle \Psi | \Psi \rangle$ is always real. It follows therefore, from Eq. (5.80), that $\langle \hat{F} \rangle$ will be real whenever $\langle \Psi | \hat{F} | \Psi \rangle$ is. We have learned, by Eq. (5.66), that $\langle \Psi | \hat{F} | \Psi \rangle$ is real if $\hat{F}$ is Hermitian. What we shall now show is, that if $\langle \Psi | \hat{F} | \Psi \rangle$ is real for any well-behaved Ψ, then $\hat{F}$ is Hermitian. We proceed as follows.

We assume that $\langle \Psi | \hat{F} | \Psi \rangle$ is in fact real for any well-behaved Ψ and let Ψ_1 and Ψ_2 be two well-behaved, but otherwise arbitrary (complex-valued) functions. We then construct the two new functions

$$\begin{aligned} \Psi_a &= \Psi_1 + \Psi_2, \\ \Psi_b &= \Psi_1 + i\Psi_2, \end{aligned} \tag{5.81}$$

and evaluate $\langle \Psi | \hat{F} | \Psi \rangle$ for each of them. The result is

$$\begin{aligned} \langle \Psi_a | \hat{F} | \Psi_a \rangle &= \langle \Psi_1 | \hat{F} | \Psi_1 \rangle + \langle \Psi_2 | \hat{F} | \Psi_2 \rangle + \{ \langle \Psi_1 | \hat{F} | \Psi_2 \rangle + \langle \Psi_2 | \hat{F} | \Psi_1 \rangle \}, \\ \langle \Psi_b | \hat{F} | \Psi_b \rangle &= \langle \Psi_1 | \hat{F} | \Psi_1 \rangle + \langle \Psi_2 | \hat{F} | \Psi_2 \rangle + i\{ \langle \Psi_1 | \hat{F} | \Psi_2 \rangle - \langle \Psi_2 | \hat{F} | \Psi_1 \rangle \} \end{aligned} \tag{5.82}$$

We have assumed that $\langle \Psi | \hat{F} | \Psi \rangle$ is real for any well-behaved function. Hence $\langle \Psi_a | \hat{F} | \Psi_a \rangle$, $\langle \Psi_b | \hat{F} | \Psi_b \rangle$, $\langle \Psi_1 | \hat{F} | \Psi_1 \rangle$, and $\langle \Psi_2 | \hat{F} | \Psi_2 \rangle$ are all real. This in turn implies that

$$\begin{aligned} &\langle \Psi_1 | \hat{F} | \Psi_2 \rangle + \langle \Psi_2 | \hat{F} | \Psi_1 \rangle \quad \text{is real,} \\ &\langle \Psi_1 | \hat{F} | \Psi_2 \rangle - \langle \Psi_2 | \hat{F} | \Psi_1 \rangle \quad \text{is imaginary.} \end{aligned} \tag{5.83}$$

But if the sum of two complex numbers is real while their difference is imaginary, then the two numbers must be complex conjugates. The proof is elementary: We assume that the relations (5.83) are fulfilled and write

$$\begin{aligned} \langle \Psi_1 | \hat{F} | \Psi_2 \rangle &= A + iB, \\ \langle \Psi_2 | \hat{F} | \Psi_1 \rangle &= C - iD, \end{aligned} \tag{5.84}$$

where A, B, C, and D are real per definition We get then

$$\begin{aligned} \langle \Psi_1 | \hat{F} | \Psi_2 \rangle + \langle \Psi_2 | \hat{F} | \Psi_1 \rangle &= (A + C) + i(B - D), \\ \langle \Psi_1 | \hat{F} | \Psi_2 \rangle - \langle \Psi_2 | \hat{F} | \Psi_1 \rangle &= (A - C) + i(B + D). \end{aligned} \tag{5.85}$$

Since the sum is real we conclude that $B = D$, and since the difference is imaginary we conclude that $A = C$. Thus, the expressions (5.83) do in fact give that

$$\langle \Psi_2 | \hat{F} | \Psi_1 \rangle = \langle \Psi_1 | \hat{F} | \Psi_2 \rangle^*. \tag{5.86}$$

But this is, according to the definition (5.42), exactly the condition for $\hat{F}$ to be Hermitian, since Ψ_1 and Ψ_2 are arbitrary.

This completes the proof of the theorem (5.79).

5.5 Expectation Values and Uncertainties

In Sec. 3.4, we introduced the statistical interpretation of the wavefunction, and touched upon it again in Sections 4.9 and 5.1. We shall now consider the general problem of extracting statistical information from a wavefunction.

Let us, for simplicity, begin by considering a particle which is restricted to move in a single dimension, as in the case of a one-dimensional box. Let $\Psi(x,t)$ be a normalized (stationary or non-stationary) wavefunction for the particle. Our previous considerations tell us then that the quantity

$$P(x,t) = \Psi^*(x,t)\Psi(x,t) \tag{5.87}$$

is a probability density, in the sense that $P(x,t)dx$ is the probability of observing the particle in the small interval dx at x, at time t. It integrates to unity:

$$\int P(x,t)dx = \int \Psi^*(x,t)\Psi(x,t)dx = 1, \tag{5.88}$$

the integration being extended over the range of x.

As in ordinary probability theory, we may now introduce the *average value* of the variable x at time t by the definition

$$\langle x\rangle = \int xP(x,t)dx, \tag{5.89}$$

The average value of x is also referred to as the *expectation value* of x. To stress that it depends on t whenever Ψ does, it is sometimes convenient to use the symbol $\overline{x}(t)$ instead of $\langle x\rangle$.

In a similar way, we may introduce the average or expectation value of an arbitrary function of the type $v(x,t)$ by the definition

$$\langle v(x,t)\rangle = \int v(x,t)P(x,t)dx. \tag{5.90}$$

The expectation value of x^2 is, in particular

$$\langle x^2\rangle = \int x^2P(x,t)dx, \tag{5.91}$$

and the average value of a constant is seen to be the constant itself.

The so-called *variance* of x is defined by the relation

$$\langle\{x - \langle x\rangle\}^2\rangle = \int \{x - \langle x\rangle\}^2 P(x,t)dx. \tag{5.92}$$

Finally, the *standard deviation* of x, denoted by Δx, is defined as the square root of the variance, i.e.,

$$\Delta x = \langle\{x - \langle x\rangle\}^2\rangle^{\frac{1}{2}}. \tag{5.93}$$

One refers to this quantity as the *uncertainty* of x, since it measures the magnitude of the fluctuation of x about its average value, at time t. We note that the variance of x, and hence also Δx, may be calculated from the expectation values of x and x^2 in the following way

$$\begin{aligned}(\Delta x)^2 &= \langle\{x - \langle x\rangle\}^2\rangle = \langle x^2 - 2x\langle x\rangle + \langle x\rangle^2\rangle \\ &= \langle x^2\rangle - 2\langle x\rangle\langle x\rangle + \langle x\rangle^2 = \langle x^2\rangle - \langle x\rangle^2.\end{aligned} \tag{5.94}$$

The above expressions are all similar to the expressions of ordinary probability theory, but they only give information about the expectation value of x and about the expectation values of functions of x. A wavefunction hides, however, much more information than that. It enables us, in fact, to calculate the expectation value of any relevant observable. Let us note, that the elementary manipulations

$$v(x,t)P(x,t) = v(x,t)\Psi^*(x,t)\Psi(x,t) = \Psi^*(x,t)v(x,t)\Psi(x,t) \tag{5.95}$$

allow us to write the expressions (5.89), (5.90) and (5.92) as follows:

$$\begin{aligned}\langle x\rangle &= \langle\Psi|x|\Psi\rangle, \\ (\Delta x)^2 &= \langle\Psi|\{x - \langle x\rangle\}^2|\Psi\rangle, \\ \langle v(x,t)\rangle &= \langle\Psi|v(x,t)|\Psi\rangle.\end{aligned} \tag{5.96}$$

These are expressions that may be generalized to arbitrary observables. This is done by the following *postulate*, in which we again use the notation q

for the coordinates and $\hat{F}$ for a general Hermitian operator:

The expectation value of the observable F
in the state $|\Psi\rangle \equiv \Psi(q,t)$, is given by the expression

$$\langle \hat{F} \rangle = \frac{\langle \Psi | \hat{F} | \Psi \rangle}{\langle \Psi | \Psi \rangle}.$$

When Ψ is normalized to unity, this becomes

$$\langle \hat{F} \rangle = \langle \Psi | \hat{F} | \Psi \rangle.$$

The uncertainty of F is

$$\Delta F = \langle \{ \hat{F} - \langle \hat{F} \rangle \}^2 \rangle^{\frac{1}{2}}.$$

ΔF is a measure of the fluctuation of F
about its average value.

(5.97)

The variance, $(\Delta F)^2$, may be calculated from the expectation values of F and F^2 by the relation

$$(\Delta F)^2 = \langle \{ \hat{F} - \langle \hat{F} \rangle \}^2 \rangle = \langle \hat{F}^2 \rangle - \langle \hat{F} \rangle^2. \tag{5.98}$$

The validity of the postulate, that the expressions in (5.97) are the correct ones to use for the expectation value and hence the uncertainty of a physical quantity, hinges of course on experimental verification. To verify it experimentally, prepare a large number of identical systems, each described by the wavefunction $\Psi(x,t)$, then measure the value of F for each system at time t. This results in a distribution of values of F. Then compare the mean value and the variance of this distribution with the values calculated for $\langle \hat{F} \rangle$ and $(\Delta F)^2$ by the expressions in (5.97). If the experimental and theoretical values are the same for any operator, then the postulate has been verified. Needless to say, one knows of no examples where the agreement between the two sets of values breaks down.

That the measurement of a physical quantity F results in a distribution of values in the above sense, implies that the result of a single experiment is, in general, irreproducible. The only thing that *is* reproducible is the form of the distribution. This is a genuine feature of quantum mechanics.

The only case in which the result of a single experiment *is* in fact reproducible, is when $\Psi(q,t)$ is an eigenfunction of $\hat{F}$, with eigenvalue f, say. For then we have that

$$\hat{F}\Psi(q,t) = f\Psi(q,t), \tag{5.99}$$

so that

$$\langle \hat{F} \rangle = \int \Psi^*(q,t)\hat{F}\Psi(q,t)dq = f\int \Psi^*(q,t)\Psi(q,t)dq = f \tag{5.100}$$

and

$$(\Delta F)^2 = \int \Psi^*(q,t)(\hat{F} - f)(\hat{F} - f)\Psi(q,t)dx = 0. \tag{5.101}$$

We have used that $\hat{F} - f$ annihilates $\Psi(q,t)$, which follows from Eq. (5.99). Thus all experiments give the value f in this case.

An important example of such a situation is encountered when $\hat{F}$ is the Hamiltonian $\widehat{H}$ and $\Psi(q,t)$ is the wavefunction associated with a stationary state. For $\Psi(q,t)$ is then an eigenfunction of $\widehat{H}$. Thus, we always get the same value when we measure the energy of a stationary state—we say that we get a *sharp value* of the energy. It is for this reason that we have been able to refer to the value of E in the time-independent Schrödinger equation as *the* energy of the state.

A non-stationary state does not have a well-defined energy. It is merely characterized by a distribution of energy values, but the average value $\langle \widehat{H} \rangle$ and the uncertainty ΔH associated with the distribution are, of course, well defined.

To illustrate the above concepts, let us again turn to the particle in a one-dimensional box.

5.6 The Particle in a Box Revisited

The stationary-state wavefunctions for the particle in a one-dimensional box are given by the expressions (4.83) and (4.84). These expressions show that

$$\boxed{\begin{array}{c}\langle \Psi_n | \hat{F} | \Psi_n \rangle = \langle \psi_n | \hat{F} | \psi_n \rangle \\ \text{whenever } \hat{F} \text{ is independent of } t.\end{array}} \tag{5.102}$$

This is a general result: In a stationary state, the expectation value of a physical quantity F is independent of time, unless the operator $\hat{F}$ depends explicitly on time. Important time-independent operators are operators like x and $\hat{p}$, and the Hamiltonian for a conservative system. For a conservative system, the potential energy function is independent of time, cf. Sec. 3.1. It is

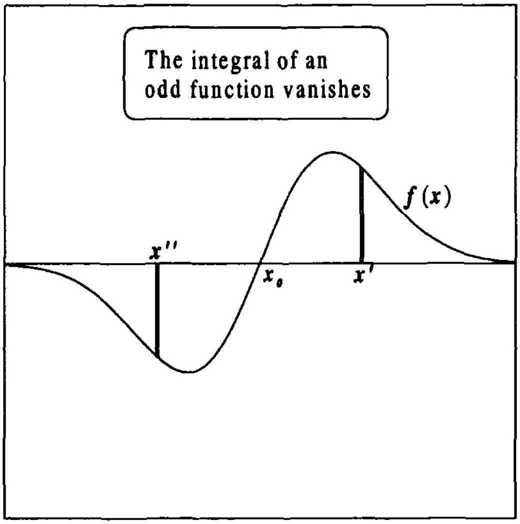

Figure 5.1: The function $f(x)$ is odd (ungerade) under inversion in the point x_0, i. e., $f(x_0-\xi)=-f(x_0+\xi)$ for all ξ. The value of the integral $\int_{-\infty}^{\infty} f(x)dx$ is equal to the sign-valued area between the curve $f(x)$ and the x-axis. With $x'-x_0=x_0-x''$, as on the figure, the two contributions $f(x')dx$ and $f(x'')dx$ to the integral are numerically equal but of opposite sign, and hence cancel out. This is true wherever x' is chosen on the x-axis, so the contribution to $\int f(x)dx$ from the interval $x>x_0$ is exactly cancelled by the contribution from the interval $x<x_0$.

only for such systems that the time-independent Schrödinger equation is at all relevant.

For the stationary states of the particle in a one-dimensional box, the probability densities defined by Eq. (5.87) become:

$$P_n(x)=\psi_n^*(x)\psi_n(x)=\frac{2}{a}\sin^2(n\pi x/a). \tag{5.103}$$

They are plotted on the right-hand side of Fig. 4.3. They are all even under inversion in the point $x=a/2$. Hence we get that

$$\int_0^a (x-a/2)P_n(x)dx=0, \tag{5.104}$$

for all n. For since the function $x-a/2$ is odd under the inversion, the product function $(x-a/2)P_n(x)$ is also odd, and the integral of an odd function is strictly zero (See Fig. (5.1)). By combining the result (5.104) with that of Eq. (5.88) we see that

$$\langle x\rangle = \int_0^a xP_n(x)dx = \int_0^a (x-a/2)P_n(x)dx + \frac{a}{2}\int_0^a P_n(x)dx = 0 + \frac{a}{2} = \frac{a}{2}. \tag{5.105}$$

This result is just what one would expect by simply looking at the graphs of $P_n(x)$. (It falls out a little easier, but now in the form $\langle x\rangle = 0$, by shifting the origin to the midpoint of the box, as in Sec. 4.5.)

To evaluate the variance and hence the uncertainty of x, we use that $(\Delta x)^2 = \langle x^2\rangle - \langle x\rangle^2$, as in Eqs. (5.94) and (5.98). For $\langle x^2\rangle$ we find

$$\begin{aligned}\langle x^2\rangle &= \frac{2}{a}\int_0^a x^2\sin^2(n\pi x/a)dx = \frac{2}{a}\left(\frac{a}{n\pi}\right)^3\int_0^{n\pi} u^2\sin^2 u du \\ &= \frac{2}{a}\left(\frac{a}{n\pi}\right)^3\left(\frac{n^3\pi^3}{6} - \frac{n\pi}{4}\right) = a^2\left(\frac{1}{3} - \frac{1}{2n^2\pi^2}\right),\end{aligned} \tag{5.106}$$

and when we combine this result with the result of Eq. (5.105), we get

$$\Delta x = \left\{a^2\left(\frac{1}{3} - \frac{1}{2n^2\pi^2}\right) - \frac{a^2}{4}\right\}^{\frac{1}{2}} = a\left(\frac{1}{12} - \frac{1}{2n^2\pi^2}\right)^{\frac{1}{2}}. \tag{5.107}$$

Thus, the uncertainty of x increases from the value $0.1808a$ in the ground state to the value $0.2887a$ in highly excited states.

Next, let us evaluate $\langle\hat{p}_x\rangle$ and Δp_x for the linear momentum which corresponds to the operator

$$\hat{p}_x = -i\hbar\frac{d}{dx}. \tag{5.108}$$

We find that

$$\begin{aligned}\langle\hat{p}_x\rangle &= \frac{2}{a}\int_0^a \sin(n\pi x/a)\left(-i\hbar\frac{d}{dx}\right)\sin(n\pi x/a)dx \\ &= \frac{2}{a}(-i\hbar)\frac{n\pi}{a}\int_0^a \sin(n\pi x/a)\cos(n\pi x/a)dx = 0,\end{aligned} \tag{5.109}$$

where the last integral vanishes because the integrand is odd under inversion in the point $x = a/2$. Alternatively, we may argue that $\langle\hat{p}_x\rangle$ must be real because $\hat{p}_x$ is Hermitian. The integral expression is, however, imaginary—so a contradiction occurs unless the integral and hence $\langle\hat{p}_x\rangle$ vanishes.

To evaluate $\langle \hat{p}_x^2 \rangle$, we observe that

$$\begin{aligned} \hat{p}_x^2 \psi_n(x) &= 2m\frac{\hat{p}_x^2}{2m}\psi_n(x) = 2m\widehat{H}\psi_n(x) = 2mE_n\psi_n(x) \\ &= \hbar^2 \left(\frac{n\pi}{a}\right)^2 \psi_n(x), \end{aligned} \tag{5.110}$$

so that

$$\langle \hat{p}_x^2 \rangle = \int_0^a \psi_n(x)^* \hat{p}_x^2 \psi_n(x) dx = \hbar^2 \left(\frac{n\pi}{a}\right)^2, \tag{5.111}$$

and hence

$$\Delta p_x = \frac{n\pi\hbar}{a}. \tag{5.112}$$

Thus, Δp_x increases linearly with n, the ground-state value being $\pi\hbar/a$.

An important quantity is the uncertainty product $\Delta x \Delta p_x$. For it follows from general operator relations to be discussed in Sections 5.7 and 5.8, that it is impossible to construct a quantum state for which this product is smaller than $\hbar/2$. This is an example of the famous *uncertainty relation*, attributed to Heisenberg,

$$\boxed{\begin{array}{c}\text{Heisenberg's uncertainty relation} \\ \text{for position and momentum:} \\ \Delta x \Delta p_x \geq \frac{1}{2}\hbar.\end{array}} \tag{5.113}$$

For the stationary states of the particle in a one-dimensional box we get, by combining Eq. (5.107) and Eq. (5.112),

$$\Delta x \Delta p_x = n\pi\hbar \left(\frac{1}{12} - \frac{1}{2n^2\pi^2}\right)^{\frac{1}{2}}. \tag{5.114}$$

The product increases roughly linearly with n, the ground-state value being $0.5679\hbar$. The values are seen to be in accordance with the relation (5.113).

After this example, let us return to the discussion of arbitrary quantum systems.

5.7 Commuting Hermitian Operators

In the light of the uncertainty principle for position and momentum, it is of interest to evaluate the uncertainty product $\Delta F \Delta G$ for arbitrary operators and states. This we shall do in the following section. In the present section, we shall consider a related important problem.

Assume that we have a set of linearly independent functions,

$$\psi_1(q), \psi_2(q), \ldots, \psi_n(q), \ldots \tag{5.115}$$

which is complete in the sense that any well-behaved function, $\Psi(q)$, may be expanded on the set. By this we mean that a unique set of coefficients, $c_1, c_2, \ldots$, exists such that we may write

$$\Psi(q) = \sum_{n=1}^{\infty} c_n \psi_n(q). \tag{5.116}$$

Assume also that each function in the set (5.115) is a common eigenfunction of two linear Hermitian operators $\hat{F}$ and $\hat{G}$,

$$\begin{aligned} \hat{F}\psi_n &= f_n \psi_n, \quad n = 1, 2, \ldots \\ \hat{G}\psi_n &= g_n \psi_n, \quad n = 1, 2, \ldots \end{aligned} \tag{5.117}$$

Under which conditions is this possible?

To answer this question, we act on the first of the above eigenvalue relations with the operator $\hat{G}$, on the second with the operator $\hat{F}$. We get

$$\begin{aligned} \hat{G}\hat{F}\psi_n &=_n \hat{G}\psi_n, = f_n g_n \psi_n \quad n = 1, 2, \ldots \\ \hat{F}\hat{G}\psi_n &= g_n \hat{F}\psi_n, = g_n f_n \psi_n \quad n = 1, 2, \ldots \end{aligned} \tag{5.118}$$

Subtraction gives

$$(\hat{G}\hat{F} - \hat{F}\hat{G})\psi_n = 0, \quad n = 1, 2, \ldots \tag{5.119}$$

and hence $(\hat{G}\hat{F} - \hat{F}\hat{G})\Psi = 0$ for any function that is a linear combination of the functions $\psi_1, \psi_2, \ldots$. But the set (5.115) is complete, so any Ψ is of that type. Thus, the commutator $[\hat{G}, \hat{F}]$ annihilates any function, and is therefore by definition zero.

A necessary condition for the relations (5.117) to be possible is, accordingly, that the commutator between the operators $\hat{F}$ and $\hat{G}$ vanish. This, then, raises the question whether one can always construct common eigenfunctions of two commuting Hermitian operators. The question may be answered in the affirmative, although we shall not go through the somewhat elaborate derivation.[1] We have, therefore, the following theorem

> A necessary and sufficient condition for two Hermitian operators to have a complete set of eigenfunctions in common, is that the operators commute. (5.120)

The theorem (5.120) is of great importance because it allows us to classify the eigenstates of a physical system by the eigenvalues of a maximum set of mutually commuting operators. We shall take great advantage of this possibility in the following chapters. In fact, we have already applied the possibility in Sec. (4.5), where we showed that the eigenfunctions of the Hamiltonian (the solutions of the time-independent Schrödinger equation) were also eigenfunctions of the inversion operator. The inversion operator is a Hermitian operator, and it commutes with the Hamiltonian for the particle in a box.

The theorem (5.120) also tells us something about the possibility of constructing quantum states for which sharp values of more than one observable may be obtained during a measurement. For the discussion at the end of Sec. 5.5 is readily generalized to other observables besides the energy. The condition that a sharp value is obtained for an observable F is, therefore, that the quantum state under observation is an eigenstate of the operator $\hat{F}$. Similarly, it must be an eigenstate of the operator $\hat{G}$ for G to have a sharp value. But according to the discussion above this is, in general, only possible when $\hat{F}$ and $\hat{G}$ commute.

If the operators $\hat{F}$ and $\hat{G}$ fail to commute, then we cannot generally have common eigenfunctions for $\hat{F}$ and $\hat{G}$. Consequently, the uncertainties ΔF and ΔG cannot both vanish for the same quantum state. For the non-commuting operators x and $\hat{p}_x$ of the previous section, we have the uncertainty relation (5.113). This relation is a special case of the general relation

> The uncertainty relation
> for two arbitrary observables F and G:
> $$\Delta F \Delta G \geq \tfrac{1}{2}|\langle i[\hat{F},\hat{G}]\rangle|. \qquad (5.121)$$

$< i[\hat{F},\hat{G}] >$ is the expectation value of i times the commutator between $\hat{F}$ and $\hat{G}$.

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[1] The derivation draws on the methods of linear algebra and the possibility of simultaneously diagonalizing two Hermitian matrices.

The commutator $[x, \hat{p}_x]$ has, according to Eq. (5.23), the value $i\hbar$. The expectation value of i times this number is $-\hbar$ for any state. The absolute value is $\hbar$. Hence, the uncertainty relation (5.113) follows immediately from the general uncertainty relation (5.121).

A proof of the relation (5.121) is given in the following section.

5.8 The General Uncertainty Principle

We begin by noticing that for any operator $\hat{A}$ and any wavefunction Ψ, we have the relation $\langle \hat{A}\Psi|\hat{A}\Psi\rangle \geq 0$. This follows immediately from the definition (5.5), which shows that $\langle \hat{A}\Psi|\hat{A}\Psi\rangle$ is the integral of a real and non-negative function, and such an integral can, of course, never be negative.

Next, let us consider two Hermitian operators, $\hat{F}$ and $\hat{G}$, a normalized wavefunction, Ψ, and a *real* constant, α. The relation

$$\langle (\hat{F} + i\alpha\hat{G})\Psi|(\hat{F} + i\alpha\hat{G})\Psi\rangle \geq 0 \tag{5.122}$$

will then hold for all values of α. A straightforward expansion of the expression on the left-hand side of this relation gives

$$\langle \hat{F}\Psi|\hat{F}\Psi\rangle + \alpha^2\langle \hat{G}\Psi|\hat{G}\Psi\rangle + i\alpha(\langle \hat{F}\Psi|\hat{G}\Psi\rangle - \langle \hat{G}\Psi|\hat{F}\Psi\rangle) \geq 0. \tag{5.123}$$

We now use the definition (5.42) of a Hermitian operator, together with Eq. (5.46), to get

$$\langle \Psi|\hat{F}^2|\Psi\rangle + \alpha^2\langle \Psi|\hat{G}^2|\Psi\rangle + i\alpha\langle \Psi|\hat{F}\hat{G} - \hat{G}\hat{F}|\Psi\rangle \geq 0. \tag{5.124}$$

Written in terms of expectation values, this becomes

$$\langle \hat{F}^2\rangle + \alpha^2\langle \hat{G}^2\rangle + \alpha\langle i(\hat{F}\hat{G} - \hat{G}\hat{F})\rangle \geq 0. \tag{5.125}$$

According to Eq. (5.60), the operator $i[\hat{F}, \hat{G}]$ is Hermitian. Its expectation value is therefore real. Thus, all three terms on the left-hand side of the above relation are real.

To appreciate the next step in the derivation, recall that a second-order polynomium in x, say Ax^2+Bx+C, has two real roots whenever $B^2-4AC > 0$. When $B^2 - 4AC < 0$, the polynomium is positive valued for all x. The condition that the relation (5.125) hold for all values of α is therefore

$$\langle i(\hat{F}\hat{G} - \hat{G}\hat{F})\rangle^2 - 4\langle \hat{G}^2\rangle\langle \hat{F}^2\rangle \leq 0, \tag{5.126}$$

or,

$$\langle \hat{F}^2\rangle\langle \hat{G}^2\rangle \geq \tfrac{1}{4}\langle i(\hat{F}\hat{G}-\hat{G}\hat{F})\rangle^2. \tag{5.127}$$

To proceed, we introduce two real constants, a and b, and note that

$$(\hat{F}-a)(\hat{G}-b)-(\hat{G}-b)(\hat{F}-a)=\hat{F}\hat{G}-\hat{G}\hat{F}=[\hat{F},\hat{G}]. \tag{5.128}$$

The relation (5.127), applied to the operators $\hat{F}-a$ and $\hat{G}-b$ instead of $\hat{F}$ and $\hat{G}$, implies therefore that

$$\langle(\hat{F}-a)^2\rangle\langle(\hat{G}-b)^2\rangle \geq \tfrac{1}{4}\langle i[\hat{F},\hat{G}]\rangle^2. \tag{5.129}$$

We now put a equal to $\langle\hat{F}\rangle$ and b equal to $\langle\hat{G}\rangle$. The definition of uncertainties, (Eq. (5.97)), gives then

$$(\Delta F)^2(\Delta G)^2 \geq \tfrac{1}{4}\langle i[\hat{F},\hat{G}]\rangle^2. \tag{5.130}$$

We may therefore conclude that

$$\Delta F\Delta G \geq \tfrac{1}{2}|\langle i[\hat{F},\hat{G}]\rangle|. \tag{5.131}$$

But this is just the uncertainty relation (5.121) which we set out to prove.

5.9 Quantum Theory and Measurements

In the preceding sections we have stressed that observables must be represented by Hermitian operators. We have also postulated that if we have a system described by a coordinate set q, then the average value, or expectation value, of a general observable F in the state $|\Psi\rangle = \Psi(q,t)$, at time t, is given by $\langle\hat{F}\rangle = \langle\Psi|\hat{F}|\Psi\rangle$, assuming of course that $\Psi(q,t)$ is properly normalized to unity. We also learned how to calculate the uncertainty ΔF that measures the fluctuations of F about its average value.

Expectation values and uncertainties play important roles in the interpretation of quantum mechanics and in the applications. Yet, they merely express the average result of a series of measurements on identical systems, in the sense spelled out in the text following Eq. (5.80). We shall now consider the possible outcome of a single measurement on a single system. As we know, the outcome of such a measurement is statistical. The predictions we can make concerning the outcome are formulated in the following. They are part of a generally accepted theory of measurements on quantum systems.

First, we have the general statement, or postulate

> The measurement of an observable F gives an eigenvalue of the operator $\hat{F}$. As a result of the measurement, the state of the system is turned into a corresponding eigenstate of $\hat{F}$. (5.132)

The very concept of an observable is delimited by the statement [2]

> An observable F is represented by a Hermitian operator $\hat{F}$ whose eigenstates form a complete set. (5.133)

That the eigenstates of the Hamiltonian must form a complete set has already been formulated as the principle of superposition, in Sec. 4.9. Now we require that a similar condition hold for any operator $\hat{F}$ that represents an observable. What the requirement really says is that if we consider a complete, orthonormal set of functions,

$$\psi_1(q), \psi_2(q), \ldots, \psi_n(q), \ldots, \quad \langle\psi_n|\psi_m\rangle = \delta_{nm}, \tag{5.134}$$

then this set may be so chosen that the basis functions are eigenfunctions of $\hat{F}$,

$$\hat{F}|\psi_n\rangle = f_n|\psi_n\rangle, \quad n = 1, 2, \ldots \tag{5.135}$$

The eigenvalues need not all be different.

Next, we consider a particular state $|\Psi\rangle = \Psi(q,t)$, at time t, and write

$$\Psi(q,t) = \sum_{n=1}^{\infty} c_n(t)\psi_n(q), \tag{5.136}$$

or

$$|\Psi(t)\rangle = \sum_{n=1}^{\infty} c_n(t)|\psi_n\rangle. \tag{5.137}$$

---

[2] Dirac lets any Hermitian operator whose eigenstates form a complete set define an observable, and he even uses the term observable for the operator itself (See Sec. 10 of reference [12] in the bibliography). This practise is today quite common, but it implies a higher level of abstraction than the one we have adopted throughout the present treatise.

Knowing the basis set (5.134) and the form of the wavefunction $\Psi(q,t)$, we may determine the value of each of the coefficients $c_n(t)$, say $c_k(t)$, by multiplication of Eq. (5.136) by $\psi_k(q)^*$ followed by integration. For in that way we get

$$\int \psi_k(q)^*\Psi(t)dq = \sum_{n=1}^{\infty} c_n(t) \int \psi_k(q)^*\psi_n(q)dq = \sum_{n=1}^{\infty} c_n(t)\delta_{kn} = c_k(t). \tag{5.138}$$

More elegantly, we may say that we take the scalar product of $|\psi_k\rangle$ with Eq. (5.137) to get

$$\langle\psi_k|\Psi(t)\rangle = \sum_{n=1}^{\infty} c_n(t)\langle\psi_k|\psi_n\rangle = \sum_{n=1}^{\infty} c_n(t)\delta_{kn} = c_k(t). \tag{5.139}$$

Thus, the values of the coefficients are given by the expression

$$\boxed{c_k(t) = \langle\psi_k|\Psi(t)\rangle = \int \psi_k(q)^*\Psi(t)dq} \tag{5.140}$$

With reference to Eq. (4.76), we note that

$$\sum_{n=1}^{\infty} c_n(t)^* c_n(t) = \sum_{n=1}^{\infty} |c_n(t)|^2 = 1, \tag{5.141}$$

provided that $\Psi(q,t)$ is normalized to unity. This leads us to the following definitions

The quantity

$$c_k(t) = \langle\psi_k|\Psi(t)\rangle$$

is the *probability amplitude* of $|\psi_k\rangle$ in $|\Psi(t)\rangle$ at time t, and (5.142)

$$c_k(t)^* c_k(t) = \langle\psi_k|\Psi(t)\rangle^*\langle\psi_k|\Psi(t)\rangle = \langle\Psi(t)|\psi_k\rangle\langle\psi_k|\Psi(t)\rangle$$

is the *weight* of $|\psi_k\rangle$ in $|\Psi(t)\rangle$ at time t.

According to Eq. (5.141) the sum of the weights equals 1, as it should for the use of the word weight to be justified in the statistical sense.

We can now make the following postulate

If the basis function $|\psi_k\rangle$ is the only eigenfunction of $\hat{F}$ that corresponds to the eigenvalue f_k, then the probability for a measurement of F at time t to give the value f_k equals the weight of $|\psi_k\rangle$ in $|\Psi(t)\rangle$, i. e., it equals $c_k(t)^* c_k(t)$. If a measurement actually gives the value f_k, then the state of the system immediately after the measurement will be $|\psi_k\rangle$.
If, on the other hand, there is a set of basis functions, $|\psi_{k1}\rangle, |\psi_{k2}\rangle, \ldots, |\psi_{km}\rangle$, corresponding to the eigenvalue f_k, then the probability that a measurement of F at time t give the value f_k equals

$$c_{k1}(t)^* c_{k1}(t) + c_{k2}(t)^* c_{k2}(t) + \cdots + c_{km}(t)^* c_{km}(t).$$

If a measurement actually gives the value f_k, then the state of the system immediately after the measurement will be a linear superposition of the states $|\psi_{k1}\rangle, |\psi_{k2}\rangle, \ldots |\psi_{km}\rangle$. (5.143)

With the above postulates, we have extended the discussion of the preceding sections, and it is therefore worth-while returning to a few of our previous definitions and results.

First, there is the definition (5.97) of the expectation value, or average value, of an observable F. Inserting the expansion (5.137) into the expression for the definition of $\langle \hat{F} \rangle$ gives

$$\langle \hat{F} \rangle = \langle \Psi | \hat{F} | \Psi \rangle = \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} c_n(t)^* c_m(t) \langle \psi_n | \hat{F} | \psi_m \rangle = \sum_{n=1}^{\infty} c_n(t)^* c_n(t) f_n. \tag{5.144}$$

We have used Eq. (5.9) and the orthonormality relation (5.134). The final expression in Eq. (5.144) is just the sum of the eigenvalues of $\hat{F}$ multiplied by their statistical weights. It corresponds to the ususal definition of an average value in probability theory. That the expectation value of F equals $\langle \Psi | \hat{F} | \Psi \rangle$ needs therefore not be introduced as an independent postulate. It is derivable from the theory of the present section. Yet, the expression plays such an important role in the applications that it is natural to give it a central position in the discussion.

Next, there is the lemma (5.120) concerning two commuting Hermitian operators $\hat{F}$ and $\hat{G}$. Letting $\hat{F}$ and $\hat{G}$ represent observables, it implies that the functions defining the basis set (5.134) may be chosen as eigenfunctions of both $\hat{F}$ and $\hat{G}$. Hence, a combined measurement of the observables F and G may be performed. The result of a single measurement wil be an eigenvalue pair (f_n, g_m) and an eigenstate of both $\hat{F}$ and $\hat{G}$.

It is also of interest to look at the time-dependent function (4.89) which is written as a linear superposition of eigenfunctions of the Hamiltonian. Here, the weight $c_n^* c_n$ gives the probability of getting the value E_n as the result of measuring the energy of the particle. After the measurement, the wavefunction will be an eigenfunction of the Hamiltonian and hence describe a stationary state.

The fact that a wavefunction like that of Eq. (5.136) is changed in a discontinuous way during a measurement is often referred to as the *reduction* or the *collapse* of a wave packet. It has given rise to much discussion in the past and together with other facets of measurement theory it is still being elaborated upon, with the purpose of clarifying all its physical and philosophical implications. But here we must refer the reader to the rich and diversified literature.[3]

We close our chapter on quantum-mechanical operators with a section on matrix algebra.

5.10 Matrix Algebra

In Sec. 5.3 we referred to an integral of the type $\langle \Psi_r | \hat{\Omega} | \Psi_s \rangle$ as a matrix element, Ω_{rs}. The use of this notation reflects a close connection between the algebra of linear operators and the algebra of square matrices. The connection is a fundamental and important one, and we shall study it in the present section.

Let us consider a general quantum system and assume that we have an operator $\hat{A}$ that operates in a linear function space $\mathcal{V}$ of dimension m. The function space is defined by an orthonormal basis of m functions,

$$\{\Phi_r\} = \Phi_1, \Phi_2, \ldots, \Phi_m, \qquad \langle \Phi_r | \Phi_s \rangle = \delta_{rs}. \tag{5.145}$$

A general function in $\mathcal{V}$ has the form

$$\Psi = \sum_{r=1}^{m} c_r \Phi_r. \tag{5.146}$$

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[3] See, for instance, the reprint collection by Wheeler and Zurek; the bibliography, entry [13].

That $\hat{A}$ operates in $\mathcal{V}$ is understood to imply that $\hat{A}\Psi$ also belongs to $\mathcal{V}$, i. e., the function

$$\Psi' = \hat{A}\Psi \tag{5.147}$$

may be written

$$\Psi' = \sum_{r=1}^{m} c'_r \Phi_r . \tag{5.148}$$

To obtain the coefficients c'_r in terms of the coefficients c_r, let us first consider the function $\hat{A}\Phi_r$. We write

$$\hat{A}\Phi_r = \sum_{t=1}^{m} A_{tr}\Phi_t \tag{5.149}$$

where the coefficients A_{tr} are to be determined. To determine these coefficients, multiply Eq. (5.149) from the left by Φ_s^* and integrate over the variables on which the Φ functions depend. In this way we get

$$\langle \Phi_s | \hat{A} | \Phi_r \rangle = \sum_{t=1}^{m} A_{tr} \langle \Phi_s | \Phi_t \rangle = \sum_{t=1}^{m} A_{tr}\delta_{st} = A_{sr} , \tag{5.150}$$

where we have utilized the orthonormality of the basis set (5.145). The desired expression for A_{tr} is therefore

$$A_{tr} = \langle \Phi_t | \hat{A} | \Phi_r \rangle , \tag{5.151}$$

i. e., A_{tr} is the tr'th element of a matrix $\boldsymbol{A}$ which, according to the definitions of Sec. 5.3, is just the matrix that we conventionally associate with the operator $\hat{A}$ and the set of functions (5.145). A relation like (5.149) holds, of course, for each Φ_r in the set (5.145). It is convenient to collect the functions in a row matrix and write

$$\hat{A}\left(\Phi_1, \Phi_2, \ldots, \Phi_m\right) = \left(\Phi_1, \Phi_2, \ldots, \Phi_m\right) \begin{pmatrix} A_{11} & A_{12} & \cdots & A_{1m} \\ A_{21} & A_{22} & \cdots & A_{2m} \\ \ldots & \ldots & \ldots & \ldots \\ A_{m1} & A_{m2} & \cdots & A_{mm} \end{pmatrix} \tag{5.152}$$

We are now prepared to determine the coefficients c'_r in Eq. (5.148). We get

$$\begin{aligned}\Psi' = \hat{A}\Psi = \sum_{r=1}^{m} c_r \hat{A}\Phi_r &= \sum_{r=1}^{m}\sum_{t=1}^{m} c_r A_{tr}\Phi_t \\ &= \sum_{t=1}^{m}\left(\sum_{r=1}^{m} A_{tr}c_r\right)\Phi_t,\end{aligned} \tag{5.153}$$

and hence

$$c'_t = \sum_{r=1}^{m} A_{tr}c_r, \tag{5.154}$$

i. e.,

$$\begin{pmatrix} c'_1 \\ c'_2 \\ \vdots \\ c'_m \end{pmatrix} = \begin{pmatrix} A_{11} & A_{12} & \cdots & A_{1m} \\ A_{21} & A_{22} & \cdots & A_{2m} \\ \cdots & \cdots & \cdots & \cdots \\ A_{m1} & A_{m2} & \cdots & A_{mm} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_m \end{pmatrix}, \tag{5.155}$$

or,

$$\boldsymbol{c}' = \boldsymbol{A}\boldsymbol{c}. \tag{5.156}$$

This is the matrix representation of Eq. (5.147). The functions Ψ and Ψ' are represented by the column vectors

$$\boldsymbol{c} = \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_m \end{pmatrix}, \qquad \boldsymbol{c}' = \begin{pmatrix} c'_1 \\ c'_2 \\ \vdots \\ c'_m \end{pmatrix} \tag{5.157}$$

respectively, and the operator $\hat{A}$ is represented by the matrix

$$\boldsymbol{A} = \begin{pmatrix} A_{11} & A_{12} & \cdots & A_{1m} \\ A_{21} & A_{22} & \cdots & A_{2m} \\ \cdots & \cdots & \cdots & \cdots \\ A_{m1} & A_{m2} & \cdots & A_{mm} \end{pmatrix}. \tag{5.158}$$

Similar matrix representations may, of course, be set up for other relations. Thus, the eigenvalue equation

$$\hat{F}\Psi = f\Psi, \tag{5.159}$$

where $\hat{F}$ is some operator acting in $\mathcal{V}$, has the matrix representation

$$\boldsymbol{F}\boldsymbol{c} = f\boldsymbol{c}. \tag{5.160}$$

In this way, the problem of determining the eigenvalues of an operator becomes transformed into the problem of determining the eigenvalues of a square matrix. In particular, the Schrödinger equation (5.3) becomes

$$\boldsymbol{H}\boldsymbol{c} = E\boldsymbol{c}, \tag{5.161}$$

where $\boldsymbol{H}$ is the *Hamiltonian matrix.*

To proceed, let us show that the matrix $\boldsymbol{C}$ corresponding to the operator product $\hat{C} = \hat{A}\hat{B}$, is the product of the matrices $\boldsymbol{A}$ and $\boldsymbol{B}$. We make successive use of the analogues of Eq. (5.149) to get

$$\begin{aligned}\hat{C}\Phi_r &= \hat{A}\hat{B}\Phi_r = \hat{A}\sum_{t=1}^{m} B_{tr}\Phi_t = \sum_{t=1}^{m} B_{tr}\hat{A}\Phi_t \\ &= \sum_{t=1}^{m} B_{tr}\sum_{s=1}^{m} A_{st}\Phi_s \\ &= \sum_{s=1}^{m}\left(\sum_{t=1}^{m} A_{st}B_{tr}\right)\Phi_s,\end{aligned} \tag{5.162}$$

which shows that

$$C_{sr} = \sum_{t=1}^{m} A_{st}B_{tr}. \tag{5.163}$$

This is just the matrix equation

$$\boldsymbol{C} = \boldsymbol{A}\boldsymbol{B}. \tag{5.164}$$

Hence $\boldsymbol{C}$ is the product of $\boldsymbol{A}$ and $\boldsymbol{B}$, as claimed.

As a special consequence of Eq. (5.164), we note that the matrix representation of a commutator between operators is the commutator between the corresponding matrices. Thus, a commutator relation like

$$[\hat{A}, \hat{B}] = i\hat{D} \tag{5.165}$$

implies the corresponding matrix relation

$$[\boldsymbol{A}, \boldsymbol{B}] = i\boldsymbol{D}. \tag{5.166}$$

The results of the present section are of great importance in many applications of quantum mechanics. A statement of warning is, however, in order. We have everywhere assumed that the operators referred to act within the finite function space $\mathcal{V}$, such that relations like (5.149) are exact. This condition will in general not be satisfied for all operators of a given physical system. It will, in particular, never be satisfied for the familiar position and momentum operators $\hat{x}_i$ and $\hat{p}_j$. In order to have the condition fulfilled for these operators, it is necessary to let the dimension m of the function space $\mathcal{V}$ go to infinity. One then encounters infinite matrices, and such matrices must be treated with great care.

It is, in this context, of interest to notice that Heisenberg's formulation of quantum mechanics, to which we alluded in the introduction to Chapter 3, was a theory based on infinite matrices. It was prior to Schrödinger's formulation. Infinite matrices, $\boldsymbol{x}_i$ and $\boldsymbol{p}_j$, were postulated to exist, and in terms of these the Hamiltonian matrix was to be constructed. A basic role was played by the commutator relation

$$[\boldsymbol{x}_i, \boldsymbol{p}_j] = i\hbar\delta_{ij}\mathbf{1} \tag{5.167}$$

where $\mathbf{1}$ is the unit matrix (of infinite dimension). The idea was to search for matrices $\boldsymbol{x}_i$ and $\boldsymbol{p}_j$ that would cause the Hamiltonian matrix to become diagonal, with the diagonal elements postulated to be the observed energies of the system. This was a difficult task, but in the cases where it could be carried through its results were reproduced by Schrödinger's theory. Amazed by this, Schrödinger produced his fifth paper[4] in which he showed that Heisenberg's matrices could be understood as the matrix representives of his own operators. The search for a diagonal Hamiltonian matrix, he showed, corresponds to choosing the basis functions (5.145) as the eigenfunctions of the Hamiltonian, for in that case we have that

$$H_{rs} = \langle \Phi_r | \widehat{H} | \Phi_s \rangle = E_r \delta_{rs}. \tag{5.168}$$

In closing the present section, it is important to stress that the relations we have derived all hinge on the assumption that the basis functions (5.145) form an orthonormal set. If the basis functions are non-orthogonal, the setup of the correspondence between operators and matrices is best performed by introducing an additional basis in $\mathcal{V}$, viz.

$$\{\Phi^r\} = \Phi^1, \Phi^2, \ldots, \Phi^m, \tag{5.169}$$

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[4] See footnote 3.2.

such that

$$\langle \Phi^r | \Phi_s \rangle = \delta_{rs} . \tag{5.170}$$

The two bases are said to be the duals of each other, and are collectively referred to as a biorthonormal basis. We shall not discuss the use of such a basis here, but refer the reader to the literature.[5]

By working with a biorthonormal basis, one may preserve relations like (5.161), (5.164) and (5.166). If, however, this is not essential and the main object is to solve the time-independent Schrödinger equation

$$(\hat{H} - E)\Psi = 0, \tag{5.171}$$

then one may proceed as follows.

Write Ψ on the form (5.146) and substitute it into Eq. (5.171), to get

$$\sum_{s=1}^{m} (\hat{H} - E) c_s \Phi_s = 0. \tag{5.172}$$

Then multiply from the left by Φ_r^* and integrate over all the coordinates of the system. We get then

$$\sum_{s=1}^{m} \langle \Phi_r | \hat{H} - E | \Phi_s \rangle c_s , \qquad r = 1, 2, \ldots, m, \tag{5.173}$$

or,

$$\boxed{\sum_{s=1}^{m} (H_{rs} - E S_{rs}) c_s = 0 , \qquad r = 1, 2, \ldots, m} \tag{5.174}$$

where

$$H_{rs} = \langle \Phi_r | \hat{H} | \Phi_s \rangle \tag{5.175}$$

is an element of the Hamiltonian matrix and

$$S_{rs} = \langle \Phi_r | \Phi_s \rangle . \tag{5.176}$$

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[5] For an introduction to the properties of biorthonormal sets and their use in quantum chemistry, see J. P. Dahl, Int. J. Quantum Chem. **14**, 191 (1978).

is an element of the overlap matrix. Eq. (5.174) may be written

$$\boldsymbol{Hc} = E\boldsymbol{Sc}. \tag{5.177}$$

Eq. (5.177) is also a matrix form of the Schrödinger equation. In the same way as Eq. (5.161), it is equivalent to the Schrödinger equation when the representation (5.146) is exact. But even if the representation is not exact, i. e., the function $\hat{H}\Psi$ does not entirely belong to $\mathcal{V}$, then Eq. (5.177) will still determine an approximate solution to the Schrödinger equation, and this solution is the best one within $\mathcal{V}$ in a variational sense, as we shall discuss it at length in Sec. 12.5. It is an observation of great practical value.

Supplementary Reading

The bibliography, entries [10], [11], [12], and [13].

Problems

5.1. Starting from the commutation relation (5.26), use the relations (5.35) to derive the first of the commutation relations (5.33).

5.2. Evaluate the commutators $[\frac{1}{x}, \hat{p}_x]$, $[\hat{p}_x, x^n]$ and $[x, \hat{p}_x^n]$, where n is a positive integer.

5.3. Evaluate the commutators $[x, \hat{l}_x]$, $[x, \hat{l}_y]$ and $[x, \hat{l}_z]$.

5.4. Determine the Hermitian conjugate to each of the operators x^2, $x\hat{p}_x$, $x\hat{p}_x^2$ and $x\hat{p}_x x$.

5.5. Let $\hat{A}$ be the operator

$$\hat{A} = x + i\hat{p}_x.$$

Write down the Hermitian conjugate operator $\hat{A}^\dagger$ and evaluate the commutator $[\hat{A}, \hat{A}^\dagger]$.

5.6. Use the fact that d/dx is an anti-Hermitian operator (Eq. (5.50)) to show that

$$\int f(x)f'(x)dx = 0$$

whenever $f(x)$ is *real* and *well-behaved*, and $f'(x) = df(x)/dx$.

5.7. Let $\Psi(t)$ be a wavefunction that develops in time in accordance with the time-dependent Schrödinger equation and a time-independent Hamiltonian $\hat{H}$. Let $\hat{F}$

be some other time-independent operator. The expectation value of $\hat{F}$ is then, in general, a function of time. We denote it $f(t)$:

$$f(t) = \langle\Psi(t)|\hat{F}|\Psi(t)\rangle.$$

In forming this expression, we have assumed that $\langle\Psi(t)|\Psi(t)\rangle = 1$ at all times. That this is a consistent assumption is shown in **b**.

a. Show that

$$\frac{df(t)}{dt} = \langle\Psi(t)|\hat{F}'|\Psi(t)\rangle,$$

where

$$\hat{F}' = \frac{i}{\hbar}[\hat{H}, \hat{F}].$$

b. By putting $\hat{F} = 1$, show that the normalization integral $\langle\Psi(t)|\Psi(t)\rangle$ is, in fact, independent of time.

c. Assume, now, that we consider a one-dimensional system with the Hamiltonian

$$\hat{H} = \frac{\hat{p}_x^2}{2m} + V(x).$$

Evaluate the expressions

$$x' = \frac{i}{\hbar}[\hat{H}, x] \quad \text{and} \quad \hat{p}_x' = \frac{i}{\hbar}[\hat{H}, \hat{p}_x]$$

for x' and $\hat{p}_x'$.

5.8. Consider the one-dimensional box, but with the origin placed at the inversion center as in Sec. (4.5), and approximate the ground-state wavefunction by the 'trial function'

$$\psi(x) = N\left(\frac{a^2}{4} - x^2\right), \quad -a/2 \le x \le a/2.$$

a. Determine the constant N such that $\psi(x)$ is normalized to 1.

b. Determine the expectation value of $\hat{H}$, i. e.,

$$\langle\hat{H}\rangle = \langle\psi|\hat{H}|\psi\rangle = -\frac{\hbar^2}{2m}\int \psi(x)^* \frac{d^2}{dx^2}\psi(x)dx$$

and verify that $\langle\hat{H}\rangle$ is larger than the true ground-state energy E_1.

c. Evaluate the overlap integral $\langle\psi_1|\psi\rangle$ between the trial function $\psi(x)$ and the true ground-state wavefunction $\psi_1(x)$.

5.9. Consider the time-dependent wavefunction (4.94) and show that the average value $\bar{E} \equiv \langle\hat{H}\rangle$ of the energy, and the uncertainty $\Delta E \equiv \Delta H$, are given by the expressions

$$\bar{E} = \frac{1}{2}(E_1 + E_2), \quad \Delta E = \frac{1}{2}(E_2 - E_1).$$

Use that $\psi_1(x)$ and $\psi_2(x)$ are eigenfunctions of $\hat{H}$.

Chapter 6

The Free Particle

Contents

After the refinement of the quantum-mechanical formalism performed in the previous chapter, let us continue our study of actual problems.

In Chapter 4 we determined the stationary states of the particle in a box. In the next chapter we shall determine the stationary states of the harmonic oscillator. In both cases the energy spectrum is entirely discrete, because the potential energy function rises to infinity in all directions. In the present chapter we shall consider the free particle, for which the potential energy function is everywhere zero. This causes the energy spectrum to become entirely continuous. It is also found that the wavefunctions associated with the stationary states no longer vanish at infinity. Hence they cannot be normalized to unity. This implies in turn that the stationary states of a free particle cannot be physically realized. The only genuine states of a free particle are the non-stationary states. The principle of superposition, (4.92), remains valid however, so it is still of great importance to study the stationary states. This we shall do in the following section. We shall see that the stationary-state wavefunctions may be considered to be de Broglie waves. A linear superposition of stationary-state wavefunctions is hence a superposition of de Broglie waves, and since any non-stationary wavefunction may, at least in principle, be written as such a superposition, one often refers to a non-stationary wavefunction as a *wave packet*.

In Sec. 2 we study the time evolution of a particular non-stationary wavefunction known as the Gaussian wave packet. This kind of wavefunction plays an important role in many applications and in general discussions on the nature of quantum mechanics. The wavefunction retains a simple analytical form as a function of time, and simple expressions hold for the statistical parameters introduced in the previous chapter. These parameters include mean values, uncertainties and uncertainty product. They are derived and discussed in Sec. 3.

Throughout the first three sections we confine the motion of the free particle to a single dimension. The generalization to ordinary three-dimensional space is presented in the last section of the chapter.

6.1 The Stationary States of the Free Particle

For the free particle, the time-independent Schrödinger equation has the form (4.1) everywhere. We may separate the variables in the same way as it was done for the particle in the box in Sec. 4.1, and we are thus led to study the Schrödinger equation

$$\widehat{H}\psi(x) = E\psi(x) \tag{6.1}$$

for a free particle in one dimension. Its Hamiltonian is

$$\widehat{H} = \frac{\hat{p}_x^2}{2m} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \tag{6.2}$$

where m is the mass of the particle as usual, and $\hat{p}_x$ is the linear momentum operator:

$$\hat{p}_x = -i\hbar\frac{d}{dx}\,. \tag{6.3}$$

Thus, Eq. (6.1) takes the familiar form

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x). \tag{6.4}$$

Apart from a slight difference in notation, this equation is the same as Eq. (4.11), and it has the same mathematical solutions.

The physically relevant solutions of Eq. (6.4) are those that stay finite for all values of x (cf. Sec. (3.2)). It follows from the discussion of Sec. 4.2 that no such solutions exist for negative values of E; for any function of the form (4.17) becomes infinite at either $+\infty$ or $-\infty$. For $E = 0$ we must put c_2 equal to zero in the expression (4.30) for the general solution, so there is just one physically acceptable solution, namely a constant. For positive values of E we have the mathematical solution (4.23); the general solution is oscillatory and stays finite everywhere; it is accordingly a physically acceptable solution for all values of E and for all values of the arbitrary coefficients c_1 and c_2.

Let us, for simplicity, write k for the k_x of Sec. 4.2. The stationary-state energies of the free particle are then

$$E = E_k = \frac{\hbar^2 k^2}{2m}. \tag{6.5}$$

The corresponding wavefunctions have the form (4.23), i. e.,

$$\psi(x) = c_1 \sin(kx) + c_2 \cos(kx). \tag{6.6}$$

This expression also covers the case $E = 0$, since $\psi(x)$ reduces to the constant c_2 when k becomes zero.

Apart from the level $E = 0$, each energy level is twofold degenerate, i. e., there are two linearly independent eigenfunctions for each value of E, and any linear combination of these functions is again an eigenfunction (cf. the discussion of degeneracy in Sec. 4.7). The two basis functions are $\sin(kx)$ and $\cos(kx)$, or any two linearly independent combinations of these functions. It is particularly useful to select the functions e^{ikx} and e^{-ikx} which are related to $\sin(kx)$ and $\cos(kx)$ by Euler's relations (See Appendix A). Thus, we may write the general eigenfunction (6.6) in the alternative form

$$\psi(x) = A_1 e^{ikx} + A_2 e^{-ikx} \tag{6.7}$$

where A_1 and A_2 are new arbitrary constants.

Not only are the basis functions e^{ikx} and e^{-ikx} eigenfunctions of the Hamiltonian (6.2). They are also eigenfunctions of the momentum operator (6.3). It is, in fact, easily verified that

$$\boxed{\hat{p}_x e^{\pm ikx} = \pm \hbar k e^{\pm ikx}} \tag{6.8}$$

We say that e^{ikx} describes a particle with momentum $\hbar k$, and e^{-ikx} a particle with momentum $-\hbar k$.

In the above expressions it is sufficient to work with non-negative k-values to cover all stationary states of the free particle, as we did in Sec. 4.2. But now it is expedient to allow k to become negative, and thus let the notation e^{ikx} cover both positive and negative k-values. Our results may then be formulated as follows:

> The functions e^{ikx}, $-\infty < k < \infty$, are common eigenfunctions of the free-particle Hamiltonian (6.2) and the momentum operator (6.3). The momentum eigenvalue is $p_x = \hbar k$, and the energy eigenvalue is $E = \hbar^2 k^2/2m = p_x^2/2m$. For a given $k \neq 0$, the two functions e^{-ikx} and e^{ikx} corresponding to opposite values of k have the same energy: The energy level is twofold degenerate, and the most general energy eigenfunction may be written as in Eq. (6.7) or Eq. (6.6). (6.9)

The complex exponential function is periodic with the period $2\pi i$ (See Appendix A). We have accordingly

$$e^{ik(x+2\pi/k)} = e^{ikx}. \tag{6.10}$$

Thus, the function e^{ikx} repeats itself when x is augmented by $2\pi/k$. In other words, the function e^{ikx} may be characterized by the wavelength $\lambda = 2\pi/|k|$. And since e^{ikx} is an eigenfunction of $\hat{p}_x$ with eigenvalue $p_x = \hbar k$, we also get that $\lambda = h/|p_x|$. But this is nothing but the expression for the de Broglie wavelength, which we introduced in Sec. 2.6. Thus, we have made an important contact with the concepts of early quantum mechanics:

> The energy- and momentum-wavefunction e^{ikx} is a de Broglie wave with the de Broglie wavelength
>
> $$\lambda = h/|p_x| = 2\pi/|k|.$$
>
> (6.11)

We shall now consider the orthogonality and normalization properties of the free-electron wavefunctions. We have already stated several times that these functions fail to be square integrable. Let us, however, consider the following integral

$$\langle e^{ik_1x}|e^{ik_2x}\rangle = \int_{-\infty}^{\infty} \left(e^{ik_1x}\right)^* e^{ik_2x} dx = \int_{-\infty}^{\infty} e^{i(k_2-k_1)x} dx \tag{6.12}$$

where the integral from $-\infty$ to ∞ is evaluated by the prescription

$$\int_{-\infty}^{\infty} f(x)dx = \lim_{a\to\infty} \int_{-a}^{a} f(x)dx. \tag{6.13}$$

This is the so-called *Cauchy value* of the integral. We get then

$$\langle e^{ik_1x}|e^{ik_2x}\rangle = \lim_{a\to\infty} \left[\frac{e^{i(k_2-k_1)x}}{i(k_2-k_1)}\right]_{-a}^{a} = 2 \lim_{a\to\infty} \frac{\sin[(k_2-k_1)a]}{k_2-k_1} \tag{6.14}$$

where we have used the Euler relation (A.5) in Appendix A.

At this stage the reader is referred to Appendix E in which the Dirac δ-function is discussed. In the appendix, the independent variable is denoted u. Here we want it to be k. The δ-function, $\delta(k)$, is defined such that

$$\begin{cases} \delta(k) = 0 \quad \text{for} \quad k \neq 0, \\ \displaystyle\int_{-\infty}^{\infty} \delta(k)dk = 1. \end{cases} \tag{6.15}$$

In addition we have, for any function $g(k)$, that

$$\int_{-\infty}^{\infty} g(k)\delta(k-k_0)dk = g(k_0). \tag{6.16}$$

These relations are the equivalents of the relations (E.4) and (E.5).

As shown in the appendix, several one-parameter families of functions have the δ-function as limit function when the parameter tends to 0 or ∞, say. Eqs. (E.10) and (E.13) show in fact that

$$\lim_{a\to\infty} \frac{1}{\pi}\frac{\sin(ak)}{k} = \delta(k). \tag{6.17}$$

Eq. (6.14) may accordingly be written

$$\boxed{\langle e^{ik_1x}|e^{ik_2x}\rangle = 2\pi\delta(k_2-k_1)} \tag{6.18}$$

Thus, functions corresponding to different values of k are mutually orthogonal.

We may avoid the factor 2π on the right-hand side of Eq. (6.18) by defining

$$\boxed{\psi_k(x) = \sqrt{\frac{1}{2\pi}}e^{ikx}} \tag{6.19}$$

for then we get

$$\boxed{\langle\psi_{k_1}(x)|\psi_{k_2}(x)\rangle = \delta(k_2 - k_1)} \tag{6.20}$$

This relation bears a strong resemblance to the orthonormality relation (4.42) for the box wavefunctions. The only difference is that the Kronecker delta symbol has been replaced by the Dirac δ-function. Hence, we also refer to the relation (6.20) as an orthonormality relation, but talk about *δ-function normalization* rather than normalization to unity.

Having determined the solutions of the time-independent Schrödinger equation for the free particle, we must as always remember that the proper stationary-state wavefunctions contain the time-dependent factor $e^{-iEt/\hbar}$ (cf. Eq. (3.5)). With this time dependence included, the stationary-state wavefunction (6.19) becomes

$$\boxed{\Psi_k(x,t) = \sqrt{\frac{1}{2\pi}}e^{ikx}e^{-iE_kt/\hbar}, \qquad E_k = \frac{\hbar^2k^2}{2m}} \tag{6.21}$$

Although we say that the function (6.21) describes a particle with momentum $\hbar k$, it is not square integrable and hence does not describe a *bona fide* state of the free particle. It may, however, be proved that the functions e^{ikx}, with k being a continuous parameter extending from $-\infty$ to ∞, form a complete set in the sense that any well-behaved and square-integrable function, $f(x)$, may be written on the form

$$f(x) = \sqrt{\frac{1}{2\pi}}\int_{-\infty}^{\infty} g(k)e^{ikx}dk. \tag{6.22}$$

This is the so-called *Fourier representation* of $f(x)$. The function $g(k)$ is called the *Fourier transform* of $f(x)$, and vice versa, since the following inverse relation also holds:

$$g(k) = \sqrt{\frac{1}{2\pi}}\int_{-\infty}^{\infty} f(x)e^{-ikx}dx. \tag{6.23}$$

To prove this inverse relation, we isolate the right-hand side of Eq. (6.23) and insert the expression (6.22) for $f(x)$, to show that the result in fact equals $g(k)$.We get

$$\sqrt{\frac{1}{2\pi}}\int_{-\infty}^{\infty} f(x)e^{-ikx}dx = \frac{1}{2\pi}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dxdk'g(k')e^{ik'x}e^{-ikx}. \tag{6.24}$$

But the integration over x results in a δ-function, according to Eq. (6.18). Hence we get

$$\sqrt{\frac{1}{2\pi}}\int_{-\infty}^{\infty} f(x)e^{-ikx}dx = \int_{-\infty}^{\infty} dk'g(k')\delta(k'-k). \tag{6.25}$$

The right-hand side is now of the form (6.16). Thus, we reproduce the expression (6.23) for $g(k)$.

It may also be proven that

$$\int_{-\infty}^{\infty} f^*(x)f(x)dx = \int_{-\infty}^{\infty} g^*(k)g(k)dk. \tag{6.26}$$

This relation is known as *Parseval's theorem.*[1] The reader may find it interesting to prove this theorem by inserting the expression (6.22) for $f(x)$ twice on the left-hand side of Eq. (6.26) and then use the properties of the δ-function to obtain the right-hand side of the equation.

In connection with our study of non-stationary states of the particle in a box in Sec. 4.9, we stressed on the principle of superposition (4.92), according to which the wavefunction associated with any non-stationary state could be written in the form (4.89), i. e., as a sum over the stationary-state wavefunctions. Because of the possibility of writing a general function in the form (6.22), a similar principle holds in the present case, the only difference being that the sum over n in Eq. (4.89) now has to be replaced by an integral over k. In this sense, the stationary states of the free particle play a similar role as the stationary states of a bound system. In the next section, we shall consider a typical time-dependent state of a free particle on this background.

6.2 Non-Stationary States of the Free Particle

Let $\Psi(x,0)$ be some properly normalized wavefunction for a free particle at time $t = 0$. As always, we may then try to determine the form of Ψ at any

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[1] The theory of Fourier transforms is discussed in a large number of textbooks. But at present it is sufficient to realize the mere existence of the relations (6.22), (6.23) and (6.26).

later time by continued iteration based on the time-dependent Schrödinger equation. But in accordance with the discussion at the end of the last section, and in analogy with the discussion in Sec. 4.9, we may prefer to start from the Fourier representation of $\Psi(x,0)$, i. e., we draw on Eq. (6.22) and write

$$\Psi(x,0) = \sqrt{\frac{1}{2\pi}} \int_{-\infty}^{\infty} \phi(k) e^{ikx} dk. \tag{6.27}$$

The analogs of Eqs. (4.88)–(4.91) give then

$$\Psi(x,t) = \sqrt{\frac{1}{2\pi}} \int_{-\infty}^{\infty} \phi(k) e^{ikx} e^{-iE_k t/\hbar} dk. \tag{6.28}$$

We shall use this expression to study the time evolution of a so-called *Gaussian wave packet* which plays an important role in many contexts. The designation *wave packet* refers to the representation (6.28), according to which the wavefunction is written as a superposition of de Broglie waves. It is, however, important to realize that one *need not* use that representation. The only thing that matters is the function $\Psi(x,t)$ itself.

A Gaussian wave packet centered at $x = 0$ at time $t = 0$ has the form [2]

$$\boxed{\Psi(x,0) = \left(\frac{\alpha^2}{\pi}\right)^{\frac{1}{4}} e^{-\frac{1}{2}\alpha^2 x^2} e^{ik_0 x}} \tag{6.29}$$

The corresponding position probability density is

$$P(x,0) = \Psi^*(x,0)\Psi(x,0) = \frac{\alpha}{\sqrt{\pi}} e^{-\alpha^2 x^2}. \tag{6.30}$$

This density is independent of the value of k_0. But we shall see below that the factor $e^{ik_0 x}$ nevertheless is essential in determining the momentum of the particle. The wavefunction (6.29) is therefore a good example of a wavefunction that carries essential information beyond that contained in its absolute square (cf. the discussion in Sec. 3.4).

The wavefunction (6.29) is normalized to unity, which is easily verified from

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[2] The term Gaussian has its origin in probability theory where a distribution described by a function of the form (6.30) is called *normal* or *Gaussian*.

the first expression in the following list of useful integrals

$$\boxed{\begin{aligned}\mathcal{I}_0(\beta) &= \int_{-\infty}^{\infty} e^{-\beta u^2} du = \sqrt{\frac{\pi}{\beta}}, \quad \beta > 0\\ \mathcal{I}_2(\beta) &= \int_{-\infty}^{\infty} u^2 e^{-\beta u^2} du = -\frac{d\mathcal{I}_0(\beta)}{d\beta} = \frac{1}{2}\sqrt{\frac{\pi}{\beta^3}}\\ \mathcal{I}_4(\beta) &= \int_{-\infty}^{\infty} u^4 e^{-\beta u^2} du = \frac{d^2\mathcal{I}_0(\beta)}{d\beta^2} = \frac{3}{4}\sqrt{\frac{\pi}{\beta^5}}\end{aligned}} \tag{6.31}$$

These integrals also allow us to evaluate $\phi(k)$ from the analog of Eq. (6.23), i. e.,

$$\phi(k) = \sqrt{\frac{1}{2\pi}} \int_{-\infty}^{\infty} \Psi(x,0) e^{-ikx} dx. \tag{6.32}$$

The result is

$$\boxed{\phi(k) = \left(\frac{1}{\pi\alpha^2}\right)^{\frac{1}{4}} e^{-\frac{1}{2\alpha^2}(k-k_0)^2}} \tag{6.33}$$

Inserting this expression into Eq. (6.28) together with the expression of Eq. (6.21) for E_k gives, after some tedious but straightforward algebra,

$$\begin{aligned}\Psi(x,t) = \left(\frac{\alpha^2}{\pi(1+it/\tau)^2}\right)^{\frac{1}{4}} \exp\left\{-\frac{1}{2}\frac{\alpha^2}{1+it/\tau}\left(x - \frac{\hbar k_0}{m}t\right)^2\right.\\ \left. +ik_0\left(x - \frac{\hbar k_0}{m}t\right) + \frac{i}{2}\frac{\hbar k_0^2}{m}t\right\}\end{aligned} \tag{6.34}$$

where

$$\tau = \frac{m}{\alpha^2\hbar}. \tag{6.35}$$

Thus, we have been able to derive an analytic expression for $\Psi(x,t)$. The associated position probability density is found to be

$$\boxed{P(x,t) = \Psi^*(x,t)\Psi(x,t) = \left(\frac{\alpha(t)^2}{\pi}\right)^{\frac{1}{2}} \exp\left\{-\alpha(t)^2\left(x - \frac{\hbar k_0}{m}t\right)^2\right\}} \tag{6.36}$$

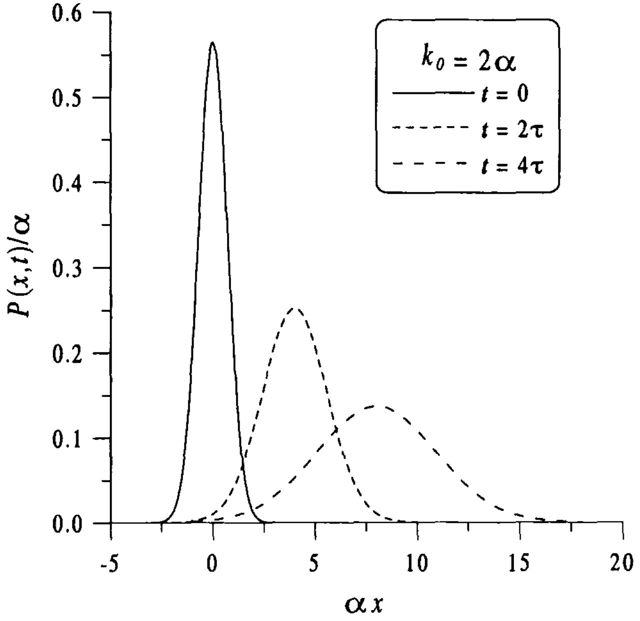

Figure 6.1: Motion of a Gaussian wave packet. τ is the natural unit of time defined by Eq. (6.35).

with

$$\alpha(t) = \left(\frac{\alpha^2}{1+(t/\tau)^2}\right)^{\frac{1}{2}}. \tag{6.37}$$

Eq. (6.36) shows that the probability density $P(x,t)$ is a Gaussian at all times. It propagates along the x-axis with velocity $v = \hbar k_0/m$, broadening as it moves. This broadening is referred to as the spreading of the wave packet. It makes predictions about the position of the particle increasingly imprecise as time goes on. The spreading of the wave packet is illustrated in Figure 6.1.

The wavefunction (6.34) contains more information than is displayed in Eq. (6.36) or Figure 6.1, in particular information about the momentum distribution. In the following section, we shall display such information in terms of expectation values and uncertainties. But in the light of the discussion of Sec. 5.9 it is possible to go further. For Eq. (6.27) is really an expansion of $\Psi(x,0)$ in terms of the eigenfunctions (6.19) of $\hat{p}_x$. In analogy with the postulate (5.143), we may therefore interpret the absolute square of the function $\phi(k)/\sqrt{\hbar}$, where $\phi(k)$ is given by Eq. (6.33), as the distribution function for the linear momentum of the particle.[3] In accordance with this, the function $\phi(k)/\sqrt{\hbar}$ becomes the wavefunction in *momentum space* if one transforms the quantum-mechanical description to the so-called *momentum-space representation.*

6.3 The Gaussian Wave Packet

An evaluation of the mean values and uncertainties for the Gaussian wave packet (6.34) is straightforward, but the calculations are rather lengthy. Hence, we only give the final results,

$$\boxed{\begin{aligned} \bar{x}(t) &= \frac{\hbar k_0}{m} t \\ \bar{p}_x(t) &= \hbar k_0 \\ \Delta x(t) &= \sqrt{\tfrac{1}{2}} \frac{1}{\alpha(t)} \\ \Delta p_x(t) &= \sqrt{\tfrac{1}{2}} \alpha \hbar \\ \Delta x(t) \Delta p_x(t) &= \tfrac{1}{2} \frac{\alpha}{\alpha(t)} \hbar \end{aligned}} \tag{6.38}$$

These expressions show that the center of the wave packet, as defined by $\bar{x}(t)$, moves with the constant velocity

$$v = \frac{\hbar k_0}{m} . \tag{6.39}$$

The expectation value of the momentum, $\bar{p}_x(t)$, is seen to be independent of time and equal to mv. Thus, the center of the wave packet moves like a free classical particle with mass m.

A Gaussian wave packet is the most precise wavefunction that we can construct for a free particle, in the sense that the uncertainty product $\Delta x(t)\Delta p_x(t)$ has its smallest possible value, $\frac{1}{2}\hbar$, at $t = 0$. This is why this kind of wavefunction is so important in the applications. For the optimal initial state is one in

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[3] The linear momentum corresponding to k is $\hbar k$, and $|\phi(k)|^2 dk = |\phi(k)/\sqrt{\hbar}|^2 d(\hbar k)$. Hence, the probability amplitude for the linear momentum is $\phi(k)/\sqrt{\hbar}$ rather than just $\phi(k)$.

which the uncertainties in the quantities by which one wants to characterize the state are as small as possible. The exact meaning of this statement is the following.

Assume that we want the momentum in our initial state to be very well defined, i.e., we want $\Delta p_x(0)$ to be quite small. Then the uncertainty principle tells us that $\Delta x(0)$ must necessarily be relatively large, for it is impossible to construct a wavefunction for which $\Delta x \Delta p_x$ is smaller than $\frac{1}{2}\hbar$. But we don't want to make $\Delta x(0)$ *unnecessarily* large; we make it as small as possible by constructing a Gaussian wave packet. Conversely, if we find it useful to construct an initial state with a small Δx value, we avoid making Δp_x unnecessarily large, again by choosing a Gaussian wave packet.

So far, so good. But our formulae also tell us that even if we have prepared an optimal state at $t = 0$, and even though the center of the wave packet moves in a classical way, we loose information about the particle as time goes on. This loss of information takes place in the position coordinate. For Eq. (6.38) shows that Δp_x is independent of time, whereas Δx increases in time. The rate of increase is governed by the parameter τ defined by Eq. (6.35). A small value of this parameter makes Δx increase fast. A larger value of the parameter leads to a slower increase.

As Eq. (6.38) and Figure 6.1 show, the rate at which the wave packet spreads is determined by the parameter τ. By choosing $t = \tau$ in Eq. (6.37) we get

$$\alpha(\tau) = \frac{\alpha}{\sqrt{2}}, \tag{6.40}$$

and hence

$$\Delta x(\tau) = \sqrt{2}\Delta x(0). \tag{6.41}$$

Thus, the width of the Gaussian increases by a factor of $\sqrt{2}$ during a time interval τ.

For an electron with $m = m_e$ and $\alpha = 1/a_0$, where a_0 is the Bohr radius, we get $\tau = 2.4 \times 10^{-17}\,\mathrm{s}$. For a particle with $m = 10^{-6}\,\mathrm{kg}$ and $\alpha = 1/(10^{-6}\,\mathrm{m})$ we find $\tau = 9.5 \times 10^{27}\,\mathrm{s} = 3.0 \times 10^{20}$ years. Thus, the spreading of the wave packet is very important in the realm of the elementary particles, but irrelevant for particles of macroscopic dimensions.

We close our discussion of the free particle with a generalization to three-dimensional space.

6.4 From One to Three Dimensions

The Schrödinger equation for a free particle in ordinary three-dimensional space is the same as that for the particle in the three-dimensional box (Eq. (4.1)). Consequently, the stationary-state wavefunctions may be constructed from those for a free particle in a single dimension in a manner which is entirely analogous to that applied in Sec. 4.6. Thus, the wavefunction $\psi_k(x)$ of Eq. (6.19) becomes replaced by the wavefunction

$$\psi_{k_x k_y k_z}(x, y, z) = \left(\frac{1}{2\pi}\right)^{\frac{3}{2}} e^{i(k_x x + k_y y + k_z z)}. \tag{6.42}$$

Let us introduce the usual notation for the position vector,

$$\boldsymbol{r} = (x, y, z) \tag{6.43}$$

and the notation $\boldsymbol{k}$ for the vector

$$\boldsymbol{k} = (k_x, k_y, k_z). \tag{6.44}$$

This vector is usually referred to as the *wave vector*. The wavefunction (6.42) may then be written

$$\psi_{\boldsymbol{k}}(\boldsymbol{r}) = \left(\frac{1}{2\pi}\right)^{\frac{3}{2}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}}. \tag{6.45}$$

This function is referred to as a *plane wave* because it is constant in any plane perpendicular to $\boldsymbol{k}$, and because it repeats itself whenever one moves the distance

$$\lambda = \frac{2\pi}{|\boldsymbol{k}|} \tag{6.46}$$

in the direction parallel to $\boldsymbol{k}$ (cf. Eq. (6.11)).

The equivalent of Eq. (6.21) becomes

$$\boxed{\Psi_{\boldsymbol{k}}(\boldsymbol{r}, t) = \left(\frac{1}{2\pi}\right)^{\frac{3}{2}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} e^{-iE_{\boldsymbol{k}}t/\hbar}, \qquad E_{\boldsymbol{k}} = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2(k_x^2 + k_y^2 + k_z^2)}{2m}} \tag{6.47}$$

Similarly, the Gaussian wave packet (6.29) becomes replaced by the three-dimensional wave packet

$$\boxed{\Psi(\boldsymbol{r},0) = \left(\frac{\alpha_x^2\alpha_y^2\alpha_z^2}{\pi^3}\right)^{\frac{1}{4}} e^{-\frac{1}{2}(\alpha_x^2x^2+\alpha_y^2y^2+\alpha_z^2z^2)}e^{i\boldsymbol{k}_0\cdot\boldsymbol{r}}} \tag{6.48}$$

The center of the wave packet moves in the direction $\boldsymbol{k}_0$ with the velocity $\hbar\boldsymbol{k}_0/m$, just like a free classical particle with mass m and linear momentum $\hbar\boldsymbol{k}_0$. The form of $\Psi(\boldsymbol{r},t)$ is the straightforward generalization of the one-dimensional form (6.34).

Supplementary Reading

The bibliography, entries [10] and [11].

Problems

6.1. Let $\hat{I}$ be the inversion operator defined by Eq. (4.48) and let $\hat{p}_x$ be the linear-momentum operator (6.3). By simplifying the expression $[\hat{I},\hat{p}_x]f(x)$, show that the commutator $[\hat{I},\hat{p}_x]$ is different from zero.

6.2. For a given value of k (> 0) , the basis functions e^{ikx} and e^{-ikx} are common eigenfunctions of the Hamiltonian (6.2) and the momentum operator (6.3), whereas the basis functions $\sin kx$ and $\cos kx$ are common eigenfunctions of the Hamiltonian and the inversion operator defined by Eq. (4.48). Relate these observations to the theorem (5.120), and relate the presence of degeneracy to the non-vanishing of the commutator $[\hat{I},\hat{p}_x]$ and the discussion at the end of Sec. 4.7.

6.3. Calculate the quantities $\bar{E} \equiv \langle\hat{H}\rangle$ and $\Delta E \equiv \Delta H$ for the free-particle wave-function (6.29). Use the integral expressions (6.31).

Chapter 7

The Harmonic Oscillator

Contents

In Sec. 2.1 we described how Planck was able to account for the intensity and spectral composition of the black-body radiation by assuming that the energy of an oscillator was quantized according to the rule

$$E_n = nh\nu, \quad n = 0, 1, 2, \ldots \tag{7.1}$$

And in Sec. 2.4 we described how Einstein, by applying the same assumption to the atomic vibrations in a monatomic crystal, could account for the temperature dependence of its specific heat. In the present chapter we shall solve the Schrödinger equation for the harmonic oscillator and thus justify the expression (7.1), albeit in the modified form

$$E_n = (n + \tfrac{1}{2})h\nu, \quad n = 0, 1, 2, \ldots \tag{7.2}$$

which differs from the older expression by the inclusion of the *zero-point energy* $\frac{1}{2}h\nu$, as already discussed at the end of Sec. 2.4.

The harmonic oscillator is one of the most important model systems in quantum mechanics. The solutions of the harmonic-oscillator problem find extensive application in theoretical physics and chemistry. Central applications include the description of vibrations in molecules and crystals, and the theory of the electromagnetic field.

We shall determine the stationary states of the harmonic oscillator by two different methods. One is the so-called *polynomial method* in which one proceeds in essentially the same manner as for the particle in a box, i. e., one determines all the mathematical solutions of a second-order differential equation and subsequently picks out the physically acceptable ones. This is the classical method. The other method is called the *algebraic method*. For the harmonic oscillator, this method simply amounts to solving a first-order differential equation for the ground state. The higher states are then determined from the known ground state by means of a *ladder operator*. The algebraic method plays an important role in modern quantum mechanics. We shall encounter it again in the following chapters.

7.1 Definitions

Let x be the coordinate associated with a one-dimensional oscillator, $-\infty < x < \infty$ and let m be the mass. The oscillator is said to be *harmonic*, with *force constant* $k > 0$, if the potential energy function has the form

$$V(x) = \tfrac{1}{2}kx^2. \tag{7.3}$$

The particle is then pulled toward the origin, $x = 0$, with an attractive force which is the negative gradient of the potential (cf. Eq. (3.2)):

$$F = -\frac{dV(x)}{dx} = -kx. \tag{7.4}$$

Classically, the oscillator performs harmonic vibrations whose frequency ν is determined by the expression

$$\omega = 2\pi\nu = \sqrt{\frac{k}{m}}, \tag{7.5}$$

with ω being the angular frequency. Eq. (7.5) allows us to write the expression (7.3) for the potential-energy function as

$$V(x) = \tfrac{1}{2}m\omega^2x^2, \tag{7.6}$$

and this is the form that we shall prefer to use in the following.

The classical kinetic energy is as usual given by the expression

$$T = \frac{p_x^2}{2m}, \tag{7.7}$$

and the Hamiltonian is

$$H = \frac{p_x^2}{2m} + \tfrac{1}{2}m\omega^2 x^2. \tag{7.8}$$

The coordinate, x, of a classical oscillator with energy E varies sinusoidally between $-x_{cl}$ and x_{cl}, where x_{cl} is the maximum amplitude. It is determined by the condition that the kinetic energy at this amplitude vanishes, i.e., the energy equals the value of the potential energy at that amplitude,

$$E = \tfrac{1}{2}m\omega^2 x_{cl}^2, \qquad x_{cl} = \sqrt{\frac{2E}{m\omega^2}}\,. \tag{7.9}$$

The points $\pm x_{cl}$ are called the *classical turning points.*.

To the quantum mechanical energies (7.2),

$$E_n = (n + \tfrac{1}{2})h\nu = (n + \tfrac{1}{2})\hbar\omega, \quad n = 0, 1, 2, \ldots \tag{7.10}$$

correspond the classical turning points

$$x_n = \sqrt{\frac{2E_n}{m\omega^2}} = \sqrt{\frac{(2n+1)\hbar}{m\omega}}\,. \tag{7.11}$$

Thus, we may expect that the quantity

$$\boxed{\frac{1}{\alpha} \equiv x_0 = \sqrt{\frac{\hbar}{m\omega}}} \tag{7.12}$$

is a characteristic length in the quantum mechanical problem, in a similar way as a_0 is a characteristic length in the quantum theory of the hydrogen atom. This is borne out in the following section.

7.2 The Schrödinger Equation for the Harmonic Oscillator

By the usual process of quantization (Sec. 3.3), the Hamiltonian (7.8) gives the time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + \tfrac{1}{2}m\omega^2 x^2\psi(x) = E\psi(x). \tag{7.13}$$

To clear the equation for dimensional constants we first divide both sides by $\hbar\omega$. This gives

$$-\frac{1}{2}\frac{\hbar}{m\omega}\frac{d^2\psi(x)}{dx^2}+\frac{1}{2}\frac{m\omega}{\hbar}x^2\psi(x)=\varepsilon\psi(x) \tag{7.14}$$

where ε is the dimensionless energy,

$$\boxed{\varepsilon=\frac{E}{\hbar\omega}} \tag{7.15}$$

Then we introduce the dimensionless coordinate

$$\boxed{Q=\alpha x=\sqrt{\frac{m\omega}{\hbar}}\,x} \tag{7.16}$$

defined in terms of the characteristic length $1/\alpha$ of Eq. (7.12), and get

$$-\frac{1}{2}\frac{d^2\varphi(Q)}{dQ^2}+\tfrac{1}{2}Q^2\varphi(Q)=\varepsilon\varphi(Q). \tag{7.17}$$

Thus, we have reduced the original equation (7.13) to a *standard form* which is the same for all harmonic oscillators, no matter what their defining parameters (m and ω) are.

The relation between $\psi(x)$ and $\varphi(Q)$ is, of course, that $\psi(x)=\varphi(\alpha x)$, or more general, that $\psi(x)=c\varphi(\alpha x)$, where c is an arbitrary constant that allows us to work with different normalization conditions for ψ and φ. Assume, in fact, that $\varphi(Q)$ is normalized to unity with respect to Q,

$$\int_{-\infty}^{\infty}\varphi^*(Q)\varphi(Q)dQ=1, \tag{7.18}$$

but that we want $\psi(x)$ to be normalized to unity with respect to x,

$$\int_{-\infty}^{\infty}\psi^*(x)\psi(x)dx=1. \tag{7.19}$$

We must then choose c such that $c^*c=\alpha$, for inserting $\psi(x)=c\varphi(\alpha x)$ into Eq. (7.19) gives

$$\begin{aligned}\int_{-\infty}^{\infty}\psi^*(x)\psi(x)dx&=c^*c\int_{-\infty}^{\infty}\varphi^*(\alpha x)\varphi(\alpha x)dx\\&=\frac{c^*c}{\alpha}\int_{-\infty}^{\infty}\varphi^*(Q)\varphi(Q)dQ=\frac{c^*c}{\alpha}.\end{aligned} \tag{7.20}$$

Eqs. (7.18) and (7.19) will thus be compatible if we choose c as $\sqrt{\alpha}$. This gives the important relation

$$\boxed{\psi(x) = \sqrt{\alpha}\,\varphi(\alpha x), \qquad \alpha = \sqrt{\frac{m\omega}{\hbar}}} \tag{7.21}$$

Together with the dimensionless coordinate Q we may introduce the dimensionless momentum operator

$$\begin{aligned} \hat{P} &= -i\frac{d}{dQ} = -i\frac{1}{\alpha}\frac{d}{dx} = \frac{1}{\alpha\hbar}\hat{p}_x \\ &= \frac{1}{\sqrt{m\omega\hbar}}\hat{p}_x . \end{aligned} \tag{7.22}$$

The new variables Q and P define the uncertainty product $\Delta Q \Delta P$, for which we find

$$\Delta Q \Delta P = (\alpha \Delta x)\left(\frac{\Delta p_x}{\alpha\hbar}\right) = \frac{1}{\hbar}\Delta x \Delta p_x . \tag{7.23}$$

So, Heisenberg's uncertainty relation (5.113) for ΔQ and ΔP becomes

$$\boxed{\Delta Q \Delta P \geq \tfrac{1}{2}} \tag{7.24}$$

We shall now go on and find the proper solutions of the Schrödinger equation as expressed in the form (7.17).

7.3 Solving the Schrödinger Equation

Let us, for convenience, rewrite the Schrödinger equation (7.17) in the form

$$\frac{d^2\varphi(Q)}{dQ^2} + (2\varepsilon - Q^2)\varphi(Q) = 0. \tag{7.25}$$

We shall solve this equation in three steps.

In the *first step* we consider the equation for so large values of $|Q|$ that 2ε may be neglected in comparison with Q^2. As it is easily verified by insertion, this gives us the *asymptotic solution*

$$\varphi(Q) \approx A_1 e^{-\frac{1}{2}Q^2} + \left(A_2 e^{\frac{1}{2}Q^2}\right), \qquad |Q| \text{ large,} \tag{7.26}$$

where A_1 and A_2 are arbitrary constants. A physically acceptable solution must stay finite in the limit $|Q| \to \infty$ and hence have A_2 equal to zero. In Eq. (7.26), we have indicated this by putting the unacceptable part of the asymptotic solution in brackets.

Inspired by the known asymptotic behavior of an acceptable $\varphi(Q)$ we proceed by writing

$$\varphi(Q) = F(Q)e^{-\frac{1}{2}Q^2}, \tag{7.27}$$

and find

$$\left\{ \begin{aligned} \frac{d\varphi}{dQ} &= \left(\frac{dF}{dQ} - QF\right) e^{-\frac{1}{2}Q^2} \\ \frac{d^2\varphi}{dQ^2} &= \left\{\frac{d^2F}{dQ^2} - 2Q\frac{dF}{dQ} + \left(Q^2 - 1\right) F\right\} e^{-\frac{1}{2}Q^2}. \end{aligned} \right. \tag{7.28}$$

Inserting these expressions in Eq. (7.25) gives

$$\frac{d^2F}{dQ^2} - 2Q\frac{dF}{dQ} + (2\varepsilon - 1)F = 0. \tag{7.29}$$

We have thus transformed the problem of solving Eq. (7.25) into that of solving Eq. (7.29). This completes the first step.

Eq. (7.29) has one very simple solution when $\varepsilon = \frac{1}{2}$, for it is then satisfied by putting $F(Q)$ equal to a constant. We are thus led to what appears to be the ground-state wavefunction:

$$\varphi_0(Q) = N_0 e^{-\frac{1}{2}Q^2}, \qquad \varepsilon_0 = \tfrac{1}{2}, \qquad E_0 = \tfrac{1}{2}\hbar\omega, \tag{7.30}$$

where N_0 is a normalization constant.

For other values of ε we must take a *second step*. This step amounts to expanding $F(Q)$ as a power series in Q and determining the coefficients in the expansion. Thus, we write

$$F(Q) = \sum_{n=0}^{\infty} a_n Q^n, \tag{7.31}$$

and find

$$\left\{ \begin{aligned} Q\frac{dF}{dQ} &= Q\sum_{n=1}^{\infty} a_n n Q^{n-1} = \sum_{n=0}^{\infty} a_n n Q^n \\ \frac{d^2F}{dQ^2} &= \sum_{n=2}^{\infty} a_n n(n-1)Q^{n-2} = \sum_{n=0}^{\infty} a_{n+2}(n+2)(n+1)Q^n. \end{aligned} \right. \tag{7.32}$$

Inserting these expressions in Eq. (7.29) gives

$$\sum_{n=0}^{\infty}\left[a_{n+2}(n+2)(n+1)-a_n(2n-2\varepsilon+1)\right]Q^n=0. \tag{7.33}$$

The various powers of Q are linearly independent functions, and hence the sum in Eq. (7.33) can only vanish if the coefficients of each power of Q are separately zero. Thus, $F(Q)$ is a solution of Eq. (7.29) if and only if

$$a_{n+2}=\frac{2n+1-2\varepsilon}{(n+1)(n+2)}a_n \tag{7.34}$$

for all n. This is called a *recursion relation.* It shows that once a value of a_0 has been chosen, then the values of a_2, a_4, $a_6, \dots$ are determined. Similarly, the values of a_3, a_5, $a_7, \dots$ are determined once the value of a_1 is fixed. A direct application of the recursion relation gives in fact

$$\begin{aligned}F(Q)&=a_0\left\{1+\frac{1-2\varepsilon}{1\cdot 2}Q^2+\frac{(1-2\varepsilon)(5-2\varepsilon)}{1\cdot 2\cdot 3\cdot 4}Q^4+\dots\right\}\\&\quad+a_1\left\{Q+\frac{3-2\varepsilon}{2\cdot 3}Q^3+\frac{(3-2\varepsilon)(7-2\varepsilon)}{2\cdot 3\cdot 4\cdot 5}Q^5+\dots\right\}\\&=a_0F_0(Q)+a_1F_1(Q)\end{aligned} \tag{7.35}$$

where a_0 and a_1 are arbitrary constants.

By multiplying the expression (7.35) by $\exp(-\frac{1}{2}Q^2)$ we obtain the complete solution of the original Eq. (7.25). As it should, the solution contains two arbitrary constants, a_0 and a_1. We must now extract the solutions that behave properly at $\pm\infty$. This defines *the third step* in our effort to solve Eq. (7.25).

In this third step, we begin by comparing the behavior of $F(Q)$ for large values of $|Q|$ with that of the function $\exp(Q^2)$. The latter has the well-known power-series expansion

$$\begin{aligned}e^{Q^2}&=1+Q^2+\frac{1}{2!}Q^4+\dots+\frac{1}{(n/2)!}Q^n+\frac{1}{(n/2+1)!}Q^{n+2}+\dots\\&=b_0+b_2Q^2+b_4Q^4+\dots+b_nQ^n+b_{n+2}Q^{n+2}+\dots\end{aligned} \tag{7.36}$$

As we see, this expansion is characterized by the recursion relation

$$b_{n+2}=\frac{2}{n+2}b_n. \tag{7.37}$$

When we compare this relation with the corresponding relation (7.34) for $F(Q)$, we observe that the two relations approach each other for sufficiently large values of n, for fixed ε. We get in fact that

$$\frac{a_{n+2}}{a_n} \approx \frac{b_{n+2}}{b_n} \approx \frac{2}{n}. \tag{7.38}$$

What this means is that both $F_0(Q)$ and $F_1(Q)$ behave like $\exp(Q^2)$ in the limits $Q \to \infty$ and $Q \to -\infty$. The function $F(Q) = a_0F_0(Q) + a_1F_1(Q)$ will accordingly also behave like $\exp(Q^2)$, at least on the side of the origin where the terms of $a_0F_0(Q)$ and $a_1F_1(Q)$ have the same sign for large values of n. When a_0 and a_1 have the same sign this corresponds to the limit $Q \to \infty$, when a_0 and a_1 have opposite signs it corresponds to the limit $Q \to -\infty$.

That $F(Q)$ behaves like $\exp(Q^2)$ implies in turn that $\varphi(Q)$, as defined by Eq. (7.27), behaves like $\exp(\frac{1}{2}Q^2)$. But this is exactly the behavior which we rejected in Eq. (7.26). So it looks as if no proper solutions exist at all.

But there is a way out. For our considerations around the relations (7.38) lose their validity if the power series (7.31) terminates after a finite number of terms. This causes $F(Q)$ to become a polynomial, and a polynomial times $\exp(-\frac{1}{2}Q^2)$ tends to zero when $|Q|$ becomes large.

So, if $F_0(Q)$ is a polynomial, we put $a_1 = 0$ and construct the function $F_0(Q)\exp(-\frac{1}{2}Q^2)$. And if $F_1(Q)$ is a polynomial, we put $a_0 = 0$ and construct the function $F_1(Q)\exp(-\frac{1}{2}Q^2)$. These functions are then the proper solutions of the Schrödinger equation (7.25).

For the power series (7.31) to become a polynomial of the nth degree, we must have that $a_n \neq 0$, with all subsequent coefficients vanishing. Eq. (7.34) shows that this situation will be met with if and only if $2\varepsilon = 2n + 1$.

Thus, we have arrived at the conclusion that acceptable solutions of Eq. (7.25) only exist when $\varepsilon = \varepsilon_n$, with

$$\boxed{\varepsilon_n = n + \tfrac{1}{2}, \qquad n = 0, 1, 2, \ldots} \tag{7.39}$$

There is one proper solution for each value of ε_n. It has the form of a Gaussian function, $\exp(-\frac{1}{2}Q^2)$, times an nth degree polynomial which we denote $H_n(Q)$. Its defining coefficients may be read off Eq. (7.35). We write the proper solutions as

$$\varphi_n(Q) = N_n H_n(Q) e^{-\frac{1}{2}Q^2} \tag{7.40}$$

where N_n is a normalization constant. We shall devote the following section to a more detailed presentation of these functions.

In closing this section, let us recall that ε is the dimensionless energy defined by Eq. (7.15). The energy spectrum of our original oscillator is accordingly given by the formula

$$\boxed{E_n = (n + \tfrac{1}{2})\hbar\omega = (n + \tfrac{1}{2})h\nu, \qquad n = 0, 1, 2, \ldots} \tag{7.41}$$

as anticipated in Eq. (7.2).

7.4 The Wavefunctions

By substituting $2n + 1$ for 2ε in Eq. (7.29) we see that the polynomial $H_n(Q)$ satisfies the differential equation

$$\frac{d^2F}{dQ^2} - 2Q\frac{dF}{dQ} + 2nF = 0. \tag{7.42}$$

This is a well-known differential equation in applied mathematics. It is called *Hermite's differential equation*, and the polynomials $H_n(Q)$ are called *Hermite polynomials*. They have a number of interesting properties, [1] but here we shall merely mention the independent definition

$$H_n(Q) = (-1)^n e^{Q^2} \frac{d^n}{dQ^n}\left(e^{-Q^2}\right), \tag{7.43}$$

the identity

$$\frac{dH_n(Q)}{dQ} = 2nH_{n-1}(Q), \tag{7.44}$$

and the recursion relation

$$H_{n+1}(Q) = 2QH_n(Q) - 2nH_{n-1}(Q). \tag{7.45}$$

The first few Hermite polynomials are listed in Table 7.1. The reader will find it easy to generate them from Eq. (7.43), or from Eq. (7.35) where the values of a_0 and a_1 are at our disposal.

The wavefunctions (7.40) have now been fully specified, apart from the normalization constant N_n. For lower values of n, it is easy to evaluate a particular N_n from the list (6.31) of integral expressions. We get, for instance,

$$\langle\varphi_0|\varphi_0\rangle = \int_{-\infty}^{\infty} \varphi_0^*(Q)\varphi_0(Q)dQ = N_0^* N_0 \int_{-\infty}^{\infty} e^{-Q^2} dQ = \sqrt{\pi} N_0^* N_0 \tag{7.46}$$

---

[1] See, for example, Chapter 22 in the reference of footnote 2.11.

Table 7.1: Hermite Polynomials

$H_0(Q) = 1$
$H_1(Q) = 2Q$
$H_2(Q) = 4Q^2 - 2$
$H_3(Q) = 8Q^3 - 12Q$
$H_4(Q) = 16Q^4 - 48Q^2 + 12$
$H_5(Q) = 32Q^5 - 16Q^3 + 120Q$
$H_6(Q) = 64Q^6 - 480Q^4 + 720Q^2 - 120$
$H_7(Q) = 128Q^7 - 1344Q^5 + 3360Q^3 - 1680Q$

and

$$\begin{aligned}\langle\varphi_1|\varphi_1\rangle &= \int_{-\infty}^{\infty} \varphi_1^*(Q)\varphi_1(Q)dQ = N_1^* N_1 \int_{-\infty}^{\infty} 4Q^2 e^{-Q^2} dQ \\ &= 4N_1^* N_1 \tfrac{1}{2}\sqrt{\pi} = 2\sqrt{\pi}\, N_1^* N_1\end{aligned} \tag{7.47}$$

and hence, by applying the normalization condition (7.18),

$$N_0 = \left(\sqrt{\pi}\right)^{-\frac{1}{2}}, \qquad N_1 = \left(2\sqrt{\pi}\right)^{-\frac{1}{2}}. \tag{7.48}$$

We have made rational phase choices similar to the one made in Eq. (4.36).

For other n-values, the normalization constant may be evaluated in a similar fashion. It is, however, also possible to use the mathematical properties of the Hermite polynomials to derive the following general expression [2]

$$N_n = \left(2^n n! \sqrt{\pi}\right)^{-\frac{1}{2}}. \tag{7.49}$$

The properly normalized solutions of Eq. (7.25) are therefore

$$\boxed{\varphi_n(Q) = \left\{\frac{1}{2^n n! \sqrt{\pi}}\right\}^{\frac{1}{2}} H_n(Q) e^{-\frac{1}{2}Q^2}} \tag{7.50}$$

They are normalized according to Eq. (7.18). We have, in fact, that

$$\boxed{\langle\varphi_n|\varphi_m\rangle = \int_{-\infty}^{\infty} \varphi_n^*(Q)\varphi_m(Q)dQ = \delta_{nm}} \tag{7.51}$$

---

[2] See, for example, the second reference of footnote 1.

Thus, these functions form an orthonormal set, just like the wavefunctions for the particle in a box (cf. Eq. (4.42)). The orthogonality of the wavefunctions may be demonstrated by using the general properties of the Hermite polynomials, but this is really not necessary, for we proved in Sec. 5.4 that eigenfunctions corresponding to different eigenvalues of a Hermitian operator are always orthogonal. The relation (7.51) is therefore tied to a very general rule.

The wavefunctions of our original oscillator are related to the functions of Eq. (7.50) through Eq. (7.21). Thus, we have

$$\boxed{\psi_n(x) = \left\{\frac{\alpha}{2^n n!\sqrt{\pi}}\right\}^{\frac{1}{2}} H_n(\alpha x)e^{-\frac{1}{2}\alpha^2x^2}, \qquad \alpha = \sqrt{\frac{m\omega}{\hbar}}} \tag{7.52}$$

These functions are normalized according to Eq. (7.19) and satisfy the orthonormality relation

$$\boxed{\langle\psi_n|\psi_m\rangle = \int_{-\infty}^{\infty} \psi_n(x)\psi_m(x)dx = \delta_{nm}} \tag{7.53}$$

Their energies are given by the familiar expression (7.41).

In Fig. 7.1 we give a graphic picture of some of the results obtained above, in the dimensionless representation based on the coordinate Q. Shown are the wavefunctions and their squares, in a presentation that allows their values at a point Q to be directly compared with the value of the potential energy function $V(Q)$ at the same point.

The base lines from which the amplitudes of the wavefunctions and their squares are measured are defined by the dimensionless energies of the states. Hence, the base lines intersect the potential energy curve at the classical turning points. A classical particle is unable to cross these points, but we see that a quantum-mechanical particle can. There is, in fact, a non-vanishing probability of finding the particle in the region beyond the turning points. We say that *the particle tunnels into the classically forbidden regions.*

Apart from this, the wavefunctions in Fig. 7.1 share some characteristic features with the wavefunctions for the particle in a one-dimensional box (Fig. 4.3): The number of nodes increases with the energy, the ground-state wavefunction being a nodeless function, and the wavefunctions are alternately even and odd. The latter feature reflects the inversion symmetry of the problem: the potential energy function, and hence the Hamiltonian, is invariant under an inversion in the origin (cf. Sec. 4.5).

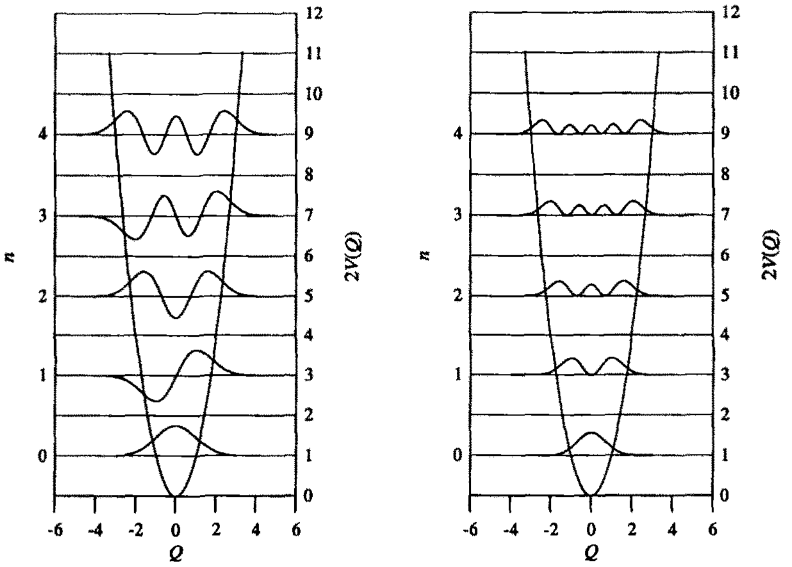

Figure 7.1: Harmonic oscillator wavefunctions $\varphi_n(Q)$, left, and probability densities $\varphi_n(Q)^*\varphi_n(Q)$, right, for $n = 0, 1, 2, 3, 4$. The amplitudes are measured from the positions of the energy levels. The potential energy function $V(Q) = \frac{1}{2}Q^2$ is also shown.

We have now determined both the energies and the wavefunctions for the one-dimensional harmonic oscillator. The method we have been using to solve the Schrödinger equation is the *polynomial method* which may be applied to a large class of quantum-mechanical eigenvalue problems. Most often, such problems may also be treated by the already mentioned *algebraic method*. This method is particularly simple and elegant for the harmonic oscillator problem. We discuss this case in the following section.

7.5 The Algebraic Method

We begin by writing the dimensionless Schrödinger equation (7.17) as

$$\hat{h}|\varphi\rangle = \varepsilon|\varphi\rangle \tag{7.54}$$

with

$$\hat{h} = \tfrac{1}{2}(\hat{P}^2 + \hat{Q}^2), \tag{7.55}$$

where $\hat{Q} = Q$ and $\hat{P} = -id/dQ$, as in Eq. (7.22). We have the commutation relation

$$[\hat{Q}, \hat{P}] = i. \tag{7.56}$$

In the following, this relation is more important than what the operators $\hat{Q}$ and $\hat{P}$ actually stand for. We have therefore kept the operator symbol on the variable Q.

Let us now introduce the operators

$$\hat{a} = \sqrt{\tfrac{1}{2}}(\hat{Q} + i\hat{P}) \tag{7.57}$$

and

$$\hat{a}^\dagger = \sqrt{\tfrac{1}{2}}(\hat{Q} - i\hat{P}). \tag{7.58}$$

They are not Hermitian, but as the notation indicates, they are the Hermitian conjugates of each other (cf. Eq. (5.61)). Utilizing the commutation relation (7.56) we get

$$\begin{aligned} \hat{a}\hat{a}^\dagger &= \tfrac{1}{2}(\hat{P}^2 + \hat{Q}^2) - \tfrac{i}{2}[\hat{Q}, \hat{P}] = \tfrac{1}{2}(\hat{P}^2 + \hat{Q}^2) + \tfrac{1}{2}\,, \\ \hat{a}^\dagger\hat{a} &= \tfrac{1}{2}(\hat{P}^2 + \hat{Q}^2) - \tfrac{1}{2}\,. \end{aligned} \tag{7.59}$$

Hence,

$$[\hat{a}, \hat{a}^\dagger] = 1 \tag{7.60}$$

and

$$\hat{h} = \hat{a}^\dagger\hat{a} + \tfrac{1}{2}\,. \tag{7.61}$$

The last equation shows that $\hat{h}$ and $\hat{a}^\dagger\hat{a}$ have the same eigenfunctions. Solving Eq. (7.54) is therefore equivalent to solving the eigenvalue equation

$$\hat{a}^\dagger\hat{a}|\varphi\rangle = \lambda|\varphi\rangle. \tag{7.62}$$

The eigenvalues are connected by the relation

$$\varepsilon = \lambda + \tfrac{1}{2}\,. \tag{7.63}$$

We note that λ must be non-negative, for Eq. (7.62) implies the relation $\langle\varphi|\hat{a}^\dagger\hat{a}|\varphi\rangle = \lambda\langle\varphi|\varphi\rangle$, or $\langle\hat{a}\varphi|\hat{a}\varphi\rangle = \lambda\langle\varphi|\varphi\rangle$, and both $\langle\varphi|\varphi\rangle$ and $\langle\hat{a}\varphi|\hat{a}\varphi\rangle$ are non-negative (See the introductory remarks of Sec. 5.8).

To determine the possible values of λ, and hence of ε, let us imagine that we already know one λ-value and the corresponding $|\varphi\rangle$. Operating with $\hat{a}$ on both sides of Eq. (7.62) gives then

$$\hat{a}\hat{a}^{\dagger}\hat{a}|\varphi\rangle = \lambda\hat{a}|\varphi\rangle. \tag{7.64}$$

The commutation relation (7.60) shows that $\hat{a}\hat{a}^{\dagger} = \hat{a}^{\dagger}\hat{a} + 1$. Inserting this in Eq. (7.64) gives

$$\hat{a}^{\dagger}\hat{a}\hat{a}|\varphi\rangle + \hat{a}|\varphi\rangle = \lambda\hat{a}|\varphi\rangle, \tag{7.65}$$

or

$$(\hat{a}^{\dagger}\hat{a})\hat{a}|\varphi\rangle = (\lambda - 1)\hat{a}|\varphi\rangle. \tag{7.66}$$

This relation shows that $\hat{a}|\varphi\rangle$ is an eigenfunction of $\hat{a}^{\dagger}\hat{a}$ with eigenvalue $\lambda - 1$, or else $\hat{a}|\varphi\rangle$ vanishes. If $\hat{a}|\varphi\rangle$ is in fact different from zero, then we may repeat the argument with $\hat{a}|\varphi\rangle$ as the target function and conclude that $\hat{a}^2|\varphi\rangle$ is an eigenfunction of $\hat{a}^{\dagger}\hat{a}$ with eigenvalue $\lambda - 2$, or else it is zero. This process may be continued, but not indefinitely, for we have learned that all eigenvalues of $\hat{a}^{\dagger}\hat{a}$ are non-negative. Consequently, there must exist a $|\varphi_0\rangle$ that is annihilated by $\hat{a}$, so that

$$\hat{a}|\varphi_0\rangle = 0. \tag{7.67}$$

Operating with $\hat{a}^{\dagger}$ gives

$$\hat{a}^{\dagger}\hat{a}|\varphi_0\rangle = 0. \tag{7.68}$$

Thus, $|\varphi_0\rangle$ has the eigenvalue 0.

Because the operator $\hat{a}$ lowers the eigenvalue of $\hat{a}^{\dagger}\hat{a}$ by one (unless it operates on $|\varphi_0\rangle$), it is called a *lowering operator*, or a *step-down operator*. Similarly, the operator $\hat{a}^{\dagger}$ is called a *raising operator*, or a *step-up operator*, because it raises the eigenvalue of $\hat{a}^{\dagger}\hat{a}$ by one. To see this, operate with $\hat{a}^{\dagger}$ on both sides of Eq. (7.62) and use the commutation relation (7.60). This gives first

$$\hat{a}^{\dagger}\hat{a}^{\dagger}\hat{a}|\varphi\rangle = \lambda\hat{a}^{\dagger}|\varphi\rangle, \tag{7.69}$$

and then

$$\hat{a}^{\dagger}(\hat{a}\hat{a}^{\dagger} - 1)|\varphi\rangle = \lambda\hat{a}^{\dagger}|\varphi\rangle. \tag{7.70}$$

Thus, we have

$$(\hat{a}^\dagger \hat{a})\hat{a}^\dagger|\varphi\rangle = (\lambda + 1)\hat{a}^\dagger|\varphi\rangle, \tag{7.71}$$

showing that $\hat{a}^\dagger|\varphi\rangle$ is in fact an eigenfunction of $\hat{a}^\dagger\hat{a}$ with eigenvalue $\lambda + 1$.

A common designation for step-up and step-down operators is the term *ladder operators.*

The algebraic method has now led us to the conclusion that $\hat{a}^\dagger\hat{a}$ has the eigenvalues $0, 1, 2, \ldots$. We may express this result by the equation

$$\hat{a}^\dagger\hat{a}|\varphi_n\rangle = n|\varphi_n\rangle, \qquad n = 0, 1, 2, \ldots \tag{7.72}$$

Since $\hat{a}^\dagger\hat{a}$ is a Hermitian operator, we know that wavefunctions corresponding to different values of n are orthogonal. We may assume that all eigenfunctions have been normalized to unity, and thus we have

$$\langle\varphi_n|\varphi_m\rangle = \delta_{nm} \tag{7.73}$$

The results of operating with $\hat{a}$ and $\hat{a}^\dagger$ may now be written

$$\begin{aligned} \hat{a}|\varphi_n\rangle &= c_n|\varphi_{n-1}\rangle, \\ \hat{a}^\dagger|\varphi_{n-1}\rangle &= d_n|\varphi_n\rangle, \end{aligned} \tag{7.74}$$

where c_n and d_n are constants to be determined. By taking the scalar product with $|\varphi_{n-1}\rangle$ in the first of these equations and with $|\varphi_n\rangle$ in the second equation, we get immediately

$$\begin{aligned} c_n &= \langle\varphi_{n-1}|\hat{a}|\varphi_n\rangle, \\ d_n &= \langle\varphi_n|\hat{a}^\dagger|\varphi_{n-1}\rangle. \end{aligned} \tag{7.75}$$

The coefficients c_n and d_n are not independent, for we know that $\hat{a}$ and $\hat{a}^\dagger$ are Hermitian conjugate operators. According to the first of the relations (5.43) we have therefore that

$$d_n = c_n^*. \tag{7.76}$$

Thus, we only need to determine the c_n coefficients.

From Eq. (7.74) we get that

$$\langle\hat{a}\varphi_n|\hat{a}\varphi_n\rangle = c_n^* c_n \langle\varphi_{n-1}|\varphi_{n-1}\rangle = c_n^* c_n. \tag{7.77}$$

But by using the second of the relations (5.43) together with Eq. (7.72) we also get that

$$\langle\hat{a}\varphi_n|\hat{a}\varphi_n\rangle = \langle\varphi_n|\hat{a}^\dagger\hat{a}|\varphi_n\rangle = n\langle\varphi_n|\varphi_n\rangle = n. \tag{7.78}$$

We may therefore conclude that $c_n = e^{i\delta_n}\sqrt{n}$ where the phase δ_n is real. We may, however, *choose* the relative phases of the $|\varphi_n\rangle$ functions such that all δ_n are zero, because the normalization condition only determines the normalization constant of $|\varphi_n\rangle$ to within a phase factor $e^{i\delta}$ (cf. Eq. (4.35)). Making the proper choice of phases gives us accordingly

$$\boxed{\begin{aligned} \hat{a}|\varphi_n\rangle &= \sqrt{n}|\varphi_{n-1}\rangle, \\ \hat{a}^\dagger|\varphi_n\rangle &= \sqrt{n+1}|\varphi_{n+1}\rangle. \end{aligned}} \tag{7.79}$$

Note that the first of these equations includes the special case $\hat{a}|\varphi_0\rangle = 0$.

The relations (7.79) allow us to determine all the eigenfunctions of $\hat{a}^\dagger\hat{a}$, and hence of $\hat{h}$, by a recursive procedure starting from $|\varphi_0\rangle$. To do so, we again put $\hat{Q} = Q$ and $\hat{P} = -id/dQ$ and get

$$\begin{aligned} \hat{a} &= \sqrt{\frac{1}{2}}\left(\frac{d}{dQ} + Q\right), \\ \hat{a}^\dagger &= \sqrt{\frac{1}{2}}\left(-\frac{d}{dQ} + Q\right). \end{aligned} \tag{7.80}$$

The relation $\hat{a}|\varphi_0\rangle = 0$ becomes then

$$\frac{d\varphi_0(Q)}{dQ} + Q\varphi_0(Q) = 0. \tag{7.81}$$

This first-order differential equation has the normalized solution

$$\varphi_0(Q) = \pi^{-\frac{1}{4}}e^{-\frac{1}{2}Q^2}. \tag{7.82}$$

To determine $\varphi_1(Q)$ we use the relation $\hat{a}^\dagger|\varphi_0\rangle = |\varphi_1\rangle$ which gives

$$\begin{aligned} \varphi_1(Q) &= \sqrt{\frac{1}{2}}\left(-\frac{d}{dQ} + Q\right)\pi^{-\frac{1}{4}}e^{-\frac{1}{2}Q^2} \\ &= \left\{\frac{1}{2\sqrt{\pi}}\right\}^{\frac{1}{2}} 2Qe^{-\frac{1}{2}Q^2}. \end{aligned} \tag{7.83}$$

Successive application of the relation $\hat{a}^\dagger|\varphi_{n-1}\rangle = \sqrt{n}|\varphi_n\rangle$ gives

$$\varphi_n(Q) = \left\{\frac{1}{2^n n!}\right\}^{\frac{1}{2}}\left(-\frac{d}{dQ} + Q\right)^n \varphi_0(Q). \tag{7.84}$$

The functions obtained in this way are the same as those presented in Eq. (7.50), as the $\varphi_0(Q)$ and $\varphi_1(Q)$ of Eqs. (7.82) and (7.83) indicate.

This concludes our present discussion of the algebraic method. The method has allowed us to determine the energy spectrum of the harmonic oscillator solely from the commutation relation (7.60) and the form (7.61) for the Hamiltonian. The ladder operators $\hat{a}$ and $\hat{a}^\dagger$ connect the various eigenstates by the scheme (7.79). For many purposes, these relations are more important than the actual form of the wavefunctions. They invite us to simply talk about the eigenkets (cf. Sec. 5.1) and the relations between them, instead of worrying about the actual form of the wavefunctions.

Supplementary Reading

The bibliography, entries [10], [11] and [14].

Problems

7.1. Consider the harmonic oscillator defined by the Hamiltonian (7.8) and write down the normalized wavefunctions $\psi_0(x)$ and $\psi_1(x)$ for the ground state and the first excited state, respectively.

a. Show that the expectation values $\langle x \rangle$ and $\langle \hat{p}_x \rangle$ both vanish for the two states. Use symmetry arguments related to the inversion operator.

b. Evaluate the expectation values $\langle x^2 \rangle$ and $\langle \hat{p}_x^2 \rangle$ and the uncertainty product $\Delta x \Delta p_x$ for both states. Exploit the integral list (6.31).

c. Evaluate $\langle \hat{T} \rangle$ and $\langle \hat{V} \rangle$ for both states and show that

$$\langle \hat{T} \rangle = \langle \hat{V} \rangle.$$

This is the *virial theorem* for the harmonic oscillator.

d. The virial theorem holds for all states of the harmonic oscillator. Use this information together with the energy expression (7.41) to calculate the uncertainty product $\Delta x \Delta p_x$ for the nth excited state.

7.2. The Schrödinger equation for the two-dimensional, isotropic harmonic oscillator reads

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2}\right) + \tfrac{1}{2} m\omega^2 (x^2 + y^2)\psi = E\psi,$$

where $\psi = \psi(x, y)$.

a. Show that the Schrödinger equation has solutions of the form

$$\psi(x,y) = X(x)Y(y), \qquad E = E_x + E_y,$$

and write the Schrödinger equations that determine X and Y. Specify also the allowed energies E_x and E_y, expressed in terms of the respective quantum numbers n_x and n_y.

b. The allowed values of E may be written

$$E_n = (n+1)\hbar\omega, \qquad n = 0, 1, 2, \ldots$$

Express n in terms of the quantum numbers n_x and n_y and construct an energy-level diagram similar to that of Fig. 4.4. Include at least four levels and specify the degeneracy of each level together with the (n_x, n_y)-values.

7.3. A particle with mass m executes a one-dimensional motion in the harmonic potential (7.6). At time $t = 0$, it may be described by the wavefunction

$$\Psi(x,0) = \sqrt{\tfrac{3}{4}}\psi_0(x) + i\sqrt{\tfrac{1}{4}}\psi_2(x)$$

where $\psi_0(x)$ and $\psi_2(x)$ are the wavefunctions for the ground state and the second excited state, respectively, of the harmonic oscillator defined by the potential $V(x)$.

a. Write down the formal expression for $\Psi(x,t)$, the wavefunction at a later time t. It is not necessary to insert the analytical expressions for $\psi_0(x)$ and $\psi_2(x)$.

b. The probability density $\Psi(x,t)^*\Psi(x,t)$ oscillates with the frequency ν. Write the expression for the probability density and determine ν.

Chapter 8

The Central Field Problem

Contents

In this chapter, we shall consider the Schrödinger equation for a particle in a central field. A central field is characterized by a potential energy function, $V(r)$, which only depends upon the distance, r, to a fixed point. This point is taken as the origin of a rectangular Cartesian coordinate system. The central-field problem may be easily set up in spaces of any dimension, but we shall confine ourselves to the familiar three-dimensional space. The position vector of the particle is then $\boldsymbol{r} = (x, y, z)$, with magnitude $r = \sqrt{x^2 + y^2 + z^2}$.

The central-field problem is of paramount importance in quantum mechanics and, of course, in classical mechanics too. The one-electron atom is a central-field problem, with $V(r)$ given by Eq. (2.65). But the central-field problem is also encountered in the theory of many-electron atoms. $V(r)$ is then the sum of the Coulomb field from the nucleus and a suitably averaged field from the electrons. Other central-field problems include, for instance, the isotropic oscillator and the particle in a spherical box. These two model systems have, in particular, been much used in simplified descriptions of the atomic nucleus.

Talking about the one-electron atom we must be aware that even this—the simplest atomic system—really is a two-body system. Both the nucleus and the electron are quantum-mechanical particles, and even though the nucleus is much heavier than the electron it cannot be brought to a complete standstill. But in a similar way as in classical mechanics, it is possible to separate the motion of two particles into the center-of-mass motion and the relative motion when the interaction between the particles only depends upon the distance r between the particles. The relative motion is then found to be a genuine one-particle problem of the central-field type, but now for a particle with a *reduced mass*. That it is the reduced mass rather than the mass of a free electron that enters the description of the one-elctron atom was, as mentioned in Sec. 2.5, properly realized by Bohr in his early theory of the hydrogen atom.

The fact, that any two-body problem in which the two particles interact through a potential-energy function of the form $V(r)$ may be reduced to a one-particle central-field problem, is also of essential importance in the description of the vibration and rotation of a diatomic molecule. There, the introduction of the reduced mass as an effective one-particle mass induces much larger effects than in the one-electron atom.

Because it is important to be aware of the reduced-mass issue in many applications, we shall begin our general description of the central-field problem by actually demonstrating how a two-particle problem may be reduced to a one-particle problem. This will be the subject matter of the following section.

After that, we address the true central-field problem. The procedure is to introduce spherical polar coordinates which in turn leads to a separation of the motion into a radial part and an angular part. The angular part is then solved by introducing the so-called surface spherical harmonics. This is a very important class of functions which is shared by all central-field problems. They also occur in many problems of classical physics and were, in fact, introduced by the French mathematician Pierre Simon de Laplace about two hundred years ago.

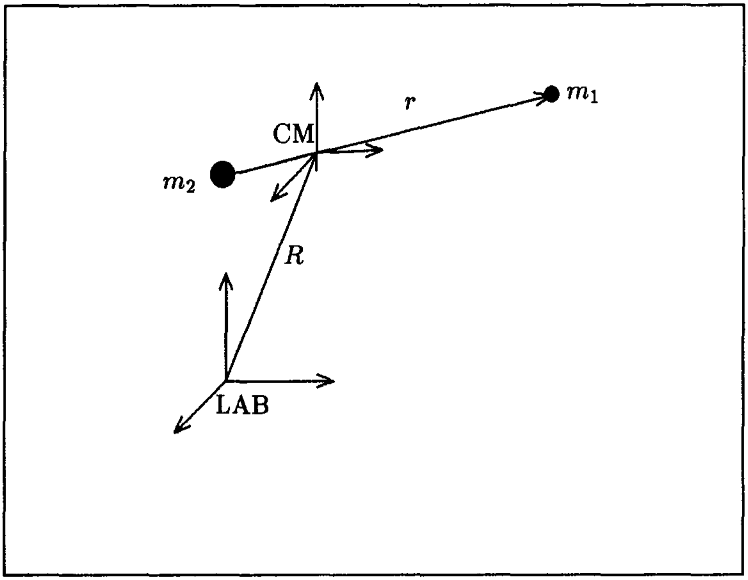

Figure 8.1: The Two-Body Problem.

We devote a fairly long section to the introduction of the surface spherical harmonics, and end the chapter with a discussion of the radial part of the central-field problem. The functions that solve this part of the problem depend on the actual form of the potential $V(r)$. Some general comments may be made, but the actual determination of the radial functions must be postponed to the ensuing sections containing the applications.

8.1 The Reduced Mass of a Two-Body System

Let us now demonstrate how the motion of a two-body system may be separated into relative motion and center-of-mass motion of a particle with reduced mass.

To this end, we introduce Figure 8.1 which shows the position of two particles (with masses m_1 and m_2) relative to two coordinate systems, namely, the *laboratory system* (marked LAB in the figure) and the *center-of-mass system* (marked CM). The position vectors of the two particles in the LAB system are

$$\left\{ \begin{array}{l} \boldsymbol{r}_1 = (x_1, y_1, z_1), \\ \boldsymbol{r}_2 = (x_2, y_2, z_2), \end{array} \right. \tag{8.1}$$

and the distance between them is

$$r = |\boldsymbol{r}_1 - \boldsymbol{r}_2| = \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2}. \tag{8.2}$$

We assume that the potential energy function of the two-body system is a function of this distance alone,[1] i. e.,

$$V = V(r). \tag{8.3}$$

Then the time-independent Schrödinger equation for the system has the form

$$-\frac{\hbar^2}{2m_1}\left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2}\right)\psi - \frac{\hbar^2}{2m_2}\left(\frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2}\right)\psi + V(r)\psi = E^{\text{total}}\psi \tag{8.4}$$

where E^{total} is the (total) energy, and the wavefunction is

$$\psi = \psi(x_1, y_1, z_1, x_2, y_2, z_2). \tag{8.5}$$

We shall show that the wavefunction may be factorized into a product of two functions provided we introduce new variables.

These new variables are defined by the vectors

$$\begin{cases} \boldsymbol{R} = (X, Y, Z), \\ \boldsymbol{r} = (x, y, z), \end{cases} \tag{8.6}$$

where

$$\begin{cases} \boldsymbol{R} = \dfrac{m_1}{M}\boldsymbol{r}_1 + \dfrac{m_2}{M}\boldsymbol{r}_2, \\ \boldsymbol{r} = \boldsymbol{r}_1 - \boldsymbol{r}_2, \end{cases} \tag{8.7}$$

and M is the total mass:

$$\boxed{M = m_1 + m_2} \tag{8.8}$$

$\boldsymbol{R}$ gives the position of the center of mass, and $\boldsymbol{r}$ gives the position of particle 1 with respect to particle 2. Both of these vectors are shown in Figure 8.1.

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[1] The reader may easily verify that it is in fact sufficient to assume that $V = V(\boldsymbol{r}_1 - \boldsymbol{r}_2)$ in order to carry the following demonstration through. A separation into relative motion and center-of-mass motion is therefore also possible when the potential is a general function of the relative position vector.

We may equally well consider the wavefunction to be a function of the new variables and write

$$\psi = \psi(X, Y, Z, x, y, z). \tag{8.9}$$

We now note that Eq. (8.7) implies that

$$\begin{cases} X = \frac{m_1}{M}x_1 + \frac{m_2}{M}x_2, \\ x = x_1 - x_2, \end{cases} \tag{8.10}$$

with similar relations for the y and z coordinates. Hence we get, by implicit differentiation,

$$\begin{cases} \frac{\partial\psi}{\partial x_1} = \frac{\partial\psi}{\partial X}\frac{\partial X}{\partial x_1} + \frac{\partial\psi}{\partial x}\frac{\partial x}{\partial x_1} = \frac{m_1}{M}\frac{\partial\psi}{\partial X} + \frac{\partial\psi}{\partial x}, \\ \frac{\partial\psi}{\partial x_2} = \frac{\partial\psi}{\partial X}\frac{\partial X}{\partial x_2} + \frac{\partial\psi}{\partial x}\frac{\partial x}{\partial x_2} = \frac{m_2}{M}\frac{\partial\psi}{\partial X} - \frac{\partial\psi}{\partial x}. \end{cases} \tag{8.11}$$

Repeating the process gives, for instance,

$$\begin{aligned} \frac{\partial^2\psi}{\partial x_1^2} &= \frac{m_1}{M}\frac{\partial^2\psi}{\partial X\partial x_1} + \frac{\partial^2\psi}{\partial x\partial x_1} \\ &= \frac{m_1}{M}\frac{\partial}{\partial X}\left[\frac{m_1}{M}\frac{\partial\psi}{\partial X} + \frac{\partial\psi}{\partial x}\right] + \frac{\partial}{\partial x}\left[\frac{m_1}{M}\frac{\partial\psi}{\partial X} + \frac{\partial\psi}{\partial x}\right], \end{aligned} \tag{8.12}$$

and hence

$$\begin{cases} \frac{\partial^2\psi}{\partial x_1^2} = \left(\frac{m_1}{M}\right)^2\frac{\partial^2\psi}{\partial X^2} + 2\frac{m_1}{M}\frac{\partial^2\psi}{\partial X\partial x} + \frac{\partial^2\psi}{\partial x^2}, \\ \frac{\partial^2\psi}{\partial x_2^2} = \left(\frac{m_2}{M}\right)^2\frac{\partial^2\psi}{\partial X^2} - 2\frac{m_2}{M}\frac{\partial^2\psi}{\partial X\partial x} + \frac{\partial^2\psi}{\partial x^2}. \end{cases} \tag{8.13}$$

Let us now insert these expressions and their y- and z-analogs into the Schrödinger equation (8.4). We then recover that equation in the form

$$\begin{aligned} -\frac{\hbar^2}{2M}\left(\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2}\right)\psi - \frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi \\ + V(r)\psi = E^{\text{total}}\psi \end{aligned} \tag{8.14}$$

where μ is the reduced mass:

$$\boxed{\mu = \frac{m_1 m_2}{m_1 + m_2} \quad \text{or} \quad \frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}} \tag{8.15}$$

Next, we make the ansatz that ψ may be written as the product

$$\psi = \psi^{trans}(X, Y, Z)\psi^{rel}(x, y, z) \tag{8.16}$$

and insert this product in the Schrödinger equation (8.14). We then proceed in a similar way as in Section 4.1 and find that Eq. (8.14) splits into the two equations

$$\boxed{-\frac{\hbar^2}{2M}\left(\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2}\right)\psi^{trans} = E^{trans}\psi^{trans}} \tag{8.17}$$

and

$$\boxed{-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi^{rel} + V(r)\psi^{rel} = E^{rel}\psi^{rel}} \tag{8.18}$$

with

$$\boxed{E^{\text{total}} = E^{trans} + E^{rel}} \tag{8.19}$$

Eq. (8.17) is equivalent to the Schrödinger equation for a free particle with mass M. It describes the motion of the center of mass and hence of the two-body system as a whole. We may imagine that our molecule is enclosed in a very large box. The center-of-mass wavefunction $\psi^{trans}(X, Y, Z)$ and the translational energy E^{trans} will then be given by the expressions of Sec. 4.6. Alternatively, we may choose $\psi^{trans}(X, Y, Z)$ to be a free-particle wavefunction of the form (6.45). Subsequently, we may form superpositions of such wavefunctions since Eq. (8.18) is the same for all values of E^{trans}. We may, for instance, choose a Gaussian wave packet of the form (6.48). In either case, we need not consider the center-of-mass motion further.

Equation (8.18) descibes the relative, or internal motion. This motion is equivalent to that of a particle with mass μ in the *central field* $V(r)$, and we have thus achieved the goal of reducing the two-body problem to a one-body problem.

In the following section we shall show that if we introduce spherical polar coordinates, then $\psi^{rel}(x, y, z)$ may be factorized into the product of a function of the angular coordinates of $\boldsymbol{r}$ and a function of r, the magnitude of $\boldsymbol{r}$.

The importance of the central-field problem transcends its natural occurrence as part of the two-body problem, as is clear from the comments made in the introductory remarks to the present chapter. In accordance with this universal importance of the problem, we shall adopt a general notation in the following section and consider Eq. (8.18) as but a special case of the Schrödinger equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\boldsymbol{r}) + V(r)\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r}), \tag{8.20}$$

in which m is a general mass and $V(r)$ a general central-field potential. For convenience, we have also introduced a new operator symbol, ∇^2, by the definition

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}. \tag{8.21}$$

∇^2 is called the *Laplacian*. We now need the expression for this operator in spherical polar coordinates.

8.2 Spherical Polar Coordinates

The spherical polar coordinates have the same natural relation to the central-field problem as the Cartesian coordinates have to the rectangular box problem, and they allow the variables in the Schrödinger equation to be separated in a similar way. The definition of the coordinates is the familiar one,

$$\begin{cases} x = r\sin\theta\cos\phi, & 0 \le r < \infty, \\ y = r\sin\theta\sin\phi, & 0 \le \theta < \pi, \\ z = r\cos\theta, & 0 \le \phi < 2\pi. \end{cases} \tag{8.22}$$

See Fig. 8.2.

To express the Laplacian (8.21) and other useful operators in spherical polar coordinates, one may take advantage of the theory of *curvilinear coordinates*, of which the spherical polar coordinates form just one example. The most fundamental ingredients of this theory are presented in Appendix C. It leads to the following expression for the Laplacian in spherical polar coordinates

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right], \tag{8.23}$$

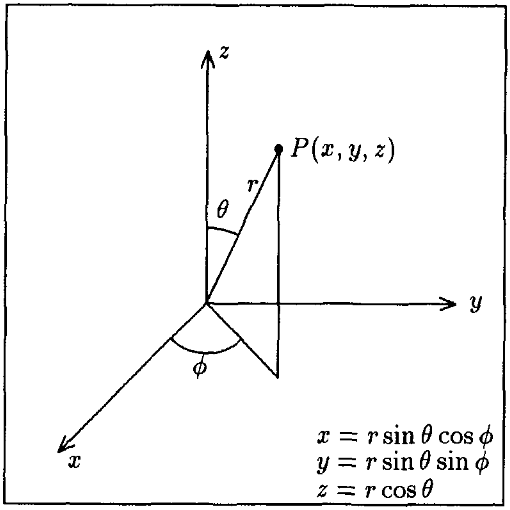

Figure 8.2: Spherical Polar Coordinates.

or

$$\boxed{\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{\hat{\ell}^2}{r^2}} \tag{8.24}$$

where the operator $\hat{\ell}^2$ only acts on the angular variables θ and ϕ:

$$\boxed{\hat{\ell}^2 = -\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) - \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}} \tag{8.25}$$

It is also found that the volume element becomes

$$\boxed{dv = r^2 \sin\theta\, dr d\theta d\phi} \tag{8.26}$$

Inserting the expression (8.24) into Eq. (8.20) gives

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial r^2} + \frac{2}{r}\frac{\partial\psi}{\partial r}\right) + \frac{\hbar^2\hat{\ell}^2}{2mr^2}\psi + V(r)\psi = E\psi. \tag{8.27}$$

This, then, is the Schrödinger equation (8.20) expressed in spherical polar coordinates.

As discussed in Appendix C, the operator $\hat{\ell}^2$ may be written

$$\hat{\ell}^2 = \hat{\ell}_x^2 + \hat{\ell}_y^2 + \hat{\ell}_z^2, \tag{8.28}$$

where $(\hat{\ell}_x, \hat{\ell}_y, \hat{\ell}_z)$ represents the dimensionless angular momentum of a particle with radius vector $\boldsymbol{r}$. The connection to the true angular momentum $\hat{\boldsymbol{l}}$ is simply

$$(\hat{l}_x, \hat{l}_y, \hat{l}_z) = \hbar(\hat{\ell}_x, \hat{\ell}_y, \hat{\ell}_z). \tag{8.29}$$

We may therefore also write Eq. (8.27) as

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial r^2} + \frac{2}{r}\frac{\partial\psi}{\partial r}\right) + \frac{\hat{l}^2}{2mr^2}\psi + V(r)\psi = E\psi. \tag{8.30}$$

To solve Eq. (8.27), we begin by rearranging terms and multiply *from the left* with $2mr^2/\hbar^2$. This gives

$$r^2\left(-\frac{\partial^2\psi}{\partial r^2} - \frac{2}{r}\frac{\partial\psi}{\partial r} + \frac{2m}{\hbar^2}[V(r) - E]\psi\right) = -\hat{\ell}^2\psi. \tag{8.31}$$

Since $\hat{\ell}^2$ only acts on the angular variables we may accomplish a partial separation of variables by writing

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi). \tag{8.32}$$

For if we insert this expression into Eq. (8.31) and subsequently divide from the left with $R(r)Y(\theta, \phi)$, we get

$$\frac{1}{R}r^2\left(-\frac{d^2R}{dr^2} - \frac{2}{r}\frac{dR}{dr} + \frac{2m}{\hbar^2}[V(r) - E]R\right) = -\frac{1}{Y}\hat{\ell}^2Y. \tag{8.33}$$

The left-hand side of this equation depends only on r. On the other hand, the right-hand side is independent of r. In a similar way as in the transition from Eq. (4.5) to Eq. (4.6) we must therefore demand that both sides equal a constant, $-\chi$ say. Thus we conclude that Eq. (8.27), together with the ansatz (8.32)), is equivalent to the following two differential equations

$$\hat{\ell}^2Y(\theta, \phi) = \chi Y(\theta, \phi) \tag{8.34}$$

and

$$-\frac{\hbar^2}{2m}\left(\frac{d^2R(r)}{dr^2} + \frac{2}{r}\frac{dR(r)}{dr}\right) + \frac{\chi\hbar^2}{2mr^2}R(r) + V(r)R(r) = ER(r). \tag{8.35}$$

The well-behaved solutions of Eq. (8.34) are called *surface spherical harmonics*. Well-behaved solutions exist only for specific values of the separation constant χ. We shall see below that these values may be written

$$\chi = \ell(\ell + 1), \quad \ell = 0, 1, 2, \ldots \tag{8.36}$$

We shall also find that there are $2\ell + 1$ linearly independent solutions of Eq. (8.34) for a given value of ℓ. Inserting $\chi = \ell(\ell + 1))$ into Eq. (8.35) gives

$$\boxed{-\frac{\hbar^2}{2m}\left(\frac{d^2R(r)}{dr^2} + \frac{2}{r}\frac{dR(r)}{dr}\right) + \frac{\ell(\ell + 1)\hbar^2}{2mr^2}R(r) + V(r)R(r) = ER(r)} \tag{8.37}$$

Solving this *radial equation* gives the allowed values of the energy E for each ℓ-value, and the corresponding *radial functions* $R(r)$.

The form of the radial functions $R(r)$ depends, of course, on the form of the potential $V(r)$. Thus, different central-field problems lead to different radial functions. But all central-field problems share the same set of angular functions since Eq. (8.34) is independent of $V(r)$. These angular functions are, as already mentioned, called surface spherical harmonics. They are of immense importance in quantum mechanics—and also in other branches of physics and theoretical chemistry. The quantum number ℓ is related to the magnitude of the angular momentum associated with the central-field motion.

The following section and its subsections is a presentation of the surface spherical harmonics.

8.3 Spherical Harmonics

Eq. (8.34) may be written in the form

$$\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \chi\right\}Y(\theta,\phi) = 0. \tag{8.38}$$

It is a second-order differential equation in θ and ϕ. It has been much studied, and there are different ways of attacking it. The complete mathematical solution for a given value of χ may be found by separation of variables, whence one obtains a second-order differential equation in ϕ and another second-order differential equation in θ. The ϕ-part is easy to handle, but to extract the physically acceptable solutions from the θ-part is a somewhat intricate matter.

However, we do not need the complete mathematical solution of Eq. (8.38), so it is really not necessary for us to write it down as an intermediate step towards obtaining the physically well-behaved solutions. We shall therefore adopt a different procedure.

8.3.1 The Dimensionless Angular-Momentum Operators

The idea is to use an algebraic method much related to the method used in Sec. 7.5 for the harmonic- oscillator problem. The operators involved are the angular-momentum operators, and it is expedient to take them in the dimensionless form given in Appendix C. Thus, we consider the operators

$$\begin{cases} \hat{\ell}_x &= -i\left(y\dfrac{\partial}{\partial z} - z\dfrac{\partial}{\partial y}\right), \\ \hat{\ell}_y &= -i\left(z\dfrac{\partial}{\partial x} - x\dfrac{\partial}{\partial z}\right), \\ \hat{\ell}_z &= -i\left(x\dfrac{\partial}{\partial y} - y\dfrac{\partial}{\partial x}\right), \end{cases} \tag{8.39}$$

and the square

$$\hat{\ell}^2 = \hat{\ell}_x^2 + \hat{\ell}_y^2 + \hat{\ell}_z^2. \tag{8.40}$$

It follows from Eqs. (5.33) and (5.34) that they obey the commutation relations

$$\begin{cases} [\hat{\ell}_x, \hat{\ell}_y] = i\hat{\ell}_z, \\ [\hat{\ell}_y, \hat{\ell}_z] = i\hat{\ell}_x, \\ [\hat{\ell}_z, \hat{\ell}_x] = i\hat{\ell}_y, \end{cases} \tag{8.41}$$

and

$$[\hat{\ell}^2, \hat{\ell}_x] = [\hat{\ell}^2, \hat{\ell}_y] = [\hat{\ell}^2, \hat{\ell}_z] = 0. \tag{8.42}$$

According to Eq. (8.34) we are looking for the eigenfunctions of the operator $\hat{\ell}^2$. As mentioned above, we may expect degeneracy, in the sense that there may be several linearly independent eigenfunctions for a given value of χ. Thus, we have a situation similar to the one discussed at length in Sec. 4.7. The eigenfunctions in question define a linear function space, any function belonging to this function space being an eigenfunction with eigenvalue χ. If the degeneracy is g, then any set of g linearly independent functions will be a basis of the function space. But which criterion should we use to determine an appropriate basis?

Here we are helped by the theorem (5.120), according to which two Hermitian operators may have a complete set of eigenfunctions in common, if the two operators commute. So, the procedure to follow is to find an operator that commutes with $\hat{\ell}^2$, and then require that the eigenfunctions defining the basis of the g-dimensional function space also be eigenfunctions of the new operator. We may hope that the basis functions determined in this way correspond to different eigenvalues of the new operator, so that these eigenvalues in fact characterize the basis in a unique way. If, however, there still is some degeneracy left with respect to the new eigenvalues, then we may go on and search for a third operator which commutes with the two operators already discussed. Hopefully, then, this will lead to a unique characterization of the basis.

The operators $\hat{\ell}_x$, $\hat{\ell}_y$ and $\hat{\ell}_z$ all commute with $\hat{\ell}^2$, so it is natural to let one of these operators define our basis in the case of degeneracy. Which one we choose is immaterial, but each choice leads to a different basis, for $\hat{\ell}_x$, $\hat{\ell}_y$ and $\hat{\ell}_z$ do not commute with each other and hence cannot have a complete set of eigenfunctions in common. Traditionally, one chooses to define the basis by the eigenvalues of $\hat{\ell}_z$ because this operator is represented by the simplest expression in spherical polar coordinates.

8.3.2 Looking for Common Eigenfunctions of $\hat{\ell}^2$ and $\hat{\ell}_z$

Consequently, we shall now be looking for the common solutions of the eigenvalue equation (8.34) and the eigenvalue equation

$$\hat{\ell}_z Y(\theta,\phi) = mY(\theta,\phi), \tag{8.43}$$

where m denotes the eigenvalue of $\hat{\ell}_z$.

The expressions for $\hat{\ell}_x$, $\hat{\ell}_y$ and $\hat{\ell}_z$ in spherical polar coordinates are presented in Appendix C. They are

$$\begin{cases} \hat{\ell}_x = i\left(\sin\phi\dfrac{\partial}{\partial\theta} + \cot\theta\cos\phi\dfrac{\partial}{\partial\phi}\right), \\ \hat{\ell}_y = -i\left(\cos\phi\dfrac{\partial}{\partial\theta} - \cot\theta\sin\phi\dfrac{\partial}{\partial\phi}\right), \\ \hat{\ell}_z = -i\dfrac{\partial}{\partial\phi}. \end{cases} \tag{8.44}$$

The eigenvalue equation (8.43) may accordingly be written

$$-i\frac{\partial}{\partial\phi}Y(\theta,\phi) = mY(\theta,\phi). \tag{8.45}$$

It has the complete mathematical solution

$$Y(\theta,\phi) = \Theta(\theta)e^{im\phi}. \tag{8.46}$$

where $\Theta(\theta)$ is an arbitrary function of θ. Thus, the ϕ-dependence of $Y(\theta,\phi)$ is given by the complex exponential function. This is not a physically acceptable ϕ-dependence for arbitrary m-values. For we must require that the function $Y(\theta,\phi)$ be single valued, and as far as the ϕ-dependence is concerned, this amounts to the condition

$$Y(\theta,\phi+2\pi) = Y(\theta,\phi), \tag{8.47}$$

since ϕ and $\phi + 2\pi$ must define the same point in space, i. e., the same point P in Fig. 8.2.

The implication of the condition (8.47) is that m must be an integer. For only then will $\exp(im\phi)$ be periodic in ϕ with period 2π (See Appendix A).

We may now let the common eigenfunctions of $\hat{\ell}^2$ and $\hat{\ell}_z$ be denoted $Y_m^{(\chi)}(\theta,\phi)$ and write

$$Y_m^{(\chi)}(\theta,\phi) = \Theta_m^{(\chi)}(\theta)e^{im\phi}. \tag{8.48}$$

For a given value of χ, we may expect not just one, but a whole set of m-values. The basis discussed above will then be characterized by this set. We must now determine the allowed values of χ and the set of m-values going with each χ.

In connection with functions of θ and ϕ, it is convenient to use a bra-ket notation based on the definition

$$\boxed{\langle Y|Y'\rangle = \int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} Y^*(\theta,\phi)Y'(\theta,\phi)\sin\theta d\theta d\phi} \tag{8.49}$$

The integration involved in this definition is "integration over the unit sphere", the surface element being the angular part of the volume element dv of Eq. (8.26). We shall assume that the functions in the set (8.48) are normalized to unity in the sense

$$\langle Y_m^{(\chi)}|Y_m^{(\chi)}\rangle = 1. \tag{8.50}$$

Now, we may derive an important relation between the value of χ and the corresponding values of m directly from the definition (8.40). The definition implies that

$$\langle Y|\hat{\ell}^2|Y\rangle = \langle Y|\hat{\ell}_x^2|Y\rangle + \langle Y|\hat{\ell}_y^2|Y\rangle + \langle Y|\hat{\ell}_z^2|Y\rangle \tag{8.51}$$

for any $Y(\theta, \phi)$. For a function in the set (8.48) this gives

$$\chi = \langle Y_m^{(\chi)} | \hat{\ell}_x^2 | Y_m^{(\chi)} \rangle + \langle Y_m^{(\chi)} | \hat{\ell}_y^2 | Y_m^{(\chi)} \rangle + m^2. \tag{8.52}$$

Since $\hat{\ell}_x$ is a Hermitian operator, we have that

$$\langle Y_m^{(\chi)} | \hat{\ell}_x^2 | Y_m^{(\chi)} \rangle = \langle \hat{\ell}_x Y_m^{(\chi)} | \hat{\ell}_x Y_m^{(\chi)} \rangle. \tag{8.53}$$

By an argument similar to that of the opening remark of Sec. 5.8, we note that the right-hand side of Eq. (8.53) is non-negative. The same holds therefore for the left-hand side. From this result, and an equivalent result for the second term on the right-hand side of Eq. (8.52), we conclude from Eq. (8.52) that

$$\chi \geq m^2. \tag{8.54}$$

This is the relation that we wanted to derive.

8.3.3 The Raising and Lowering Operators

To proceed, let us introduce the operators

$$\begin{cases} \hat{\ell}_+ = \hat{\ell}_x + i\hat{\ell}_y, \\ \hat{\ell}_- = \hat{\ell}_x - i\hat{\ell}_y, \end{cases} \tag{8.55}$$

which are the Hermitian conjugates of each other (cf. Eq. (5.62)). They both commute with $\hat{\ell}^2$ (because $\hat{\ell}_x$ and $\hat{\ell}_y$ do). Utilizing this we get

$$\hat{\ell}^2 \hat{\ell}_\pm Y_m^{(\chi)}(\theta, \phi) = \hat{\ell}_\pm \hat{\ell}^2 Y_m^{(\chi)}(\theta, \phi) = \chi \hat{\ell}_\pm Y_m^{(\chi)}(\theta, \phi), \tag{8.56}$$

showing that the functions $\hat{\ell}_+ Y_m^{(\chi)}$ and $\hat{\ell}_- Y_m^{(\chi)}$ both belong to the function space defined by the eigenvalue χ.

To learn more about the functions $\hat{\ell}_+ Y_m^{(\chi)}$ and $\hat{\ell}_- Y_m^{(\chi)}$, let us express $\hat{\ell}_+$ and $\hat{\ell}_-$ in spherical polar coordinates. The expressions (8.44) give immediately

$$\begin{cases} \hat{\ell}_+ = e^{i\phi} \left(\dfrac{\partial}{\partial \theta} + i \cot\theta \dfrac{\partial}{\partial \phi} \right), \\ \hat{\ell}_- = e^{-i\phi} \left(-\dfrac{\partial}{\partial \theta} + i \cot\theta \dfrac{\partial}{\partial \phi} \right). \end{cases} \tag{8.57}$$

Applying these relations to the function $Y_m^{(\chi)}(\theta, \phi)$ of Eq. (8.48) shows that the ϕ-dependence of the function $\hat{\ell}_+ Y_m^{(\chi)}(\theta, \phi)$ is $\exp(i(m+1)\phi)$ (unless the function vanishes), while that of the function $\hat{\ell}_- Y_m^{(\chi)}(\theta, \phi)$ is $\exp(i(m-1)\phi)$ (unless this function vanishes). The first function is accordingly an eigenfunction of $\hat{\ell}_z$ with eigenvalue $m+1$, and the second function is an eigenfunction of $\hat{\ell}_z$ with eigenvalue $m-1$.

The same conclusions may be arrived at in a more formal way by considering the commutation relations $[\hat{\ell}_z, \hat{\ell}_+]$ and $[\hat{\ell}_z, \hat{\ell}_-]$. We find easily that

$$\begin{aligned}[\hat{\ell}_z, \hat{\ell}_+] &= [\hat{\ell}_z, \hat{\ell}_x] + i[\hat{\ell}_z, \hat{\ell}_y] = i\hat{\ell}_y + i(-i\hat{\ell}_x) \\ &= \hat{\ell}_x + i\hat{\ell}_y = \hat{\ell}_+,\end{aligned} \tag{8.58}$$

and similarly,

$$[\hat{\ell}_z, \hat{\ell}_-] = -\hat{\ell}_-. \tag{8.59}$$

Exploiting these results gives

$$\hat{\ell}_z\hat{\ell}_+Y_m^{(\chi)} = (\hat{\ell}_+\hat{\ell}_z + \hat{\ell}_+)Y_m^{(\chi)} = (m+1)\hat{\ell}_+Y_m^{(\chi)} \tag{8.60}$$

and

$$\hat{\ell}_z\hat{\ell}_-Y_m^{(\chi)} = (\hat{\ell}_-\hat{\ell}_z - \hat{\ell}_-)Y_m^{(\chi)} = (m-1)\hat{\ell}_-Y_m^{(\chi)}. \tag{8.61}$$

The first of these relations tell us that unless $\hat{\ell}_+Y_m^{(\chi)}$ vanishes, it is an eigenfunction of $\hat{\ell}_z$ with eigenvalue $m+1$. Similarly, the function $\hat{\ell}_-Y_m^{(\chi)}$ is an eigenfunction of $\hat{\ell}_z$ with eigenvalue $m-1$, unless it vanishes. These conclusions are the same as those obtained above.

Thus, the operator $\hat{\ell}_+$ raises the eigenvalue of $\hat{\ell}_z$ by one (unless $\hat{\ell}_+Y_m^{(\chi)}$ vanishes), and it is therefore called a *raising operator*, or a *step-up operator*. Similarly, $\hat{\ell}_-$ is called a *lowering operator*, or a *step-down operator*. One also refers to both types of operators as *ladder operators*. This is a similar notation as that used for the operators $\hat{a}^\dagger$ and $\hat{a}$ in the discussion of the harmonic-oscillator problem (Sec. 7.5).

These findings now lead to the conclusion, that if we repeatedly apply the operators $\hat{\ell}_+$ and $\hat{\ell}_-$ to the function $Y_m^{(\chi)}$, then we generate a set of functions,

$$Y_{m''}^{(\chi)}, \ldots, Y_{m-1}^{(\chi)}, Y_m^{(\chi)}, Y_{m+1}^{(\chi)}, \ldots Y_{m'}^{(\chi)}, \tag{8.62}$$

which successively differ in their m quantum numbers by 1, but are eigenfunctions of $\hat{\ell}^2$ with the same eigenvalue χ (cf. Eq. (8.56)). The sequence must terminate in both directions since the values of m are bounded by the relation (8.54). Thus, we must have that

$$\hat{\ell}_-Y_{m''}^{(\chi)} = 0, \tag{8.63}$$

and

$$\hat{\ell}_+ Y_{m'}^{(\chi)} = 0. \tag{8.64}$$

We shall now show that $m'' = -m'$.

8.3.4 The Quantum Number ℓ

We may relate m'' and m' to the value of χ in the following way.

From the definitions of $\hat{\ell}^2$, $\hat{\ell}_+$ and $\hat{\ell}_-$, and the commutation relations (8.41) we first get

$$\begin{aligned}\hat{\ell}_+\hat{\ell}_- &= (\hat{\ell}_x + i\hat{\ell}_y)(\hat{\ell}_x - i\hat{\ell}_y) = \hat{\ell}_x^2 + \hat{\ell}_y^2 - i[\hat{\ell}_x, \hat{\ell}_y] \\ &= \hat{\ell}_x^2 + \hat{\ell}_y^2 + \hat{\ell}_z = \hat{\ell}^2 - \hat{\ell}_z^2 + \hat{\ell}_z,\end{aligned} \tag{8.65}$$

and similarly,

$$\hat{\ell}_-\hat{\ell}_+ = \hat{\ell}^2 - \hat{\ell}_z^2 - \hat{\ell}_z. \tag{8.66}$$

We then note that the relations (8.63) and (8.64) of course imply that also $\hat{\ell}_+\hat{\ell}_- Y_{m''}^{(\chi)}$ and $\hat{\ell}_-\hat{\ell}_+ Y_{m'}^{(\chi)}$ vanish. When this observation is combined with the results of Eqs. (8.65) and (8.66) we get

$$\hat{\ell}_+\hat{\ell}_- Y_{m''}^{(\chi)} = (\chi - m''^2 + m'')Y_{m''}^{(\chi)} = 0 \tag{8.67}$$

and

$$\hat{\ell}_-\hat{\ell}_+ Y_{m'}^{(\chi)} = (\chi - m'^2 - m')Y_{m'}^{(\chi)} = 0. \tag{8.68}$$

But the functions $Y_{m''}^{(\chi)}$ and $Y_{m'}^{(\chi)}$ are not supposed to vanish since they are defined as the terminal functions in the set (8.62). Eqs. (8.67) and (8.68) imply therefore that

$$\chi = m''^2 - m'' = m''(m'' - 1) \tag{8.69}$$

and

$$\chi = m'^2 + m' = m'(m' + 1). \tag{8.70}$$

For both of these two equations to be true, we must have that $m''(m'' - 1) = m'(m' + 1)$, or,

$$(m' + m'')(m' - m'' + 1) = 0. \tag{8.71}$$

But the setup of the sequence (8.62) implies that $m' \geq m''$. The second factor on the right-hand side of Eq. (8.71) is consequently different from zero. Hence, we conclude that $m'' = -m'$ and therefore also that $m' \geq 0$.

The value of χ as well as the range of m-values is accordingly determined by the value of m'. Let us change the notation and write ℓ instead of m', and hence also $-\ell$ instead of m''. We have then that $\chi = \ell(\ell+1)$, according to Eq. (8.70). Let us also write write $Y_{\ell m}(\theta, \phi)$ instead of $Y_m^{(\ell(\ell+1))}(\theta, \phi)$. Our finding is then (cf. the setup (8.62)) that each possible ℓ-value ($\ell = 0, 1, 2, \ldots$) defines a sequence of $2\ell + 1$ functions,

$$Y_{\ell,-\ell}, \ldots, Y_{\ell,m-1}, Y_{\ell m}, \ldots, Y_{\ell\ell}, \tag{8.72}$$

which are eigenfunctions of $\hat{\ell}^2$ with the same eigenvalue, and eigenfunctions of $\hat{\ell}_z$ with eigenvalues that vary in steps of one from $-\ell$ to ℓ, i. e.,

$$\boxed{\begin{aligned} &\hat{\ell}^2 Y_{\ell m}(\theta, \phi) = \ell(\ell+1) Y_{\ell m}(\theta, \phi), \\ &\hat{\ell}_z Y_{\ell m}(\theta, \phi) = m Y_{\ell m}(\theta, \phi), \qquad m = -\ell, -\ell+1, \ldots, \ell-1, \ell. \end{aligned}} \tag{8.73}$$

That the only possible values of ℓ are the numbers $0, 1, 2, \ldots$ is obvious from the definition of ℓ, namely, $\ell \equiv m' = -m''$, and from the condition that any m must be an integer. The latter condition was derived from the actual form of $\hat{\ell}_z$ via the relation (8.47) which required that any $Y(\theta, \phi)$ be a single-valued function.

It is interesting to note that we may obtain a condition on the possible values of ℓ from the pure algebra without worrying about the form of $\hat{\ell}_z$, and that this condition is milder than the one above. The argument is the following.

From the very way the sequence (8.62), and hence the sequence (8.72), was constructed, it is obvious that the difference between m' and m'' must be an integer. But this difference is just 2ℓ. Hence, 2ℓ must be an integer. The values of ℓ that the algebraic formalism allows are, therefore, $0, \frac{1}{2}, 1, \frac{3}{2}, 2, \ldots$. This set of values differs from the above set by the inclusion of half-integral values of ℓ. We shall refer to this finding when we come to discuss the introduction of spin, in Chapter 10. As far as the spherical harmonics are concerned, only integral values of ℓ come into play.

8.3.5 A Phase Convention

The spherical harmonics in the set (8.72) are transformed into each other under the action of the step-up and step-down operators $\hat{\ell}_+$ and $\hat{\ell}_-$. We assume that each $Y_{\ell m}$ is normalized according to the prescription of Eqs. (8.49) and (8.50). In addition, we know that any two members of the set (8.72) are orthogonal, because they correspond to different eigenvalues of the Hermitian operator $\hat{\ell}_z$ (This is the theorem (5.67)). Thus, we have

$$\langle Y_{\ell m}|Y_{\ell m'}\rangle = \delta_{mm'}. \tag{8.74}$$

The results of acting with $\hat{\ell}_+$ and $\hat{\ell}_-$ may be written

$$\begin{aligned} \hat{\ell}_+ Y_{\ell m}(\theta,\phi) &= c_m Y_{\ell,m+1}(\theta,\phi), \\ \hat{\ell}_- Y_{\ell,m+1}(\theta,\phi) &= d_m Y_{\ell,m}(\theta,\phi), \end{aligned} \tag{8.75}$$

where c_m and d_m are constants to be determined. The constants are, however, not independent, for if we take the scalar product with $Y_{\ell,m+1}(\theta,\phi)$ in the first of the equations, and the scalar product with $Y_{\ell m}(\theta,\phi)$ in the second equation we get

$$\begin{aligned} \langle Y_{\ell,m+1}|\hat{\ell}_+|Y_{\ell m}\rangle &= c_m, \\ \langle Y_{\ell m}|\hat{\ell}_-|Y_{\ell,m+1}\rangle &= d_m, \end{aligned} \tag{8.76}$$

and since $\hat{\ell}_+$ and $\hat{\ell}_-$ are Hermitian conjugate operators, we have that

$$\langle Y_{\ell m}|\hat{\ell}_-|Y_{\ell,m+1}\rangle = \langle Y_{\ell,m+1}|\hat{\ell}_+|Y_{\ell m}\rangle^*, \tag{8.77}$$

according to the definition (5.43). This implies that

$$d_m = c_m^*. \tag{8.78}$$

Thus, we only need to worry about the determination of the c_m coefficients.

To determine the c_m coefficients, we first note that the first of the relations (8.75) gives

$$\langle \hat{\ell}_+ Y_{\ell m}|\hat{\ell}_+ Y_{\ell m}\rangle = \langle c_m Y_{\ell,m+1}(\theta,\phi)|c_m Y_{\ell,m+1}(\theta,\phi)\rangle = c_m^* c_m = |c_m|^2. \tag{8.79}$$

Next, we use the turn-over rule (5.43) and then the relation (8.66) to get

$$\begin{aligned} \langle \hat{\ell}_+ Y_{\ell m}|\hat{\ell}_+ Y_{\ell m}\rangle &= \langle Y_{\ell m}|\hat{\ell}_-\hat{\ell}_+|Y_{\ell m}\rangle = \langle Y_{\ell m}|\hat{\ell}^2 - \hat{\ell}_z^2 - \hat{\ell}_z|Y_{\ell m}\rangle \\ &= \ell(\ell+1) - m^2 - m = (\ell - m)(\ell + m + 1). \end{aligned} \tag{8.80}$$

A comparison of these results shows that $c_m = e^{i\delta_m}\sqrt{(\ell - m)(\ell + m + 1)}$ where the phase δ_m is real. We now *choose* the relative phases of the functions

$Y_{\ell m}(\theta,\phi)$ such that all δ_m become zero. This is possible because the normalization condition only determines each $Y_{\ell m}(\theta,\phi)$ to within a phase factor (cf. Eq. (4.35) and the discussion in Sec. 7.5). With this choice we get that

$$\begin{aligned} c_m = d_m &= \sqrt{(\ell-m)(\ell+m+1)}, \\ c_{m-1} = d_{m-1} &= \sqrt{(\ell+m)(\ell-m+1)}, \end{aligned} \tag{8.81}$$

and hence

$$\boxed{\begin{aligned} \hat{\ell}_+ Y_{\ell m}(\theta,\phi) &= \sqrt{(\ell-m)(\ell+m+1)}\,Y_{\ell,m+1}(\theta,\phi) \\ \hat{\ell}_- Y_{\ell m}(\theta,\phi) &= \sqrt{(\ell+m)(\ell-m+1)}\,Y_{\ell,m-1}(\theta,\phi) \end{aligned}} \tag{8.82}$$

Note that these relations show that $\hat{\ell}_+ Y_{\ell\ell}(\theta,\phi)$ and $\hat{\ell}_- Y_{\ell,-\ell}(\theta,\phi)$ vanish, in accordance with Eqs. (8.63) and (8.64).

The convention, by which the relative phases of the surface spherical harmonics are so chosen that the relations (8.82) are valid, is called the *Condon-Shortley phase convention*, in tribute to a classic book by Condon and Shortley.[2]

8.3.6 The Analytical Expressions

We are now able to derive the analytical expressions for the surface spherical harmonics $Y_{\ell m}(\theta,\phi)$. From Eq. (8.46) we know that they have the general form

$$Y_{\ell m}(\theta,\phi) = \Theta_{\ell m}(\theta)e^{im\phi}. \tag{8.83}$$

The problem is therefore to determine the analytical form of the functions $\Theta_{\ell m}(\theta)$. To do so, we settle on a given ℓ-value and begin by determining the form of $\Theta_{\ell,-\ell}(\theta)$ from the condition that $\hat{\ell}_- Y_{\ell,-\ell}(\theta,\phi)$ vanish. With the expression for $\hat{\ell}_-$ as given in Eq. (8.57), the condition reads

$$e^{-i\phi}\left(-\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right)\Theta_{\ell,-\ell}(\theta)e^{-i\ell\phi} = 0. \tag{8.84}$$

Hence, we must solve the first-order differential equation

$$\left(-\frac{d}{d\theta} + \ell\cot\theta\right)\Theta_{\ell,-\ell}(\theta) = 0. \tag{8.85}$$

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[2] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra*. See the bibliography, entry [15].

The complete solution of this equation is an arbitrary constant, A, times $\sin^\ell\theta$. Thus, we have found that

$$Y_{\ell,-\ell}(\theta,\phi) = A\sin^\ell\theta e^{-i\ell\phi}. \tag{8.86}$$

The constant A is obtained by normalizing $Y_{\ell,-\ell}(\theta,\phi)$ according to the general normalization condition contained in Eq. (8.74), i. e.,

$$\langle Y_{\ell m}|Y_{\ell m}\rangle = \int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} Y^*_{\ell m}(\theta,\phi)Y_{\ell m}(\theta,\phi)\sin\theta d\theta d\phi = 1. \tag{8.87}$$

For $\ell = 0$ we get

$$Y_{00}(\theta,\phi) = \sqrt{\frac{1}{4\pi}}, \tag{8.88}$$

and for $\ell \neq 0$,

$$Y_{\ell,-\ell}(\theta,\phi) = \sqrt{\frac{1}{4\pi}\frac{(2\ell+1)(2\ell-1)\cdots1}{2\ell(2\ell-2)\cdots2}}\sin^\ell\theta e^{-i\ell\phi}, \tag{8.89}$$

where we have chosen the sign of the normalization constant to be positive.

Having determined the function $Y_{\ell,-\ell}(\theta,\phi)$, we may determine the remaining 2ℓ functions belonging to the same ℓ-value by means of the first of the relations in (8.82). We illustrate this for $\ell = 1$.

For $\ell = 0$, there is only one spherical harmonic, namely the function $Y_{00}(\theta,\phi)$ given by Eq. (8.88). For $\ell = 1$, we have the three functions Y_{11}, Y_{10} and Y_{1-1}. Eq. (8.89) gives immediately:

$$Y_{1-1}(\theta,\phi) = \sqrt{\frac{3}{8\pi}}\sin\theta e^{-i\phi}. \tag{8.90}$$

Next, we note that the first of the relations in (8.82) requires that

$$\hat{\ell}_+ Y_{1-1}(\theta,\phi) = \sqrt{(1+1)(1-1+1)}Y_{10}(\theta,\phi). \tag{8.91}$$

With the expression (8.57) for $\hat{\ell}_+$, we may therefore determine Y_{10} as follows

$$\begin{aligned} Y_{10}(\theta,\phi) &= \sqrt{\frac{1}{2}}\hat{\ell}_+ Y_{1-1}(\theta,\phi) \\ &= \sqrt{\frac{1}{2}}e^{i\phi}\left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right)\sqrt{\frac{3}{8\pi}}\sin\theta e^{-i\phi} \\ &= \sqrt{\frac{3}{4\pi}}\cos\theta. \end{aligned} \tag{8.92}$$

Y_{11} may be determined by a similar procedure,

$$\begin{aligned} Y_{11}(\theta,\phi) &= \sqrt{\frac{1}{2}}\,\hat{\ell}_+ Y_{10}(\theta,\phi) \\ &= \sqrt{\frac{1}{2}}\,e^{i\phi}\left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right)\sqrt{\frac{3}{4\pi}}\cos\theta \qquad (8.93) \\ &= -\sqrt{\frac{3}{8\pi}}\sin\theta e^{i\phi}. \end{aligned}$$

For higher ℓ-values we may proceed in a similar fashion and thus generate any spherical harmonic needed. Table 8.1 gives all the spherical harmonics with $\ell = 0$, 1, 2, and 3.[3] Note the factor -1 which occurs whenever m is odd and positive. This factor is a consequence of the Condon-Shortley phase convention, as the transition from Eq. (8.92) to Eq. (8.93) exemplifies.

The spherical harmonics in Table 8.1 are eigenfunctions of $\hat{\ell}^2$ and $\hat{\ell}_z$. The square of the true angular momentum (8.29) has the sharp value $\ell(\ell+1)\hbar^2$, and the projection of the true angular momentum onto the z-axis has the sharp value $m\hbar$. (The term *sharp value* was defined in Secs. 5.5 and 5.7. That an observable has a sharp value, implies that the wavefunction of the system is an eigenfunction of the operator representing the observable.)

For a given value of ℓ, the $2\ell+1$ spherical harmonics define a basis in the function space defined by the eigenvalue $\ell(\ell+1)$ of $\hat{\ell}^2$. Other bases may be obtained by taking linear combinations of the functions $Y_{\ell m}(\theta,\phi)$. In this way, one might for instance construct $2\ell+1$ functions that are eigenfunctions of $\hat{\ell}^2$ and $\hat{\ell}_x$. But one may also construct bases for which no component of the angular momentum has a sharp value. A very useful basis of this type is obtained by replacing each two functions of the type $Y_{\ell m}$ and $Y_{\ell,-m}$ by the sum and difference of the two functions (normalization introduces an extra factor of $1/\sqrt{2}$). After multiplication by i or $-i$, if necessary, one ends up with a set of *real* surface spherical harmonics. Such a set is presented in Table 8.2. It finds great application in, for instance, molecular-orbital theory.

The equivalent of the orthonormality relation (8.74) holds for the functions of Table 8.2. We also note that spherical harmonics with different ℓ-values must be orthogonal, for such functions correspond to eigenfunctions of $\hat{\ell}^2$ with different eigenvalues, so the theorem (5.67) may be applied once again. Thus,

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[3] The symbols s, p, d, f associated with the ℓ-values $0, 1, 2, 3$, respectively, refer to the use of the spherical harmonics in atomic theory (See the following chapter).

we may write

$$\boxed{\langle Y_{\ell\gamma}|Y_{\ell'\gamma'}\rangle = \int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} Y_{\ell\gamma}^{*}(\theta,\phi)Y_{\ell'\gamma'}(\theta,\phi)\sin\theta d\theta d\phi = \delta_{\ell\ell'}\delta_{\gamma\gamma'}} \tag{8.94}$$

The index γ takes on $2\ell+1$ values for a given value of ℓ. When the complex harmonics of Table 8.1 are considered, it may be identified with the quantum number m. For the real harmonics of Table 8.2, it is simply some symbol that identifies the $2\ell+1$ different harmonics for fixed ℓ.

We have now given a thorough description of the physically acceptable solutions of Eq. (8.34). They are the surface spherical harmonics. We have determined these functions by an algebraic procedure, but as mentioned at the beginning of Sec. 8.3 they may also be determined by more classical means. One then realizes that the θ-dependence of the functions is that of the associated Legendre functions. For the sake of completeness, we present this dependence in Appendix D.

After this thorough discussion of the solutions of Eq. (8.38), we must now turn to the radial equation (8.37).

8.4 The Radial Function $P(r)$

In this short section, we shall replace the radial equation (8.37) with an equivalent radial equation obtained in the following way.

We may assume that the general wavefunction (8.32) is a normalized wavefunction. The expression for the volume element in spherical polar coordinates is given by Eq. (8.26), and the normalization condition is therefore

$$\langle\psi|\psi\rangle = \int_{r=0}^{\infty} R^{*}(r)R(r)r^{2}dr\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} Y^{*}(\theta,\phi)Y(\theta,\phi)\sin\theta d\theta d\phi = 1. \tag{8.95}$$

The spherical harmonic $Y(\theta,\phi)$ is supposed to be normalized to unity in analogy with Eq. (8.87). Hence, we require that $R(r)$ be normalized such that

$$\boxed{\int_{r=0}^{\infty}[R(r)]^{2}r^{2}dr = 1} \tag{8.96}$$

where we have assumed that $R(r)$ is real .

The form of the normalization expression for $R(r)$ suggests that we introduce a new radial function, $P(r)$, by the definition

$$\boxed{P(r) = rR(r)} \tag{8.97}$$

which will then be normalized such that

$$\boxed{\int_{r=0}^{\infty} [P(r)]^2 dr = 1} \tag{8.98}$$

The differential equation to be satisfied by $P(r)$ is obtained by multiplying Eq. (8.37) from the left with r and noting that Eq. (8.97) implies that

$$\frac{d^2P}{dr^2} = r\frac{d^2R}{dr^2} + 2\frac{dR}{dr}. \tag{8.99}$$

Thus, we get

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2P(r)}{dr^2} + \frac{\ell(\ell+1)\hbar^2}{2mr^2}P(r) + V(r)P(r) = EP(r)} \tag{8.100}$$

The structure of this equation is somewhat simpler than that of Eq. (8.37), and we shall accordingly base much of our future discussion of central-field problems on the radial function $P(r)$ instead of the original function $R(r)$.

In terms of $P(r)$, we may write the wavefunction (8.32) as

$$\boxed{\psi(r,\theta,\phi) = \tfrac{1}{r}P(r)Y(\theta,\phi)} \tag{8.101}$$

Eq. (8.100) has the same structure for all central-field problems. But since the explicit form of $V(r)$ is different for different problems, each problem must be handled as a new case. In the following chapter, we shall solve Eq. (8.100) for the hydrogen atom.

Table 8.1: Normalized Surface Spherical Harmonics. Complex Form

$\ell = 0$ s	$Y_{00} = \sqrt{\frac{1}{4\pi}}$		
$\ell = 1$ p	$Y_{1\,-1}$	$= \sqrt{\frac{3}{8\pi}}\frac{x-iy}{r}$	$= \sqrt{\frac{3}{8\pi}}\sin\theta e^{-i\phi}$
	$Y_{1\,0}$	$= \sqrt{\frac{3}{4\pi}}\frac{z}{r}$	$= \sqrt{\frac{3}{4\pi}}\cos\theta$
	$Y_{1\,1}$	$= -\sqrt{\frac{3}{8\pi}}\frac{x+iy}{r}$	$= -\sqrt{\frac{3}{8\pi}}\sin\theta e^{i\phi}$
$\ell = 2$ d	$Y_{2\,-2}$	$= \sqrt{\frac{15}{32\pi}}\frac{(x-iy)^2}{r^2}$	$= \sqrt{\frac{15}{32\pi}}\sin^2\theta e^{-2i\phi}$
	$Y_{2\,-1}$	$= \sqrt{\frac{15}{8\pi}}\frac{z(x-iy)}{r^2}$	$= \sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{-i\phi}$
	$Y_{2\,0}$	$= \sqrt{\frac{5}{16\pi}}\frac{3z^2-r^2}{r^2}$	$= \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1)$
	$Y_{2\,1}$	$= -\sqrt{\frac{15}{8\pi}}\frac{z(x+iy)}{r^2}$	$= -\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{i\phi}$
	$Y_{2\,2}$	$= \sqrt{\frac{15}{32\pi}}\frac{(x+iy)^2}{r^2}$	$= \sqrt{\frac{15}{32\pi}}\sin^2\theta e^{2i\phi}$
$\ell = 3$ f	$Y_{3\,-3}$	$= \sqrt{\frac{35}{64\pi}}\frac{(x-iy)^3}{r^3}$	$= \sqrt{\frac{35}{64\pi}}\sin^3\theta e^{-3i\phi}$
	$Y_{3\,-2}$	$= \sqrt{\frac{105}{32\pi}}\frac{z(x-iy)^2}{r^3}$	$= \sqrt{\frac{105}{32\pi}}\sin^2\theta\cos\theta e^{-2i\phi}$
	$Y_{3\,-1}$	$= \sqrt{\frac{21}{64\pi}}\frac{(5z^2-r^2)(x-iy)}{r^3}$	$= \sqrt{\frac{21}{64\pi}}(5\cos^2\theta - 1)\sin\theta e^{-i\phi}$
	$Y_{3\,0}$	$= \sqrt{\frac{7}{16\pi}}\frac{z(5z^2-3r^2)}{r^3}$	$= \sqrt{\frac{7}{16\pi}}\cos\theta(5\cos^2\theta - 3)$
	$Y_{3\,1}$	$= -\sqrt{\frac{21}{64\pi}}\frac{(5z^2-r^2)(x+iy)}{r^3}$	$= -\sqrt{\frac{21}{64\pi}}(5\cos^2\theta - 1)\sin\theta e^{i\phi}$
	$Y_{3\,2}$	$= \sqrt{\frac{105}{32\pi}}\frac{z(x+iy)^2}{r^3}$	$= \sqrt{\frac{105}{32\pi}}\sin^2\theta\cos\theta e^{2i\phi}$
	$Y_{3\,3}$	$= -\sqrt{\frac{35}{64\pi}}\frac{(x+iy)^3}{r^3}$	$= -\sqrt{\frac{35}{64\pi}}\sin^3\theta e^{3i\phi}$

Table 8.2: Normalized Surface Spherical Harmonics. Real Form

$\ell = 0$ s	$Y_{00} = \sqrt{\frac{1}{4\pi}}$
$\ell = 1$ p	$Y_x = \sqrt{\frac{3}{4\pi}}\frac{x}{r} = \sqrt{\frac{3}{4\pi}}\sin\theta\cos\phi$
	$Y_y = \sqrt{\frac{3}{4\pi}}\frac{y}{r} = \sqrt{\frac{3}{4\pi}}\sin\theta\sin\phi$
	$Y_z = \sqrt{\frac{3}{4\pi}}\frac{z}{r} = \sqrt{\frac{3}{4\pi}}\cos\theta$
$\ell = 2$ d	$Y_{z^2} = \sqrt{\frac{5}{16\pi}}\frac{3z^2-r^2}{r^2} = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1)$
	$Y_{zx} = \sqrt{\frac{15}{4\pi}}\frac{zx}{r^2} = \sqrt{\frac{15}{4\pi}}\sin\theta\cos\theta\cos\phi$
	$Y_{zy} = \sqrt{\frac{15}{4\pi}}\frac{zy}{r^2} = \sqrt{\frac{15}{4\pi}}\sin\theta\cos\theta\sin\phi$
	$Y_{x^2-y^2} = \sqrt{\frac{15}{16\pi}}\frac{x^2-y^2}{r^2} = \sqrt{\frac{15}{16\pi}}\sin^2\theta\cos 2\phi$
	$Y_{xy} = \sqrt{\frac{15}{4\pi}}\frac{xy}{r^2} = \sqrt{\frac{15}{16\pi}}\sin^2\theta\sin 2\phi$
$\ell = 3$ f	$Y_{z^3} = \sqrt{\frac{7}{16\pi}}\frac{z(5z^2-3r^2)}{r^3} = \sqrt{\frac{7}{16\pi}}\cos\theta(5\cos^2\theta - 3)$
	$Y_{z^2x} = \sqrt{\frac{21}{32\pi}}\frac{(5z^2-r^2)x}{r^3} = \sqrt{\frac{21}{32\pi}}(5\cos^2\theta - 1)\sin\theta\cos\phi$
	$Y_{(5z^2-r^2)y} = \sqrt{\frac{21}{32\pi}}\frac{(5z^2-r^2)y}{r^3} = \sqrt{\frac{21}{32\pi}}(5\cos^2\theta - 1)\sin\theta\sin\phi$
	$Y_{z(x^2-y^2)} = \sqrt{\frac{105}{16\pi}}\frac{z(x^2-y^2)}{r^3} = \sqrt{\frac{105}{16\pi}}\sin^2\theta\cos\theta\cos 2\phi$
	$Y_{zxy} = \sqrt{\frac{105}{4\pi}}\frac{zxy}{r^3} = \sqrt{\frac{105}{16\pi}}\sin^2\theta\cos\theta\sin 2\phi$
	$Y_{x^2y} = \sqrt{\frac{35}{32\pi}}\frac{3x^2y-y^3}{r^3} = \sqrt{\frac{35}{32\pi}}\sin^3\theta\cos 3\phi$
	$Y_{y^2x} = \sqrt{\frac{35}{32\pi}}\frac{x^3-3y^2x}{r^3} = \sqrt{\frac{35}{32\pi}}\sin^3\theta\sin 3\phi$

Supplementary Reading

The bibliography, entry [15] and [16].

Problems

8.1. By actually evaluating the integrals involved, check that the surface spherical harmonic Y_x of Table 8.2 is normalized to unity. Check also that the harmonics Y_x and Y_{zx} are mutually orthogonal.

8.2. The normalized surface spherical harmonic $Y_{40}(\theta,\phi)$ is

$$Y_{40}(\theta,\phi) = \frac{3}{16}\sqrt{\frac{1}{\pi}}\left(35\cos^4\theta - 30\cos^2\theta + 3\right).$$

By applying the operators $\hat{\ell}_+$ and $\hat{\ell}_-$, determine the normalized surface spherical harmonics $Y_{41}(\theta,\phi)$ and $Y_{4,-1}(\theta,\phi)$.

8.3. A useful way of looking at a surface spherical harmonic is to relate it to the function

$$U_{\ell\gamma}(x,y,z) = r^\ell Y_{\ell\gamma}(\theta,\phi)$$

because this function, as the tables 8.1 and 8.2 show, is a homogeneous polynomial of order ℓ, i. e., a polynomial of the form

$$U_{\ell\gamma}(x,y,z) = \sum_{rst} a_{rst}x^r y^s z^t, \quad r+s+t=\ell.$$

The function $U_{\ell\gamma}(x,y,z)$ is called a *solid spherical harmonic.*

a. Show that $U_{\ell\gamma}(x,y,z)$ is a solution of the *Laplace equation*

$$\nabla^2 U = 0,$$

by identifying the Laplace equation with the central-field equation (8.20) for $V(r)=0$ and $E=0$, and by showing that Eq. (8.37) then is satisfied by $R(r)=r^\ell$.

b. Equation (8.37) has two linearly independent solutions for a given value of ℓ. As just shown, one of them is $R(r)=r^\ell$ for $V(r)=0$ and $E=0$. Try to guess the other solution.

c. There are 6 linearly independent homogeneous polynomials of order 2, for instance:

$$x^2,\ y^2,\ z^2,\ xy,\ yz,\ zx,$$

but they do not all satisfy the Laplace equation. Find 5 linearly independent polynomials that do, and compare these with the solid spherical harmonics that may be read off Table (8.2) for $\ell = 2$.

An alternative way of introducing the surface spherical harmonics is, in fact, to start out from the solid spherical harmonics, defined as the homogeneous polynomials that satisfy the Laplace equation. The relation $U_{\ell\gamma}(x, y, z) = r^{\ell} Y_{\ell\gamma}(\theta, \phi)$ gives then the form of the surface spherical harmonics.

Chapter 9

The Hydrogen Atom

Contents

In continuation of the previous chapter, let us now determine the energies and wavefunctions for the electron in a one-electron atom. We consider the general case corresponding to a nuclear charge Ze, and take the nucleus to be infinitely heavy so that we may neglect its motion. But we understand that we may correct for the finite nuclear mass by simply replacing the electronic mass, m_e, with the reduced mass as discussed in Sec. 8.1. In light of this, it might seem preferable to work with the reduced mass from the very outset, but some natural physical quantities that occur on the way are conventionally defined in terms of the mass m_e rather than the reduced mass (which varies from atom to atom). So it is better to work with m_e throughout and, when it is needed, correct the final expressions by simply replacing m_e with the proper reduced mass.

As mentioned in Sec. 4.8, it is customary to refer to a one-electron wavefunction as an *orbital*. The wavefunctions of a one-electron atom are hence called *atomic orbitals*. The angular dependence of atomic orbitals is given by the surface spherical harmonics, so the starting point of the present chapter will be the radial equation (8.100).

We begin the chapter by introducing a standard notation for the radial wavefunctions. The radial equation is then solved by the polynomial method which is familiar to us from the harmonic-oscillator problem. Three equivalent analytical expressions are set up for the radial functions, and the functions defining the lowest energy levels are also represented as graphs. In the final section, we consider the total wavefunctions obtained by multiplying the radial functions by the proper surface spherical harmonics.

Wavefunctions on a three-dimensional space are, of course, more difficult to visualize than wavefunctions on a one-dimensional space. But much may be achieved by drawing contour curves in selected planes together with contour surfaces in three-dimensional space. Because the orbitals of the one-electron atom in various ways serve as elementary units in the construction of wavefunctions for many-electron atoms and molecules, it is important to form good mental pictures of them. As a help in building such pictures, we present a number of contour curves and contour surfaces for orbitals of the hydrogen atom in the last section.

The wavefunctions determined in the present chapter are said to describe the *orbital motion* of the electron, and the angular momentum $\hat{l}$ is similarly called the *orbital angular momentum*, a notation which reminds us of the presence of the electron spin. As remarked in Sec. 3.1, we may safely neglect the spin as long as we exclude magnetic fields and only treat single-particle problems. We can live with these limitations throughout this chapter, but in order to proceed we must definitely learn how to incorporate the spin. A proper discussion of the spin problem will be included in the following chapter.

9.1 The Effective Potential. General Notation

As mentioned above, the starting point of the present chapter is the radial equation (8.100), with the arbitrary mass m replaced by m_e. The potential-energy function $V(r)$ is given by the Coulomb expression (2.65), so the actual form of Eq. (8.100) becomes

$$-\frac{\hbar^2}{2m_e}\frac{d^2P(r)}{dr^2}+\left(\frac{\ell(\ell+1)\hbar^2}{2m_er^2}-\frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r}\right)P(r)=EP(r). \qquad (9.1)$$

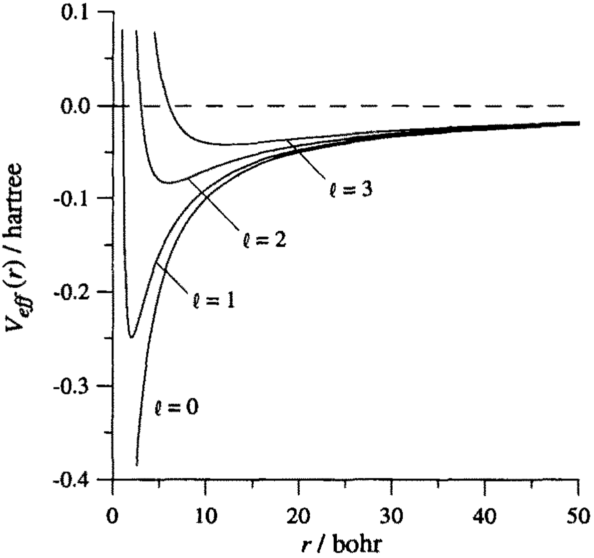

Figure 9.1: Effective radial potential for the hydrogen atom ($Z = 1$). Atomic units as defined in Appendix B.

We note that each ℓ-value gives a genuinely new equation.

We may interpret Eq. (9.1) as the Schrödinger equation for a one-dimensional problem in which the particle moves between $r = 0$ and $r \approx \infty$, in the *effective potential*

$$V_{eff}(r) = \frac{\ell(\ell+1)\hbar^2}{2m_e r^2} - \frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r}, \tag{9.2}$$

made up of the original Coulomb potential and an ℓ-dependent *centrifugal potential.* Each ℓ-value gives a new effective potential and hence its own one-dimensional Schrödinger equation. The effective potential for the four lowest ℓ-values, $\ell = 0, 1, 2, 3$, is shown in Fig. 9.1.

For a given ℓ-value, we number the admissible energies and radial functions by an additional index n which increases with the energy. It would seem natural to let n take on the consecutive values $1, 2, 3, \ldots$, but traditionally one lets n start with the value $\ell + 1$. So, for a given ℓ-value we number the energy levels by the n-values

$$n = \ell + 1, \ell + 2, \ldots \tag{9.3}$$

The reason is, that this numbering is natural for the hydrogen-like atom because n turns out to be the quantum number that determines the energy, through the Bohr formula (2.68). Thus, we have the following radial wavefunctions, $P_{n\ell}(r)$,

$$\left.\begin{array}{llllr} P_{1s}, & P_{2s}, & P_{3s}, & P_{4s}, \ldots & \text{for } \ell = 0 \\ & P_{2p}, & P_{3p}, & P_{4p}, \ldots & \text{for } \ell = 1 \\ & & P_{3d}, & P_{4d}, \ldots & \text{for } \ell = 2 \\ & & \ldots & \ldots & \ldots \ldots \end{array}\right\} \tag{9.4}$$

As is customary, we have referred to the ℓ-value by a letter symbol defined by the following correspondence

ℓ–value	0	1	2	3	4	5	6	7	8	9	...
Symbol	s	p	d	f	g	h	i	k	l	m	...

(9.5)

This correspondence was also included in Tables 8.1 and 8.2. The radial functions $R_{n\ell}(r)$ are indexed in a similar way as the functions $P_{n\ell}(r)$. When the radial function $R_{1s}(r)$ is combined with the surface spherical harmonic Y_{00}, we get the $1s$ orbital. When the radial function $R_{2p}(r)$ is combined with the three spherical harmonics with $\ell = 1$, we get the three $2p$ orbitals, etc. The notation is of spectroscopic origin: the letters s, p, d, and f refer, respectively, to the so-called *sharp*, *principal*, *diffuse*, and *fundamental* series of the alkali atom spectra.

After these introductory remarks, let us now attack the radial Schrödinger equation (9.1). As the form of the effective potentials in Fig. 9.1 indicates, the energy spectrum is found to be discrete for $E < 0$ (bound states) and continuous for $E > 0$ (dissociative states). We shall only be interested in the bound-state solutions, corresponding to states with negative energy. As we shall see, there are infinitely many such states, for each value of ℓ.

9.2 The Radial Equation for the Hydrogen-Like Atom

For a radial function $P(r)$ to represent a bound state of the electron, it must vanish at infinity. In addition, $R(r)$ must stay finite at the origin, and hence $P(r)$—which equals $rR(r)$—must tend to zero with r. The boundary conditions on $P(r)$ are therefore

$$P(0) = 0, \quad P(\infty) = 0. \tag{9.6}$$

To implement these conditions, we consider the limiting form of Eq. (9.1) for small and for large values of r.

For sufficiently small values of r, and $\ell \neq 0$, it is obvious that the centrifugal term in Eq. (9.1) will completely dominate the term containing E, and also the term containing the Coulomb potential. Thus, we may replace Eq. (9.1) by the equation

$$-\frac{\hbar^2}{2m_e}\left(\frac{d^2P(r)}{dr^2}-\frac{\ell(\ell+1)}{r^2}P(r)\right)=0. \tag{9.7}$$

It has the complete solution

$$P(r)=a_1r^{\ell+1}+a_2r^{-\ell}, \tag{9.8}$$

and we must evidently take a_2 to be zero, to satisfy the first of the boundary conditions (9.6). When $\ell = 0$, there is no centrifugal term, and we must go back to Eq. (9.1). Inserting a power series expansion, $P(r) = a_1r + a_2r^2 + \ldots$, into this equation shows that a_1 must be different from zero. Hence, the well-behaved solution goes as a constant times r for small values of r, and is covered by the general expression $P(r) = a_1r^{\ell+1}$.

In the other limit, i. e, for very large values of r, we replace Eq. (9.1) by the equation

$$-\frac{\hbar^2}{2m_e}\frac{d^2P(r)}{dr^2}=EP(r), \tag{9.9}$$

or,

$$\frac{d^2P(r)}{dr^2}=\frac{\kappa^2}{4}P(r), \tag{9.10}$$

where we have put

$$E=-\frac{\kappa^2\hbar^2}{8m_e}. \tag{9.11}$$

Real values of κ correspond to negative energies, imaginary values of κ to positive energies. Eq. (9.10) has the complete solution

$$P(r)=b_1e^{-\kappa r/2}+b_2e^{\kappa r/2}. \tag{9.12}$$

For imaginary values of κ, this is an oscillatory solution which stays finite at infinity. Accordingly, it cannot represent a bound state, so bound states must correspond to real values of κ, and hence to negative energies, as claimed in the Introduction. We shall only consider bound states in the following, and consequently always take κ to be real, and in fact positive (since this is no restriction, as Eqs. (9.11) and (9.12) show). With κ being positive, it follows that the second of the boundary conditions in Eq. (9.6) requires b_2 to be zero.

We have thus seen that an acceptable solution of Eq. (9.1) must behave like $r^{\ell+1}$ for small values of r, and like $e^{-\kappa r/2}$ for large values of r. As we would expect, such a solution only exists for certain discrete values of E. Let us determine these values.

We begin by simplifying the look of Eq. (9.1) by introducing the new variable

$$\rho = \kappa r, \tag{9.13}$$

whereby the equation becomes

$$\frac{d^2P(r)}{d\rho^2} - \left(\frac{\ell(\ell+1)}{\rho^2} - \frac{n}{\rho} + \frac{1}{4}\right) P(r) = 0, \tag{9.14}$$

with the constant n defined as

$$n = \frac{Ze^2}{4\pi\epsilon_0}\frac{2m_e}{\hbar^2\kappa}. \tag{9.15}$$

The values of n for which Eq. (9.14) has acceptable solutions determine the corresponding values of κ and E, through Eqs. (9.15) and (9.11). For κ we get

$$\kappa = \frac{2Z}{na_0} \tag{9.16}$$

where a_0 is the Bohr radius which we introduced in Sec. 2.5, Eq. (2.60),

$$\boxed{a_0 = \frac{\hbar^2}{m_e}\frac{4\pi\epsilon_0}{e^2}} \tag{9.17}$$

Similarly, we get for E:

$$\boxed{E_n = -\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \frac{Z^2 m_e}{2\hbar^2 n^2}} \tag{9.18}$$

This is the Bohr expression (2.68) for the allowed energies of a one-electron atom, provided n is an integer. This will turn out to be the case, but we are not supposed to know yet.

To actually determine the possible values of n, we take advantage of what we know about $P(r)$ for small and for large values of r and write

$$P(r) = \rho^{\ell+1} e^{-\rho/2} F(\rho). \tag{9.19}$$

Inserting this expression in Eq. (9.14) gives, after some algebra,

$$\rho \frac{d^2F}{d\rho^2} + (2\ell + 2 - \rho)\frac{dF}{d\rho} + (n - \ell - 1)F = 0. \tag{9.20}$$

We shall see that this equation has an infinite number of solutions, corresponding to $n = \ell + 1, \ell + 2, \ldots$, in accordance with the discussion around Eq. (9.4). In fact, we immediately see that we get a solution by putting $n = \ell + 1$, namely, $F = A$, where A is a constant. Thus, we find that $P_{1s}, P_{2p}, P_{3d}, \ldots$ must have the general form

$$P_{n,n-1}(r) = A\rho^n e^{-\rho/2}. \tag{9.21}$$

To determine A, which we take to be real and positive, we invoke the normalization condition (8.98) and get

$$1 = \int_0^\infty P(r)^2 dr = \frac{1}{\kappa}\int_0^\infty P^2 d\rho = \frac{A^2}{\kappa}\int_0^\infty \rho^{2n} e^{-\rho} d\rho = \frac{A^2}{\kappa}(2n)! \tag{9.22}$$

We have used the standard integral

$$\boxed{\int_0^\infty t^n e^{-t} dt = n!} \tag{9.23}$$

With A as determined from Eq. (9.22), and with κ taken from Eq. (9.16), Eq. (9.21) becomes

$$P_{n,n-1}(r) = \sqrt{\frac{2Z}{na_0}}\sqrt{\frac{1}{(2n)!}}\left(\frac{2Zr}{na_0}\right)^n \exp\left(-\frac{Zr}{na_0}\right). \tag{9.24}$$

Hence, we get that the corresponding R-function, $R(r) = P(r)/r$, becomes

$$\boxed{R_{n,n-1}(r) = \left(\frac{2Z}{na_0}\right)^{3/2}\sqrt{\frac{1}{(2n)!}}\left(\frac{2Zr}{na_0}\right)^{n-1} \exp\left(-\frac{Zr}{na_0}\right)} \tag{9.25}$$

where $n = 1, 2, 3, \ldots$

In the general case, we solve Eq. (9.20) by expanding $F(\rho)$ in a power series, i. e., we write

$$F(\rho) = \sum_{s=0}^{\infty} c_s \rho^s \tag{9.26}$$

where we know that $c_0 \neq 0$, for otherwise $P(r)$ would not have the correct limit form for small values of r. For the first derivative of F we find

$$\frac{dF}{d\rho} = \sum_{s=1}^{\infty} c_s s \rho^{s-1} = \sum_{s=0}^{\infty} c_{s+1}(s+1)\rho^s. \tag{9.27}$$

By evaluating also the second derivative and grouping terms with the same power of ρ together, we get

$$\sum_{s=0}^{\infty} \{c_{s+1}[(s+1)s + (2\ell+2)(s+1)] - c_s[s - (n-\ell-1)]\} \rho^s = 0. \tag{9.28}$$

The various powers of ρ are linearly independent functions, and hence the coefficient of ρ^s must vanish for each s. This requirement gives the recursion relation

$$c_{s+1} = \frac{\ell+1-n+s}{(1+s)(2\ell+2+s)} c_s \tag{9.29}$$

which determines the subsequent coefficients in terms of c_0.

By iterating Eq. (9.29) we easily find that

$$F(\rho) = c_0 \left\{ 1 + \sum_{s=1}^{\infty} \frac{(\ell+1-n)(\ell+2-n)\cdots(\ell+s-n)}{s!(2\ell+2)(2\ell+3)\cdots(2\ell+1+s)} \rho^s \right\}, \tag{9.30}$$

where c_0 now plays the role of an arbitrary constant. The function

$${}_1F_1(\alpha, \beta; x) = 1 + \frac{\alpha}{1 \cdot \beta} x + \frac{\alpha(\alpha+1)}{2!\beta(\beta+1)} x^2 + \ldots \tag{9.31}$$

is called a *confluent hypergeometric function.*[1] It allows us to write $F(\rho)$ as

$$F(\rho) = {}_1F_1(\ell+1-n, 2\ell+2; \rho) c_0. \tag{9.32}$$

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[1] See, for example, Chapter 13 in the reference of footnote 2.11.

We now observe that as s increases without limit, the recursion formula (9.29) states that

$$\frac{c_{s+1}}{c_s} \approx \frac{1}{s}. \tag{9.33}$$

This is the same ratio that we get from the exponential function

$$e^{\rho} = \sum_0^{\infty} \frac{\rho^s}{s!}, \tag{9.34}$$

so when the expression for $F(\rho)$ is inserted in Eq. (9.19) we find that $P(\rho)$ behaves like $\exp(\rho/2)$ for large r. In other words, the solution which is regular at the origin will in general not tend to zero at infinity, i.e., the coefficient b_2 in Eq. (9.12) will not vanish.

This behavior will hold for any n-value which is not a positive integer. We see, however, from Eq. (9.29), that if n is a positive integer larger than or equal to $\ell + 1$ then c_{n-1} and all subsequent coefficients will vanish, and $F(\rho)$ will become a polynomial of degree $n - \ell - 1$.

Thus, we have arrived at the result that Eq. (9.14) has acceptable solutions if and only if, for a given value of ℓ, n takes on one of the values

$$\boxed{n = \ell + 1, \ell + 2, \ldots} \tag{9.35}$$

The corresponding form of $P(r)$ is, according to Eqs. (9.19) and (9.32),

$$\boxed{P_{n\ell}(r) = A\rho^{\ell+1}e^{-\rho/2}{}_1F_1(\ell + 1 - n, 2\ell + 2; \rho)} \tag{9.36}$$

where A is a normalization constant. We note that $P_{n\ell}(r)$ equals $e^{-\rho/2}$ times a polynomial of degree n, starting with the term $A\rho^{\ell+1}$. We also note, from Eqs. (9.13) and (9.16) that

$$\boxed{\rho = \frac{2Z}{na_0}r} \tag{9.37}$$

n is called the *principal quantum number*. The quantum number ℓ is often called the *azimuthal quantum number*. Similarly, one often refers to the quantum number m that appears when the complex spherical harmonics are applied, as the *magnetic quantum number*. These designations have their origin in the old Bohr-Sommerfeld theory. We shall usually refer to ℓ and m as angular-momentum quantum numbers.

We have now, for each value of ℓ, found all the acceptable solutions of the radial Schrödinger equation (9.1). The allowed energies are those given by Bohr's formula (9.18). Eq. (9.35) shows that the solutions may be labeled as in the diagram (9.4), each line in the diagram going with a different effective potential of the type (9.2). The energy expression (9.18) shows that if we also *order* the solutions as in the diagram (9.4), then functions in the same column correspond to the same energy. To be specific,

$$\boxed{P_{n0}(r), P_{n1}(r), \ldots, P_{n,n-1}(r) \text{ go with the same energy.}} \tag{9.38}$$

This is a remarkable result, for each line in the diagram (9.4) represents a different radial equation—as discussed at length in the Introduction. So there is no immediate reason why functions in the same column should have the same energy. As a matter of fact, this will no longer be the case if the Coulomb potential in Eq. (9.1) is replaced by a slightly different potential. The energy is then found to depend on both n and ℓ.

Let us now study the radial functions that we have determined in more detail.

9.3 The Normalized Radial Functions

For lower values of n, the actual form of $P_{n\ell}(r)$, and hence of $R_{n\ell}(r)$, is easily written down from Eq. (9.36). $R_{n\ell}(r)$ may then be normalized by the same procedure as the $R_{n,n-1}(r)$ of Eq. (9.25). In this way, one obtains Table 9.1, which shows $R_{n\ell}(r)$ for all (n, ℓ) values corresponding to $n = 1, 2, 3$.

In the general case, we need an analytic expression for the normalization constant A in Eq. (9.36). Such an expression has been derived and is contained in the following general formula for $R_{n\ell}(r)$

$$\boxed{\begin{aligned} R_{n\ell}(r) = {} & (-1)^{n-\ell-1}\left(\frac{2Z}{na_0}\right)^{3/2}\frac{1}{(2\ell+1)!}\sqrt{\frac{(n+\ell)!}{2n(n-\ell-1)!}} \\ & \times\left(\frac{2Zr}{na_0}\right)^{\ell}{}_1F_1(\ell+1-n, 2\ell+2; 2Zr/na_0)\exp\left(-\frac{Zr}{na_0}\right)\end{aligned}} \tag{9.39}$$

The sign factor has been chosen such as to make $R_{n\ell}(r)$ positive for large values of r.

It is customary to state this result in terms of the so-called *Laguerre polynomials*. There are essentially two different, albeit related, definitions of these polynomials in the literature. The one most often used in textbook discussions of the hydrogen atom is the following

$$L_n^m(x) = (-1)^m \frac{(n!)^2}{m!(n-m)!}\, {}_1F_1(-n+m, m+1; x). \tag{9.40}$$

$L_n^m(x)$ is called the *associated Laguerre polynomial of degree $n-m$*. An independent definition is

$$L_n^m(x) = \frac{d^m}{dx^m} L_n^0(x), \tag{9.41}$$

where the *Laguerre polynomial* $L_n^0(x)$ is defined as

$$L_n^0(x) = e^x \frac{d^n}{dx^n}\left(x^n e^{-x}\right). \tag{9.42}$$

When $R_{n\ell}(r)$ is expressed in terms of these functions by comparing Eqs. (9.39) and (9.40), we get

$$\boxed{\begin{aligned} R_{n\ell}(r) = {} & (-1)^{n-\ell}\left(\frac{2Z}{na_0}\right)^{3/2}\sqrt{\frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}} \\ & \times \left(\frac{2Zr}{na_0}\right)^{\ell} L_{n+\ell}^{2\ell+1}(2Zr/na_0)\exp\left(-\frac{Zr}{na_0}\right) \end{aligned}} \tag{9.43}$$

The alternative definition of the Laguerre polynomials is[2]

$$L_n^{(m)}(x) = \frac{(m+n)!}{m!n!}\, {}_1F_1(-n, m+1; x). \tag{9.44}$$

We refer to these polynomials as *generalized Laguerre polynomials*, because the independent definition that may be introduced does not presume that m is a non-negative integer as in Eq. (9.41). The independent definition is

$$L_n^{(m)}(x) = \frac{1}{n!} e^x x^{-m} \frac{d^n}{dx^n}\left(x^{n+m} e^{-x}\right). \tag{9.45}$$

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[2] See, for example, Chapters 13 and 22 in the reference of footnote 2.11.

In terms of these polynomials we get

$$\boxed{\begin{aligned} R_{n\ell}(r) = &\ (-1)^{n-\ell-1}\left(\frac{2Z}{na_0}\right)^{3/2}\sqrt{\frac{(n-\ell-1)!}{2n(n+\ell)!}} \\ &\times\left(\frac{2Zr}{na_0}\right)^{\ell} L_{n-\ell-1}^{(2\ell+1)}(2Zr/na_0)\exp\left(-\frac{Zr}{na_0}\right) \end{aligned}} \tag{9.46}$$

The reader will find it rather easy to generate the functions in Table 9.1 from any of these formulae. As an intermediate step in this process we list the first few Laguerre polynomials, derived by the definition of Eq. (9.42),

$$\begin{cases} L_0^0(x) = 1, \qquad L_1^0(x) = 1 - x, \qquad L_2^0(x) = 2 - 4x + x^2, \\ L_3^0(x) = 6 - 18x + 9x^2 - x^3, \\ L_4^0(x) = 24 - 96x + 72x^2 - 16x^3 + x^4, \\ L_5^0(x) = 120 - 600x + 600x^2 - 200x^3 + 25x^4 - x^5. \end{cases} \tag{9.47}$$

Let us finally point out that the radial functions satisfy the orthonormality relation

$$\boxed{\int_0^\infty R_{n\ell}(r)R_{n'\ell}(r)r^2dr = \int_0^\infty P_{n\ell}(r)P_{n'\ell}(r)dr = \delta_{nn'}} \tag{9.48}$$

which supplements the orthonormality relation (8.94) for the angular part of the complete wavefunction. Eq. (9.48) follows as a straightforward consequence of applying the theorem (5.67) to the solutions of Eq. (9.1).

9.4 Radial Probability Densities

In Figs. 9.2, 9.3 and 9.4 we present the graphs of the radial functions $R_{n\ell}(r)$ of Table 9.1, together with graphs of the corresponding functions $P_{n\ell}(r)$. We have put $Z = 1$, and thus let the graphs refer to the hydrogen atom. In addition, we have put $a_0 = 1$, as in the system of atomic units. Atomic units are discussed in Appendix B.

According to the statistical interpretation of the wavefunction (Sec. 3.4), the quantity $\psi^*(\boldsymbol{r})\psi(\boldsymbol{r})$ is a probability density, and $\psi^*(\boldsymbol{r})\psi(\boldsymbol{r})dv$ is the probability of finding the electron in the volume element dv around the point $\boldsymbol{r}$. The probability of finding the electron within a certain volume V is the integral of $\psi^*\psi$ over that volume.

Table 9.1: Hydrogen-Like Radial Functions

$n=1$	$R_{1s}(r) = \left(\frac{Z}{a_0}\right)^{3/2} 2\exp\left(-\frac{Zr}{a_0}\right)$
$n=2$	$R_{2s}(r) = \left(\frac{Z}{2a_0}\right)^{3/2} \left(\frac{Zr}{a_0} - 2\right)\exp\left(-\frac{Zr}{2a_0}\right)$ $R_{2p}(r) = \left(\frac{Z}{2a_0}\right)^{3/2} \sqrt{\frac{1}{3}}\frac{Zr}{a_0}\exp\left(-\frac{Zr}{2a_0}\right)$
$n=3$	$R_{3s}(r) = \left(\frac{Z}{3a_0}\right)^{3/2} \frac{1}{3}\left\{\left(\frac{2Zr}{3a_0}\right)^2 - 6\left(\frac{2Zr}{3a_0}\right) + 6\right\}\exp\left(-\frac{Zr}{3a_0}\right)$ $R_{3p}(r) = \left(\frac{Z}{3a_0}\right)^{3/2} \sqrt{\frac{1}{18}}\left\{\left(\frac{2Zr}{3a_0}\right)^2 - 4\left(\frac{2Zr}{3a_0}\right)\right\}\exp\left(-\frac{Zr}{3a_0}\right)$ $R_{3d}(r) = \left(\frac{Z}{3a_0}\right)^{3/2} \sqrt{\frac{1}{90}}\left(\frac{2Zr}{3a_0}\right)^2\exp\left(-\frac{Zr}{3a_0}\right)$

Thus, we understand that the probability of finding the electron of the hydrogen-like atom in the spherical shell between the radii r_1 and r_2 is given by the integral

$$\int_{r_1}^{r_2} r^2 dr \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta\, R_{n\ell}(r)^2 |Y_{\ell\gamma}(\theta,\phi)|^2 = \int_{r_1}^{r_2} P_{n\ell}(r)^2 dr \tag{9.49}$$

where we have inserted the form of the total wavefunction as given by Eqs. (8.32) and (8.101). So, the quantity $P_{n\ell}(r)^2 dr$ may be interpreted as the probability of finding the electron between r and $r + dr$, irrespective of its angular coordinates. Consequently, we may refer to the functions $P_{n\ell}(r)$ and $P_{n\ell}(r)^2$ as the *radial probability amplitude* and the *radial probability density*, respectively.

We also see, that if $f(r)$ is some function of r, then its average value, the so-called expectation value (Sec. 5.5), is given by the integral

$$\langle f(r)\rangle = \int_0^{\infty} r^2 dr \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta\, f(r) R_{n\ell}(r)^2 |Y_{\ell\gamma}(\theta,\phi)|^2, \tag{9.50}$$

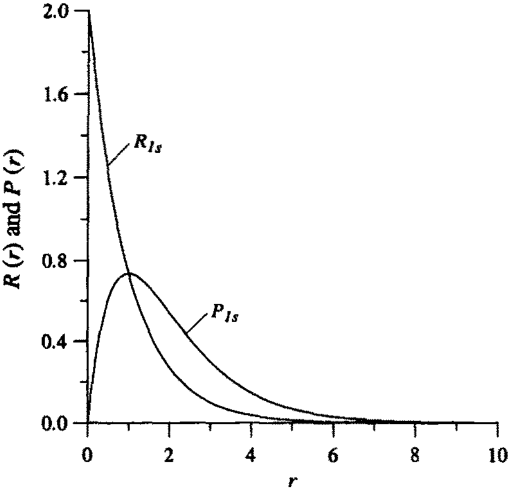

Figure 9.2: Radial wavefunctions for the $n = 1$ level of the hydrogen atom ($Z = 1$). Atomic units as defined in Appendix B.

which after integration over θ and ϕ becomes

$$\langle f(r)\rangle = \int_0^\infty f(r)P_{n\ell}(r)^2 dr. \tag{9.51}$$

These results demonstrate that the function $P(r)$ plays a natural role in the applications of the theory.

Eq. (9.51) may, for instance, be used to calculate the expectation values of the various powers of r. We list the following useful results [3]

$$\left\{\begin{aligned} &\langle r\rangle = \frac{1}{2}\left[3n^2 - \ell(\ell+1)\right]\frac{a_0}{Z}, \\ &\langle r^2\rangle = \frac{n^2}{2}\left[5n^2 + 1 - 3\ell(\ell+1)\right]\left(\frac{a_0}{Z}\right)^2, \\ &\left\langle \frac{1}{r}\right\rangle = \frac{1}{n^2}\frac{Z}{a_0}, \\ &\left\langle \frac{1}{r^2}\right\rangle = \frac{2}{n^3(2\ell+1)}\left(\frac{Z}{a_0}\right)^2, \\ &\left\langle \frac{1}{r^3}\right\rangle = \frac{2}{n^3\ell(\ell+1)(2\ell+1)}\left(\frac{Z}{a_0}\right)^3, \quad \ell \neq 0. \end{aligned}\right. \tag{9.52}$$

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[3] For other powers of r, see Chapter 5 in the reference of footnote 8.2.

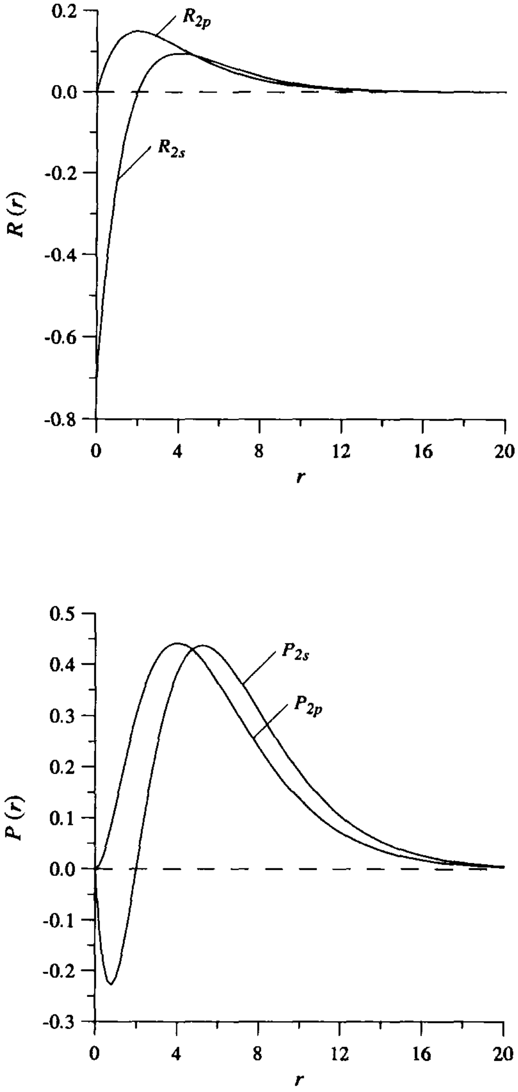

Figure 9.3: Radial wavefunctions for the $n = 2$ level of the hydrogen atom ($Z = 1$). Atomic units as defined in Appendix B.

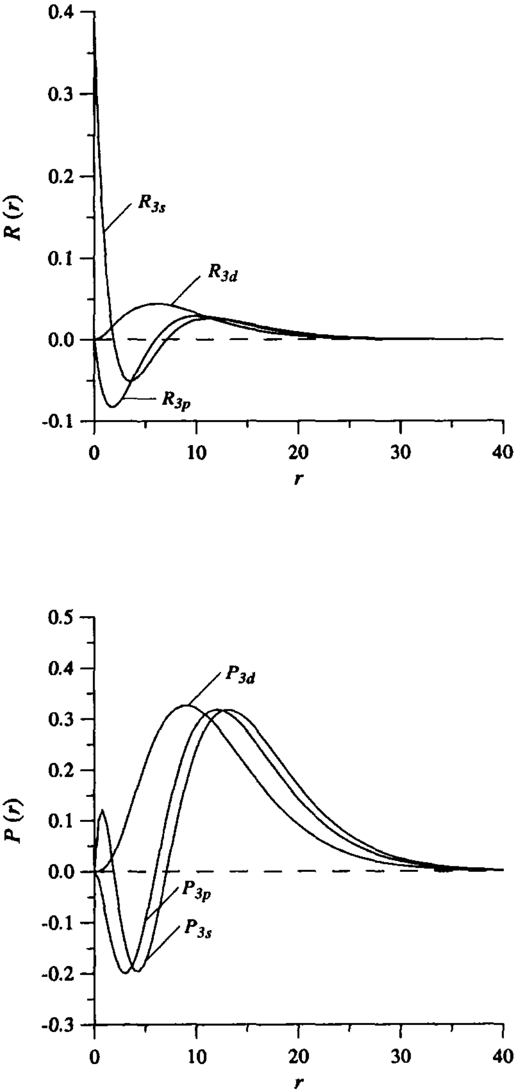

Figure 9.4: Radial wavefunctions for the $n = 3$ level of the hydrogen atom ($Z = 1$). Atomic units as defined in Appendix B.

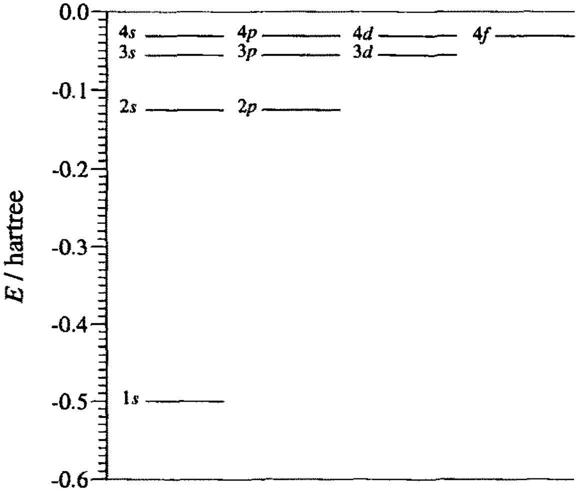

Figure 9.5: The lowest energy levels of the hydrogen atom.

9.5 The Complete Wavefunctions

The complete wavefunctions for the hydrogen-like atom have the form (8.32), or (8.101). In particular, the complex wavefunctions are obtained by multiplying the complex spherical harmonics in Table 8.1 by the radial functions in Table 9.1. They may accordingly be written

$$\psi_{n\ell m_\ell}(r,\theta,\phi) = R_{n\ell}(r)Y_{\ell m_\ell}(\theta,\phi), \tag{9.53}$$

where we have introduced a generally accepted standard notation by writing m_ℓ instead of m.

Similarly, the real wavefunctions are obtained by multiplying the real spherical harmonics in Table 8.2 by the radial functions in Table 9.1. In either case, there are $2\ell+1$ independent wavefunctions. We may construct a notation that embraces both cases by writing

$$\psi_{n\ell\gamma_\ell}(r,\theta,\phi) = R_{n\ell}(r)Y_{\ell\gamma_\ell}(\theta,\phi), \tag{9.54}$$

where γ_ℓ is a label that identifies the members of a chosen set of $2\ell+1$ independent wavefunctions for a given ℓ-value. In the special case where the chosen set is the set (9.53), we identify γ_ℓ with m_ℓ. In any case, a wavefunction (atomic orbital) is characterized by three "quantum numbers", (n,ℓ,γ_ℓ). Obviously, we have the orthonormality relation

$$\begin{aligned}\langle \psi_{n\ell\gamma_\ell} | \psi_{n'\ell'\gamma'_\ell} \rangle &= \int_{r=0}^{\infty} R_{n\ell}(r) R_{n'\ell'}(r) r^2 dr \\ &\quad \times \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} Y^*_{\ell\gamma_\ell}(\theta,\phi) Y_{\ell'\gamma'_\ell}(\theta,\phi) \sin\theta d\theta d\phi \\ &= \delta_{nn'} \delta_{\ell\ell'} \delta_{\gamma_\ell \gamma'_\ell}\end{aligned} \tag{9.55}$$

which combines the orthonormality relations (8.94) and (9.48).

The quantum number n determines the energy through Bohr's expression (9.18). By introducing atomic units as discussed in Appendix B, we may write the Bohr expression in the form

$$E_n = -\frac{Z^2}{2n^2} \text{ hartree}, \qquad n = 1, 2, 3, \ldots \tag{9.56}$$

with 1 hartree $= 4.35975 \times 10^{-18}$ J $= 27.2114$ eV. For any n, the quantum number ℓ takes on the values $0, 1, \ldots, n-1$, and for any ℓ we have $2\ell + 1$ different values of γ_ℓ. The degeneracy g_n, i.e., the total number of wavefunctions corresponding to the energy E_n, is accordingly

$$\boxed{g_n = \sum_{\ell=0}^{n-1} (2\ell + 1) = n^2} \tag{9.57}$$

For other central potentials, the energy depends on both n and ℓ, so the degeneracy of an energy level will only be $2\ell + 1$. Thus, the Coulomb potential leads to a high degree of *accidental degeneracy*.

This degeneracy is often said to reflect the presence of a *hidden*, or *dynamical*, four-dimensional symmetry. For it turns out that if one constructs an angular-momentum theory in a four-dimensional world, then an additional quantum number—which we may also call n—appears. For each n, there are n^2 surface spherical harmonics. It is possible to set up a well-defined correspondence between those harmonics and the hydrogenic wavefunctions with the same n-value. The correspondence breaks down as soon as one makes the slightest change to the Coulomb potential.[4]

---

[4] The dynamical symmetry associated with the Coulomb potential has attracted much attention in the scientific literature. For an entrance to the literature and a discussion of the physical origin of the symmetry, see J. P. Dahl, J. Phys. A **30**, 6831 (1997). See also the bibliography, entry [18], Sec. 30.

The energy levels of the hydrogen atom ($Z = 1$) are shown in Fig. 9.5. The accidental degeneracy is accentuated by showing separate energy levels for each ℓ value.

It is important to note that the designations (9.53) and (9.54) may be used for any central field. But the Bohr expression holds only for hydrogen-like atoms. For other central fields, the energy will depend on both n and ℓ. The quantum number n is then nothing more than a useful index which, for each value of ℓ, increases with the energy in accordance with the setup (9.4).

In Figs. 9.6-9.9 we illustrate some of the real hydrogen atomic orbitals by means of contour maps in suitably chosen planes through the nucleus. The specific form of the orbitals is commented on in the respective figure captions. Each figure also includes a so-called *polar plot*, the origin of which is the following.

A polar plot is a plot of the angular part of an orbital. Let the angular part be $Y(\theta,\phi)$. The polar plot is then the surface such that the distance from the origin to a point on the surface, in the direction (θ,ϕ), equals $|Y(\theta,\phi)|$. The surface has, accordingly, the following parametric representation

$$\begin{aligned} x &= |Y(\theta,\phi)|\sin\theta\cos\phi, \\ y &= |Y(\theta,\phi)|\sin\theta\sin\phi, \\ z &= |Y(\theta,\phi)|\cos\theta, \end{aligned} \tag{9.58}$$

with θ varying between 0 and π, and ϕ varying between 0 and 2π, as in Eq. (8.22).

The intersection between the above described surface and a coordinate plane leads to the two-dimensional polar plots shown in Figs. 9.6-9.9. As one sees from these figures, there is a close qualitative resemblance between the two-dimensional polar plots and the planar contour plots for the complete wavefunctions. The three-dimensional contour surfaces of the complete wavefunctions will consequently also have a similar appearance as the three-dimensional polar plots. The polar plots are therefore often used for qualitative purposes where the exact form of the radial function $R(r)$ doesn't matter so much. As described above, the polar plots are completely defined by the angular part of an orbital. The proper contour surface of the orbital is, however, also sensitive to the form of $R(r)$.

Fig. 9.10 shows proper three-dimensional pictures of the hydrogenic $1s$, $2p_x$, $3d_{zx}$, and $3d_{z^2}$ orbitals, viewed along the direction perpendicular to the zx-plane. Each orbital is rendered as an *isosurface*, made up of contour surfaces on which the wavefunction has the same *absolute* value. For example, the

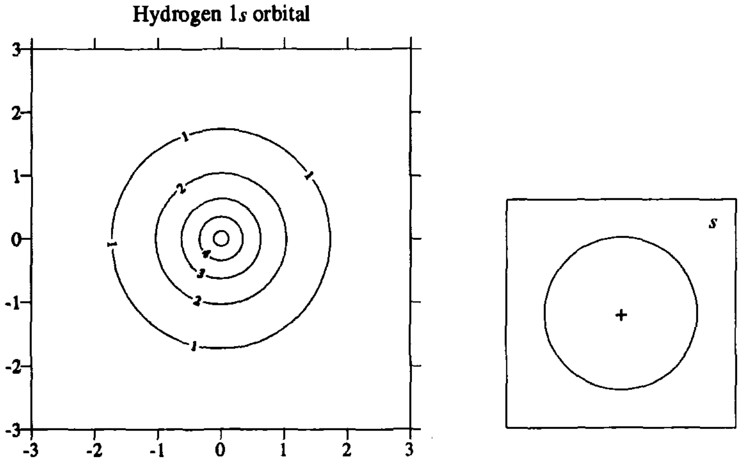

Figure 9.6: This figure shows the $n = 1$ orbital of the hydrogen atom ($Z = 1$), in atomic units ($a_0 = 1$). The analytic form of the orbital is obtained by multiplying the R_{1s} radial function of Table 9.1 by the spherical harmonic Y_{00} of Table 8.2. We get

$$\psi_{1s} = \sqrt{\frac{1}{\pi}}\exp(-r).$$

The big drawing is a *contour map* showing the contour curves of the 1s-function in any plane through the nucleus. A *contour curve* is defined as a curve through points with the same value of the function (the *contour value*). The contour curves of any s-orbital are circles centered on the nucleus. The corresponding three-dimensional *contour surfaces* are spherical surfaces.

The numbers specified on the contours are the contour values multiplied by 10.

The smaller drawing is a polar plot of the 1s orbital. It shows its spherical shape and its constant sign.

$2p_x$ isosurface consists of two similar lobes, one on which the wavefunction is positive, and another on which it has the same absolute value but is negative. On the left part of the figure, each isosurface is shown as a *shaded surface*. On the right part of the figure, each orbital is displayed by a *wire mesh* formed by contour curves on the isosurface, drawn in equidistant planes parallel to the zx-plane.

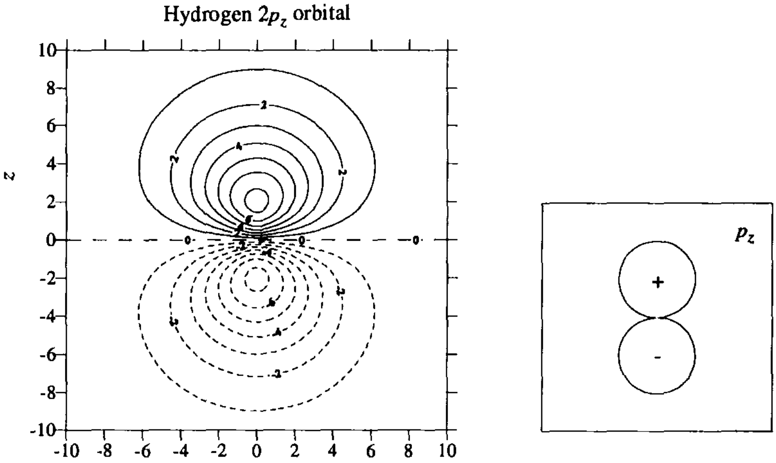

Figure 9.7: The big map shows the contour curves of the hydrogenic $2p_z$ orbital, in any plane through the z-axis. The analytic form of the orbital is obtained by multiplying the R_{2p} function of Table 9.1 by the Y_z function from Table 8.2. It is

$$\psi_{2p_z} = \sqrt{\frac{1}{32\pi}}\, z \exp(-r/2) = \sqrt{\frac{1}{32\pi}}\, r \exp(-r/2) \cos\theta.$$

The numbers specified on the contours are the contour values multiplied by 100.

The contour surfaces of the $2p_z$ orbital are surfaces of revolution. They may be generated by rotating the above contour curves about the z-axis.

The $2p_x$ and $2p_y$ orbitals are similar to the $2p_z$ orbital, but with the z-axis replaced by the x- and y-axes, respectively.

The smaller drawing is a polar plot of a p_z orbital, focusing on the directional character of the orbital and the signs of its lobes.

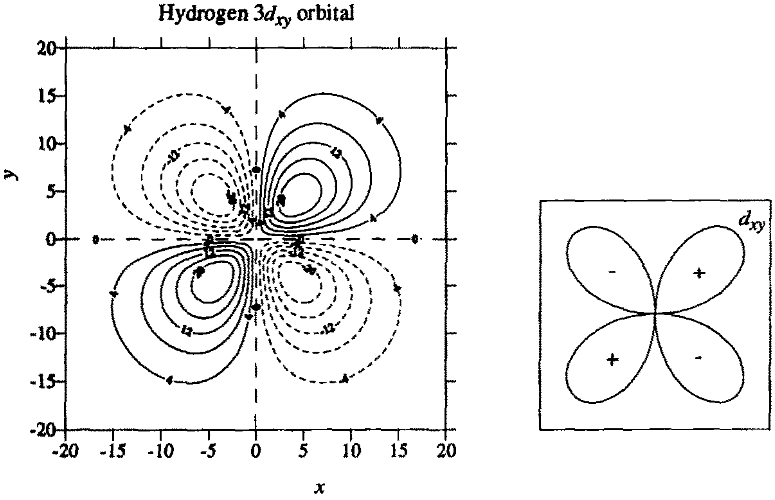

Figure 9.8: The big map shows the contour curves of the hydrogenic $3d_{xy}$ orbital, in the xy-plane. The analytic form of the orbital, as obtained from Table 9.1 and Table 8.2, is

$$\psi_{3d_{xy}} = \frac{1}{81}\sqrt{\frac{2}{\pi}}\, xy \exp(-r/3) = \frac{1}{81}\sqrt{\frac{1}{2\pi}}\, r^2 \exp(-r/3) \sin^2\theta \sin 2\phi.$$

The numbers specified on the contours are the contour values multiplied by 1000.

The smaller drawing is a polar plot, showing the directional character of the orbital and the signs of its lobes.

The $3d_{yz}$ and $3d_{zx}$ orbitals are similar to the $3d_{xy}$ orbital, but with the xy plane replaced by the yz and zx planes, respectively.

The $3d_{x^2-y^2}$ orbital is obtained from the $3d_{xy}$ orbital by a clockwise rotation through $\pi/4$ about the z-axis.

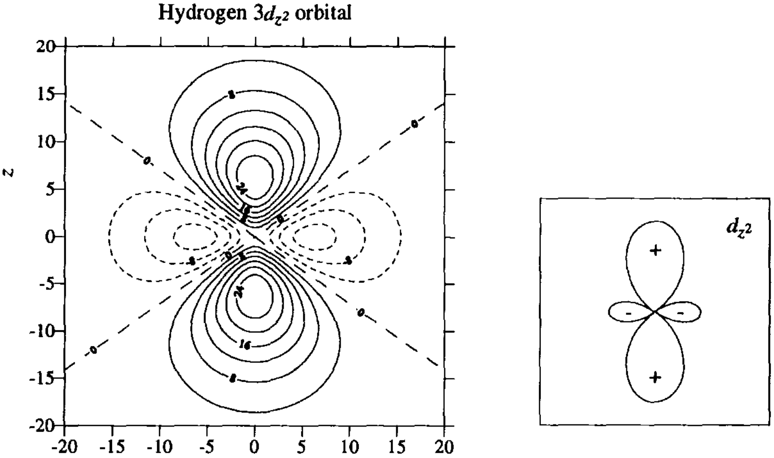

Figure 9.9: The big map shows the contour curves of the hydrogenic $3d_{z^2}$ orbital, in any plane through the z-axis. The analytic form of the orbital, as obtained from Table 9.1 and Table 8.2, is

$$\psi_{3d_{z^2}} = \frac{1}{81}\sqrt{\frac{1}{6\pi}}\,(3z^2 - r^2)\exp(-r/3) = \frac{1}{81}\sqrt{\frac{1}{6\pi}}\,r^2 \exp(-r/3)(3\cos^2\theta - 1).$$

The numbers specified on the contours are the contour values multiplied by 1000.

The smaller drawing is a polar plot, showing the directional character of the orbital and the signs of its lobes and its central collar.

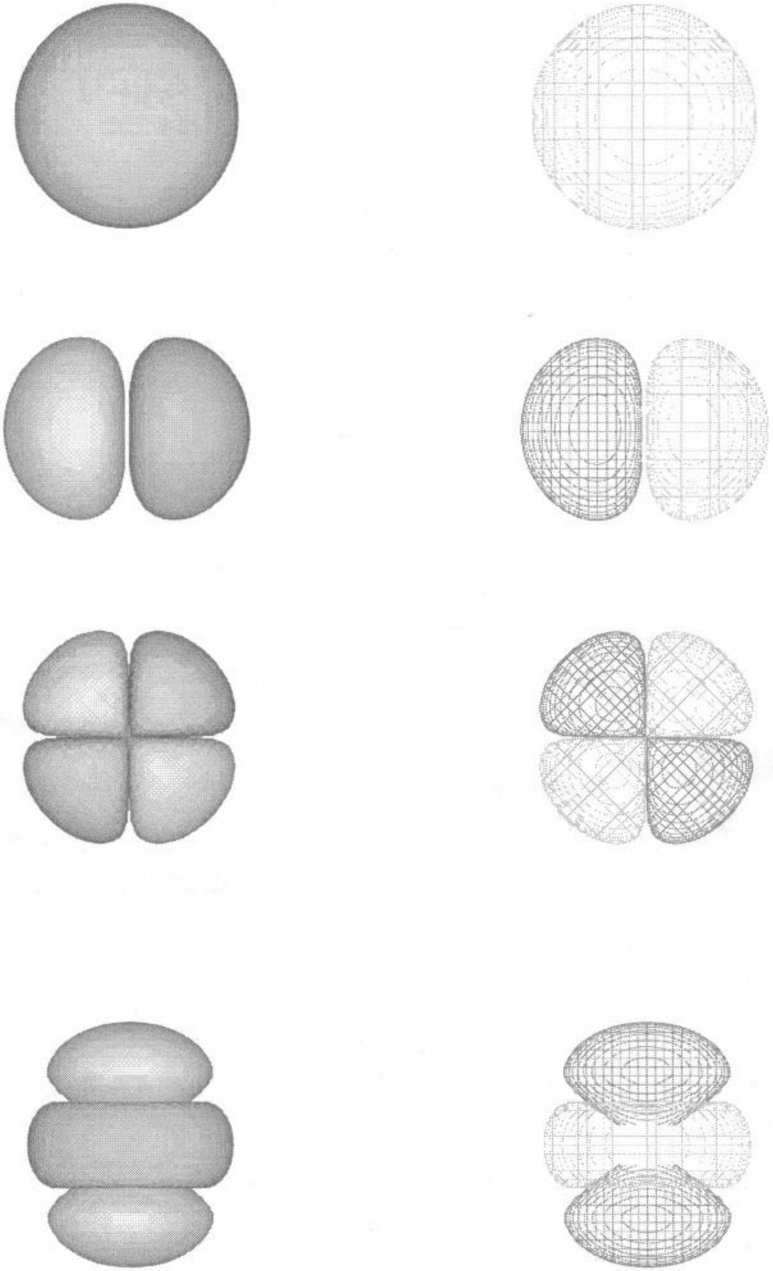

Figure 9.10: s, p and d isosurfaces.

Supplementary Reading

The bibliography, entries [10], [11], [17], and [18].

Problems

9.1. The $1s$ orbital for a hydrogen-like atom has the form

$$\psi_{1s}(r,\theta,\phi) = \sqrt{\frac{Z^3}{\pi a_0^3}}\, e^{-Zr/a_0}.$$

Verify this from Table 8.1 and Table 9.1.

a. Show that ψ_{1s} is normalized to 1.
Use the expression (8.26) for the volume element and draw on the general integral expression (9.23).

b. Determine the expectation value of r, i. e.,

$$\langle r\rangle = \int r\psi_{1s}(r,\theta,\phi)^2 dv,$$

in terms of Z and a_0.

c. Likewise, determine the expectation value of $1/r$, i. e.,

$$\left\langle \frac{1}{r}\right\rangle = \int \frac{1}{r}\psi_{1s}(r,\theta,\phi)^2 dv.$$

9.2. Consider the so-called *hybrid orbital*

$$\psi = \sqrt{\frac{1}{1+\lambda^2}}\,(\psi_{2s} + \lambda\psi_{2p_z})$$

where ψ_{2s} and ψ_{2p_z} are the normalized atomic orbitals for a hydrogen-like atom with nuclear charge Ze, i. e.,

$$\begin{cases} \psi_{2s} = R_{2s}(r)Y_{00}(\theta,\phi), \\ \psi_{2p_z} = R_{2p}(r)Y_z(\theta,\phi). \end{cases}$$

Adopt atomic units and write down the explicit expressions for ψ_{2s} and ψ_{2p_z}.

a. Determine the *dipole moment*

$$\mu = \langle z\rangle = \int \psi^* z\psi dv = \int \psi^* r\cos\theta\psi dv$$

as a function of λ and Z.
For some of the integrals that occur, exploit that the integral of an odd function vanishes. This is true in any dimension, as one sees by a straightforward generalization of Fig. 5.1 to higher dimensions.

b. Which *positive* value of λ gives the largest dipole moment?

c. Still using atomic units, calculate the value of μ for an *sp* hybrid orbital ($\lambda = 1$), an sp^2 hybrid orbital ($\lambda = \sqrt{2}$) and an sp^3 hybrid orbital ($\lambda = \sqrt{3}$).

d. Sketch the above mentioned hybrid orbitals by drawing contour curves in a plane containing the z-axis.

9.3. The *positron* is the *antiparticle* of the electron. It has the same mass as the electron, but while the electron has the charge $-e$, the positron has the charge $+e$. Under suitable conditions, the two particles may bind to each other, forming a *positronium* atom (average lifetime 0.5×10^{-9} s).
What is the ground-state energy of the positronium atom?

9.4. Starting from Table 9.1, write down the analytic expressions for the radial functions $P_{1s}(r)$, $P_{2s}(r)$ and $P_{2p}(r)$.

a. Adapt the bra-ket notation

$$\langle P_{nl}|P_{n'l'}\rangle = \int_0^\infty P_{nl}^*(r)P_{n'l'}(r)dr$$

and conclude, on the basis of suitable theoretical arguments, that

$$\langle P_{1s}|P_{2s}\rangle = 0.$$

b. Show, by direct evaluation of the integral, that

$$\langle P_{2s}|\frac{1}{r^2}|P_{2p}\rangle = \int_0^\infty P_{2s}^*(r)\frac{1}{r^2}P_{2p}(r)dr = \int_0^\infty R_{2s}^*(r)R_{2p}(r)dr = 0.$$

Next, construct theoretical arguments for this result, by writing down the differential equations that P_{2s} and P_{2p} must satisfy and using that $-d^2/dr^2$ is a Hermitian operator.

Chapter 10

The Spinning Electron

Contents

In the previous two chapters, we have seen the important role that the orbital angular momentum plays in the central-field problem. The orbital angular momentum of a single particle is, however, not the only kind of angular momentum that occurs in the description of atoms and molecules. Another important kind of angular momentum is the spin, and yet another kind is obtained by adding individual angular momenta of any type.

In the first section of this chapter, we shall extend the algebraic treatment of the angular-momentum problem set up in Sec. 8.3 to cover any type of angular momentum. This is, in fact, an easy thing to do, because the whole theory is governed by the commutation relations between the angular-momentum components and the requirement that the components be Hermitian operators. The general theory is *representation independent* in the sense that it only works with the eigenkets of the angular-momentum operators and the relations between them. The explicit form of the angular-momentum eigenfunctions is irrelevant in so far as the general theory is concerned. It is determined by the system to which the theory is applied.

The general theory allows both integral and half-integral angular-momentum quantum numbers. Thus, it enables us to give a quantitative discussion of the electron spin. Such a discussion is given in the second section and further elaborated in the third section. In the fourth section, with its three subsections, we give a detailed account of how a one-electron Hamiltonian is modified by the presence of the spin and external electromagnetic fields.

An important companion of the spin is the intrinsic magnetic moment of the electron which is often given the epithet *anomalous*. The background for this designation is also given in the fourth section. In the fifth section, we estimate the magnitude of the effects induced by the spin terms and an external magnetic field, and show that the effects are relatively small, at least for light atoms.

When discussing magnetic effects, one often writes the Hamiltonian as a two-by-two matrix and the wavefunction as a two-component quantity. The resulting Schrödinger equation is known as the Pauli equation. It is set up in the sixth section.

The final section of the chapter touches on the relation between angular-momentum theory and the theory of rotations, and we arrive at the important conclusion that wavefunctions describing particles with half-integral spin must change sign during a rotation through 2π about any axis.

10.1 General Angular Momentum Theory

The definition of a general angular momentum is the following

> A set of three Hermitian operators satisfying the commutation relations
>
> $$\begin{aligned}[\hat{J}_x,\, \hat{J}_y] &= i\hbar \hat{J}_z,\\ [\hat{J}_y,\, \hat{J}_z] &= i\hbar \hat{J}_x,\\ [\hat{J}_z,\, \hat{J}_x] &= i\hbar \hat{J}_y,\end{aligned}$$
>
> defines an angular momentum. The vector operator (10.1)
>
> $$\hat{\boldsymbol{J}} = (\hat{J}_x, \hat{J}_y, \hat{J}_z)$$
>
> is called an angular-momentum vector, and the operator
>
> $$\hat{J}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2$$
>
> is called the square of the angular momentum.

The commutation relations between $\hat{J}_x$, $\hat{J}_y$ and $\hat{J}_z$ are the same as the commutation relations (5.33) between the orbital angular-momentum operators $\hat{l}_x$, $\hat{l}_y$ and $\hat{l}_z$. Hence, the equivalent of the exercise (5.38) gives

$$[\hat{J}^2, \hat{J}_x] = [\hat{J}^2, \hat{J}_y] = [\hat{J}^2, \hat{J}_z] = 0, \tag{10.2}$$

showing that $\hat{J}^2$ commutes with any component of $\hat{\boldsymbol{J}}$.

The commutation relations in (10.1) show that $\hat{J}_x$, $\hat{J}_y$ and $\hat{J}_z$ must have the same dimension as $\hbar$. The operators

$$(\hat{\mathcal{J}}_x, \hat{\mathcal{J}}_y, \hat{\mathcal{J}}_z) = \frac{1}{\hbar}(\hat{J}_x, \hat{J}_y, \hat{J}_z) \tag{10.3}$$

are therefore dimensionless operators. They satisfy the same commutation relations as the operators $(\hat{\ell}_x, \hat{\ell}_y, \hat{\ell}_z)$ of Sec. 8.3. This implies that any result of Sec. 8.3 that could be derived from the commutation relations alone must also hold in the general case. In particular, there must be a sequence of eigenkets similar to the sequence (8.72). Let us write J and M instead of ℓ and m, and also $|JM\rangle$ instead of $Y_{\ell m}$. We have, then, relations similar to the relations (8.73). Expressed in terms of the operators $(\hat{J}_x, \hat{J}_y, \hat{J}_z)$ rather than

$(\hat{\mathcal{J}}_x, \hat{\mathcal{J}}_y, \hat{\mathcal{J}}_z)$, these relations become

$$\boxed{\begin{aligned} &\hat{J}^2|JM\rangle = J(J+1)\hbar^2|JM\rangle, \\ &\hat{J}_z|JM\rangle = M\hbar|JM\rangle, \qquad M = -J, -J+1, \dots, J-1, J. \end{aligned}} \tag{10.4}$$

The orthonormality relation (8.74) reads

$$\langle JM|JM'\rangle = \delta_{MM'}, \tag{10.5}$$

and the step-up and step-down relations (8.82) become

$$\boxed{\begin{aligned} &\hat{J}_+|JM\rangle = \hbar\sqrt{(J-M)(J+M+1)}\,|J, M+1\rangle, \\ &\hat{J}_-|JM\rangle = \hbar\sqrt{(J+M)(J-M+1)}\,|J, M-1\rangle \end{aligned}} \tag{10.6}$$

where

$$\begin{cases} J_+ = J_x + iJ_y, \\ J_- = J_x - iJ_y. \end{cases} \tag{10.7}$$

As to the possible values of J, we conclude from the discussion at the end of Sec. (8.3.4) that the general algebra allows the values $J = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \dots$. That the quantum number ℓ had to be restricted to integral values was derived from the actual form of $\hat{\ell}_z$, via the relation (8.47). In other words, it was a result that was obtained for a particular physical system. The algebra itself allows for the possibility that physical systems exist for which the situation could be different.

The formalism behind the relations (10.1)–(10.7) enables us to treat any angular-momentum sytem, whether it refers to a single particle or a collection of particles. In the present chapter, we are primarily interested in the spin problem, so we shall postpone the discussion of many-particle systems. As a foretaste of what is involved for a many-particle system, let us, however, verify that the total orbital angular momentum of an N-electron system is a *bona-fide* angular-momentum vector, in regard to the definitions of this section.

The total orbital angular momentum of an N-electron system is customarily denoted by $\hat{\boldsymbol{L}}$. It is defined as the vector sum of the individual orbital angular momenta:

$$\hat{\boldsymbol{L}} = \sum_{i=1}^{N} \hat{\boldsymbol{l}}_i. \tag{10.8}$$

The components of $\hat{\boldsymbol{L}}$ are given by the operators

$$(\hat{L}_x, \hat{L}_y, \hat{L}_z) = \left(\sum_{i=1}^{N} \hat{l}_{ix}, \sum_{i=1}^{N} \hat{l}_{iy}, \sum_{i=1}^{N} \hat{l}_{iz} \right). \tag{10.9}$$

When these operators act on a function of the coordinates $(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)$, operators referring to different particles will commute. Hence, we get

$$[\hat{L}_x, \hat{L}_y] = \sum_{i=1}^{N}\sum_{j=1}^{N} [\hat{l}_{ix}, \hat{l}_{jy}] = \sum_{i=1}^{N} [\hat{l}_{ix}, \hat{l}_{iy}] = i\hbar \sum_{i=1}^{N} \hat{l}_{iz} = i\hbar \hat{L}_z, \tag{10.10}$$

plus the analogous expressions for $[\hat{L}_y, \hat{L}_z]$ and $[\hat{L}_z, \hat{L}_x]$. Thus, $\hat{L}_x$, $\hat{L}_y$ and $\hat{L}_z$ satisfy the commutation relations (10.1) and $\hat{\boldsymbol{L}}$ is, in fact, a proper angular-momentum vector.

10.2 Spin, Spin Functions and Spin-Orbitals

We shall now attack the problem of describing the spin of the electron. Formally, this is quite simple, because everything we need is included in the previous section. The only thing we have to do is to treat the spin problem as a special case of the general angular-momentum problem. This will be the leading philosophy of this section.

The spin is described by a vector operator $\hat{\boldsymbol{s}} = (\hat{s}_x, \hat{s}_y, \hat{s}_z)$ and its square, $\hat{s}^2 = \hat{s}_x^2 + \hat{s}_y^2 + \hat{s}_z^2$. These operators are assumed to be Hermitian, and they satisfy commutation relations similar to those in (10.1),

$$\left\{ \begin{array}{l} [\hat{s}_x, \hat{s}_y] = i\hbar \hat{s}_z, \\ [\hat{s}_y, \hat{s}_z] = i\hbar \hat{s}_x, \\ [\hat{s}_z, \hat{s}_x] = i\hbar \hat{s}_y, \\ [\hat{s}^2, \hat{s}_x] = [\hat{s}^2, \hat{s}_y] = [\hat{s}^2, \hat{s}_z] = 0, \end{array} \right. \tag{10.11}$$

so the formal machinery set up in the previous section applies to them. But to indicate that the particular problem is a spin problem, one traditionally denotes the J and M quantum numbers by s and m_s, respectively.

As already mentioned in Sec. 1.7, the electron is a spin one-half particle. What this says is that the only s-value that appears is $s = \frac{1}{2}$. Thus, the s-value is an invariable property of the electron. There is no way of changing it. This situation contrasts the orbital angular-momentum case. An orbital angular-momentum must be described by an integral ℓ-value, but the ℓ-value may be changed by letting the electron interact with other particles, including photons.

With $s = \frac{1}{2}$, there are only two linearly independent spin functions. We may choose them as eigenfunctions of $\hat{s}_z$, and they are then denoted by α and β. Thus, we have

$$\boxed{\begin{array}{ll} \hat{s}_z\alpha(\varsigma) = \frac{1}{2}\hbar\alpha(\varsigma), & \hat{s}^2\alpha(\varsigma) = \frac{1}{2}(\frac{1}{2}+1)\hbar^2\alpha(\varsigma), \\ \hat{s}_z\beta(\varsigma) = -\frac{1}{2}\hbar\beta(\varsigma), & \hat{s}^2\beta(\varsigma) = \frac{1}{2}(\frac{1}{2}+1)\hbar^2\beta(\varsigma). \end{array}} \tag{10.12}$$

The α and β spin functions are eigenfunctions of the operator $\hat{s}_z$ with different eigenvalues and are hence orthogonal. We shall also assume that α and β are normalized to unity. The spin variable ς is a purely formal quantity which allows us to express these statements in a familiar way:[1]

$$\left\{ \begin{array}{l} \langle\alpha|\alpha\rangle = \int \alpha(\varsigma)^*\alpha(\varsigma)d\varsigma = 1, \\ \langle\beta|\beta\rangle = \int \beta(\varsigma)^*\beta(\varsigma)d\varsigma = 1, \\ \langle\alpha|\beta\rangle = \int \alpha(\varsigma)^*\beta(\varsigma)d\varsigma = 0. \end{array} \right. \tag{10.13}$$

The relations (10.6) take the simple form

$$\boxed{\begin{array}{ll} \hat{s}_+\alpha(\varsigma) = 0, & \hat{s}_-\alpha(\varsigma) = \hbar\beta(\varsigma), \\ \hat{s}_+\beta(\varsigma) = \hbar\alpha(\varsigma), & \hat{s}_-\beta(\varsigma) = 0, \end{array}} \tag{10.14}$$

where

$$\left\{ \begin{array}{l} \hat{s}_+ = \hat{s}_x + i\hat{s}_y, \\ \hat{s}_- = \hat{s}_x - i\hat{s}_y. \end{array} \right. \tag{10.15}$$

Since there are only two linearly independent spin functions, the most general, normalized spin function has the form

$$\eta(\varsigma) = c_1\alpha(\varsigma) + c_2\beta(\varsigma), \qquad c_1^*c_1 + c_2^*c_2 = 1. \tag{10.16}$$

In accordance with the discussion of Sec. 5.9, its statistical interpretation is that $c_1^*c_1$ is the probability of observing the z-projection of the spin to be $\frac{1}{2}\hbar$, while $c_2^*c_2$ is the probability of observing its value to be $-\frac{1}{2}\hbar$. In a given physical situation c_1 and c_2 may, of course, be functions of time.

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[1] The symbol ς is a typographical variant of the greek letter σ (sigma). It should not be mistaken for the greek letter ζ (zeta).

Thus we are able to give a purely formal description of the spin without demanding that it emerge from a more fundamental analysis. This type of description is fully adequate for most purposes.

Considering both the spatial and the spin degrees of freedom for a spin one-half particle, one introduces a so-called *spin-orbital*,

$$\psi(\boldsymbol{r},\varsigma) = \varphi_1(\boldsymbol{r})\alpha(\varsigma) + \varphi_2(\boldsymbol{r})\beta(\varsigma). \tag{10.17}$$

Any wavefunction for a spin one-half particle may be written in this form. The statistical interpretation is that $\varphi_1(\boldsymbol{r})^*\varphi_1(\boldsymbol{r})dv$ is the probability of finding the particle in the volume element dv at $\boldsymbol{r}$, with the z-projection of the spin being $\frac{1}{2}\hbar$. Similarly, $\varphi_2(\boldsymbol{r})^*\varphi_2(\boldsymbol{r})dv$ is the probability of finding the particle with the z-projection being $-\frac{1}{2}\hbar$. Again, the functions $\varphi_1(\boldsymbol{r})$ and $\varphi_2(\boldsymbol{r})$ may be made time-dependent.

Having introduced the concept of spin-orbitals, we must also be prepared to include terms containing the spin operators $\hat{s}_x$, $\hat{s}_y$ and $\hat{s}_z$ into the Hamiltonian. The Schrödinger equation must then be written

$$\widehat{H}\psi(\boldsymbol{r},\varsigma) = E\psi(\boldsymbol{r},\varsigma). \tag{10.18}$$

Its solutions will be of the form (10.17). We shall meet spin-dependent Hamiltonians later in this chapter (Sec. 10.4). If, however, the Hamiltonian is taken to be independent of spin, as when we retain the familiar form

$$\widehat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 + V(\boldsymbol{r}), \tag{10.19}$$

then the solutions of Eq. (10.18) will be $\varphi(\boldsymbol{r})\eta(\varsigma)$, where $\eta(\varsigma)$ is an arbitrary spin function of the form (10.16), and $\varphi(\boldsymbol{r})$ is a solution of the Schrödinger equation

$$\widehat{H}\varphi(\boldsymbol{r}) = E\varphi(\boldsymbol{r}). \tag{10.20}$$

For since the spin-independent Hamiltonian $\widehat{H}$ has no effect on $\eta(\varsigma)$, it is obvious that $\varphi(\boldsymbol{r})\eta(\varsigma)$ satisfies the Schrödinger equation (10.18) whenever $\varphi(\boldsymbol{r})$ satisfies Eq. (10.20). In this way, each $\varphi(\boldsymbol{r})$ defines two linearly independent solutions of Eq. (10.18), and it is customary to take these to be

$$\left\{\begin{aligned} \overset{+}{\varphi}(x) &= \varphi(\boldsymbol{r})\alpha(\varsigma), \\ \bar{\varphi}(x) &= \varphi(\boldsymbol{r})\beta(\varsigma), \end{aligned}\right. \tag{10.21}$$

where + and − refer to the α and β spin-functions respectively. The degeneracy of each energy level is thus doubled by the inclusion of the spin.

In Eq. (10.21), we have used x as a convenient designation for the combination of the space coordinates (x, y, z) and the spin variable ς. Similarly, we shall let dx denote integration over x, y, and z plus integration over ς, i. e., we shall write

$$dx = dv d\varsigma. \tag{10.22}$$

We get then, provided that $\varphi(\boldsymbol{r})$ is normalized to unity,

$$\left\{ \begin{array}{l} \langle \overset{+}{\varphi} \,|\, \overset{+}{\varphi} \rangle = \int \overset{+}{\varphi}(x)^* \, \overset{+}{\varphi}(x) dx = \int \varphi^*(\boldsymbol{r}) \varphi(\boldsymbol{r}) dv \int \alpha^*(\varsigma) \alpha(\varsigma) d\varsigma = 1, \\ \langle \bar{\varphi} \,|\, \bar{\varphi} \rangle = \int \bar{\varphi}(x)^* \, \bar{\varphi}(x) dx = \int \varphi^*(\boldsymbol{r}) \varphi(\boldsymbol{r}) dv \int \beta^*(\varsigma) \beta(\varsigma) d\varsigma = 1, \\ \langle \overset{+}{\varphi} \,|\, \bar{\varphi} \rangle = \int \overset{+}{\varphi}(x)^* \, \bar{\varphi}(x) dx = \int \varphi^*(\boldsymbol{r}) \varphi(\boldsymbol{r}) dv \int \alpha^*(\varsigma) \beta(\varsigma) d\varsigma = 0. \end{array} \right. \tag{10.23}$$

Hence, the spin-orbitals $\overset{+}{\varphi}$ and $\bar{\varphi}$ are normalized and mutually orthogonal.

As an important example, let us assume that the potential in Eq. (10.19) only depends upon the distance r to a center. We are then dealing with a central-field problem, and the spatial orbitals may be written as in Eq. (9.53) or Eq. (9.54). Hence, the associated spin-orbitals take the form

$$\psi_{n\ell m_\ell m_s}(x) = R_{n\ell}(r) Y_{\ell m_\ell}(\theta, \phi) \left\{ \begin{array}{ll} \alpha(\varsigma), & m_s = \frac{1}{2} \\ \beta(\varsigma), & m_s = -\frac{1}{2} \end{array} \right. \tag{10.24}$$

or, more general,

$$\psi_{n\ell\gamma_\ell\gamma_s}(x) = R_{n\ell}(r) Y_{\ell\gamma_\ell}(\theta, \phi) \eta_{\gamma_s}(\varsigma) \tag{10.25}$$

where γ_s labels two independent linear combinations of $\alpha(\varsigma)$ and $\beta(\varsigma)$, in a similar way as γ_ℓ labels $2\ell + 1$ independent linear combinations of the surface spherical harmonics $Y_{\ell m_\ell}(\theta, \phi)$. In any case, a central-field spin-orbital is characterized by four "quantum numbers", (n, ℓ, m_ℓ, m_s) or $(n, \ell, \gamma_\ell, \gamma_s)$.

In the next chapter, we shall see that the inclusion of spin, and in particular the replacement of ordinary spatial orbitals by spin-orbitals, is of fundamental importance for the understanding of the electronic structure of many-electron atoms and molecules. But apart from this, the spin also manifests itself through its accompanying magnetic moment. The presence of the magnetic moment leads to additional terms in the Hamiltonian, in particular when the atom or the molecule is embedded in an electromagnetic field. We shall introduce these terms in Sec. 10.4.

As already mentioned in Sec. 3.1, the hypothesis that the electron possesses an intrinsic angular momentum was introduced in 1925 by Uhlenbeck and

Goudsmit.[2] At the time, attempts to give a rational interpretation of the simpler atomic spectra had led to much confusion, and it was the merit of Uhlenbeck and Goudsmit that they were able to point to a mechanism by which the confusion might be eliminated in a convincing way. It appears that the young American physicist Ralph de Laer Kronig had come upon a similar idea earlier the same year, but since it was ridiculed by the authorative Austrian physicist Wolfgang Pauli, he did not publish it. Notwithstanding his early opposition, it was Pauli who first constructed an operator description of the spin, along essentially the same lines as we have presented above. (See Sec. 10.6.)

In continuation of the above discussion, let us emphasize that spin is an intrinsic property of all elementary particles. Particles with half-integral spin are called *fermions*, particles with integral spin are called *bosons*. The photon is a spin 1 particle, the mesons are spin 0 particles, so they are all examples of bosons. Among the fermions, we find the electron, the proton and the neutron, the neutrinos, etc. A spin formalism similar to the one set up for the electron in this section may equally well be established for the other elementary particles, *mutatis mutandis*.

The fact that our present spin operators $\hat{s}_x$, $\hat{s}_y$ and $\hat{s}_z$ refer to a spin one-half system endows them with some special properties that general angular-momentum operators do not share. We derive these properties in the following section by exploiting that $\hat{s}_x$, $\hat{s}_y$ and $\hat{s}_z$ always act on functions in the two-dimensional function space spanned by the functions $\alpha(\varsigma)$ and $\beta(\varsigma)$, namely, the set of functions given by Eq. (10.16).

10.3 Properties of the Spin One-Half Operators

It is convenient to replace the spin operators $\hat{s}_x$, $\hat{s}_y$ and $\hat{s}_z$ by three dimensionless operators $\hat{\sigma}_x$, $\hat{\sigma}_y$ and $\hat{\sigma}_z$ according to the definition[3]

$$(\hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z) = \frac{2}{\hbar}(\hat{s}_x, \hat{s}_y, \hat{s}_z). \tag{10.26}$$

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[2] G. E. Uhlenbeck and S. Goudsmit, Naturwiss. 13, 953 (1925).

[3] Note that this definition includes an extra factor of 2 as compared with the otherwise similar definition in Eq. (10.3).

In terms of these operators, the relations (10.12) become

$$\boxed{\begin{array}{ll} \hat{\sigma}_z\alpha = \alpha, & \hat{\sigma}^2\alpha = 3\alpha, \\ \hat{\sigma}_z\beta = -\beta, & \hat{\sigma}^2\beta = 3\beta \end{array}} \qquad (10.27)$$

where we have omitted the formal spin variable ς. Similarly, the relations (10.14) become

$$\boxed{\begin{array}{ll} \hat{\sigma}_+\alpha = 0, & \hat{\sigma}_-\alpha = 2\beta, \\ \hat{\sigma}_+\beta = 2\alpha, & \hat{\sigma}_-\beta = 0 \end{array}} \qquad (10.28)$$

where

$$\left\{ \begin{array}{l} \hat{\sigma}_+ = \hat{\sigma}_x + i\hat{\sigma}_y, \\ \hat{\sigma}_- = \hat{\sigma}_x - i\hat{\sigma}_y. \end{array} \right. \qquad (10.29)$$

By inserting the expressions (10.29) into the relations (10.28) and subsequently adding and subtracting equations, one obtains simple expressions for the action of $\hat{\sigma}_x$ and $\hat{\sigma}_y$ on the functions α and β. Including also the result of acting with $\hat{\sigma}_z$, from Eq. (10.27), we arrive at the important formulae

$$\boxed{\begin{array}{lll} \hat{\sigma}_x\alpha = \beta, & \hat{\sigma}_y\alpha = i\beta, & \hat{\sigma}_z\alpha = \alpha, \\ \hat{\sigma}_x\beta = \alpha, & \hat{\sigma}_y\beta = -i\alpha, & \hat{\sigma}_z\beta = -\beta. \end{array}} \qquad (10.30)$$

By means of these formulae we find, for instance, that

$$\left\{ \begin{array}{l} \hat{\sigma}_x\hat{\sigma}_y(c_1\alpha + c_2\beta) = i\hat{\sigma}_x(c_1\beta - c_2\alpha) = i(c_1\alpha - c_2\beta) \\ \hat{\sigma}_y\hat{\sigma}_x(c_1\alpha + c_2\beta) = \hat{\sigma}_y(c_1\beta + c_2\alpha) = -i(c_1\alpha - c_2\beta) \\ \hat{\sigma}_z(c_1\alpha + c_2\beta) = c_1\alpha - c_2\beta. \end{array} \right. \qquad (10.31)$$

Since $c_1\alpha + c_2\beta$ is an entirely arbitrary spin one-half function, these expressions allow us to write

$$\hat{\sigma}_x\hat{\sigma}_y = -\hat{\sigma}_y\hat{\sigma}_x = i\hat{\sigma}_z. \qquad (10.32)$$

The formulae (10.30) also give that

$$\hat{\sigma}_x\hat{\sigma}_x(c_1\alpha + c_2\beta) = \hat{\sigma}_x(c_1\beta + c_2\alpha) = c_1\alpha + c_2\beta, \qquad (10.33)$$

so that we may write

$$\hat{\sigma}_x\hat{\sigma}_x = 1. \tag{10.34}$$

Proceeding in a similar manner, we end up with the following set of relations

$$\boxed{\begin{aligned} \hat{\sigma}_x\hat{\sigma}_x &= \hat{\sigma}_y\hat{\sigma}_y = \hat{\sigma}_z\hat{\sigma}_z = 1, \\ \hat{\sigma}_x\hat{\sigma}_y &= -\hat{\sigma}_y\hat{\sigma}_x = i\hat{\sigma}_z, \\ \hat{\sigma}_y\hat{\sigma}_z &= -\hat{\sigma}_z\hat{\sigma}_y = i\hat{\sigma}_x, \\ \hat{\sigma}_z\hat{\sigma}_x &= -\hat{\sigma}_x\hat{\sigma}_z = i\hat{\sigma}_y. \end{aligned}} \tag{10.35}$$

The relations (10.35) imply the commutation relations

$$[\hat{\sigma}_x, \hat{\sigma}_y] = 2i\hat{\sigma}_z, \quad [\hat{\sigma}_y, \hat{\sigma}_z] = 2i\hat{\sigma}_x, \quad [\hat{\sigma}_z, \hat{\sigma}_x] = 2i\hat{\sigma}_y, \tag{10.36}$$

which, of course, could have been written down from the very outset by substituting the definition (10.26) into the commutation relations of Eq. (10.11). However, the relations (10.35) also imply that

$$\left\{ \begin{aligned} \hat{\sigma}_x\hat{\sigma}_y + \hat{\sigma}_y\hat{\sigma}_x &= 0, \\ \hat{\sigma}_y\hat{\sigma}_z + \hat{\sigma}_z\hat{\sigma}_y &= 0, \\ \hat{\sigma}_z\hat{\sigma}_x + \hat{\sigma}_x\hat{\sigma}_z &= 0. \end{aligned} \right. \tag{10.37}$$

These relations only hold for spin one-half systems. One says that the spin operators $\hat{\sigma}_x$, $\hat{\sigma}_y$ and $\hat{\sigma}_z$ *anticommute* with one another. By introducing the so-called *anticommutator* by the definition

$$[\hat{\Omega}_a, \hat{\Omega}_b]_+ = \hat{\Omega}_a\hat{\Omega}_b + \hat{\Omega}_b\hat{\Omega}_a, \tag{10.38}$$

with $\hat{\Omega}_a$ and $\hat{\Omega}_b$ being arbitrary operators, we may collect the anticommutation relations in a single compact expression as follows

$$\boxed{[\hat{\sigma}_i, \hat{\sigma}_j]_+ = 2\delta_{ij}} \tag{10.39}$$

where i and j independently take on the values 1, 2 and 3, with 1 referring to index x, 2 to index y and 3 to index z. The anticommutation relations are peculiar to spin one-half systems, because they are a consequence of the spin one-half formulae (10.30).

The formulae (10.30) are often presented in a matrix notation, viz.,

$$\hat{\sigma}_x(\alpha, \beta) = (\alpha, \beta)\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \tag{10.40}$$

$$\hat{\sigma}_y(\alpha,\beta) = (\alpha,\beta)\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \tag{10.41}$$

$$\hat{\sigma}_z(\alpha,\beta) = (\alpha,\beta)\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{10.42}$$

The matrices

$$\boxed{\boldsymbol{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \boldsymbol{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \boldsymbol{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}} \tag{10.43}$$

are called the *Pauli spin matrices.* They satisfy all the relations (10.35), and therefore also the commutation relations (10.36) and the anticommutation relations (10.39). This is readily verified, but it also follows from the general discussion of Sec. 5.10, by considering $\alpha(\varsigma)$ and $\beta(\varsigma)$ as basis functions in a two-dimensional function space $\mathcal{V}$ and, in particular, by comparing with Eqs. (5.152) and (5.164) of that section. Eqs. (5.151) and (5.152) also imply that

$$\boldsymbol{\sigma}_k = \begin{pmatrix} \langle\alpha|\hat{\sigma}_k|\alpha\rangle & \langle\alpha|\hat{\sigma}_k|\beta\rangle \\ \langle\beta|\hat{\sigma}_k|\alpha\rangle & \langle\beta|\hat{\sigma}_k|\beta\rangle \end{pmatrix}, \qquad k = x, y, z. \tag{10.44}$$

By the rules laid out in Sec. 5.10, the spin matrices $\boldsymbol{\sigma}_x$, $\boldsymbol{\sigma}_y$ and $\boldsymbol{\sigma}_z$ become the representatives of the operators $\hat{\sigma}_x$, $\hat{\sigma}_y$ and $\hat{\sigma}_z$ when one represents the α and β spin functions, and the general spin function (10.16), by the column vectors

$$\begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \quad \begin{pmatrix} c_1 \\ c_2 \end{pmatrix},$$

respectively. In such a representation, a relation like

$$\hat{\sigma}_y(c_1\alpha + c_2\beta) = -ic_2\alpha + ic_1\beta \tag{10.45}$$

becomes

$$\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} -ic_2 \\ ic_1 \end{pmatrix}. \tag{10.46}$$

Matrix expressions of this type are useful in several contexts and are frequently met in the literature (See also Sec. 10.6).

10.4 The One-Electron Atom in External Fields

The motion of a single electron in a central field has so far been defined by a Hamiltonian of the form

$$\widehat{H}_0 = \frac{\hat{p}^2}{2m_e} + V(r) = -\frac{\hbar^2}{2m_e}\nabla^2 + V(r). \tag{10.47}$$

As indicated, we now call this Hamiltonian $\widehat{H}_0$. We ask how it is modified by the inclusion of the spin and the addition of an external electromagnetic field, and answer this equation in three steps to be described in the following three subsections.

10.4.1 The Hamiltonian With Spin Neglected

Let us begin by still neglecting the spin. The procedure to follow is then to first construct the proper classical Hamiltonian, in a similar way as in Sec. 3.3, and next turn this dynamical function into an operator by the prescription given in that section. To set up the classical Hamiltonian for a particle in the presence of an external electromagnetic field is a somewhat advanced problem. It is properly described in many textbooks,[4] so we shall merely give the result, which is

$$H_{cl}(\boldsymbol{p}, \boldsymbol{r}) = \frac{1}{2m}\left(\boldsymbol{p} - q\boldsymbol{A}(\boldsymbol{r}, t)\right)^2 + q\varphi(\boldsymbol{r}, t) + V(\boldsymbol{r}). \tag{10.48}$$

$V(\boldsymbol{r})$ is the potential energy without the field. For the one-electron atom it is the central field, $V(r)$. q is the charge of the particle and m is its mass. For an electron, $m = m_e$ and $q = -e$, so Eq. (10.48) becomes

$$\boxed{H_{cl}(\boldsymbol{p}, \boldsymbol{r}) = \frac{1}{2m_e}\left(\boldsymbol{p} + e\boldsymbol{A}(\boldsymbol{r}, t)\right)^2 - e\varphi(\boldsymbol{r}, t) + V(\boldsymbol{r})} \tag{10.49}$$

$\boldsymbol{A}(\boldsymbol{r}, t)$ is the *vector potential* of the field and $\varphi(\boldsymbol{r}, t)$ is the *scalar potential.*

The field potentials $\boldsymbol{A}(\boldsymbol{r}, t)$ and $\varphi(\boldsymbol{r}, t)$ represent the *magnetic induction* $\boldsymbol{B}(\boldsymbol{r}, t)$ and the *electric field* $\boldsymbol{E}(\boldsymbol{r}, t)$ through the relations

$$\begin{cases} \boldsymbol{B} = \nabla \times \boldsymbol{A}, \\ \boldsymbol{E} = -\nabla\varphi - \dfrac{\partial \boldsymbol{A}}{\partial t}, \end{cases} \tag{10.50}$$

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[4] See, for instance, Refs. [19], [20], [21], or [22] in the bibliography.

where

$$\nabla\varphi = \left(\frac{\partial\varphi}{\partial x}, \frac{\partial\varphi}{\partial y}, \frac{\partial\varphi}{\partial z}\right) \tag{10.51}$$

and

$$\nabla \times \boldsymbol{A} = \left(\frac{\partial A_z}{\partial y} - \frac{\partial A_y}{\partial z}, \frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x}, \frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y}\right). \tag{10.52}$$

$\nabla\varphi$ is the gradient of the scalar potential φ (cf. Eq. (3.2)). $\nabla \times \boldsymbol{A}$ is the *curl* of the vector potential $\boldsymbol{A}$.

This is not the place to enter into a deeper discussion of the relations (10.50). For the present, we shall focus our attention on fields that are *constant* (independent of time) and *uniform* (independent of position). We may then put

$$\left\{\begin{array}{l} \boldsymbol{A}(\boldsymbol{r}) = \frac{1}{2}\boldsymbol{B} \times \boldsymbol{r} = \frac{1}{2}\left(B_y z - B_z y, B_z x - B_x z, B_x y - B_y x\right), \\ \varphi(\boldsymbol{r}) = -\boldsymbol{E} \cdot \boldsymbol{r} = -\left(E_x x + E_y y + E_z z\right), \end{array}\right. \tag{10.53}$$

where $\boldsymbol{B}$ and $\boldsymbol{E}$ are the constant and uniform fields. It is readily verified that the above expressions do, in fact, generate the fields $\boldsymbol{B}$ and $\boldsymbol{E}$ from the relations (10.50). We get, for instance,

$$\begin{aligned} (\nabla \times \boldsymbol{A})_x &= \frac{\partial A_z}{\partial y} - \frac{\partial A_y}{\partial z} = \frac{1}{2}\frac{\partial}{\partial y}\left(B_x y - B_y x\right) - \frac{1}{2}\frac{\partial}{\partial z}\left(B_z x - B_x z\right) \\ &= \frac{1}{2}B_x + \frac{1}{2}B_x = B_x \end{aligned} \tag{10.54}$$

and

$$-\frac{\partial\varphi}{\partial x} - \frac{\partial A_x}{\partial t} = \frac{\partial}{\partial x}\left(E_x x + E_y y + E_z z\right) + 0 = E_x. \tag{10.55}$$

We must now substitute the expressions (10.53) for $\boldsymbol{A}$ and φ into the Hamiltonian (10.49). This leads to the following result, for constant and uniform fields,

$$\boxed{H_{cl}(\boldsymbol{p}, \boldsymbol{r}) = \frac{p^2}{2m_e} + V(r) + \frac{e}{2m_e}\boldsymbol{l} \cdot \boldsymbol{B} + e\boldsymbol{r} \cdot \boldsymbol{E} + \frac{e^2}{8m_e}\left(\boldsymbol{B} \times \boldsymbol{r}\right)^2} \tag{10.56}$$

where $\boldsymbol{l} = \boldsymbol{r} \times \boldsymbol{p}$ is the usual orbital angular momentum. As an intermediate step in obtaining this result, write

$$\begin{aligned} \left(\boldsymbol{p} + e\boldsymbol{A}(\boldsymbol{r})\right)^2 &= \left(\boldsymbol{p} + e\boldsymbol{A}(\boldsymbol{r})\right) \cdot \left(\boldsymbol{p} + e\boldsymbol{A}(\boldsymbol{r})\right) \\ &= p^2 + 2e\boldsymbol{A}(\boldsymbol{r}) \cdot \boldsymbol{p} + e^2 A(\boldsymbol{r})^2, \end{aligned} \tag{10.57}$$

substitute $\boldsymbol{A}(\boldsymbol{r}) = \frac{1}{2}\boldsymbol{B} \times \boldsymbol{r}$ and use that the elementary rules of vector analysis allow us to write $(\boldsymbol{B} \times \boldsymbol{r}) \cdot \boldsymbol{p} = \boldsymbol{B} \cdot (\boldsymbol{r} \times \boldsymbol{p}) = (\boldsymbol{r} \times \boldsymbol{p}) \cdot \boldsymbol{B}$.

To obtain the quantum-mechanical Hamiltonian, we must replace the vector $\boldsymbol{p}$ in Eq. (10.49) by the vector operator

$$\hat{\boldsymbol{p}} = -i\hbar\nabla = -i\left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right) \tag{10.58}$$

and write

$$\widehat{H}_{cl} = \frac{1}{2m_e}\left(\hat{\boldsymbol{p}} + e\boldsymbol{A}(\boldsymbol{r},t)\right)^2 - e\varphi(\boldsymbol{r},t) + V(\boldsymbol{r}). \tag{10.59}$$

We must then substitute the expressions for $\boldsymbol{A}$ and φ as before. But during this process, we must now reconsider the step represented by Eq. (10.57) and examine whether the commutation relations (5.26) allow us to put

$$\hat{\boldsymbol{p}} \cdot \boldsymbol{A} = \boldsymbol{A} \cdot \hat{\boldsymbol{p}} \tag{10.60}$$

For this to be the case, the commutators $[\hat{p}_x, A_x]$, $[\hat{p}_y, A_y]$ and $[\hat{p}_z, A_z]$ must all vanish. They do, for we see from Eq. (10.53) that A_x is independent of x, A_y is independent of y, and A_z is independent of z. Thus, Eq. (10.60) does hold, and the quantum-mechanical Hamiltonian becomes

$$\widehat{H}_{cl} = \frac{\hat{p}^2}{2m_e} + V(\boldsymbol{r}) + \frac{e}{2m_e}\hat{\boldsymbol{l}} \cdot \boldsymbol{B} + e\boldsymbol{r} \cdot \boldsymbol{E} + \frac{e^2}{8m_e}(\boldsymbol{B} \times \boldsymbol{r})^2. \tag{10.61}$$

10.4.2 The Hamiltonian With Spin Included

We must now worry about the inclusion of the electron's spin. This is not a straightforward problem, for the concept of spin lies outside the realm of classical mechanics.

To tackle the problem, we remark that the classical Hamiltonian (10.49) is the *non-relativistic classical Hamiltonian*. We are looking for the corresponding *non-relativistic quantum-mechanical Hamiltonian*. The way to derive the form of this Hamiltonian is to infer it from the Dirac equation[5] which gives the proper *relativistic* description of the electron, as already pointed out in the Introduction to Chapter 3. From the Dirac equation, one arrives at the remarkable result that the Hamiltonian in question becomes

$$\boxed{\widehat{H} = \frac{1}{2m_e}\{\hat{\boldsymbol{\sigma}} \cdot (\hat{\boldsymbol{p}} + e\boldsymbol{A}(\boldsymbol{r},t))\}^2 - e\varphi(\boldsymbol{r},t) + V(\boldsymbol{r})} \tag{10.62}$$

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[5] See, for instance, Refs. [18] or [27] in the bibliography.

where $\hat{\boldsymbol{\sigma}}$ is the dimensionless spin vector defined by Eq. (10.26), i. e.,

$$\hat{\boldsymbol{\sigma}} = (\hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z). \tag{10.63}$$

Thus, the effect of the spin is to modify the first term in the Hamiltonian (10.59).

We shall now show that the modification is illusory when $\boldsymbol{A}$ is zero. For in that case the first term merely contains the operator $(\hat{\boldsymbol{\sigma}} \cdot \hat{\boldsymbol{p}})^2$, for which we get

$$\begin{aligned}(\hat{\boldsymbol{\sigma}} \cdot \hat{\boldsymbol{p}})^2 &= (\hat{\sigma}_x\hat{p}_x + \hat{\sigma}_y\hat{p}_y + \hat{\sigma}_z\hat{p}_z)^2 \\ &= \hat{\sigma}_x^2\hat{p}_x^2 + \hat{\sigma}_y^2\hat{p}_y^2 + \hat{\sigma}_z^2\hat{p}_z^2 + (\hat{\sigma}_x\hat{\sigma}_y + \hat{\sigma}_y\hat{\sigma}_x)\hat{p}_x\hat{p}_y \\ &\quad + (\hat{\sigma}_y\hat{\sigma}_z + \hat{\sigma}_z\hat{\sigma}_y)\hat{p}_y\hat{p}_z + (\hat{\sigma}_z\hat{\sigma}_x + \hat{\sigma}_x\hat{\sigma}_z)\hat{p}_z\hat{p}_x,\end{aligned} \tag{10.64}$$

where we have used that $\hat{p}_x\hat{p}_y = \hat{p}_y\hat{p}_x$, etc. The right-hand side of this equation looks complicated enough, but because of the anticommutation relations (10.39)—or more explicitly, because of the relations (10.37) and the first set of the relations (10.35)—we simply get that

$$(\hat{\boldsymbol{\sigma}} \cdot \hat{\boldsymbol{p}})^2 = \hat{p}^2. \tag{10.65}$$

Thus, the Hamiltonians (10.59) and (10.62) are identical when $\boldsymbol{A}$ vanishes.

The relation (10.65) is a special case of the more general relation

$$(\hat{\boldsymbol{\sigma}} \cdot \hat{\boldsymbol{a}})(\hat{\boldsymbol{\sigma}} \cdot \hat{\boldsymbol{b}}) = \hat{\boldsymbol{a}} \cdot \hat{\boldsymbol{b}} + i\hat{\boldsymbol{\sigma}} \cdot (\hat{\boldsymbol{a}} \times \hat{\boldsymbol{b}}), \tag{10.66}$$

where $\hat{\boldsymbol{a}}$ and $\hat{\boldsymbol{b}}$ are arbitrary vector operators. To verify this relation, expand $(\hat{\boldsymbol{\sigma}} \cdot \hat{\boldsymbol{a}})(\hat{\boldsymbol{\sigma}} \cdot \hat{\boldsymbol{b}})$ and use the relations (10.35):

$$\begin{aligned}(\hat{\boldsymbol{\sigma}} \cdot \hat{\boldsymbol{a}})(\hat{\boldsymbol{\sigma}} \cdot \hat{\boldsymbol{b}}) &= (\hat{\sigma}_x\hat{a}_x + \hat{\sigma}_y\hat{a}_y + \hat{\sigma}_z\hat{a}_z)(\hat{\sigma}_x\hat{b}_x + \hat{\sigma}_y\hat{b}_y + \hat{\sigma}_z\hat{b}_z) \\ &= \hat{\sigma}_x^2\hat{a}_x\hat{b}_x + \hat{\sigma}_y^2\hat{a}_y\hat{b}_y + \hat{\sigma}_z^2\hat{a}_z\hat{b}_z + \hat{\sigma}_x\hat{\sigma}_y\hat{a}_x\hat{b}_y + \hat{\sigma}_y\hat{\sigma}_x\hat{a}_y\hat{b}_x \\ &\quad + \hat{\sigma}_x\hat{\sigma}_z\hat{a}_x\hat{b}_z + \hat{\sigma}_z\hat{\sigma}_x\hat{a}_z\hat{b}_x + \hat{\sigma}_y\hat{\sigma}_z\hat{a}_y\hat{b}_z + \hat{\sigma}_z\hat{\sigma}_y\hat{a}_z\hat{b}_y \\ &= \hat{a}_x\hat{b}_x + \hat{a}_y\hat{b}_y + \hat{a}_z\hat{b}_z + i\hat{\sigma}_z(\hat{a}_x\hat{b}_y - \hat{a}_y\hat{b}_x) \\ &\quad + i\hat{\sigma}_y(\hat{a}_z\hat{b}_x - \hat{a}_x\hat{b}_z) + i\hat{\sigma}_x(\hat{a}_y\hat{b}_z - \hat{a}_z\hat{b}_y) \\ &= \hat{\boldsymbol{a}} \cdot \hat{\boldsymbol{b}} + i\hat{\boldsymbol{\sigma}} \cdot (\hat{\boldsymbol{a}} \times \hat{\boldsymbol{b}}).\end{aligned} \tag{10.67}$$

As the form of Eq. (10.62) shows, we need the relation (10.66) if $\boldsymbol{A}$ is different from zero (with $\hat{\boldsymbol{a}} = \hat{\boldsymbol{b}}$ in the relation). We get

$$\{\hat{\boldsymbol{\sigma}} \cdot (\hat{\boldsymbol{p}} + e\boldsymbol{A}(\boldsymbol{r}, t))\}^2 = (\hat{\boldsymbol{p}} + e\boldsymbol{A}(\boldsymbol{r}, t))^2 + ie\hat{\boldsymbol{\sigma}} \cdot (\hat{\boldsymbol{p}} \times \hat{\boldsymbol{A}} + \hat{\boldsymbol{A}} \times \hat{\boldsymbol{p}}), \tag{10.68}$$

where we have used that $\hat{\boldsymbol{p}} \times \hat{\boldsymbol{p}}$ and $\boldsymbol{A} \times \boldsymbol{A}$ vanish.

We now note that

$$\begin{aligned}(\hat{\boldsymbol{p}} \times \hat{\boldsymbol{A}})_x + (\hat{\boldsymbol{A}} \times \hat{\boldsymbol{p}})_x &= (\hat{p}_y \hat{A}_z - \hat{p}_z \hat{A}_y) + (\hat{A}_y \hat{p}_z - \hat{A}_z \hat{p}_y) \\ &= \left\{ \hat{A}_z \hat{p}_y - i\hbar \frac{\partial A_z}{\partial y} - \hat{A}_y \hat{p}_z + i\hbar \frac{\partial A_y}{\partial z} \right\} \\ &\quad + (\hat{A}_y \hat{p}_z - \hat{A}_z \hat{p}_y) = -i\hbar (\nabla \times \boldsymbol{A})_x,\end{aligned} \tag{10.69}$$

etc. But $\nabla \times \boldsymbol{A} = \boldsymbol{B}$, according to the first of the relations (10.50). When this result is inserted into Eq. (10.68), we find that the Hamiltonian (10.62) may be written

$$\hat{H} = \frac{1}{2m_e}(\hat{\boldsymbol{p}} + e\boldsymbol{A}(\boldsymbol{r},t))^2 + \frac{e\hbar}{2m_e}\hat{\boldsymbol{\sigma}} \cdot \boldsymbol{B}(\boldsymbol{r},t) - e\varphi(\boldsymbol{r},t) + V(\boldsymbol{r}). \tag{10.70}$$

This Hamiltonian differs from the Hamiltonian (10.59) by the term containing $\hat{\boldsymbol{\sigma}} \cdot \boldsymbol{B}(\boldsymbol{r},t)$.

By reintroducing the original spin $\hat{\boldsymbol{s}}$ by Eq. (10.26), we get

$$\boxed{\hat{H} = \frac{1}{2m_e}(\hat{\boldsymbol{p}} + e\boldsymbol{A}(\boldsymbol{r},t))^2 + \frac{e}{m_e}\hat{\boldsymbol{s}} \cdot \boldsymbol{B}(\boldsymbol{r},t) - e\varphi(\boldsymbol{r},t) + V(\boldsymbol{r})} \tag{10.71}$$

This expression holds for arbitrary external fields. If, however, the external fields are constant and uniform, then we may again perform the reduction that led to Eq. (10.61), and we get

$$\boxed{\hat{H} = \frac{\hat{p}^2}{2m_e} + V(\boldsymbol{r}) + \frac{e}{2m_e}\hat{\boldsymbol{l}} \cdot \boldsymbol{B} + \frac{e}{m_e}\hat{\boldsymbol{s}} \cdot \boldsymbol{B} + e\boldsymbol{r} \cdot \boldsymbol{E} + \frac{e^2}{8m_e}(\boldsymbol{B} \times \boldsymbol{r})^2} \tag{10.72}$$

10.4.3 The Refined Hamiltonian

The Hamiltonian (10.72) is the correct non-relativistic Hamiltonian for an electron in constant and uniform external fields. But because electrons may move at quite high speeds in the interior of an atom—in particular when the nuclear charge is large—there are many situations for which a purely non-relativistic description does not suffice. In very precise work, it is becoming increasingly common to introduce the Dirac equation in such cases, but often one may go a long way by simply adopting the Hamiltonian (10.72) with a single relativistic correction term which accounts for the so-called *spin-orbit coupling*. The term may be derived from the Dirac equation, and for a central field problem it has the following form

$$\boxed{\widehat{H}_{\mathrm{so}} = \xi(r)\hat{\boldsymbol{s}}\cdot\hat{\boldsymbol{l}}} \tag{10.73}$$

where $\xi(r)$ is derived from the potential-energy function $V(r)$,

$$\xi(r) = \frac{1}{2m_e^2c^2}\frac{1}{r}\frac{dV(r)}{dr}\,. \tag{10.74}$$

For a hydrogen-like atom, we insert the Coulomb expression (2.65) for $V(r)$ and get

$$\xi(r) = \frac{Ze^2}{8\pi\epsilon_0 m_e^2c^2}\frac{1}{r^3}\,. \tag{10.75}$$

With the spin-orbit term included, we may write the Hamiltonian on the following form

$$\boxed{\widehat{H} = \widehat{H}_0 + \widehat{H}_{\mathrm{so}} + e\boldsymbol{r}\cdot\boldsymbol{E} + \frac{e}{2m_e}\hat{\boldsymbol{l}}\cdot\boldsymbol{B} + \frac{e}{m_e}\hat{\boldsymbol{s}}\cdot\boldsymbol{B} + \widehat{H}_{\mathrm{diam}}} \tag{10.76}$$

where $\widehat{H}_0$ is the "zero order Hamiltonian" (10.47) and we have denoted the last term in Eq. (10.72) by $\widehat{H}_{\mathrm{diam}}$,

$$\widehat{H}_{\mathrm{diam}} = \frac{e^2}{8m_e}(\boldsymbol{B}\times\boldsymbol{r})^2. \tag{10.77}$$

It is quadratic in $\boldsymbol{B}$ and gives rise to the phenomenon of diamagnetism. Hence it is called the diamagnetic term. If, for instance, the z-axis is chosen to point along the $\boldsymbol{B}$ direction it simplifies to

$$\widehat{H}_{\mathrm{diam}} = \frac{e^2}{8m_e}B^2(x^2+y^2). \tag{10.78}$$

Apart from this, the form of the Hamiltonian (10.76) gives occasion for the following interpretative comments.

The term $e\boldsymbol{E}\cdot\boldsymbol{r}$ represents the interaction between the external electric field and the charge of the electron. By the prescription (3.2), it gives the familiar electric force

$$\boldsymbol{F} = -\nabla(e\boldsymbol{E}\cdot\boldsymbol{r}) = -e\boldsymbol{E}. \tag{10.79}$$

The direction of the force is opposite to that of the electric field, because the electron is negatively charged (the symbol e is as usual understood to represent the *positive* elementary charge).

In classical electrodynamics, an electric dipole is a vector quantity whose potential energy in an electric field is

$$H' = -\boldsymbol{d} \cdot \boldsymbol{E}, \tag{10.80}$$

where $\boldsymbol{d}$ is the electric moment of the dipole. The term $e\boldsymbol{E} \cdot \boldsymbol{r}$ has, therefore, the form of the interaction between an electric dipole

$$\boldsymbol{d} = -e\boldsymbol{r} \tag{10.81}$$

and the electric field $\boldsymbol{E}$.

Similarly, a magnetic dipole is a vector quantity whose potential energy in a magnetic field is

$$H' = -\boldsymbol{\mu} \cdot \boldsymbol{B}, \tag{10.82}$$

with $\boldsymbol{\mu}$ being the magnetic moment of the dipole. The terms $(e/2m_e)\hat{\boldsymbol{l}} \cdot \boldsymbol{B}$ and $(e/m_e)\hat{\boldsymbol{s}} \cdot \boldsymbol{B}$ may, therefore, be said to represent the interaction between the magnetic field and the two dipoles

$$\hat{\boldsymbol{\mu}}_{\text{orbit}} = -\frac{e}{2m_e}\hat{\boldsymbol{l}} \tag{10.83}$$

and

$$\hat{\boldsymbol{\mu}}_{\text{spin}} = -\frac{e}{m_e}\hat{\boldsymbol{s}}. \tag{10.84}$$

The presence of an orbital angular momentum, $\hat{\boldsymbol{l}}$, is seen to imply the presence of a corresponding magnetic moment proportional to $\hat{\boldsymbol{l}}$. The factor of proportionality is called the *gyromagnetic ratio*, and is usually denoted by γ. Thus, we have

$$\gamma = -\frac{e}{2m_e} = -8.79411 \times 10^{10}\,\mathrm{Hz\,T^{-1}}. \tag{10.85}$$

Its negative sign indicates that $\hat{\boldsymbol{l}}$ and $\hat{\boldsymbol{\mu}}_{\text{orbit}}$ are antiparallel.

The spin, $\hat{\boldsymbol{s}}$, also has a magnetic moment associated with it. The magnetic moment is proportional to $\hat{\boldsymbol{s}}$, but the factor of proportionality is twice as large as that for the orbital motion.

By summing an equation like Eq. (10.72) over several electrons, it is readily seen that the total orbital-angular momentum of a many-electron system, as defined by Eq. (10.8), defines a magnetic moment proportional to it, with the same gyromagnetic ratio as in Eq. (10.85). Generally, one finds that a system of particles with a common charge-to-mass ratio, q/m, may be characterized by a gyromagnetic ratio equal to $q/2m$. In view of this, it is remarkable that the gyromagnetic ratio associated with the spin of the electron equals $-e/m_e$ rather than $-e/2m_e$. The derivation that we have presented above gives the origin of this difference. It simply arises because the spin enters into the Hamiltonian (10.62) in a different way than the orbital motion does.

In proceeding, let us replace Eq. (10.76) by the expression

$$\boxed{\hat{H} = \hat{H}_0 + \hat{H}_{\mathrm{so}} + e\boldsymbol{r} \cdot \boldsymbol{E} + \mu_{\mathrm{B}} \tfrac{1}{\hbar} \left(\hat{\boldsymbol{l}} + g_s \hat{\boldsymbol{s}}\right) \cdot \boldsymbol{B} + \hat{H}_{\mathrm{diam}}} \tag{10.86}$$

Here, we have introduced the natural unit of magnetism, the *Bohr magneton* which we already met in Sec. 1.7,

$$\boxed{\mu_{\mathrm{B}} = \frac{e\hbar}{2m_e} = 9.27402 \times 10^{-24}\,\mathrm{J\,T^{-1}}} \tag{10.87}$$

We have also introduced the dimensionless quantity g_s which is called the *g-factor*, or the *g-value*, of the electron spin. According to Eq. (10.76), and also according to the Dirac equation, g_s must equal 2, but a more precise value is in fact

$$\boxed{g_s = 2.0023193044.} \tag{10.88}$$

The reason for the small deviation from the value 2 is that even the Dirac equation has its limitations. These limitations are that the Dirac theory describes the electromagnetic field by its scalar potential and its vector potential just as we have done above. An electromagnetic field is, however, also a quantum system, with its own degrees of freedom. The field potentials and the field vectors $\boldsymbol{E}$ and $\boldsymbol{B}$ are therefore operators in *quantum electrodynamics*, and when we say that the fields vanish, this merely implies that the expectation values of the operators corresponding to $\boldsymbol{E}$ and $\boldsymbol{B}$ vanish. There are, however, uncertainties associated with the field vectors, and these uncertainties will always be different from zero, because the general uncertainty relation (5.121) holds in all branches of quantum mechanics. An electron senses the fluctuations causing the nonvanishing uncertainties and even has an influence upon them.

When the quantum fluctuations of the electromagnetic field are properly taken into account, one ends up with the g-value of Eq. (10.88), with its eleven significant figures. The theoretical value has been confirmed by extremely precise measurements that have been conducted more or less simultaneously with the advanced calculations. The calculation of the g-value is one of the great triumphes of modern physics, because it confirms the validity of quantum electrodynamics which, in turn, is the prototype of modern field theories for elementary particles and their interactions.

The intrinsic magnetic moment of the electron is often called *anomalous*, either because the g-factor is 2 rather than 1 (as it is for orbital motion), or because the g-factor is not exactly equal to 2 (as it is in the Dirac theory).

Let us now turn to the spin-orbit term (10.73). It emerges in a natural way from the Dirac theory, when that theory is compared with the Schrödinger theory by means of a series expansion in $1/c$.[6] But its form may also be obtained by an analysis based on classical mechanics, by the following arguments.

In the central field described by the potential $V(r)$ of Eq. (10.47), an electron at rest will experience an electric field $\boldsymbol{E} = -\frac{1}{(-e)}\nabla V(r)$, but no magnetic field. A moving electron will, however, also experience a certain magnetic field due to $V(r)$, according to the theory of relativity. The magnetic moment of the electron must interact with this field in a similar way as it interacts with an external magnetic field. But when the interaction is actually calculated, one finds twice the value given by the expressions (10.73) and Eq. (10.74). In other words, one only obtains the correct result by using a g-value of 1 instead of 2. A more careful analysis is, however, able to explain why this is so by realizing that an orbital electron is an accelerated electron; the direction of its velocity changes all the time. As shown by the English physicist Llewellyn Hilleth Thomas,[7] the acceleration causes a precession of the spin, and it is this precession that leads to a formal reduction of the g-value from 2 to 1.[8]

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[6] The expansion also contains other terms of the same order as the spin-orbit term, and in very accurate work these terms may not be ignored.

[7] L. H. Thomas, Nature **117**, 514 (1926).

[8] The reader who, as a splendid exercise in special relativity, wants to verify the expression (10.73) is recommended to consult Ref. [19] in the bibliography, where a comprehensive treatment of the problem is presented.

10.5 The Zeeman Effect

With reference to the Hamiltonian (10.86), let us now briefly consider the energetic effects of the spin-orbit term $\widehat{H}_{\mathrm{so}}$ and the term

$$\widehat{H}_Z = \mu_{\mathrm{B}}\tfrac{1}{\hbar}(\hat{\boldsymbol{l}} + g_s\hat{\boldsymbol{s}}) \cdot \boldsymbol{B}. \tag{10.89}$$

which is customarily referred to as the *Zeeman term.* We shall neglect the effect of the diamagnetic term and assume that the electric field is zero.

It is convenient to choose the z-axis in the direction of the magnetic field, so that $\boldsymbol{B}$ may be written

$$\boldsymbol{B} = (0, 0, B). \tag{10.90}$$

The Zeeman term becomes then

$$\widehat{H}_Z = \mu_{\mathrm{B}}B\tfrac{1}{\hbar}(\hat{l}_z + 2\hat{s}_z). \tag{10.91}$$

We have put g_s equal to 2 as an excellent approximation.

Let us begin by also neglecting the spin-orbit term, so that the Zeeman term is the only correction to $\widehat{H}_0$. We then choose the eigenfunctions of $\widehat{H}_0$ on the form (10.24), for they are then also eigenfunctions of $\hat{l}_z$ and $\hat{s}_z$, and hence of $\widehat{H}_Z$ as well. We get

$$\left\{\begin{array}{l} (\widehat{H}_0 + \widehat{H}_Z)\psi_{n\ell m_\ell m_s}(x) = \{E_0 + \mu_{\mathrm{B}}B(m_\ell + 2m_s)\}\,\psi_{n\ell m_\ell m_s}(x), \\ E = E_0 + \mu_{\mathrm{B}}B(m_\ell + 2m_s). \end{array}\right. \tag{10.92}$$

Thus, the $2(2\ell + 1)$ fold degenerate level with the *zero-order energy* E_0 is split into several components with different energies. We find, for instance, that a p level ($\ell = 1$) is split into five components, of which four are non-degenerate and one is doubly degenerate. An s level ($\ell = 0$) is split into two non-degenerate components. This splitting of levels is known as the *Zeeman effect.* More specifically, we are considering the *strong-field case* because $\widehat{H}_{\mathrm{so}}$ has been neglected.

The just mentioned splitting of s and p levels is illustrated in Table 10.1. We see that, if we introduce the energy quantity

$$\Delta E = \mu_{\mathrm{B}}B, \tag{10.93}$$

then the separation between neighboring components becomes ΔE for the p level and $2\Delta E$ for the s level. With $B = 0.5\,\mathrm{T}$ as an experimentally realistic choice, and with the value of μ_{B} taken from Eq. (10.87), we get

$$\Delta E = 0.5 \times 9.27402 \times 10^{-24}\,\mathrm{J} = 4.63701 \times 10^{-24}\,\mathrm{J}, \tag{10.94}$$

Table 10.1: The Zeeman Effect, Strong-Field Case.(See Eq. (10.58))

(ℓ, m_ℓ, m_s)	$(m_\ell + 2m_s)$
$(0, 0, \frac{1}{2})$	1
$(0, 0, -\frac{1}{2})$	−1
$(1, 1, \frac{1}{2})$	2
$(1, 0, \frac{1}{2})$	1
$(1, -1, \frac{1}{2})$	0
$(1, 1, -\frac{1}{2})$	0
$(1, 0, -\frac{1}{2})$	−1
$(1, -1, -\frac{1}{2})$	−2

or

$$\frac{\Delta E}{h} = 6.9981 \times 10^9\,\text{Hz}, \qquad \frac{\Delta E}{hc} = 0.23343\,\text{cm}^{-1}. \tag{10.95}$$

This is a very small energy separation as compared with normal energy separations between levels of the Hamiltonian $\widehat{H}_0$. Thus, the energy separation between the $n = 2$ and $n = 3$ levels of the hydrogen atom corresponds to $15241\,\text{cm}^{-1}$. The Zeeman effect is, for instance, exploited in *electron spin resonance* (ESR) experiments, where a sample containing "free" electrons is subjected to a uniform magnetic field in the Tesla region and, simultaneously, an oscillating electromagnetic field in the GHz region (1 GHz = 10^9 Hz).

If we don't neglect the spin-orbit term as we have done above, then we have a more complicated situation, except for s levels which are unaffected by $\widehat{H}_{\text{so}}$ because $(\hat{l}_x, \hat{l}_y, \hat{l}_z)Y_{00} = (0, 0, 0)$. Levels with $\ell \neq 0$ are split into two new levels by $\widehat{H}_{\text{so}}$. They may be characterized by their j-values, $j = \ell \pm \frac{1}{2}$. Here, j is the angular-momentum quantum number corresponding to the angular momentum $\hat{\boldsymbol{j}} = \hat{\boldsymbol{l}} + \hat{\boldsymbol{s}}$. The wavefunctions of the new levels may be determined by procedures for coupling of angular momenta. Having determined these wavefunctions, the effect of the Zeeman term may be found by *perturbation theory*, provided the spin-orbit effect dominates (the *weak-field case*). Otherwise, the spin-orbit term and the Zeeman term must be treated together by means of perturbation theory or the *variational method* (the intermediate case). We have not yet discussed the procedures mentioned, so we shall not consider the effects of the spin-orbit term and the Zeeman term further, but only mention that the spin-orbit splittings are very small for light atoms but appreciable for heavier atoms. Thus, the splittings in hydrogen are of the order of fractions of a cm^{-1}. It is of the order of hundreds of cm^{-1} in iron, and much larger for very heavy atoms. For hydrogenic ions, the expression (10.76) for $\xi(r)$ leads to a Z^4 dependence of the splittings.

Let us finally mention that the term $e\boldsymbol{r}\cdot\boldsymbol{E}$ in the Hamiltonian (10.86) gives rise to the so-called *Stark effect* which may likewise be studied by perturbation theory or the variational method (cf. Problem 12.3).

10.6 The Pauli Equation

In the previous sections, we have constructed the spin terms in the Hamiltonian for an electron in an external field by referring to the Dirac equation. In this description, the electron acquires an anomalous magnetic moment because of the special way the spin enters into the Hamiltonian (10.62). The Dirac equation was set up in 1928. The spin had, however, already been introduced by Uhlenbeck and Goudsmit in 1925, and Schrödinger presented his equation in 1926. Needless to say, it was felt urgent to modify Schrödinger's equation so that it would also describe the effects due to spin. The modification came soon and was due to Pauli.[9] He introduced the spin operators and their commutation relations, and by accepting the anomalous moment as an empirical fact he constructed what has become known as the *Pauli equation*. It may be reproduced from the equations above by replacing the spin operators by a set of two-by-two matrices and the spin functions by two-dimensional column vectors.

Let us put $\boldsymbol{E}=0$ in the Hamiltonian (10.86) and neglect the diamagnetic term. Let us also put $g_s = 2$, $\hat{\boldsymbol{l}} = \hbar\hat{\boldsymbol{\ell}}$, $\hat{\boldsymbol{s}} = \frac{\hbar}{2}\hat{\boldsymbol{\sigma}}$, and insert the resulting Hamiltonian in the Schrödinger equation set up in Eq. (10.18). With the expression (10.17) inserted for $\psi(\boldsymbol{r},\varsigma)$, this gives

$$\begin{aligned}\left\{\widehat{H}_0+\widehat{H}_{\rm so}+\mu_{\rm B}\hat{\boldsymbol{\ell}}\cdot\boldsymbol{B}+\mu_{\rm B}\hat{\boldsymbol{\sigma}}\cdot\boldsymbol{B}\right\}&\{\varphi_1(\boldsymbol{r})\alpha(\varsigma)+\varphi_2(\boldsymbol{r})\beta(\varsigma)\}\\&=E\{\varphi_1(\boldsymbol{r})\alpha(\varsigma)+\varphi_2(\boldsymbol{r})\beta(\varsigma)\}\,. \qquad (10.96)\end{aligned}$$

By referring to the general discussion on matrix algebra in Sec. 5.10, and in particular to the setup of Eq. (5.161), we may convert this equation into a matrix equation containing the Pauli spin matrices (10.43). This goes in a similar way as Eq. (10.45) was converted into the matrix equation (10.46), at

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[9] W. Pauli, Z. Phys. **43**, 601 (1926).

the end of Sec. 10.3. The operator $\hat{\boldsymbol{\sigma}} \cdot \boldsymbol{B}$ is thus replaced by the matrix

$$\boldsymbol{\sigma} \cdot \boldsymbol{B} = \boldsymbol{\sigma}_x B_x + \boldsymbol{\sigma}_y B_y + \boldsymbol{\sigma}_z B_z = \begin{pmatrix} B_z & B_x - iB_y \\ B_x + iB_y & -B_z \end{pmatrix}, \tag{10.97}$$

and the operator $\widehat{H}_{\mathrm{so}}$ is replaced by the matrix

$$\begin{aligned} \boldsymbol{H}_{\mathrm{so}} &= \frac{\hbar^2}{2}\xi(r)\left(\boldsymbol{\sigma}_x \hat{\ell}_x + \boldsymbol{\sigma}_y \hat{\ell}_y + \boldsymbol{\sigma}_z \hat{\ell}_z\right) \\ &= \frac{\hbar^2}{2}\xi(r)\begin{pmatrix} \hat{\ell}_z & \hat{\ell}_x - i\hat{\ell}_y \\ \hat{\ell}_x + i\hat{\ell}_y & -\hat{\ell}_z \end{pmatrix}. \end{aligned} \tag{10.98}$$

Hence, Eq. (10.96) becomes

$$\begin{aligned} &\begin{pmatrix} \widehat{H}_0 & 0 \\ 0 & \widehat{H}_0 \end{pmatrix}\begin{pmatrix} \varphi_1(\boldsymbol{r}) \\ \varphi_2(\boldsymbol{r}) \end{pmatrix} + \frac{\hbar^2}{2}\xi(r)\begin{pmatrix} \hat{\ell}_z & \hat{\ell}_x - i\hat{\ell}_y \\ \hat{\ell}_x + i\hat{\ell}_y & -\hat{\ell}_z \end{pmatrix}\begin{pmatrix} \varphi_1(\boldsymbol{r}) \\ \varphi_2(\boldsymbol{r}) \end{pmatrix} \\ &\quad + \mu_{\mathrm{B}}\begin{pmatrix} B_z & B_x - iB_y \\ B_x + iB_y & -B_z \end{pmatrix}\begin{pmatrix} \varphi_1(\boldsymbol{r}) \\ \varphi_2(\boldsymbol{r}) \end{pmatrix} = E\begin{pmatrix} \varphi_1(\boldsymbol{r}) \\ \varphi_2(\boldsymbol{r}) \end{pmatrix}. \end{aligned} \tag{10.99}$$

This is Pauli's equation.[10] It is, of course, equivalent to Eq. (10.96), but the spin-orbital $\varphi_1(\boldsymbol{r})\alpha(\varsigma) + \varphi_2(\boldsymbol{r})\beta(\varsigma)$ has been replaced by the *two-component wavefunction* $(\varphi_1(\boldsymbol{r}), \varphi_2(\boldsymbol{r}))$, often referred to as a *Pauli spinor*.

10.7 Angular-Momentum Theory and Rotations

In closing this chapter, we point out that there is a close connection between angular-momentum theory and the group theory of rotations. This connection implies that the behavior of an angular-momentum eigenfunction under rotations is entirely determined by the values of its angular-momentum quantum numbers. It is, in particular, independent of the type of coordinates upon which the function depends.

To illustrate the connection, let $\hat{R}_z(u)$ be the operator that performs a rotation, u, about the z-axis. It can then be shown that

$$\hat{R}_z(u)|JM\rangle = e^{-iuM}|JM\rangle, \tag{10.100}$$

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[10] Actually, Pauli also introduced a relativistic modification of the $\widehat{H}_0$ term, but it was an incomplete modification and is hence ignored.

no matter which system the ket $|JM\rangle$ represents. A rotation through 2π gives, in particular,

$$\hat{R}_z(2\pi)|JM\rangle = e^{-2\pi i M}|JM\rangle. \tag{10.101}$$

The relation (10.101) has a very important consequence, for it shows that

$$\hat{R}_z(2\pi)|JM\rangle = \begin{cases} +|JM\rangle, & M = 0, \pm 1, \pm 2, \ldots \\ -|JM\rangle, & M = \pm\frac{1}{2}, \pm\frac{3}{2}, \pm\frac{5}{2}, \ldots \end{cases} \tag{10.102}$$

As might be expected, there is a similar result for a rotation through 2π about any axis. This allows us to replace M by J in Eq. (10.102). So, we have the more general result

$$\hat{R}_z(2\pi)|JM\rangle = \begin{cases} +|JM\rangle, & J = 0, 1, 2, \ldots \\ -|JM\rangle, & J = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots \end{cases} \tag{10.103}$$

Thus, angular-momentum kets with integral J-values remain unchanged after a rotation through 2π, whereas angular-momentum kets with half-integral J-values change sign.

For half-integral J-values, this result violates the requirement that acceptable wavefunctions must be single-valued (cf. Sec. 3.2). This requirement seemed perfectly reasonable, yet we may replace it by the milder one without having to change the formalism that we have developed so far. For when we extract physical information from wavefunctions, and when we construct matrix elements of operators, we always work with combinations like $\psi_1^*(q)\psi_2(q)$. So all that we really need require is that such combinations remain single-valued, and this will obviously be the case when ψ_1 and ψ_2 behave similarly under a rotation through 2π, i. e., they must both remain unchanged or both change sign.

We conclude from the above discussion that the spin function of a fermion must change sign during a rotation through 2π about any axis. The spin function of a boson remains, however, unchanged. This interesting behavior of the elementary particles has been fully verified, but due to the complexity of the experiments only fairly recently.[11]

With our new knowledge, we have to reexamine the argument of Sec. 8.3.2, according to which the m-value associated with an orbital angular momentum

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[11] H. Rauch, A. Zeilinger, G. Badurek, A. Wilfing, W. Bauspiess, and U. Bonse, Phys. Lett. A **54**, 425 (1975).
S. A. Werner, R. Corella, A. W. Overhauser, and C. E. Eagen, Phys. Rev. Lett. **35**, 1053 (1975).

must be integral because of the requirement that $Y(\theta, \phi + 2\pi) = Y(\theta, \phi)$. So let us for the time being assume that it is possible to find "surface spherical harmonics" with half-integral ℓ and m. We then go through the first part of Sec. 8.3.2 again and conclude that also the new functions must have the form (8.46), but m is now half-integral. Thus, there must exist $2\ell + 1$ functions of the form (8.83). To determine the form of the functions $\Theta_{\ell m}(\theta)$, we proceed as in Sec. 8.3.6. We find again Eq. (8.86), but when we start to operate with the $\hat{\ell}_+$ operator to determine the remaining 2ℓ functions, we sooner or later create functions with singularitites. What this means is, that we can easily construct eigenfunctions of $\hat{\ell}_z$ with half-integral m-values, but these functions do not behave properly under the action of $\hat{\ell}_x$ and $\hat{\ell}_y$.

As a simple example, let us write

$$Y_{\frac{1}{2},-\frac{1}{2}}(\theta, \phi) = A \sin^{\frac{1}{2}} \theta e^{-i\phi/2} \tag{10.104}$$

and then try to apply the step-up operator in the form (8.57). The result is readily found to be

$$\hat{\ell}_+ Y_{\frac{1}{2},-\frac{1}{2}}(\theta, \phi) = A \frac{\cos \theta}{\sin^{\frac{1}{2}} \theta} e^{i\phi/2}. \tag{10.105}$$

This function has singularities at $\theta = 0$ and $\theta = \pi$ and is therefore not an acceptable function.

The above discussion leads again to the result that wavefunctions which solely depend upon the spatial variables must always be single-valued. But the spatial degrees of freedom taken alone do not suffice for a proper description of an elementary particle. It is essential that we also include the spin, and with spin included we do in fact encounter functions that change sign during a rotation through 2π.

With this and the previous two chapters we have discussed the most important aspects of the one-electron central-field problem and the one-electron spin problem. We shall now turn to the discussion of atoms with more than a single electron.

Supplementary Reading

The bibliography, entries [4], [8], [11], [18], [19], [22], [23], [24], [26], and [27] .

Problems

10.1. In connection with the general definition of an angular momentum, Eq. (10.1), we wrote:

$$\hat{\boldsymbol{J}} = (\hat{J}_x, \hat{J}_y, \hat{J}_z),$$

implying that $\hat{J}_x$, $\hat{J}_y$ and $\hat{J}_z$ are the components of the angular-momentum vector $\hat{\boldsymbol{J}}$ along the three coordinate axes. In accordance with this, we have that the component of $\hat{\boldsymbol{J}}$ along an arbitrary axis defined by the unit vector

$$\boldsymbol{n} = (n_x, n_y, n_z), \quad n_x^2 + n_y^2 + n_z^2 = 1,$$

is given by the operator

$$\boldsymbol{n} \cdot \hat{\boldsymbol{J}} = n_x \hat{J}_x + n_y \hat{J}_y + n_z \hat{J}_z.$$

It is, therefore, of interest to derive an expression for the commutation relation $[\boldsymbol{n}_1 \cdot \hat{\boldsymbol{J}},\, \boldsymbol{n}_2 \cdot \hat{\boldsymbol{J}}]$, where $\boldsymbol{n}_1$ and $\boldsymbol{n}_2$ are two arbitrary unit vectors. Show that

$$\left[\boldsymbol{n}_1 \cdot \hat{\boldsymbol{J}},\, \boldsymbol{n}_2 \cdot \hat{\boldsymbol{J}}\right] = i\hbar\, (\boldsymbol{n}_1 \times \boldsymbol{n}_2) \cdot \hat{\boldsymbol{J}}.$$

10.2. The spin functions $\alpha(\varsigma)$ and $\beta(\varsigma)$ are *eigenfunctions* of the operators $\hat{s}^2$ and $\hat{s}_z$.

a. Determine the corresponding normalized eigenfunctions of $\hat{s}^2$ and $\hat{s}_x$.

b. Similarly, determine the normalized eigenfunctions of $\hat{s}^2$ and $\hat{s}_y$.

Hint: Add and subtract suitable pairs of relations in the set (10.30).

10.3. Consider the spin function

$$\eta(\varsigma) = e^{i\delta} \left\{ \cos{(u/2)}\alpha(\varsigma) + e^{iv} \sin{(u/2)}\beta(\varsigma) \right\}$$

where $e^{i\delta}$ is an arbitrary phase factor (δ real).

a. Show that $\eta(\varsigma)$ is eigenfunction of the operator $\boldsymbol{n} \cdot \hat{\boldsymbol{s}}$ with eigenvalue $\frac{1}{2}\hbar$, where $\boldsymbol{n}$ is the unit vector

$$\boldsymbol{n} = (\sin u \cos v, \sin u \sin v, \cos u).$$

b. An electron with the above spin function is said to be *polarized* in the direction $\boldsymbol{n}$.
Show that any spin function of the general form (10.16) describes an electron with a uniquely defined direction of polarization.

Chapter 11

The Periodic Table by Electron Counting

Contents

In Sec. 1.2 we described the theory of the chemical atom as it was developed during the nineteenth century. A principal event was the construction of the periodic table of the elements, in 1869. The position of an element in the periodic table is given by its atomic number, Z, and in the beginning of the twentieth century this number was experimentally identified with the number of electrons in the neutral atom, as we discussed it in Sec. 1.6. But it was not until 1921 that it became possible to understand the background for the periodic variation of chemical and physical properties with atomic number.

As we mentioned it in Sec. 2.5, the explanation was given by Niels Bohr who constructed a qualitative model of the many-electron atom, according to which the electrons of the atom were arranged in rings about the nucleus. The proper quantum mechanical substitution for this ring structure is the *shell structure* of the atom. This shell structure, and its correlation with the chemical and physical properties of the elements, is described in most university text books on general chemistry. Accordingly, it primarily remains for us to establish the proper connection with the Schrödinger equation, so this is the aim of the present chapter.

11.1 The Many-Electron Atom

Throughout the present chapter, we shall neglect the spin-orbit coupling effects that we discussed in Sec. 10.4.3. They are relatively small and may always be included later, for instance by perturbation theory. The Schrödinger equation for a hydrogen-like atom with nuclear charge Z is accordingly taken to be

$$\left(-\frac{\hbar^2}{2m_e}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r}\right)\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r}). \tag{11.1}$$

For the present, we shall neglect spin altogether. The bound-state solutions of Eq. (11.1) are then the atomic orbitals (9.54),

$$\psi_{n\ell\gamma_\ell}(\boldsymbol{r}) = R_{n\ell}(r)Y_{\ell\gamma_\ell}(\theta,\phi), \tag{11.2}$$

with the radial functions as given in Table 9.1 and the spherical harmonics as given in Table 8.1 or 8.2. The corresponding energies are given by the Bohr expression (9.18). The energy depends only on the principal quantum number n, and the number of orbitals corresponding to the energy E_n is n^2 (See Eq. (9.57)).

For simplicity of notation, and for convenience in numerical work, we shall now completely adopt the *atomic units* described in Appendix B, i.e., we shall choose the basic units such that m_e, e, $\hbar$, and $4\pi\epsilon_0$ all become equal to one. We may then put a_0 equal to 1 in the expressions for the radial functions of Table 9.1, and Eq. (11.1) becomes

$$\left(-\frac{1}{2}\nabla^2 - \frac{Z}{r}\right)\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r}). \tag{11.3}$$

The operator $-\frac{1}{2}\nabla^2$ represents the kinetic energy of the electron, and $-Z/r$ is the potential energy of the electron in the electrostatic field of the nucleus.

The Bohr expression (9.18) for the energy becomes $E_n = -Z^2/2n^2$, as already emphasized in Sec. 9.5, Eq. (9.56). Figure 9.5 shows the lowest energy levels of the hydrogen atom ($Z = 1$) in atomic units.

For an atom or ion with N electrons and nuclear charge Z we get the Schrödinger equation

$$\boxed{\left\{\sum_{i=1}^{N}\left(-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i}\right) + \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}{}' \frac{1}{r_{ij}}\right\}\Phi = E\Phi} \tag{11.4}$$

where Φ is the many-electron wavefunction,

$$\Phi = \Phi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N). \tag{11.5}$$

We have numbered the electrons from 1 to N and denoted the position vector of the ith electron with respect to the nucleus by $\boldsymbol{r}_i$,

$$\boldsymbol{r}_i = (x_i, y_i, z_i). \tag{11.6}$$

So, the expression for the Laplacian ∇_i^2 becomes

$$\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}. \tag{11.7}$$

r_{ij} is the distance between electron i and electron j,

$$r_{ij} = |\boldsymbol{r}_i - \boldsymbol{r}_j|. \tag{11.8}$$

The prime on the double sum in Eq. (11.4) indicates that terms for which $i = j$ are omitted in the sum. But otherwise i and j run independently from 1 to N, and the sum includes for instance both $1/r_{12}$ and $1/r_{21}$ which are identical. The factor $\frac{1}{2}$ ensures, however, that such two terms only count as one. Thus, the double sum is effectively a sum over pairs,

$$\frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}{}' \frac{1}{r_{ij}} = \sum_{i=1}^{N}\sum_{j>i}^{N} \frac{1}{r_{ij}}. \tag{11.9}$$

In the Schrödinger equation (11.4), the term

$$\boxed{\hat{h}(i) = -\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i}} \tag{11.10}$$

represents the kinetic energy of electron i plus its potential energy in the field of the nucleus. The term $1/r_{ij}$ represents the Coulomb repulsion between electron i and electron j. As usual, the Schrödinger equation may be written in the form

$$\widehat{H}\Phi = E\Phi, \tag{11.11}$$

the Hamiltonian being

$$\boxed{\widehat{H} = \sum_{i=1}^{N} \hat{h}(i) + \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}{}' \frac{1}{r_{ij}}} \tag{11.12}$$

Each (Z, N) pair defines a separate Hamiltonian and a separate Schrödinger equation with its own set of eigenfunctions and energies. But it is only for the hydrogen-like atom ($N = 1$) that the problem may be solved exactly. To determine the electronic structure of all possible atoms and ions is consequently a formidable task. Yet it has by now become possible to calculate good wavefunctions for the lower states of almost any atom or ion, at various levels of approximations. But at present, we shall be content with some fairly qualitative considerations.

11.2 Neglect of Electron-Electron Repulsion

To get a first idea of the form of the solutions of Eq. (11.11), let us neglect the double sum in the Hamiltonian (11.12), i.e., let us replace $\widehat{H}$ by the simpler operator

$$\boxed{\widehat{H}^{(0)} = \sum_{i=1}^{N} \hat{h}(i)} \tag{11.13}$$

and the Schrödinger equation (11.11) by the simpler Schrödinger equation

$$\widehat{H}^{(0)}\Phi^{(0)} = E^{(0)}\Phi^{(0)}. \tag{11.14}$$

This is a great simplification, for Eq. (11.14) may be solved exactly by separation of variables. For if $\varphi_1^0(\boldsymbol{r}), \varphi_2^0(\boldsymbol{r}), \ldots$ are the usual solutions (11.2) of the hydrogen-like equation (11.3) for the appropriate value of Z, with energies $\varepsilon_1^0, \varepsilon_2^0, \ldots$, then the product function

$$\boxed{\Phi^{(0)} = \varphi_{k_1}^0(\boldsymbol{r}_1)\varphi_{k_2}^0(\boldsymbol{r}_2)\cdots\varphi_{k_N}^0(\boldsymbol{r}_N)} \tag{11.15}$$

is a solution of Eq. (11.14) with the energy

$$\boxed{E^{(0)} = \varepsilon_{k_1}^0 + \varepsilon_{k_2}^0 + \ldots + \varepsilon_{k_N}^0} \tag{11.16}$$

for any set of indices $k_1, k_2, \ldots, k_N$. This is easily seen by insertion, which amounts to adding the following set of equations

$$\begin{aligned} \hat{h}(1)\varphi_{k_1}^0(\boldsymbol{r}_1)\varphi_{k_2}^0(\boldsymbol{r}_2)\cdots\varphi_{k_N}^0(\boldsymbol{r}_N) &= \varepsilon_{k_1}^0\varphi_{k_1}^0(\boldsymbol{r}_1)\varphi_{k_2}^0(\boldsymbol{r}_2)\cdots\varphi_{k_N}^0(\boldsymbol{r}_N), \\ \hat{h}(2)\varphi_{k_1}^0(\boldsymbol{r}_1)\varphi_{k_2}^0(\boldsymbol{r}_2)\cdots\varphi_{k_N}^0(\boldsymbol{r}_N) &= \varepsilon_{k_2}^0\varphi_{k_1}^0(\boldsymbol{r}_1)\varphi_{k_2}^0(\boldsymbol{r}_2)\cdots\varphi_{k_N}^0(\boldsymbol{r}_N), \\ \cdots\cdots\cdots\cdots \quad & \quad \cdots\cdots\cdots\cdots \\ \hat{h}(N)\varphi_{k_1}^0(\boldsymbol{r}_1)\varphi_{k_2}^0(\boldsymbol{r}_2)\cdots\varphi_{k_N}^0(\boldsymbol{r}_N) &= \varepsilon_{k_N}^0\varphi_{k_1}^0(\boldsymbol{r}_1)\varphi_{k_2}^0(\boldsymbol{r}_2)\cdots\varphi_{k_N}^0(\boldsymbol{r}_N). \end{aligned} \tag{11.17}$$

Eqs. (11.13)–(11.16) are characteristic for the description of a set of independent particles in quantum mechanics: The Hamiltonian is the sum of the Hamiltonians of the individual particles, and the total energy is the sum of the single energies. The wavefunction is, on the other hand, the *product* of the single- particle wavefunctions.

That the wavefunction is a product implies, in turn, that the N-electron probability distribution is the product of the single-particle distributions. To make the content of this statement clear, let us write

$$dv = dv_1 dv_2 \cdots dv_N, \tag{11.18}$$

with

$$dv_1 = dx_1 dy_1 dz_1,\ dv_2 = dx_2 dy_2 dz_2,\ \cdots, dv_N = dx_N dy_N dz_N. \tag{11.19}$$

Let us then consider a general many-electron function of the type (11.15), say

$$\Phi = \varphi_1(\boldsymbol{r}_1)\varphi_2(\boldsymbol{r}_2)\cdots\varphi_N(\boldsymbol{r}_N), \tag{11.20}$$

where $\varphi_1, \varphi_2, \ldots, \varphi_N$ are N one-electron functions (orbitals). They need not all be different, but each of them is supposed to be normalized to unity. We get then

$$\Phi^*\Phi dv = \varphi_1^*(\boldsymbol{r}_1)\varphi_1(\boldsymbol{r}_1)dv_1 \cdot \varphi_2^*(\boldsymbol{r}_2)\varphi_2(\boldsymbol{r}_2)dv_2 \cdots \varphi_N^*(\boldsymbol{r}_N)\varphi_N(\boldsymbol{r}_N)dv_N, \quad (11.21)$$

and hence,

$$\int \Phi^*\Phi dv = \int \varphi_1^*(\boldsymbol{r}_1)\varphi_1(\boldsymbol{r}_1)dv_1 \cdot \int \varphi_2^*(\boldsymbol{r}_2)\varphi_2(\boldsymbol{r}_2)dv_2 \cdots \int \varphi_N^*(\boldsymbol{r}_N)\varphi_N(\boldsymbol{r}_N)dv_N = 1 \cdot 1 \cdots 1 = 1. \quad (11.22)$$

Eq. (11.22) shows that Φ is normalized to unity, and so we may safely consider $\Phi^*\Phi$ as a probability density. The interpretation of this density is in turn that the quantity

$$\Phi^*\Phi dv = \Phi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)^*\Phi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)dv_1 dv_2 \cdots dv_N \quad (11.23)$$

is the joint probability of observing particle 1 in the volume element dv_1 around the point $\boldsymbol{r}_1$, particle 2 in the volume element dv_2 around the point $\boldsymbol{r}_2$, etc. This interpretation applies whether Φ is a product function or not, but when Φ is in fact a product function of the type (11.20), then the joint probability factors into a product of single-particle probabilities, as shown by Eq. (11.21). In other words, the joint probability distribution is the product of single-particle distributions. *This is the statistical expression of independence.*

Let us now return to the solutions of Eq. (11.14) for our simplified N-electron atom. The expression (9.56) for the energies of a hydrogen-like atom leads to the following expression for the energy $E^{(0)}$ of Eq. (11.16),

$$E^{(0)} = -\frac{Z^2}{2}\left(\frac{1}{n(k_1)^2} + \frac{1}{n(k_2)^2} + \cdots + \frac{1}{n(k_N)^2}\right), \quad (11.24)$$

where $n(k_1)$ is the principal quantum number of the atomic orbital $\varphi^0_{k_1}$, etc. Eq. (11.24) shows that we get the lowest energy by putting all principal quantum numbers equal to 1. The ground-state solution is therefore

$$\Phi^{(0)} = \varphi^0_{1s}(\boldsymbol{r}_1)\varphi^0_{1s}(\boldsymbol{r}_2)\cdots\varphi^0_{1s}(\boldsymbol{r}_N), \qquad E^{(0)} = -\tfrac{1}{2}NZ^2. \quad (11.25)$$

Eq. (11.25) leads, in particular, to the following ground states for the atoms H, He and Li

$$\left\{\begin{array}{ll} \Phi^{(0)}_{\mathrm{H}} = \varphi^0_{1s}(\boldsymbol{r}_1) & E^{(0)}_{\mathrm{H}} = -\frac{1}{2}\,\mathrm{au}, \\ \Phi^{(0)}_{\mathrm{He}} = \varphi^0_{1s}(\boldsymbol{r}_1)\varphi^0_{1s}(\boldsymbol{r}_2), & E^{(0)}_{\mathrm{He}} = -4\,\mathrm{au}, \\ \Phi^{(0)}_{\mathrm{Li}} = \varphi^0_{1s}(\boldsymbol{r}_1)\varphi^0_{1s}(\boldsymbol{r}_2)\varphi^0_{1s}(\boldsymbol{r}_3), & E^{(0)}_{\mathrm{Li}} = -\frac{27}{2}\,\mathrm{au}, \end{array}\right. \quad (11.26)$$

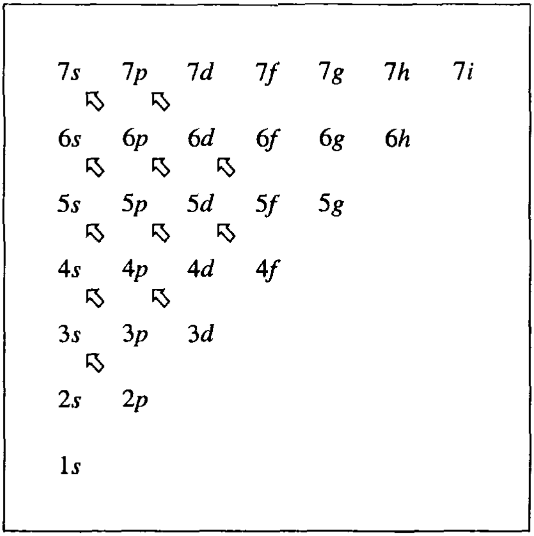

Figure 11.1: The $n + \ell$ rule:
According to Bohr's aufbau principle, electrons are filled into orbitals in the order $1s, 2s, 2p, 3s, 3p, 4s, 3d, \ldots$ No orbital may hold more than two electrons.

where it is understood that the $1s$ functions for H, He and Li are different because of the Z dependence of the radial function $R_{1s}(r)$ (See Table 9.1).

$\Phi_{\mathrm{H}}^{(0)}$, $\Phi_{\mathrm{He}}^{(0)}$ and $\Phi_{\mathrm{Li}}^{(0)}$ are all exact eigenfunctions of the simplified Schrödinger equation (11.14) for the respective values of Z and N. Yet, $\Phi_{\mathrm{H}}^{(0)}$ and $\Phi_{\mathrm{He}}^{(0)}$ are the only ones that are physically acceptable, $\Phi_{\mathrm{Li}}^{(0)}$ is not. It is excluded by the so-called Pauli principle. We discuss this principle below, after a presentation of Bohr's *aufbau principle.*

11.3 The Aufbau Principle

The model of the many-electron atom which Niels Bohr constructed in order to explain the structure of the periodic table was based on detailed spectroscopic and chemical evidence. The principle behind the model is the aufbau principle which implies the following considerations, in the terminology based on orbitals of the central-field form (8.32) rather than the classical orbits used by Bohr.

The formation of an atom may be viewed as the result of successive capture and binding of electrons. Thus, the hydrogen atom is formed when the proton captures a single electron. The electron goes into the energetically lowest orbital which is the $1s$ orbital. We say that the hydrogen atom has the *electron configuration* $1s^1$.

For the helium atom, we start with an atomic nucleus with charge 2 (atomic units). The first electron that is captured goes into the $1s$ orbital, and so does the second electron. The electron configuration of He is accordingly $1s^2$.

Coming to the lithium atom, we start with a nucleus with charge 3. The capture of the first two electrons goes exactly as in helium, but when we come to the third electron, we are taught by spectroscopic evidence that it goes into the $2s$ orbital. Thus, the $1s$ *shell* is found to be *filled*, or *closed*, when it has received two electrons. The electron configuration of Li is therefore $1s^2 2s^1$.

In the beryllium atom, the first three electrons are captured in the same way as in lithium. The fourth electron completes the $2s$ shell. The electron configuration of Be is $1s^2 2s^2$.

Continuing with the heavier atoms, it is always found by spectroscopic and chemical evidence that no orbital can hold more than two electrons. Thus the three $2p$ orbitals can hold at most six electrons. They are filled successively by going through the elements B, C, N, O, F, and Ne. The electron configuration of the neon atom is accordingly $1s^2 2s^2 2p^6$. The filled shell is found to endow the atom with an enhanced stability; neon belongs to the noble gases.

In Tables 11.2–11.4 we present the ground-state electron configuration of the elements with $Z = 1$ to $Z = 108$ (together with the so-called term symbol which will be discussed later). One might perhaps expect that the orbitals were filled in an order compatible with the energy level diagram for the hydrogen atom, shown in Figure 9.5. But this is not the case. Rather, it is found that the orbitals are filled according to the

$n + \ell$ rule:

The electron configuration of an element may be determined by filling the orbitals after increasing values of $n + \ell$. For a fixed value of $n + \ell$, orbitals with lower n-values are filled first. (11.27)

The rule is only approximate, as a study of the tables shows, but it really works surprisingly well. A graphical illustration of the rule is presented in Figure 11.1.

That the orbitals are filled in an order different from that expected by looking at Figure 9.5, is due to the interplay between nuclear-electron attraction and electron-electron repulsion. We shall return to this point later, but first we must look for the reason why an orbital can hold at most two electrons.

11.4 Exchange Degeneracy

According to the aufbau principle, a wavefunction like the $\Phi_{\mathrm{Li}}^{(0)}$ of Eq. (11.26) is physically inaccessible because it describes a $1s^3$ configuration. But this is an ad hoc argument, and we must look for a proper explanation. Let us begin by considering the function

$$\Phi_{\mathrm{Li}}^{(0)} = \varphi_{1s}^{0}(\boldsymbol{r}_1)\varphi_{1s}^{0}(\boldsymbol{r}_2)\varphi_{2s}^{0}(\boldsymbol{r}_3), \tag{11.28}$$

where we have "lifted" electron 3 from the $1s$ orbital to the $2s$ orbital, thus creating a wavefunction of the $1s^2 2s^1$ electron configuration. Such a wavefunction is apparently in harmony with the aufbau principle.

Still, there is a problem. For it was quite arbitrary that we lifted electron 3 from the $1s$ orbital to the $2s$ orbital. We might equally well have changed the orbital for electron 1 or electron 2. Thus we realize that the $1s^2 2s^1$ configuration actually defines three wavefunctions with the same energy, namely,

$$\left\{\begin{array}{l} \Phi_A^{(0)} = \varphi_{1s}^{0}(\boldsymbol{r}_1)\varphi_{1s}^{0}(\boldsymbol{r}_2)\varphi_{2s}^{0}(\boldsymbol{r}_3), \\ \Phi_B^{(0)} = \varphi_{1s}^{0}(\boldsymbol{r}_1)\varphi_{2s}^{0}(\boldsymbol{r}_2)\varphi_{1s}^{0}(\boldsymbol{r}_3), \qquad E_{\mathrm{Li}}^{(0)} = -\frac{81}{8}\,\mathrm{au}, \\ \Phi_C^{(0)} = \varphi_{2s}^{0}(\boldsymbol{r}_1)\varphi_{1s}^{0}(\boldsymbol{r}_2)\varphi_{1s}^{0}(\boldsymbol{r}_3). \end{array}\right. \tag{11.29}$$

If these wavefunctions are to give an approximate description of the ground state of the lithium atom as they stand, then the proper ground state should be three-fold degenerate. But the degeneracy is only found to be 2 and is, in fact, a spin degeneracy.

At this stage we might get the idea that the Schrödinger equation which we set up for a many-electron atom is wrong. After all, it seems to lead to spurious solutions. This is, however, the wrong angle of approach. There is, in fact, nothing wrong with the Schrödinger equation. The difficulties are instead tied to a particular symmetry of the problem.

This is the so-called *permutation symmetry* which expresses the fact that the Hamiltonian (11.12), and also the Hamiltonian (11.13), is invariant under any renumbering, or permutation, of the electrons. We say that the Hamiltonian is a *symmetric operator*. We have discussed the interplay between symmetry and the Schrödinger equation in Secs. 4.5 and 4.7. The arguments here run very similarly.

Let $\widehat{P}$ be the operator that performs a definite renumbering of the N electrons in our problem. We have then that

$$\begin{aligned}\widehat{P}\widehat{H}\Phi(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N) &= \widehat{H}\widehat{P}\Phi(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)\\ &= \widehat{H}\Phi(\boldsymbol{r}_{P1},\boldsymbol{r}_{P2},\ldots,\boldsymbol{r}_{PN})\end{aligned} \tag{11.30}$$

where $(P1,P2,\ldots,PN)$ is a permutation of the numbers $(1,2,\ldots,N)$, and we have used that $\widehat{H}$ is a symmetric operator. Assume now that Φ is an eigenfunction of $\widehat{H}$ corresponding to the energy E,

$$\widehat{H}\Phi(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N) = E\Phi(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N). \tag{11.31}$$

Applying the operator $\widehat{P}$ on both sides of the equation gives then

$$\widehat{H}\Phi(\boldsymbol{r}_{P1},\boldsymbol{r}_{P2},\ldots,\boldsymbol{r}_{PN}) = E\Phi(\boldsymbol{r}_{P1},\boldsymbol{r}_{P2},\ldots,\boldsymbol{r}_{PN}). \tag{11.32}$$

In words: If $\Phi(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)$ is a solution of the Schrödinger equation with energy E, then so is $\Phi(\boldsymbol{r}_{P1},\boldsymbol{r}_{P2},\ldots,\boldsymbol{r}_{PN})$. This argument holds for each of the $N!$ permutations $(P1,P2,\ldots,PN)$. The level with energy E possesses therefore a degeneracy equal to the number of linearly independent functions that may be generated from $\Phi(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N)$ by permuting the N coordinates (We also count the identity permutation). The degeneracy is known as *exchange degeneracy.*

Applying the above procedure to the function (11.28) and the Hamiltonian $\widehat{H}^{(0)}$ leads immediately to the three functions given by Eq. (11.29). The exchange degeneracy is accordingly 3 in this case.

But, as we mentioned above, this degeneracy is not observed. Nor are similar degeneracies observed for other many-electron systems. The reason was discovered by Dirac and Pauli:[1]

$$\boxed{\text{Electrons are identical particles.}} \tag{11.33}$$

What this means is that it is impossible to distinguish different electrons in a system individually from each other. The outcome of an experiment must therefore be independent of any attempt to label the electrons.

To appreciate the implications of such a situation, let us consider the N-electron quantity (11.23), i. e., the joint probability of observing electron 1 in

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[1] P. A. M. Dirac, Proc. Roy. Soc. (London) A **112**, 661 (1926); W. Pauli, Z. Phys. **43**, 601 (1927).

the volume element dv_1 around the point $\boldsymbol{r}_1$, electron 2 in the volume element dv_2 around the point $\boldsymbol{r}_2$, etc. According to the above requirement, this must be the same as the probability of observing electron 2 around $\boldsymbol{r}_1$ and electron 1 around $\boldsymbol{r}_2$, with the remaining electrons in the same positions as before. Thus, we must have that

$$\begin{aligned}\Phi(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3, \ldots \boldsymbol{r}_N)^* \Phi(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3, \ldots . \boldsymbol{r}_N) dv_1 dv_2 dv_3 \cdots dv_N \\ = \Phi(\boldsymbol{r}_2, \boldsymbol{r}_1, \boldsymbol{r}_3, \ldots \boldsymbol{r}_N)^* \Phi(\boldsymbol{r}_2, \boldsymbol{r}_1, \boldsymbol{r}_3, \ldots . \boldsymbol{r}_N) dv_1 dv_2 dv_3 \cdots dv_N \qquad (11.34)\end{aligned}$$

or,

$$\begin{aligned}\Phi(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3, \ldots \boldsymbol{r}_N)^* \Phi(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3, \ldots . \boldsymbol{r}_N) \\ = \Phi(\boldsymbol{r}_2, \boldsymbol{r}_1, \boldsymbol{r}_3, \ldots \boldsymbol{r}_N)^* \Phi(\boldsymbol{r}_2, \boldsymbol{r}_1, \boldsymbol{r}_3, \ldots . \boldsymbol{r}_N). \qquad (11.35)\end{aligned}$$

For a *real* wavefunction, this leads to the requirement

$$\Phi(\boldsymbol{r}_2, \boldsymbol{r}_1, \boldsymbol{r}_3, \ldots . \boldsymbol{r}_N) = \pm \Phi(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3, \ldots . \boldsymbol{r}_N). \qquad (11.36)$$

A similar condition must of course hold for the interchange of any pair of electrons. But when should we expect the plus sign to hold, and when the minus sign?

The answer to this question relates to both real and complex wavefunctions and has the form of a postulate embracing both fermions and bosons (Sec. 10.2). It has been fully vindicated: For a system of identical fermions we must always choose the minus sign, for a system of identical bosons always the plus sign. For electrons, which are fermions, we must choose the minus sign. A wavefunction that changes sign under the interchange of any two particles is called *antisymmetric*. Similarly, a wavefunction is called *symmetric* if it remains the same after such an interchange. For electrons, we thus have the following fundamental symmetry principle

> A many-electron wavefunction must be antisymmetric, that is, it must change sign under the interchange of any pair of electrons. (11.37)

It was emphasized by Pauli[2] that the interchange of a pair of electrons not only interchanges the positions and the momenta of the two particles, but also their spins. Hence, we cannot apply the principle correctly without worrying

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[2] See the reference of footnote 1.

about the spin. We must give up our attempt to describe a many-electron system by the spin-free solutions of Eq. (11.4), and instead consider how to construct proper spin-dependent solutions. This we shall do in the following section.

In closing the present section, we note that the indistinguishableness of electrons correlates well with Heisenberg's uncertainty relation (5.113). For this relation makes it impossible to specify the positions and velocities of the individual particles with sufficient accuracy to distinguish them from each other during a collective motion.

11.5 Pauli's Exclusion Principle. Slater Determinants

It follows from what we learned in Sec. 10.2 that if we have an orthonormal set of spatial orbitals, then we obtain an orthonormal set of spin-orbitals of twice the size by multiplying each spatial orbital by $\alpha(\varsigma)$ and by $\beta(\varsigma)$. Let us consider N such spin-orbitals: $\psi_1(x), \psi_2(x), \ldots, \psi_N(x)$, where $x = (\boldsymbol{r}, \varsigma)$ as in Sec. 10.2. We may then form the $N!$ product functions

$$\psi_{P1}(x_1)\psi_{P2}(x_2)\cdots\psi_{PN}(x_N), \tag{11.38}$$

where $x_1 = (\boldsymbol{r}_1, \varsigma_1)$ is the combined space and spin variables for electron 1 etc., and $(P1, P2, \ldots, PN)$ is a permutation of the numbers $1, 2, \ldots, N$. We now form a specific linear combination of these $N!$ product functions, namely, the determinant

$$\Psi(x_1, x_2, \ldots, x_N) = \sqrt{\frac{1}{N!}} \begin{vmatrix} \psi_1(x_1) & \psi_1(x_2) & \ldots & \psi_1(x_N) \\ \psi_2(x_1) & \psi_2(x_2) & \ldots & \psi_2(x_N) \\ \ldots & \ldots & \ldots & \ldots \\ \psi_N(x_1) & \psi_N(x_2) & \ldots & \psi_N(x_N) \end{vmatrix} . \tag{11.39}$$

This many-electron wavefunction satisfies the antisymmetry requirement formulated in (11.37), for interchanging a pair of electrons amounts to interchanging two columns in the determinant, and it is well known that the value of a determinant is multiplied by -1 when two of its columns are interchanged.

A determinant is also multiplied by -1 when two of its rows are interchanged. Hence a determinant with two or more identical rows must vanish. The wavefunction (11.39) is accordingly zero unless the N spin-orbitals $\psi_1(x), \psi_2(x), \ldots, \psi_N(x)$ are all different. Also, it is not very difficult to show that the determinant is in fact the only antisymmetric linear combination of the product functions (11.38) that may be constructed.

The determinant (11.39) is called a *Slater determinant*, in honor of the American physicist John Clarke Slater who invented it. It allows us to eliminate the difficulties with the exchange degeneracy in a simple fashion.

We note that when the spin-orbitals $\psi_1(x), \psi_2(x), \ldots, \psi_N(x)$ are members of an orthonormal set and all different, then the $N!$ product functions (11.38) will be normalized and mutually orthogonal. Hence the determinant (11.39) is also normalized (according to the theorem (4.76)). For simplicity, we shall denote the normalized determinant by $|\psi_1\psi_2\ldots\psi_N|$ and understand that it depends on the variables $(x_1, x_2, \ldots, x_N)$,

$$|\psi_1\psi_2\ldots\psi_N| \equiv \sqrt{\frac{1}{N!}}\begin{vmatrix} \psi_1(x_1) & \psi_1(x_2) & \ldots & \psi_1(x_N) \\ \psi_2(x_1) & \psi_2(x_2) & \ldots & \psi_2(x_N) \\ \ldots & \ldots & \ldots & \ldots \\ \psi_N(x_1) & \psi_N(x_2) & \ldots & \psi_N(x_N) \end{vmatrix}. \tag{11.40}$$

We shall now reconsider the ground-state solutions of the simplified N-electron Schrödinger equation (11.14) in the light of the above analysis.

The hydrogen atom:

Before we introduced the spin, the ground state of the hydrogen atom was found to be non-degenerate. It was described by the wavefunction $\varphi^0_{1s}(\boldsymbol{r})$. After the introduction of the spin, the ground state becomes two-fold degenerate, the independent wavefunctions being the two spin-orbitals $\overset{+}{\varphi}{}^0_{1s}(x)$ and $\overset{-}{\varphi}{}^0_{1s}(x)$, in the notation of Sec. 10.2, Eq. (10.21).

The degeneracies of the excited states are likewise doubled, the degeneracy of the nth state now being $2n^2$. The $2n^2$ spin-orbitals describing the state are

$$\psi_{n\ell\gamma_\ell m_s}(x) = R_{n\ell}(r)Y_{\ell\gamma_\ell}(\theta,\phi)\left\{\begin{array}{c}\alpha(\varsigma)\\ \beta(\varsigma)\end{array}\right. \tag{11.41}$$

as in Sec. 10.2. As usual, the quantum number m_s is understood to be 1/2 when the spin-function is $\alpha(\varsigma)$ and $-1/2$ when the spin-function is $\beta(\varsigma)$. Each spin-orbital is defined by four "quantum numbers", $(n, \ell, \gamma_\ell, m_s)$.

The helium atom:

The ground-state wavefunction for helium which we listed in Eq. (11.26) was the simple product function $\varphi^0_{1s}(\boldsymbol{r}_1)\varphi^0_{1s}(\boldsymbol{r}_2)$. With the spin included, it is replaced by the four product functions

$$\overset{+}{\varphi}{}^0_{1s}(x_1)\overset{+}{\varphi}{}^0_{1s}(x_2),\ \overset{+}{\varphi}{}^0_{1s}(x_1)\overset{-}{\varphi}{}^0_{1s}(x_2),\ \overset{-}{\varphi}{}^0_{1s}(x_1)\overset{+}{\varphi}{}^0_{1s}(x_2),\ \overset{-}{\varphi}{}^0_{1s}(x_1)\overset{-}{\varphi}{}^0_{1s}(x_2).$$

Each of these product functions corresponds to the energy −4 au, and so does any linear combination of them. But the four product functions are not antisymmetric, nor is the arbitrary linear combination so. The only antisymmetric wavefunction is the Slater determinant

$$\begin{aligned}\Psi^{(0)}_{\mathrm{He}} &= |\overset{+}{\varphi}{}^{0}_{1s}\,\overset{-}{\varphi}{}^{0}_{1s}| = \sqrt{\frac{1}{2}}\begin{vmatrix} \overset{+}{\varphi}{}^{0}_{1s}(x_1) & \overset{+}{\varphi}{}^{0}_{1s}(x_2) \\ \overset{-}{\varphi}{}^{0}_{1s}(x_1) & \overset{-}{\varphi}{}^{0}_{1s}(x_2) \end{vmatrix} \\ &= \sqrt{\frac{1}{2}}\begin{vmatrix} \varphi^{0}_{1s}(\boldsymbol{r}_1)\alpha(\varsigma_1) & \varphi^{0}_{1s}(\boldsymbol{r}_2)\alpha(\varsigma_2) \\ \varphi^{0}_{1s}(\boldsymbol{r}_1)\beta(\varsigma_1) & \varphi^{0}_{1s}(\boldsymbol{r}_2)\beta(\varsigma_2) \end{vmatrix} \qquad (11.42) \\ &= \sqrt{\frac{1}{2}}\,\varphi^{0}_{1s}(\boldsymbol{r}_1)\varphi^{0}_{1s}(\boldsymbol{r}_2)\left\{\alpha(\varsigma_1)\beta(\varsigma_2) - \beta(\varsigma_1)\alpha(\varsigma_2)\right\}.\end{aligned}$$

This, then, is the proper ground-state wavefunction. The ground state is non-degenerate and corresponds to the electron configuration $1s^2$.

Eq. (11.42) shows that the ground-state determinant factors into a two-electron spatial function and a two-electron spin-function. For systems with more than two electrons a similar factorization will in most cases be impossible.

The lithium atom:

If the lithium wavefunction of Eq. (11.26) is converted into a product of three spin-orbitals, at least two spin-orbitals will be identical for each product function. Hence, no antisymmetric wavefunction exists for the configuration $1s^3$. This configuration is accordingly excluded.

For the $1s^2 2s^1$ configuration we have the three product functions of Eq. (11.29) as our starting point. After the introduction of spin, they are converted into products of spin-orbitals, and these are again converted into Slater determinants. Thus, the spin-orbitals $\overset{+}{\varphi}{}^{0}_{1s}$, $\overset{-}{\varphi}{}^{0}_{1s}$, and $\overset{+}{\varphi}{}^{0}_{2s}$ give the determinant

$$\Psi^{(0)}_{\mathrm{Li,I}} = |\overset{+}{\varphi}{}^{0}_{1s}\,\overset{-}{\varphi}{}^{0}_{1s}\,\overset{+}{\varphi}{}^{0}_{2s}|, \qquad (11.43)$$

while the spin-orbitals $\overset{+}{\varphi}{}^{0}_{1s}$, $\overset{-}{\varphi}{}^{0}_{1s}$, and $\overset{-}{\varphi}{}^{0}_{2s}$ give the determinant

$$\Psi^{(0)}_{\mathrm{Li,II}} = |\overset{+}{\varphi}{}^{0}_{1s}\,\overset{-}{\varphi}{}^{0}_{1s}\,\overset{-}{\varphi}{}^{0}_{2s}|, \qquad (11.44)$$

The two Slater determinants both correspond to the energy $-\frac{81}{8}$ au, and the ground state is doubly degenerate.

For the ground states of other atoms we may proceed in a similar way. Thus, the ground state of the beryllium atom is non-degenerate. It is described by the Slater determinant

$$\Psi^{(0)}_{\mathrm{Be}} = |\overset{+}{\varphi}{}^{0}_{1s}\,\overset{-}{\varphi}{}^{0}_{1s}\,\overset{+}{\varphi}{}^{0}_{2s}\,\overset{-}{\varphi}{}^{0}_{2s}|. \qquad (11.45)$$

The fact that no spin-orbital can occur more than once in a Slater determinant is known as *Pauli's exclusion principle*. For an atom, each spin-orbital may be characterized by four quantum numbers as in Eq. (11.41). Thus, we get the familiar formulation of the principle

Pauli's exclusion principle:
No two electrons can have the same set of quantum numbers. (11.46)

The principle may, of course, also be used for excited states where orbitals with higher quantum numbers enter into the determinant.

We have now shown how we may derive the antisymmetric solutions of the simplified Schrödinger equation (11.14) and thus construct a rational correspondence with the aufbau principle. It is, however, entirely impossible to give anything like a *quantitative* description of atoms as long as the electron-electron repulsion is neglected. Hence, we shall now leave the approximate Hamiltonian (11.13) and consider the problem of including the fact that electrons in an atom repel each other with strong forces.

11.6 Including Electron-Electron Repulsion

When the electron-electron repulsion (11.9)) is properly included in the many-electron Hamiltonian (11.12), it is no longer possible to separate the variables associated with different particles, and the exact wavefunctions can no longer be written as Slater determinants derived from simple product functions.

It is, however, often possible to obtain reasonably good approximate wavefunctions in the form of Slater determinants built from atomic spin-orbitals of the form (11.41). But the radial functions $R_{n\ell}(r)$ are then no longer hydrogenic. They may be determined as the solutions of a one-electron Schrödinger equation in which the central field $V(r)$ is a sum of the Coulomb field from the nucleus and a suitably averaged field from the electrons.

The one-electron Schrödinger equation alluded to is a so-called *Hartree–Fock equation*. It may be derived by the variational method which we shall take up in the next chapter. The orbitals obtained by solving the Hartree–Fock equation are known as *Hartree–Fock orbitals*. We shall use the same notation for Hartree–Fock orbitals and approximations to them as for the orbitals of the preceding sections, but with the superscript ^{0} removed. A similar remark holds for the determinants built from Hartree–Fock orbitals. Thus, we write the Hartree–Fock wavefunction for the ground state of the beryllium atom as

$$\Psi_{\mathrm{Be}} = |\overset{+}{\varphi}_{1s}\,\overset{-}{\varphi}_{1s}\,\overset{+}{\varphi}_{2s}\,\overset{-}{\varphi}_{2s}|. \tag{11.47}$$

Although a Slater determinant built from atomic Hartree–Fock orbitals quite often give a fairly good many-electron wavefunction, the function is by no means exact. One way to improve it is to replace the single determinant by a linear combination of determinants. These determinants will usually correspond to different electron configurations, and hence one talks about the method of *configuration interaction.* The coefficients in the linear combination are again determined by the variational method.

Since a Hartree–Fock wavefunction is not exact, the electron density that may be derived from it is not exact either, although it is usually a quite good approximation to the true density. During configuration interaction the wavefunction, and hence also the electron density, becomes improved.

A different approach to many-electron theory is the so-called *density functional theory* in which one focuses on the electron density rather than the total wavefunction, and requires that the true electron density be derivable from a single Slater determinant. The orbitals defining that determinant are known as the *Kohn–Sham orbitals.* They may be determined from a one-electron Schrödinger equation known as the *Kohn–Sham equation.* The Kohn–Sham orbitals are usually quite similar to the Hartree–Fock orbitals.

We shall consider both the Hartree–Fock and Kohn–Sham descriptions in more detail later. But at present, we shall stick to the language of Hartree-Fock theory and close the present chapter with a section on approximate Hartree–Fock orbitals.

11.7 Slater Type Orbitals

The Hartree–Fock orbitals referred to above have the general form (11.2), i. e., each Hartree–Fock orbital is the product of a radial function and a surface spherical harmonic, but the radial functions $R_{n\ell}(r)$ can no longer be represented by simple analytical expressions. But if high accuracy is not at issue, then it is of course possible to *approximate* the radial functions by simple analytical functions, and this is often done.

The first set of simplified atomic orbitals for many-electron atoms was deviced by Slater. He wrote, in atomic units,

$$R_{n\ell}(r) = \left\{ \frac{(2\zeta_{n\ell})^{2n+1}}{(2n)!} \right\}^{\frac{1}{2}} r^{n-1} e^{-\zeta_{n\ell} r}\,, \tag{11.48}$$

Table 11.1: Variationally determined orbital exponents $\zeta_{n\ell}$

	Z	$1s$	$2s$	$2p$	$3s$	$3p$
He	2	1.6875				
Li	3	2.6906	0.6396			
Be	4	3.6848	0.9560			
B	5	4.6795	1.2881	1.2107		
C	6	5.6727	1.6083	1.5679		
N	7	6.6651	1.9237	1.9170		
O	8	7.6579	2.2458	2.2266		
F	9	8.6501	2.5638	2.5500		
Ne	10	9.6421	2.8792	2.8792		
Na	11	10.6259	3.2857	3.4009	0.8358	
Mg	12	11.6089	3.6960	3.9129	1.1025	
Al	13	12.5910	4.1068	4.4817	1.3724	1.3552
Si	14	13.5745	4.5100	4.9725	1.6344	1.4284
P	15	14.5577	4.9125	5.4806	1.8806	1.6288
S	16	15.5409	5.3144	5.9885	2.1223	1.8273
Cl	17	16.5239	5.7152	6.4966	2.3561	2.0387
Ar	18	17.5075	6.1152	7.0041	2.5856	2.2547

with

$$\zeta_{n\ell} = \frac{Z - \sigma_{n\ell}}{n} . \tag{11.49}$$

$\zeta_{n\ell}$ is called the *orbital exponent.*

We see that the radial functions prescribed by Slater are of a similar form as the hydrogen-like functions in Table 9.1, but only the maximum power of r is included. Thus, the radial functions are all taken to be nodeless, and the nuclear charge Z is replaced by the *screened nuclear charge* $Z - \sigma_{n\ell}$. The screening (or shielding) constant $\sigma_{n\ell}$ reflects the fact that the other electrons in the atom spend part of their time in the region between the nucleus and the electron considered, thereby effectively screening the nucleus from the electron.

By combining the radial function (11.48) with the appropriate surface spherical harmonic, a so-called *Slater-type orbital* (STO), results. Slater's rules for determining the screening constant for a particular orbital are the following:[3]

> (1) For a given atom, divide the orbitals into the following groups, each having a different screening constant: $1s$; $2s, 2p$; $3s, 3p$; $3d$; $4s, 4p$; $4d$; $4f$; $5s, 5p$; etc. Thus the s and p of a given shell are grouped together and get the same radial function, but the d and f are separated. The groups are considered to be arranged from inside out in the order named (note that this order is that of Figure 9.5 rather than that of Figure 11.1).
>
> (2) The screening constant $\sigma_{n\ell}$ is formed as the sum of the following contributions
>
> > (*a*) nothing from any group outside the one considered;
> > (*b*) an amount of 0.35 from each other electron in the group considered (except for the $1s$ group, where 0.30 is used instead);
> > (*c*) if the group considered is an s, p group, an amount 0.85 from each electron in the next inner group, and 1.00 from each electron still further in; but if the group is a d or f, an amount 1.00 from every electron inside it.
>
> Slater also assigned non-integer values to the n on the right-hand side of Eq. (11.48) for values of n larger than 3, but his rules are no longer used for such high n-values.

To illustrate Slater's rules, let us calculate the orbital exponents $\zeta_{n\ell}$ for the helium atom ($Z = 2$) and the carbon atom ($Z = 6$). The helium atom has the electron configuration $1s^2$, so we get immediately

$$\zeta_{1s} = (2 - 0.30)/1 = 1.70.$$

For the carbon atom, with the electron configuration $1s^2 2s^2 2p^2$, we get

$$\begin{aligned} \zeta_{1s} &= (6 - 0.30)/1 = 5.70, \\ \zeta_{2s} &= \zeta_{2p} = (6 - 3 \times 0.35 - 2 \times 0.85)/2 = 3.25/2 = 1.625. \end{aligned}$$

Slater obtained his rules from an empirical analysis of successive ionization energies and total energies of atoms. Over the years, his rules have been

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[3] J. C. Slater, Phys. Rev. **36**, 57 (1930).

modified and refined in various directions by different authors, but it is questionable if these refinements are of lasting value. Now that computers are generally available, it is in fact more natural to determine orbital exponents by means of the variational method by procedures that will be illustrated in the following chapter.

As shown in that chapter, the variational method leads to a ζ_{1s} value of 1.6875 for helium. For carbon, one allows the $2s$ and $2p$ exponents to become different and finds

$$\zeta_{1s} = 5.6727,\ \zeta_{2s} = 1.6083,\ \zeta_{2p} = 1.5679.$$

Variationally determined orbital exponents for other atoms are available in the scientific literature.[4] For the lighter atoms, they are reproduced in Table 11.1. For heavier atoms, it becomes an increasingly bad approximation to simulate a Hartree–Fock orbital by a simple Slater-type orbital. Reasonable approximations may, however, be obtained by using a linear combination of two or three Slater-type orbitals for each Hartree–Fock orbital instead.

Table 11.2: Ground-state electronic structure of the elements 1–36

Z	Element	Symbol	Configuration	Term
1	hydrogen	H	$1s^1$	$^2S_{1/2}$
2	helium	He	$1s^2$	$^1S_0$
3	lithium	Li	$1s^22s^1$	$^2S_{1/2}$
4	beryllium	Be	$1s^22s^2$	$^1S_0$
5	boron	B	$1s^22s^22p^1$	$^2P_{1/2}$
6	carbon	C	$1s^22s^22p^2$	$^3P_0$
7	nitrogen	N	$1s^22s^22p^3$	$^4S_{3/2}$
8	oxygen	O	$1s^22s^22p^4$	$^3P_2$
9	fluorine	F	$1s^22s^22p^5$	$^2P_{3/2}$
10	neon	Ne	$1s^22s^22p^6$	$^1S_0$
11	sodium	Na	$[\mathrm{Ne}]3s^1$	$^2S_{1/2}$
12	magnesium	Mg	$[\mathrm{Ne}]3s^2$	$^1S_0$
13	aluminium	Al	$[\mathrm{Ne}]3s^23p^1$	$^2P_{1/2}$
14	silicon	Si	$[\mathrm{Ne}]3s^23p^2$	$^3P_0$
15	phosphorus	P	$[\mathrm{Ne}]3s^23p^3$	$^4S_{3/2}$
16	sulfur	S	$[\mathrm{Ne}]3s^23p^4$	$^3P_2$
17	chlorine	Cl	$[\mathrm{Ne}]3s^23p^5$	$^2P_{3/2}$
18	argon	Ar	$[\mathrm{Ne}]3s^23p^6$	$^1S_0$
19	potassium	K	$[\mathrm{Ar}]4s^1$	$^2S_{1/2}$
20	calcium	Ca	$[\mathrm{Ar}]4s^2$	$^1S_0$
21	scandium	Sc	$[\mathrm{Ar}]3d^14s^2$	$^2D_{3/2}$
22	titanium	Ti	$[\mathrm{Ar}]3d^24s^2$	$^3F_2$
23	vanadium	V	$[\mathrm{Ar}]3d^34s^2$	$^4F_{3/2}$
24	chromium	Cr	$[\mathrm{Ar}]3d^54s^1$	$^7S_3$
25	manganese	Mn	$[\mathrm{Ar}]3d^54s^2$	$^6S_{5/2}$
26	iron	Fe	$[\mathrm{Ar}]3d^64s^2$	$^5D_4$
27	cobalt	Co	$[\mathrm{Ar}]3d^74s^2$	$^4F_{9/2}$
28	nickel	Ni	$[\mathrm{Ar}]3d^84s^2$	$^3F_4$
29	copper	Cu	$[\mathrm{Ar}]3d^{10}4s^1$	$^2S_{1/2}$
30	zinc	Zn	$[\mathrm{Ar}]3d^{10}4s^2$	$^1S_0$
31	gallium	Ga	$[\mathrm{Ar}]3d^{10}4s^24p^1$	$^2P_{1/2}$
32	germanium	Ge	$[\mathrm{Ar}]3d^{10}4s^24p^2$	$^3P_0$
33	arsenic	As	$[\mathrm{Ar}]3d^{10}4s^24p^3$	$^4S_{3/2}$
34	selenium	Se	$[\mathrm{Ar}]3d^{10}4s^24p^4$	$^3P_2$
35	bromine	Br	$[\mathrm{Ar}]3d^{10}4s^24p^5$	$^2P_{3/2}$
36	krypton	Kr	$[\mathrm{Ar}]3d^{10}4s^24p^6$	$^1S_0$

Table 11.3: Ground-state electronic structure of the elements 37–72

Z	Element	Symbol	Configuration	Term
37	rubidium	Rb	[Kr]$5s^1$	$^2S_{1/2}$
38	strontium	Sr	[Kr]$5s^2$	$^1S_0$
39	yttrium	Y	[Kr]$4d^1 5s^2$	$^2D_{3/2}$
40	zirconium	Zr	[Kr]$4d^2 5s^2$	$^3F_2$
41	niobium	Nb	[Kr]$4d^4 5s^1$	$^6D_{1/2}$
42	molybdenum	Mo	[Kr]$4d^5 5s^1$	$^7S_3$
43	technetium	Tc	[Kr]$4d^6 5s^1$	$^6S_{5/2}$
44	ruthenium	Ru	[Kr]$4d^7 5s^1$	$^5F_5$
45	rhodium	Rh	[Kr]$4d^8 5s^1$	$^4F_{9/2}$
46	palladium	Pd	[Kr]$4d^{10}$	$^1S_0$
47	silver	Ag	[Kr]$4d^{10} 5s^1$	$^2S_{1/2}$
48	cadmium	Cd	[Kr]$4d^{10} 5s^2$	$^1S_0$
49	indium	In	[Kr]$4d^{10} s^2 5p^1$	$^2P_{1/2}$
50	tin	Sn	[Kr]$4d^{10} 5s^2 5p^2$	$^3P_0$
51	antimony	Sb	[Kr]$4d^{10} 5s^2 5p^3$	$^4S_{3/2}$
52	tellurium	Te	[Kr]$4d^{10} 5s^2 5p^4$	$^3P_2$
53	iodine	I	[Kr]$4d^{10} 5s^2 5p^5$	$^2P_{3/2}$
54	xenon	Xe	[Kr]$4d^{10} 5s^2 5p^6$	$^1S_0$
55	cesium	Cs	[Xe]$6s^1$	$^2S_{1/2}$
56	barium	Ba	[Xe]$6s^2$	$^1S_0$
57	lanthanum	La	[Xe]$5d^1 6s^2$	$^2D_{3/2}$
58	cerium	Ce	[Xe]$4f^1 5d^1 6s^2$	$^1G_4$
59	praseodymium	Pr	[Xe]$4f^3 6s^2$	$^4I_{9/2}$
60	neodymium	Nd	[Xe]$4f^4 6s^2$	$^5I_4$
61	promethium	Pm	[Xe]$4f^5 6s^2$	$^6H_{5/2}$
62	samarium	Sm	[Xe]$4f^6 6s^2$	$^7F_0$
63	europium	Eu	[Xe]$4f^7 6s^2$	$^8S_{7/2}$
64	gadolinium	Gd	[Xe]$4f^7 5d^1 6s^2$	$^9D_2$
65	terbium	Tb	[Xe]$4f^9 6s^2$	$^6H_{15/2}$
66	dysprosium	Dy	[Xe]$4f^{10} 6s^2$	$^5I_8$
67	holmium	Ho	[Xe]$4f^{11} 6s^2$	$^4I_{15/2}$
68	erbium	Er	[Xe]$4f^{12} 6s^2$	$^3H_6$
69	thulium	Tm	[Xe]$4f^{13} 6s^2$	$^2F_{7/2}$
70	ytterbium	Yb	[Xe]$4f^{14} 6s^2$	$^1S_0$
71	lutetium	Lu	[Xe]$4f^{14} 5d^1 6s^2$	$^2D_{3/2}$
72	hafnium	Hf	[Xe]$4f^{14} 5d^2 6s^2$	$^3F_2$

Table 11.4: Ground-state electronic structure of the elements 73–108

Z	Element	Symbol	Configuration	Term
73	tantalum	Ta	[Xe]$4f^{14}5d^{3}6s^{2}$	$^{4}F_{3/2}$
74	tungsten	W	[Xe]$4f^{14}5d^{4}6s^{2}$	$^{5}D_{0}$
75	rhenium	Re	[Xe]$4f^{14}5d^{5}6s^{2}$	$^{6}S_{5/2}$
76	osmium	Os	[Xe]$4f^{14}5d^{6}6s^{2}$	$^{5}D_{4}$
77	iridium	Ir	[Xe]$4f^{14}5d^{7}6s^{2}$	$^{4}F_{9/2}$
78	platinum	Pt	[Xe]$4f^{14}5d^{9}6s^{1}$	$^{3}D_{3}$
79	gold	Au	[Xe]$4f^{14}5d^{10}6s^{1}$	$^{2}S_{1/2}$
80	mercury	Hg	[Xe]$4f^{14}5d^{10}6s^{2}$	$^{1}S_{0}$
81	thallium	Tl	[Xe]$4f^{14}5d^{10}6s^{2}6p^{1}$	$^{2}P_{1/2}$
82	lead	Pb	[Xe]$4f^{14}5d^{10}6s^{2}6p^{2}$	$^{3}P_{0}$
83	bismuth	Bi	[Xe]$4f^{14}5d^{10}6s^{2}6p^{3}$	$^{4}S_{3/2}$
84	polonium	Po	[Xe]$4f^{14}5d^{10}6s^{2}6p^{4}$	$^{3}P_{2}$
85	astatine	At	[Xe]$4f^{14}5d^{10}6s^{2}6p^{5}$	$^{2}P_{3/2}$
86	radon	Rn	[Xe]$4f^{14}5d^{10}6s^{2}6p^{6}$	$^{1}S_{0}$
87	francium	Fr	[Rn]$7s^{1}$	$^{2}S_{1/2}$
88	radium	Ra	[Rn]$7s^{2}$	$^{1}S_{0}$
89	actinium	Ac	[Rn]$6d^{1}7s^{2}$	$^{2}D_{3/2}$
90	thorium	Th	[Rn]$6d^{2}7s^{2}$	$^{3}F_{2}$
91	protactinium	Pa	[Rn]$5f^{2}6d^{1}7s^{2}$	$^{4}K_{11/2}$
92	uranium	U	[Rn]$5f^{3}6d^{1}7s^{2}$	$^{5}L_{6}$
93	neptunium	Np	[Rn]$5f^{4}6d^{1}7s^{2}$	$^{6}L_{11/2}$
94	plutonium	Pu	[Rn]$5f^{6}7s^{2}$	$^{7}F_{0}$
95	americium	Am	[Rn]$5f^{7}7s^{2}$	$^{8}S_{7/2}$
96	curium	Cm	[Rn]$5f^{7}6d^{1}7s^{2}$	$^{9}D_{2}$
97	berkelium	Bk	[Rn]$5f^{9}7s^{2}$	$^{6}H_{15/2}$
98	californium	Cf	[Rn]$5f^{10}7s^{2}$	$^{5}I_{8}$
99	einsteinium	Es	[Rn]$5f^{11}7s^{2}$	$^{4}I_{15/2}$
100	fermium	Fm	[Rn]$5f^{12}7s^{2}$	$^{3}H_{6}$
101	mendelevium	Md	[Rn]$5f^{13}7s^{2}$	$^{2}F_{7/2}$
102	nobelium	No	[Rn]$5f^{14}7s^{2}$	$^{1}S_{0}$
103	lawrencium	Lr	[Rn]$5f^{14}7s^{2}7p^{1}$	$^{2}P_{1/2}$
104	rutherfordium	Rf	[Rn]$5f^{14}6d^{2}7s^{2}$	$^{3}F_{2}$
105	dubnium	Db	[Rn]$5f^{14}6d^{3}7s^{2}$	$^{4}F_{3/2}$
106	seaborgium	Sg	[Rn]$5f^{14}6d^{4}7s^{2}$	$^{5}D_{0}$
107	bohrium	Bh	[Rn]$5f^{14}6d^{5}7s^{2}$	$^{6}S_{5/2}$
108	hassium	Hs	[Rn]$5f^{14}6d^{6}7s^{2}$	$^{5}D_{4}$

Supplementary Reading

The bibliography, entries [6], [7], [15], and [23].

Problems

11.1. Table 11.1 lists a set of "best" orbital exponents for the phosphorous atom ($Z = 15$). Which values would be obtained by applying Slater's rules?

11.2. In the following, we consider the wavefunction

$$\Psi = |\overset{+}{\varphi}_{1s}\overset{+}{\varphi}_{2s}|$$

belonging to the excited $1s^1 2s^1$ electron configuration for the helium atom. The radial functions that define the φ_{1s} and φ_{2s} orbitals are supposed to be of the form (11.48), with the orbital exponents determined by Slater's rules, as applied to the configuration $1s^1 2s^1$.

a. The electron configuration $1s^1 2s^1$ gives rise to a total of four Slater determinants. Write down the three remaining determinants.

b. Determine the values of the orbital exponents ζ_{1s} and ζ_{2s}.

c. The orbitals φ_{1s} and φ_{2s} are not mutually orthogonal. Determine the value of the overlap integral $\langle\varphi_{1s}|\varphi_{2s}\rangle$. (Use the standard integral (9.23), and be aware that Eq. (11.48) merely gives the radial part of a Slater orbital.)

d. We now construct a new $2s$ orbital φ'_{2s} of the form

$$\varphi'_{2s} = \varphi_{2s} - \lambda\varphi_{1s}.$$

Determine the constant λ such that $\langle\varphi_{1s}|\varphi'_{2s}\rangle = 0$.
This procedure is called Schmidt orthogonalization. It is a well known procedure in the field of linear algebra. (See also Problem 4.3.)

e. Write down the Slater determinant

$$\Psi' = |\overset{+}{\varphi}_{1s}\overset{+}{\varphi}{}'_{2s}|$$

and expand both this function and the original Ψ, in a similar way as done in Eq. (11.42).

f. Show that Ψ og Ψ' are identical!

g. The orbital φ'_{2s} is not normalized to unity. Hence, write

$$\varphi'_{2s} = N(\varphi_{2s} - \lambda\varphi_{1s})$$

and determine the normalization constant N such that

$$\langle\varphi'_{2s}|\varphi'_{2s}\rangle = 1.$$

h. Also expand the three determinants found under **a.**, in a similar way as done in Eq. (11.42).

i. As pointed out in the text, the symbol $|\overset{+}{\varphi}_{1s}\overset{+}{\varphi}_{2s}|$ includes the prefactor $\sqrt{\frac{1}{2}}$ which normalizes the determinant to unity, provided the orbitals φ_{1s} and φ_{2s} are mutually orthogonal. What is the proper prefactor in the present case, where φ_{1s} and φ_{2s} are non-orthogonal?

Chapter 12

The Variational Method

Contents

12.1 Introduction

In the preceding chapters we have been able to solve a number of quantum mechanical problems by analytical means. Thus, we have determined the exact solutions of the time-independent Schrödinger equation for the particle in a box (Chapter 4), the harmonic oscillator (Chapter 7), and the hydrogen-like atom (Chapter 9).

There are further quantum mechanical problems that lend themselves to an exact treatment, but the list is rapidly exhausted: The electronic Schrödinger equation may be solved exactly for the hydrogen atom and the H_2^+ ion, but not for the helium atom and the H_2 molecule. Also, we may solve the Schrödinger equation exactly for the harmonic potential and the Morse potential, but not for an exact diatomic potential (cf. Sec. 14.2). So, for the majority of problems it is necessary to turn to approximate methods in order to make progress. Most commonly, such methods are based either on numerical analysis, a variational principle, or perturbation theory.

In perturbation theory, one writes the Hamiltonian in the form

$$\widehat{H} = \widehat{H}^{(0)} + \lambda \widehat{H}^{(1)} + \lambda^2 \widehat{H}^{(2)} + \dots \tag{12.1}$$

where λ is an expansion parameter and the solutions of the *zero order problem* defined by the Hamiltonian $\widehat{H}^{(0)}$ are supposed to be known. It is then assumed that the effect of the *perturbation* $\lambda \widehat{H}^{(1)} + \lambda^2 \widehat{H}^{(2)} + \dots$ is sufficiently small that the solutions of the full problem may also be expanded as a power series in λ. This allows one to set up expressions by means of which the various terms in the expansions may be determined.

The theory of perturbations is a powerful and indispensable tool for the solution of many problems, both time-dependent and time-independent ones. But we shall postpone a discussion of the theory to a later chapter. The present chapter is devoted to methods based on variational principles.

12.2 Variational Principles

Variational principles play a fundamental role in theoretical physics and chemistry. As an exact concept, they were first used in optics by the seventeenth century French mathematician Pierre de Fermat. He postulated the following

> Fermat's principle of least time:
> No matter to what kind of reflection or refraction a ray of light is subjected, it travels from one point to another in such a way as to make the time taken a minimum. (12.2)

It is easy to demonstrate the validity of this principle for the particular case where the ray is reflected by a mirror. This is done in Fig. 12.1 by comparing the length of the actual path, for which the angles of incidence and reflection are equal, with the length of any other path.

This example contains the essence of a variational principle: Each path is characterized by some numerical value, here its length, and the values for

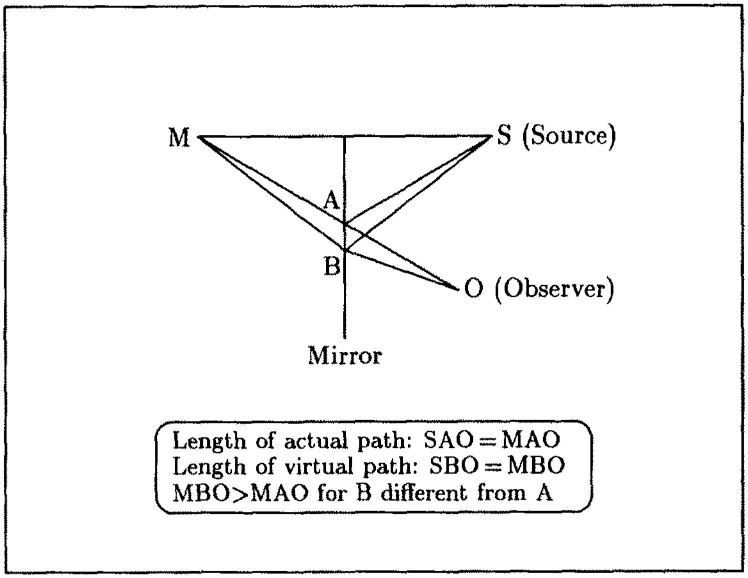

Figure 12.1: Fermat's principle.

different paths are compared. The path for which the value is stationary (not necessarily a minimum as above) is the actual path. The other paths are called virtual paths. That the value is stationary for a given path is understood to mean that it remains unchanged under an infinitesimal variation of the path.

The laws of classical mechanics, in the elegant formulations by Lagrange and Hamilton, are most easily derived by variational principles, and so are Maxwell's equations of electrodynamics. Also the Schrödinger equation may be derived from a variational principle. This holds for both the time-dependent equation and the time-independent equation. The variational principle for the time- independent equation is the simpler one and the only one we shall consider here.

12.3 The Time-Independent Schrödinger Equation

Let us consider a quantum mechanical system described by the Hamiltonian $\widehat{H}$ and let Ψ be any square-integrable function of the coordinates of the system.

The expectation value of $\widehat{H}$ is then, by the definition (5.97),

$$\mathcal{E}=\frac{\langle\Psi|\widehat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle}. \tag{12.3}$$

The value of $\mathcal{E}$ varies of course with the form of Ψ. But we shall now assume that we have found a function Ψ for which $\mathcal{E}$ is stationary. This means that the value of $\mathcal{E}$ remains unchanged when Ψ is replaced by $\Psi+\delta\Psi$, where $\delta\Psi$ is infinitesimal but otherwise arbitrary. We shall denote a stationary value of $\mathcal{E}$ by E.

The variation of $\mathcal{E}$ is generally defined as

$$\delta\mathcal{E}=\frac{\langle\Psi+\delta\Psi|\widehat{H}|\Psi+\delta\Psi\rangle}{\langle\Psi+\delta\Psi|\Psi+\delta\Psi\rangle}-\frac{\langle\Psi|\widehat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle}. \tag{12.4}$$

That Ψ is known to be a function for which $\mathcal{E}$ is stationary, means that $\delta\mathcal{E}$ is zero to first order, i. e., it is zero when second-order terms in $\delta\Psi$ are neglected on the right-hand side of Eq. (12.4). Putting the right-hand side equal to zero, and utilizing that $a/b-c/d=0$ implies that $ad=bc$, gives to first order in $\delta\Psi$

$$\begin{aligned}\langle\Psi|\Psi\rangle&\Big\{\langle\Psi|\widehat{H}|\Psi\rangle+\langle\delta\Psi|\widehat{H}|\Psi\rangle+\langle\Psi|\widehat{H}|\delta\Psi\rangle\Big\}\\&-\langle\Psi|\widehat{H}|\Psi\rangle\Big\{\langle\Psi|\Psi\rangle+\langle\delta\Psi|\Psi\rangle+\langle\Psi|\delta\Psi\rangle\Big\}=0.\end{aligned} \tag{12.5}$$

Next, cancellation of equal terms and division by $\langle\Psi|\Psi\rangle$ gives

$$\langle\delta\Psi|\widehat{H}|\Psi\rangle+\langle\Psi|\widehat{H}|\delta\Psi\rangle-\frac{\langle\Psi|\widehat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle}\{\langle\delta\Psi|\Psi\rangle+\langle\Psi|\delta\Psi\rangle\}=0. \tag{12.6}$$

By using the definition of $\mathcal{E}$, Eq. (12.3), and the fact that $\mathcal{E}$ is assumed to be stationary (and hence to be denoted by E), we may write Eq. (12.6) as

$$\langle\delta\Psi|\widehat{H}-E|\Psi\rangle+\langle\Psi|\widehat{H}-E|\delta\Psi\rangle=0. \tag{12.7}$$

Since this equation must hold for any $\delta\Psi$, we may replace $\delta\Psi$ by $i\delta\Psi$:

$$-i\langle\delta\Psi|\widehat{H}-E|\Psi\rangle+i\langle\Psi|\widehat{H}-E|\delta\Psi\rangle=0. \tag{12.8}$$

Multiplying this equation by i and adding it to Eq. (12.7) gives

$$\langle\delta\Psi|\widehat{H}-E|\Psi\rangle=0. \tag{12.9}$$

But this can only be true for *arbitrary* $\delta\Psi$ if

$$(\widehat{H}-E)\Psi=0. \tag{12.10}$$

For if the integral $\langle \delta\Psi|\hat{H}-E|\Psi\rangle$ were found to be zero for a specific $\delta\Psi$ without Eq. (12.10) being fulfilled, then we could easily violate Eq. (12.9) by changing $\delta\Psi$.

Eq. (12.10) is, of course, the time-independent Schrödinger equation. We have thus shown that this equation may be derived from the variational principle

$$\boxed{\delta\mathcal{E} = 0} \tag{12.11}$$

where $\mathcal{E}$ is the expectation value of the energy.

12.4 The Variational Method

In continuation of the preceding section, we shall now show that $\mathcal{E}$, the expectation value of $\hat{H}$ as defined by Eq. (12.3), is an absolute minimum when Ψ is the true ground-state wavefunction, Ψ_0. This is the so-called variational theorem:

The variational theorem states that

$$\mathcal{E} \equiv \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle} \geq E_0 \tag{12.12}$$

for any square-integrable Ψ.
The equality holds only if $\Psi = c\Psi_0$, where c is an arbitrary complex constant.

To prove the theorem, we take advantage of the fact that the eigenfunctions of $\hat{H}$ form a complete set (See Secs. 4.9 and 5.7). This implies that any Ψ may be written in the form

$$\Psi = \sum_{n=0}^{\infty} c_n\Psi_n \tag{12.13}$$

Usually we don't know the explicit form of the eigenfunctions, nor are they needed for the proof. We do know, however, that the eigenfunctions are mutually orthogonal (this is the theorem (5.67)), and we may also assume that they are normalized to unity. We may therefore write

$$\begin{aligned}\mathcal{E}-E_0 &= \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle}-E_0=\frac{\langle\Psi|\hat{H}-E_0|\Psi\rangle}{\langle\Psi|\Psi\rangle}\\ &=\frac{1}{\langle\Psi|\Psi\rangle}\sum_n\sum_m c_n^*c_m\langle\Psi_n|\hat{H}-E_0|\Psi_m\rangle\\ &=\frac{1}{\langle\Psi|\Psi\rangle}\sum_n\sum_m c_n^*c_m(E_m-E_0)\langle\Psi_n|\Psi_m\rangle\\ &=\frac{1}{\langle\Psi|\Psi\rangle}\sum_n c_n^*c_n(E_n-E_0)\,.\end{aligned} \tag{12.14}$$

But because E_0 is the ground-state energy, we have that $E_n - E_0 \geq 0$ for all n. Furthermore, $c_n^*c_n \geq 0$ for all n. The sum in the last expression is accordingly non-negative for any set of coefficients, and hence for any Ψ. The factor $1/\langle\Psi|\Psi\rangle$ is inherently positive, so $\mathcal{E} - E_0$ is non-negative for any Ψ. We also see that the condition for $\mathcal{E} - E_0$ to be strictly zero, is that c_n vanish for all $n > 0$, thus making Ψ equal to Ψ_0 apart from a complex constant. This proves the validity of the variational theorem (12.12).

The variational theorem is the basis for approximate ground-state calculations by *the Rayleigh-Ritz variational method.* The idea behind this method is to use a *trial function* Φ which depends on a set of variational parameters. The expectation value $\mathcal{E}$ is then evaluated as a function of these parameters, and by minimizing $\mathcal{E}$ with respect to the parameters one obtains the best approximation to Ψ_0 and E_0 that the form of Φ allows. Let us illustrate this through a couple of examples.

The hydrogen-like atom:

Pretend that we don't know the ground-state wavefunction for the Hamiltonian

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{Z}{r}\,, \tag{12.15}$$

but that we *guess* a function of the form $\exp(-\zeta r)$, i. e. , a *Slater-type* 1s *orbital* (Sec. 11.7), and treat ζ as a variational parameter. We add a normalization factor, and the trial function becomes

$$\varphi(\mathbf{r}) = \left(\frac{\zeta^3}{\pi}\right)^{\frac{1}{2}} e^{-\zeta r}. \tag{12.16}$$

This function is, in fact, the $R_{1s}(r)$ of Eq. (11.48) multiplied by $Y_{00}(\theta, \phi)$ which equals $\sqrt{1/4\pi}$. The expectation value of $\widehat{H}$ is found to be [1]

$$\mathcal{E} = \langle\varphi|\widehat{H}|\varphi\rangle = \tfrac{1}{2}\zeta^2 - Z\zeta, \tag{12.17}$$

and since

$$\frac{d\mathcal{E}}{d\zeta} = \zeta - Z, \tag{12.18}$$

we obtain the lowest value of $\mathcal{E}$ for $\zeta = Z$. The best description based on a function of the form (12.16) is accordingly obtained when

$$\varphi(\boldsymbol{r}) = \left(\frac{Z^3}{\pi}\right)^{1/2} e^{-Zr}, \qquad E = -\tfrac{1}{2}Z^2\,\text{au}. \tag{12.19}$$

This is, of course, the exact solution.

We would have been less fortunate if we had chosen a trial function of the form $\exp(-\alpha r^2)$ instead, a so-called *Gaussian-type orbital* (GTO). We normalize it to unity,

$$\varphi(\boldsymbol{r}) = \left(\frac{2\alpha}{\pi}\right)^{\frac{3}{4}} e^{-\alpha r^2}, \tag{12.20}$$

and get

$$\mathcal{E} = \langle\varphi|\widehat{H}|\varphi\rangle = \tfrac{3}{2}\alpha - 2Z\left(\frac{2\alpha}{\pi}\right)^{\frac{1}{2}}. \tag{12.21}$$

The optimal description in terms of a Gaussian-type $1s$ orbital is then obtained when

$$\alpha = \frac{8Z^2}{9\pi}, \qquad E = -\frac{4Z^2}{3\pi} = -0.4244Z^2\,\text{au}. \tag{12.22}$$

This energy lies well above the true ground-state energy, so even the best Gaussian-type $1s$ orbital is a poor approximation to the true wavefunction.

The helium-like atom:

As an example of greater physical interest, because we cannot solve the problem exactly, let us consider the Hamiltonian (11.12) with $N = 2$, i. e.,

$$\widehat{H} = -\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_2} + \frac{1}{r_{12}}. \tag{12.23}$$

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[1] To perform the actual calculations behind this and the following example is the exercise of problem 12.1.

For $Z = 2$, this is the Hamiltonian for the helium atom, for $Z > 2$ it is the Hamiltonian for a positive ion with charge $Z-2$. We take as our trial function a Slater determinant of the form (11.42), but with $\varphi^0_{1s}(\boldsymbol{r})$ replaced by the more general Slater-type 1s orbital:

$$\varphi_{1s}(\boldsymbol{r}) = \left(\frac{\zeta^3}{\pi}\right)^{\frac{1}{2}} e^{-\zeta r}. \tag{12.24}$$

Our trial function is then

$$\Psi(x_1, x_2) = \Phi(\boldsymbol{r}_1, \boldsymbol{r}_2)\Theta(\varsigma_1, \varsigma_2), \tag{12.25}$$

where

$$\Phi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \varphi_{1s}(\boldsymbol{r}_1)\varphi_{1s}(\boldsymbol{r}_2), \tag{12.26}$$

and

$$\Theta(\varsigma_1, \varsigma_2) = \sqrt{\tfrac{1}{2}}\,\{\alpha(\varsigma_1)\beta(\varsigma_2) - \beta(\varsigma_1)\alpha(\varsigma_2)\}\,. \tag{12.27}$$

Since the Hamiltonian is independent of the spin variables ς_1 and ς_2 we get

$$\mathcal{E} = \langle\Psi|\widehat{H}|\Psi\rangle = \langle\Phi\Theta|\widehat{H}|\Phi\Theta\rangle = \langle\Phi|\widehat{H}|\Phi\rangle\langle\Theta|\Theta\rangle = \langle\Phi|\widehat{H}|\Phi\rangle, \tag{12.28}$$

where we have used that Θ is normalized to unity, i. e.,

$$\langle\Theta|\Theta\rangle = \iint \Theta(\varsigma_1, \varsigma_2)^*\Theta(\varsigma_1, \varsigma_2)d\varsigma_1 d\varsigma_2 = 1. \tag{12.29}$$

This relation is readily verified from the relations (10.13).

Next, we get, from Eqs. (12.23) and (12.28), and by using that φ_{1s} is a normalized function,

$$\begin{aligned}
\mathcal{E} &= \iint dv_1 dv_2 \varphi_{1s}(\boldsymbol{r}_1)\varphi_{1s}(\boldsymbol{r}_2)\widehat{H}\varphi_{1s}(\boldsymbol{r}_1)\varphi_{1s}(\boldsymbol{r}_2) \\
&= \int dv_1 \varphi_{1s}(\boldsymbol{r}_1)\left\{-\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1}\right\}\varphi_{1s}(\boldsymbol{r}_1)\int dv_2 \varphi_{1s}(\boldsymbol{r}_2)\varphi_{1s}(\boldsymbol{r}_2) \\
&\quad + \int dv_2 \varphi_{1s}(\boldsymbol{r}_2)\left\{-\frac{1}{2}\nabla_2^2 - \frac{Z}{r_2}\right\}\varphi_{1s}(\boldsymbol{r}_2)\int dv_1 \varphi_{1s}(\boldsymbol{r}_1)\varphi_{1s}(\boldsymbol{r}_1) \\
&\quad + \iint dv_1 dv_2 \varphi_{1s}(\boldsymbol{r}_1)\varphi_{1s}(\boldsymbol{r}_2)\frac{1}{r_{12}}\varphi_{1s}(\boldsymbol{r}_1)\varphi_{1s}(\boldsymbol{r}_2) \\
&= 2\left\langle\varphi_{1s}(\boldsymbol{r})\middle| -\frac{1}{2}\nabla^2 - \frac{Z}{r}\middle|\varphi_{1s}(\boldsymbol{r})\right\rangle + J,
\end{aligned} \tag{12.30}$$

where the so-called *Coulomb integral* J is defined as

$$J = \iint dv_1 dv_2 \varphi_{1s}(\boldsymbol{r}_1)\varphi_{1s}(\boldsymbol{r}_2)\frac{1}{r_{12}}\varphi_{1s}(\boldsymbol{r}_1)\varphi_{1s}(\boldsymbol{r}_2). \tag{12.31}$$

The one-electron integral in the last line of Eq. (12.30) is nothing but the integral (12.17), and it may be shown that J has the value

$$J = \tfrac{5}{8}\zeta. \tag{12.32}$$

Hence we get

$$\mathcal{E} = 2\left(\tfrac{1}{2}\zeta^2 - Z\zeta\right) + \tfrac{5}{8}\zeta = \zeta^2 - \left(2Z - \tfrac{5}{8}\right)\zeta, \tag{12.33}$$

and

$$\frac{d\mathcal{E}}{d\zeta} = 2\left\{\zeta - \left(Z - \tfrac{5}{16}\right)\right\}. \tag{12.34}$$

The best wavefunction of the form (12.25) is consequently obtained when

$$\zeta = Z - \tfrac{5}{16}. \tag{12.35}$$

Its energy is obtained by inserting the value of ζ just obtained into the expression (12.33). It is found to be

$$E = -Z^2 + \tfrac{5}{8}Z - \tfrac{25}{256}. \tag{12.36}$$

For the helium atom ($Z = 2$), this becomes

$$E_{\mathrm{He}} = -\tfrac{729}{256}\,\mathrm{au} = -2.8477\,\mathrm{au}. \tag{12.37}$$

The experimental energy is known to be -2.9037 au. The simple trial function (12.25) is accordingly able to reproduce this value to within less than 2%. Note that our calculated value of E lies *above* the exact value as it should according to the variational theorem (12.12).

Also note that Eq. (12.35) applied to the helium atom ($Z = 2$) gives $\zeta = 1.6875$. This is just the value given for ζ_{1s} in Table 11.1, in accordance with the fact that the $1s$ orbital (12.24) derives from the radial function (11.48) by multiplication by $Y_{00}(\theta, \phi)$.

The variational method is obviously a method of great strength. We shall now consider a variant of the method in which one works with trial functions of the form

$$\Psi = \sum_{r=1}^{m} a_r \Phi_r,$$

where the functions Φ_r are supposed to be known from the outset. The variational parameters are thus the expansion coefficients a_r. This variant of the method is called the *linear variational method*, for obvious reasons. It is, for instance, by this method that we may construct molecular orbitals as linear combinations of atomic orbitals.

12.5 The Linear Variational Method

As mentioned above, we shall now consider a trial function of the form

$$\Psi = \sum_{r=1}^{m} a_r \Phi_r, \tag{12.38}$$

where $\{\Phi_1, \Phi_2, \dots, \Phi_m\}$ is a set of known functions, and the set of coefficients $\{a_1, a_2, \dots, a_m\}$ serve as variational parameters. We get then

$$\langle \Psi | \widehat{H} | \Psi \rangle = \sum_{r=1}^{m} \sum_{s=1}^{m} a_r^* a_s \langle \Phi_r | \widehat{H} | \Phi_s \rangle = \sum_{r=1}^{m} \sum_{s=1}^{m} a_r^* a_s H_{rs}, \tag{12.39}$$

and

$$\langle \Psi | \Psi \rangle = \sum_{r=1}^{m} \sum_{s=1}^{m} a_r^* a_s \langle \Phi_r | \Phi_s \rangle = \sum_{r=1}^{m} \sum_{s=1}^{m} a_r^* a_s S_{rs}, \tag{12.40}$$

where the H_{rs} are the elements of the *Hamiltonian matrix* and the S_{rs} the elements of the *overlap matrix*, in the notation introduced in connection with Eq. (5.39) of Sec. 5.3. The expectation value of $\widehat{H}$, i. e.,

$$\mathcal{E} = \frac{\langle \Psi | \widehat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \tag{12.41}$$

appears then formally as a function of both the coefficients $\{a_1, a_2, \dots, a_m\}$ and their complex conjugates $\{a_1^*, a_2^*, \dots, a_m^*\}$, but these two sets are of course not independent.

Let us write

$$\begin{cases} a_r = u_r + i v_r, \\ a_r^* = u_r - i v_r, \end{cases} \tag{12.42}$$

with u_r and v_r being real. Then u_r and v_r are truly independent, and we must therefore require that $\partial\mathcal{E}/\partial u_r$ and $\partial\mathcal{E}/\partial v_r$ both be zero for all r. The derivatives may be determined by the chain rule:

$$\begin{cases} \dfrac{\partial \mathcal{E}}{\partial u_r} = \dfrac{\partial \mathcal{E}}{\partial a_r}\dfrac{\partial a_r}{\partial u_r} + \dfrac{\partial \mathcal{E}}{\partial a_r^*}\dfrac{\partial a_r^*}{\partial u_r} = \dfrac{\partial \mathcal{E}}{\partial a_r} + \dfrac{\partial \mathcal{E}}{\partial a_r^*}, \\ \dfrac{\partial \mathcal{E}}{\partial v_r} = \dfrac{\partial \mathcal{E}}{\partial a_r}\dfrac{\partial a_r}{\partial v_r} + \dfrac{\partial \mathcal{E}}{\partial a_r^*}\dfrac{\partial a_r^*}{\partial v_r} = i\dfrac{\partial \mathcal{E}}{\partial a_r} - i\dfrac{\partial \mathcal{E}}{\partial a_r^*} \end{cases}. \tag{12.43}$$

The conditions that they vanish may therefore be written

$$\begin{cases} \dfrac{\partial \mathcal{E}}{\partial a_r} + \dfrac{\partial \mathcal{E}}{\partial a_r^*} = 0, \\ \dfrac{\partial \mathcal{E}}{\partial a_r} - \dfrac{\partial \mathcal{E}}{\partial a_r^*} = 0, \end{cases} \tag{12.44}$$

or, by adding and subtracting the two equations,

$$\frac{\partial \mathcal{E}}{\partial a_r} = 0 \qquad \text{and} \qquad \frac{\partial \mathcal{E}}{\partial a_r^*} = 0. \tag{12.45}$$

Thus, we may in fact treat the coefficients $\{a_1, a_2, \dots, a_m\}$ and their complex conjugates $\{a_1^*, a_2^*, \dots, a_m^*\}$ as if they were truly independent parameters.

Let a be one of these $2m$ parameters. We get then, from Eq. (12.41),

$$\begin{aligned} \frac{\partial \mathcal{E}}{\partial a} &= \frac{\langle\Psi|\Psi\rangle \frac{\partial}{\partial a}\langle\Psi|\widehat{H}|\Psi\rangle - \langle\Psi|\widehat{H}|\Psi\rangle \frac{\partial}{\partial a}\langle\Psi|\Psi\rangle}{\langle\Psi|\Psi\rangle^2} \\ &= \frac{\frac{\partial}{\partial a}\langle\Psi|\widehat{H}|\Psi\rangle - \mathcal{E}\frac{\partial}{\partial a}\langle\Psi|\Psi\rangle}{\langle\Psi|\Psi\rangle}. \end{aligned} \tag{12.46}$$

The condition for this to vanish is

$$\frac{\partial}{\partial a}\langle\Psi|\widehat{H}|\Psi\rangle - \mathcal{E}\frac{\partial}{\partial a}\langle\Psi|\Psi\rangle = 0. \tag{12.47}$$

When a is identified with a_r^*, and we insert the expressions (12.39) and (12.40) for $\langle\Psi|\widehat{H}|\Psi\rangle$ and $\langle\Psi|\Psi\rangle$ respectively, we get first

$$\begin{cases} \dfrac{\partial}{\partial a_r^*}\langle\Psi|\widehat{H}|\Psi\rangle = \displaystyle\sum_{s=1}^{m} H_{rs}a_s, \\ \dfrac{\partial}{\partial a_r^*}\langle\Psi|\Psi\rangle = \displaystyle\sum_{s=1}^{m} S_{rs}a_s, \end{cases} \tag{12.48}$$

and then

$$\sum_{s=1}^{m}(H_{rs} - \mathcal{E}S_{rs})a_s = 0. \tag{12.49}$$

Identifying a with a_r gives, on the other hand,

$$\sum_{s=1}^{m}(H_{sr} - \mathcal{E}S_{sr})a_s^* = 0. \tag{12.50}$$

But Eq. (5.7) shows that $S_{sr} = S_{rs}^*$, and since $\widehat{H}$ is Hermitian we also have, by Eq. (5.42), that $H_{sr} = H_{rs}^*$. Eq. (12.50) may accordingly be written

$$\sum_{s=1}^{m}(H_{rs}^* - \mathcal{E}S_{rs}^*)a_s^* = 0. \tag{12.51}$$

But this equation is nothing but the complex conjugate of Eq. (12.49) and hence gives no new condition.

The full condition, that Eq. (12.45) be satisfied for all r, reads consequently

$$\boxed{\sum_{s=1}^{m}(H_{rs} - ES_{rs})a_s = 0\,, \quad r = 1, 2, \ldots, m} \tag{12.52}$$

where we have written E instead of $\mathcal{E}$ to indicate that Eq. (12.45) is satisfied. This is a set of simultaneous equations for the coefficients $\{a_1, a_2, \ldots, a_m\}$. The problem of solving them is called the *secular problem.*

The equations may be expressed as a single matrix equation:

$$\begin{bmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \ldots & H_{1m} - ES_{1m} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \ldots & H_{2m} - ES_{2m} \\ \vdots & \vdots & & \vdots \\ H_{m1} - ES_{m1} & H_{m2} - ES_{m2} & \ldots & H_{mm} - ES_{mm} \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \\ \vdots \\ a_m \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ \vdots \\ 0 \end{bmatrix} \tag{12.53}$$

The determinant

$$\det|H_{rs} - ES_{rs}| = \begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \ldots & H_{1m} - ES_{1m} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \ldots & H_{2m} - ES_{2m} \\ \vdots & \vdots & & \vdots \\ H_{m1} - ES_{m1} & H_{m2} - ES_{m2} & \ldots & H_{mm} - ES_{mm} \end{vmatrix} \tag{12.54}$$

is called the *secular determinant.* Assume that its value is non-zero. The big matrix in Eq. (12.53) will then have an inverse. Multiplying Eq. (12.53) from the left by this inverse matrix gives $\{a_1, a_2, \ldots, a_m\} = \{0, 0, \ldots, 0\}$ which is called the *trivial solution*. It is of no interest to us, because the wavefunction (12.38) that it defines, is everywhere zero.

Non-trivial solutions of Eq. (12.53) exist only when the secular determinant vanishes, i. e., when

$$\det |H_{rs} - ES_{rs}| = 0. \tag{12.55}$$

This equation is called the *secular equation*. It is an algebraic equation of the mth degree in E, and therefore has m roots:

$$E = E_1 \leq E_2 \leq \ldots \leq E_m. \tag{12.56}$$

They are the eigenvalues of Eq. (12.53). It is only for these eigenvalues that the secular problem (12.53) has non-trivial solutions.

To determine the solution corresponding to the eigenvalue E_1, insert the value of E_1 everywhere in Eq. (12.53) and solve for the unknown coefficients $\{a_1, a_2, \ldots, a_m\}$. It is obvious from the form of Eq. (12.53) that if the set $\{a_1, a_2, \ldots, a_m\}$ is a solution, then so is the set $c\{a_1, a_2, \ldots, a_m\}$ where c is any complex constant. The wavefunction (12.38) is accordingly only determined to within an arbitrary constant. This is a familiar situation, and as usual it allows us to choose c such that Ψ be properly normalized. The normalization integral is, of course, given by Eq. (12.40).

Having determined a wavefunction Ψ_1 from the value of E_1, we may proceed in a similar way to determine a wavefunction Ψ_2 corresponding to E_2, and so on, until we have determined m linearly independent wavefunctions. If two or more E values in the list (12.56) are equal, we have a multiple root of the secular equation. Such a root is found to determine p linearly independent solutions, where p is the multiplicity of the root. Hence, the total number of linearly independent solutions will always be m.

In order to represent the energies of our physical problem, the eigenvalues that constitute the set $\{E_1, E_2, \ldots, E_m\}$ must be the expectation values of $\widehat{H}$ defined by the wavefunctions $\{\Psi_1, \Psi_2, \ldots, \Psi_m\}$. To see that this condition is actually fulfilled, multiply Eq. (12.52) by a_r^* and sum over r. This gives

$$\sum_{r=1}^{m} \sum_{s=1}^{m} a_r^* a_s (H_{rs} - ES_{rs}) = 0, \tag{12.57}$$

or, by observing Eqs. (12.39) and (12.40),

$$\langle \Psi | \widehat{H} | \Psi \rangle - E \langle \Psi | \Psi \rangle = 0. \tag{12.58}$$

But this relation implies that

$$E = \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle}, \qquad (12.59)$$

and this is precisely the expectation value of $\hat{H}$, according to the usual definition in Eq. (12.41).

Thus, E_1 must approximate the ground-state energy, and Ψ_1 must approximate the ground-state wavefunction for our system. The other solutions of the secular problem approximate the energies and wavefunctions of excited states. By the variational theorem (12.12), E_1 is an upper bound of the ground-state energy. It may be shown that the other energies in the list (12.56) likewise are upper bounds of excited state energies.

Having studied the problem of finding approximate solutions of the Schrödinger equation as linear combinations of a set of known functions, it is worth realizing that in some favorable situations it may even be possible to express exact solutions in this way. Such solutions must of course also satisfy the equations (12.52), a fact that we already discussed at the end of Sec. 5.10 on matrix algebra. But as shown in that section, the equations may then be derived in a much simpler way than the one used here.

We have now presented the basic variants of the variational method, namely, the linear variational method (this section) and methods based on non-linear parameters (the examples of the previous section). In advanced applications, these two methods may be mixed, and this makes the variational method an extremely powerful method of obtaining approximate solutions of the Schrödinger equation for even very complicated problems in the theory of atoms, molecules and solids.

We close the present chapter with an important comment on the solution of the secular problem (12.53) in the presence of operators that commute with the Hamiltonian.

12.6 Factorization of Secular Problems

It often happens that many of the matrix elements in the secular problem (12.53) vanish. This may, for instance, be the case if there is an operator present that commutes with the Hamiltonian. Let $\hat{B}$ be such an operator. We have then

$$\hat{H}\hat{B} - \hat{B}\hat{H} = 0. \qquad (12.60)$$

Assume now, that the functions $\{\Phi_1, \Phi_2, \ldots, \Phi_m\}$ in (12.38) are eigenfunctions of $\widehat{B}$ with eigenvalues $\{b_1, b_2, \ldots, b_m\}$, i. e.,

$$\widehat{B}\Phi_r = b_r\Phi_r\,, \qquad r = 1, 2, \ldots, m. \tag{12.61}$$

Assume also that $\widehat{B}$ is a Hermitian operator. We get then

$$\begin{aligned}\langle\Phi_r|\widehat{H}\widehat{B}|\Phi_s\rangle - \langle\Phi_r|\widehat{B}\widehat{H}|\Phi_s\rangle &= \langle\Phi_r|\widehat{H}\widehat{B}|\Phi_s\rangle - \langle\widehat{B}\Phi_r|\widehat{H}|\Phi_s\rangle \\ &= (b_s - b_r)\langle\Phi_r|\widehat{H}|\Phi_s\rangle\end{aligned} \tag{12.62}$$

where we have used the turn-over rule (5.42) and the fact that the eigenvalues of a Hermitian operator are real.

Due to the assumption (12.60), the result in (12.62) must be zero. The matrix element $\langle\Phi_r|\widehat{H}|\Phi_s\rangle$ will consequently vanish whenever b_r and b_s are different. The only matrix elements of $\widehat{H}$ that don't necessarily vanish are the diagonal elements ($r = s$) and matrix elements between basis functions with the same eigenvalue of $\widehat{B}$.[2]

Assume, for instance, that we use the linear variational method within a four-dimensional function space, and that the basis functions Φ_1 and Φ_2 are eigenfunctions of $\widehat{B}$ with one and the same eigenvalue, and that Φ_3 and Φ_4 are eigenfunctions of $\widehat{B}$ with another eigenvalue. The eigenvalue equation (12.53) becomes then

$$\begin{bmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & 0 & 0 \\ H_{21} - ES_{21} & H_{22} - ES_{22} & 0 & 0 \\ 0 & 0 & H_{33} - ES_{33} & H_{34} - ES_{34} \\ 0 & 0 & H_{43} - ES_{43} & H_{44} - ES_{44} \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} \tag{12.63}$$

By direct substitution, one finds that the eigenvectors of this *factorized eigenvalue problem* are of the form $(a_1, a_2, 0, 0)$ and $(0, 0, a_3, a_4)$, where (a_1, a_2) and (a_3, a_4) are eigenvectors of the smaller secular problems

$$\begin{pmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \tag{12.64}$$

and

$$\begin{pmatrix} H_{33} - ES_{33} & H_{34} - ES_{34} \\ H_{43} - ES_{43} & H_{44} - ES_{44} \end{pmatrix} \begin{pmatrix} a_3 \\ a_4 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}. \tag{12.65}$$

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[2] The reader will note that we have just rederived the theorem (5.74).

The functions that solve the secular problem (12.63) are consequently of the form $a_1\Phi_1 + a_2\Phi_2$ and $a_3\Phi_3 + a_4\Phi_4$. The generalization of this finding is:

> Assume that we have some m-dimensional function space, and that it is possible to choose a basis $\{\Phi_1, \Phi_2, \dots, \Phi_m\}$ in this space such that each basis function is an eigenfunction of a given Hermitian operator, $\widehat{B}$, that commutes with the Hamiltonian. Then only functions with the same eigenvalue for $\widehat{B}$ can combine in a linear variational calculation. As a result, the solutions of the secular problem will again be eigenfunctions of $\widehat{B}$. (12.66)

Needless to say, this is a result of great value, both conceptually and computationally.

Supplementary Reading

The bibliography, entries [25], [26], and [28].

Problems

12.1. In the present exercise, we perform the instructive calculations behind the examples on the pages 275–278. Thus, we shall consider the Hamiltonian

$$\widehat{H} = -\frac{1}{2}\nabla^2 - \frac{Z}{r} \quad \text{(atomic units)},$$

and evaluate its expectation value $\langle\widehat{H}\rangle$ for each of the two normalized trial functions

$$\varphi = \sqrt{\frac{\zeta^3}{\pi}}e^{-\zeta r} \quad \text{and} \quad \chi = \left(\frac{2\alpha}{\pi}\right)^{\frac{3}{4}} e^{-\alpha r^2}.$$

a. Calculate the expectation value $\langle\widehat{T}\rangle$ of the kinetic energy

$$\widehat{T} = -\tfrac{1}{2}\nabla^2$$

for φ og χ, as function of ζ og α, respectively.

b. Similarly, calculate the expectation value $\langle\widehat{V}\rangle$ of the potential energy

$$\widehat{V} = -\frac{Z}{r}$$

for φ og χ.

c. Next, form the expectation value $\langle \hat{H} \rangle$ for each of the two trial functions.

d. Determine the value of ζ, for which $\langle \varphi|\hat{H}|\varphi\rangle$ is minimal.

e. Similarly, determine the value of α, for which $\langle \chi|\hat{H}|\chi\rangle$ is minimal.

f. For $Z = 1$, calculate the values of $\langle \varphi|\hat{H}|\varphi\rangle$ and $\langle \chi|\hat{H}|\chi\rangle$ corresponding to the optimal values of ζ og α determined above.

g. Show that $\langle \hat{T} \rangle = -\frac{1}{2}\langle \hat{V} \rangle$ for both of the optimized functions.
This is the *virial theorem* for the motion in a Coulomb potential.
(For the motion in a harmonic potential, the virial theorem reads $\langle \hat{T} \rangle = \langle \hat{V} \rangle$, cf. Problem 7.1.)

h. Compare the graphs of the radial function R_{1s} for the two optimized functions φ and χ.
Similarly, compare the graphs of the radial function P_{1s}.
(Use the standard integrals (6.31) and (9.23).)

12.2. In continuation of the previous exercise, let us approximate the hydrogen 1*s* orbital by a function of the form

$$\varphi_{1s}(\boldsymbol{r}) = a_1\chi_1(\boldsymbol{r}) + a_2\chi_2(\boldsymbol{r}),$$

where $\chi_1(\boldsymbol{r})$ and $\chi_2(\boldsymbol{r})$ are normalized Gaussian-type orbitals:

$$\chi_1(\boldsymbol{r}) = \left(\frac{2\alpha_1}{\pi}\right)^{\frac{3}{4}} e^{-\alpha_1 r^2}, \quad \alpha_1 = 0.2015,$$
$$\chi_2(\boldsymbol{r}) = \left(\frac{2\alpha_2}{\pi}\right)^{\frac{3}{4}} e^{-\alpha_2 r^2}, \quad \alpha_2 = 1.3321,$$

in atomic units.

a. The overlap integral $S_{12} = \langle \chi_1|\chi_2\rangle$ has the value 0.5554.
Verify this value.

b. By evaluating integrals similar to those in Problem 12.1, the matrix elements of the Hamiltonian

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{Z}{r}$$

are found to to be

$$H_{11} = -0.4141\,\text{au},$$
$$H_{22} = 0.1564\,\text{au},$$
$$H_{12} = -0.4844\,\text{au}.$$

Set up the secular problem defined by the trial wavefunction $\varphi_{1s}(\boldsymbol{r})$ and determine the best approximation, E, to the ground-state energy.
Does the determined E-value satisfy the variational theorem (12.12)?

c. Find the coefficients a_1 and a_2 going with the determined energy value E, and write down the corresponding trial wavefunction $\varphi_{1s}(\boldsymbol{r})$, properly normalized to unity.

d. Compare the graphs of the radial functions R_{1s} and P_{1s} from $\varphi_{1s}(\boldsymbol{r})$, with the graphs determined in the previous problem.

12.3. In this exercise, we consider the Stark effect and the Zeeman effect for a hydrogen atom with principal quantum number $n = 3$. In atomic units, the Bohr magneton (10.87) has the value 1/2, and the Hamiltonian (10.86) becomes

$$\widehat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r} + \frac{1}{2}(\hat{\ell}_z + 2\hat{s}_z)B + zE,$$

where we have assumed that both the magnetic field $\boldsymbol{B}$ and the electric field $\boldsymbol{E}$ point in the direction of the positive z-axis. The spin-orbit coupling term and the diamagnetic term in the Hamiltonian have been neglected.

a. Consider first the Zeeman effect, by putting E equal to 0. The resulting Hamiltonian is denoted $\widehat{H}_{Zeeman}$. Show that the 18 spin-orbitals $\psi_{3\ell m_\ell m_s}$ obtained by letting the quantum numbers ℓ, m_ℓ, m_s assume all allowed values, are eigenfunctions of $\widehat{H}_{Zeeman}$. In analogy with Table 10.1, write down all the corresponding energies, and hence discuss the number of energy levels and their degeneracies.

b. Next, consider the Stark effect, by putting B equal to 0. The resulting Hamiltonian is denoted $\widehat{H}_{Stark}$. It is spin independent, and we therefore neglect the spin of the electron and merely consider the 9 spatial orbitals $\varphi_{3\ell m_\ell}$ obtained by letting the quantum numbers ℓ, m_ℓ assume all allowed values. Using the linear variational method, we look for approximate eigenfunctions of $\widehat{H}_{Stark}$ as linear combinations of the 9 (complex valued) orbitals $\varphi_{3\ell m_\ell}$. The matrix corresponding to the operator $z = r\cos\theta$ is given below.

Write down the form of the normalized orbitals φ_{3p_0} and φ_{3d_0} and verify that the matrix element $\langle\varphi_{3p_0}|z|\varphi_{3d_0}\rangle = \langle R_{3p}|r|R_{3d}\rangle\langle Y_{10}|\cos\theta|Y_{20}\rangle$ does have the value $3\sqrt{3}$.

c. For two of the approximate eigenfunctions of $\widehat{H}_{Stark}$, one finds

$$\varepsilon_1 = \varepsilon_0 - 9E, \qquad \varphi_1 = \frac{1}{\sqrt{6}}\left(\sqrt{2}\varphi_{3s} - \sqrt{3}\varphi_{3p_0} + \varphi_{3d_0}\right)$$

and

$$\varepsilon_2 = \varepsilon_0 + 9E, \qquad \varphi_2 = \frac{1}{\sqrt{6}}\left(\sqrt{2}\varphi_{3s} + \sqrt{3}\varphi_{3p_0} + \varphi_{3d_0}\right),$$

where ε_0 is the energy of a hydrogen atom without field ($n = 3$, $\varepsilon_0 = -\frac{1}{18}$ hartree).

	$3s$	$3p_0$	$3d_0$	$3p_1$	$3d_1$	$3p_{-1}$	$3d_{-1}$	$3d_2$	$3d_{-2}$
$3s$	0	$3\sqrt{6}$	0	0	0	0	0	0	0
$3p_0$	$3\sqrt{6}$	0	$3\sqrt{3}$	0	0	0	0	0	0
$3d_0$	0	$3\sqrt{3}$	0	0	0	0	0	0	0
$3p_1$	0	0	0	0	9/2	0	0	0	0
$3d_1$	0	0	0	9/2	0	0	0	0	0
$3p_{-1}$	0	0	0	0	0	0	9/2	0	0
$3d_{-1}$	0	0	0	0	0	9/2	0	0	0
$3d_2$	0	0	0	0	0	0	0	0	0
$3d_{-2}$	0	0	0	0	0	0	0	0	0

By referring to Sec. 12.6, determine the remaining 7 approximate eigenfunctions of $\widehat{H}_{Stark}$, together with their energies. Like φ_1 and φ_2, the eigenfunctions should be properly normalized.

Chapter 13

Diatomic Molecules

Contents

Now that we are familiar with the language of quantum mechanics and know how to describe atoms we are well prepared to discuss the structure of molecules. But beware, we are about to enter a complicated field. The name of molecules is legion, and each molecule hides a wonderful world all its own. We can make many generalizations, and we can divide molecules into separate classes; and in this way we gain solid fundamental understanding. But we must never forget that no two molecules are entirely alike. A molecule has several degrees of freedom and an incredible number of stationary states, and in many of these *molecular eigenstates* the various degrees of freedom interact in an intricate way.

It is, however, found that the ground and lower excited states of most molecules submit to a fairly simple theoretical description. This is the so-called *adiabatic description* which is built on the conception that the electrons, because of their much smaller mass, move so much faster than the nuclei that they adjust to the motion of the latter almost instantaneously. Following this idea, one writes the wavefunction of a molecular eigenstate in the form

$$\Psi_{\text{mol}}(x,\rho)=\Psi(x;\rho)\kappa(\rho) \tag{13.1}$$

where x collectively denotes all electron coordinates and ρ all nuclear coordinates. In words: The probability amplitude $\Psi_{\text{mol}}(x,\rho)$ is supposed to be the product of the probability amplitude $\kappa(\rho)$ for the nuclei to be at the geometry ρ, and the probability amplitude $\Psi(x;\rho)$ for the electrons to be at the configuration x, assuming that the nuclei are at the geometry ρ. $\kappa(\rho)$ is the *nuclear wavefunction*. $\Psi(x;\rho)$ is called the *electronic wavefunction*. As we shall see, it is determined by solving an *electronic Schrödinger equation* with the nuclei clamped at the geometry defined by ρ. We have a new electronic Schrödinger equation for each value of ρ. Thus, $\Psi(x;\rho)$ becomes a parametric function of ρ.

The present chapter will be devoted to the problem of determining electronic wavefunctions. Let us, however, first discuss the basis of the adiabatic description.

13.1 The Adiabatic Approximation

Consider a system of N electrons and K nuclei, interacting through Coulomb forces. With the neglect of all spin terms its Hamiltonian is, in atomic units,

$$\boxed{\begin{aligned}\widehat{H}_{\text{mol}}= & -\sum_{g=1}^{K}\frac{1}{2M_g}\nabla_g^2+\frac{1}{2}\sum_{g=1}^{K}\sum_{h=1}^{K}{}'\frac{Z_gZ_h}{r_{gh}}\\ & -\sum_{i=1}^{N}\frac{1}{2}\nabla_i^2-\sum_{g=1}^{K}\sum_{i=1}^{N}\frac{Z_g}{r_{ig}}+\frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}{}'\frac{1}{r_{ij}}\end{aligned}} \tag{13.2}$$

where i and j label the electrons, and g and h the nuclei. M_g is the mass of the gth nucleus in atomic units, that is, the nuclear mass in units of the electron mass. As usual, the primes on the summation signs indicate that terms for which the two indices become equal are omitted from the sums.

The first term in the Hamiltonian (13.2) represents the kinetic energy of the nuclei, and the second term the repulsion between the nuclei. The third term represents the kinetic energy of the electrons, and the fourth term the attraction between the electrons and the nuclei. Finally, the last term represents the electron-electron repulsion. The full *molecular Schrödinger equation* is

$$\widehat{H}_{\text{mol}}\Psi_{\text{mol}}(x,\rho) = E_{\text{mol}}\Psi_{\text{mol}}(x,\rho). \tag{13.3}$$

To arrive at approximate solutions of the form (13.1) we proceed as follows.

We introduce an *electronic Hamiltonian*, which we shall denote by $\widehat{H}$. It is taken to be the sum of the three last terms of $\widehat{H}_{\text{mol}}$, i. e., we make the definition

$$\boxed{\widehat{H} = -\sum_{i=1}^{N}\frac{1}{2}\nabla_i^2 - \sum_{g=1}^{K}\sum_{i=1}^{N}\frac{Z_g}{r_{ig}} + \frac{1}{2}\sum_{i=1}^{N}{\sum_{j=1}^{N}}'\frac{1}{r_{ij}}} \tag{13.4}$$

The Hamiltonian (13.2) may then be written

$$\boxed{\widehat{H}_{\text{mol}} = -\sum_{g=1}^{K}\frac{1}{2M_g}\nabla_g^2 + \widehat{H} + \frac{1}{2}\sum_{g=1}^{K}{\sum_{h=1}^{K}}'\frac{Z_gZ_h}{r_{gh}}} \tag{13.5}$$

and the full molecular Schrödinger equation (13.3) takes the form

$$\begin{aligned} -\sum_{g=1}^{K}\frac{1}{2M_g}\nabla_g^2\Psi_{\text{mol}}(x,\rho) + \widehat{H}\Psi_{\text{mol}}(x,\rho) + \frac{1}{2}\sum_{g=1}^{K}{\sum_{h=1}^{K}}'\frac{Z_gZ_h}{r_{gh}}\Psi_{\text{mol}}(x,\rho)& \\ = E_{\text{mol}}\Psi_{\text{mol}}(x,\rho).& \end{aligned} \tag{13.6}$$

We now insert the adiabatic expression (13.1) in this equation and proceed as we have done before, when a separation of variables was proposed (cf. Secs. 4.1, 8.1 and 8.2). Thus, we divide the equation by $\Psi(x;\rho)\kappa(\rho)$ to get

$$\begin{aligned} \frac{-1}{\Psi(x;\rho)\kappa(\rho)}\sum_{g=1}^{K}\frac{1}{2M_g}\nabla_g^2\Psi(x;\rho)\kappa(\rho) + \frac{1}{\Psi(x;\rho)}\widehat{H}\Psi(x;\rho)& \\ + \frac{1}{2}\sum_{g=1}^{K}{\sum_{h=1}^{K}}'\frac{Z_gZ_h}{r_{gh}} = E_{\text{mol}}.& \end{aligned} \tag{13.7}$$

We have used that $\widehat{H}\Psi(x;\rho)\kappa(\rho) = \kappa(\rho)\widehat{H}\Psi(x;\rho)$, which follows from the fact that the action of $\widehat{H}$ does not involve differentiations with respect to the nuclear coordinates.

In the first term on the right-hand side of Eq. (13.7) the operators ∇_g^2 act on both $\Psi(x;\rho)$ and $\kappa(\rho)$. However, we now make the assumption that $\Psi(x;\rho)$ varies sufficiently slowly with ρ that we may be allowed to neglect the action of ∇_g^2 on $\Psi(x;\rho)$. *Under that assumption* Eq. (13.7) becomes

$$\frac{-1}{\kappa(\rho)}\sum_{g=1}^{K}\frac{1}{2M_g}\nabla_g^2\kappa(\rho) + \frac{1}{\Psi(x;\rho)}\widehat{H}\Psi(x;\rho) + \frac{1}{2}\sum_{g=1}^{K}\sum_{h=1}^{K}{}'\frac{Z_gZ_h}{r_{gh}} = E_{\text{mol}}. \tag{13.8}$$

Here, the only term that contains the electronic coordinates x is the second term on the left-hand side. Obviously, it must simplify to a function that is independent of x for the equation to be satisfied. We call this function $E(\rho)$ and get thereby the requirement

$$\boxed{\widehat{H}\Psi(x;\rho) = E(\rho)\Psi(x;\rho)} \tag{13.9}$$

Inserting this relation in Eq. (13.8) gives, after multiplication by $\kappa(\rho)$,

$$\boxed{\left\{-\sum_{g=1}^{K}\frac{1}{2M_g}\nabla_g^2 + U(\rho)\right\}\kappa(\rho) = E_{\text{mol}}\kappa(\rho)} \tag{13.10}$$

where

$$\boxed{U(\rho) = E(\rho) + \frac{1}{2}\sum_{g=1}^{K}\sum_{h=1}^{K}{}'\frac{Z_gZ_h}{r_{gh}}} \tag{13.11}$$

Eq. (13.9) is the electronic Schrödinger equation that we alluded to in the introductory remarks. It must be solved for each nuclear geometry. A definite nuclear geometry is obtained by clamping the nuclei at a particular set of values of the nuclear coordinates ρ. When the electronic Schrödinger equation is solved for all nuclear geometries, $E(\rho)$ becomes a function of ρ. This function, which we denote the *electronic-energy function*, defines an *electronic-energy surface*. To each point on the surface there corresponds an electronic wavefunction $\Psi(x;\rho)$.

Adding the internuclear repulsion to the electronic-energy function leads to the function $U(\rho)$ of Eq. (13.11). It is called the *potential-energy function*, and the surface it defines is called a *potential-energy surface* (PES). Sometimes one also refers to $U(\rho)$ as the electronic energy including internuclear repulsion.

Eq. (13.10) may be interpreted as the Schrödinger equation for the nuclear motion. Obviously, the function $U(\rho)$ serves as the potential energy function for the motion of the nuclei, or, as it is often said: "The motion of the nuclei takes place on the potential-energy surface."

Imagine, now, a certain conformation of the atomic nuclei and subject this conformation with its surrounding electrons to overall translations and rotations. Such transformations do not change inter-particle distances and leave, therefore, the electronic Hamiltonian (13.4) and the internuclear-repulsion energy unchanged. The electronic wavefunction $\Psi(x;\rho)$ and the potential-energy function $U(\rho)$ are therefore independent of the orientation and location in space of the nuclear conformation. For a diatomic molecule this implies, in particular, that $\Psi(x;\rho)$ and $U(\rho)$ only depend upon the nuclear positions through the internuclear distance R.

This completes the derivation of the adiabatic description from the molecular Schrödinger equation (13.3). The description is an approximate one, obtained by neglecting the action of ∇_g on $\Psi(x;\rho)$, and thereby what may be said to be the dynamical interaction between the electronic and nuclear motions. The validity of the adiabatic description must be separately judged in each actual case. But as we indicated in the introduction, it is a good approximation for most molecules, for the states associated with the lower potential-energy surfaces.

In using the plural form of the word surface, we realize that the electronic Schrödinger equation (13.9) has, not just one, but a whole series of solutions for each nuclear geometry. Thus, the adiabatic description does in fact involve *a set* of electronic wavefunctions $\Psi_n(x;\rho)$, with corresponding electronic-energy functions $E_n(\rho)$, corresponding potential-energy surfaces and potential-energy functions $U_n(\rho)$, and with corresponding nuclear wavefunctions $\kappa_n(\rho)$.

It should be noted that electronic wavefunctions belonging to different potential-energy surfaces are mutual orthogonal for each nuclear geometry. This follows from the general theorem (5.67), by realizing that the said functions are eigenfunctions of the same Hamiltonian, namely, the electronic Hamiltonian $\widehat{H}$. As always, we may take the electronic wavefunctions to be normalized to unity, and we may therefore write

$$\int \Psi_m^*(x;\rho)\Psi_n(x;\rho)dx = \delta_{mn}. \tag{13.12}$$

Note, however, that there is no similar condition on nuclear wavefunctions associated with different potential-energy surfaces, because such functions are eigenfunctions of different Hamiltonians, specified by different $U_n(\rho)$ potentials in Eq. (13.10). On the other hand, Eq. (13.10) may have several eigenfunctions for the same $U_n(\rho)$ potential, and these functions must be mutually orthogonal. To specify the different nuclear wavefunctions for a given $U_n(\rho)$ potential, additional indices are of course needed. These indices refer to the vibrational and rotational motions of the molecule, as discussed in the following chapter.

The idea of separating the electronic and nuclear motions goes back to a famous paper by Born and Oppenheimer,[1] and the approximation of writing the total wavefunction in the form (13.1) is accordingly often referred to as the *Born-Oppenheimer approximation*. It should be noted, however, that Born and Oppenheimer's discussion only pertained to situations where $U(\rho)$ has a minimum for some nuclear geometry ρ_0, the so-called equilibrium geometry. Also, Born and Oppenheimer wrote the electronic wavefunction as $\Psi(x;\rho_0)$ rather than $\Psi(x;\rho)$ as we have done. Thus, they did not allow the electrons to follow the nuclei. By actually writing $\Psi(x;\rho)$ it becomes possible to describe situations where the nuclei make large excursions from an equilibrium conformation, and also situations where no such conformation exists at all.

Although the adiabatic description is a successful one, there are of course many situations where it is poor or breaks down completely. In such cases one must take refuge in other methods. A possibility that is often used is to write the total molecular wavefunction in the form[2]

$$\Psi_{\mathrm{mol}}(x,\rho) = \sum_n \Psi_n(x;\rho)\kappa_n(\rho), \tag{13.13}$$

where the meaning of the electronic wavefunctions $\Psi_n(x;\rho)$ is the same as before, i. e., they are solutions of the electronic Schrödinger equation (13.6). By substituting the expansion (13.13) into the molecular Schrödinger equation (13.3), successively multiplying from the left with $\Psi_1^*(x;\rho)$, $\Psi_2^*(x;\rho)$, etc., and finally integrating over the electronic coordinates, one obtains a set of coupled differential equations from which the nuclear functions $\kappa_n(\rho)$ may be determined. That the total molecular wavefunction has the form (13.13) implies, of

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[1] M. Born and R. Oppenheimer, Ann. Phys. **84**, 457 (1927).

[2] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices*, Oxford, 1954.

course, that *the motion cannot be confined to a single potential-energy surface.* This situation occurs, in particular, when different potential surfaces come close together for some nuclear geometry.

The representation (13.13) is also a good starting point for the evaluation of approximate descriptions. A careful review, including a discussion and classification of different variants of the adiabatic approximation, has been presented by Ballhausen and Hansen.[3] In their notation, the description that we have presented constitutes the *Born-Oppenheimer adiabatic approximation.* Another important variant, denoted the *Born-Huang adiabatic approximation,* includes an additional term

$$C(\rho) = \int \Psi^*(x;\rho)\left(-\sum_{g=1}^{K}\frac{1}{2M_g}\nabla_g^2\right)\Psi(x;\rho)dx \tag{13.14}$$

in the expression (13.11) for $U(\rho)$. It emerges naturally as a contribution to the diagonal terms in the above-mentioned coupled equations, based on the representation (13.13). The numerical effect of the term is not large, but it does have the theoretically important effect of making the corresponding E_{mol} in Eq. (13.10) an upper bound for the exact molecular ground-state energy, in a similar way as the expectation value $\mathcal{E}$ in Eq. (12.12) is an upper bound for the exact ground-state energy E_0.

We shall now leave the general discussion and study the solutions of the electronic Schrödinger equation (13.6) for some actual molecules. As the expansion (13.13) suggests, we need the solutions of Eq. (13.6) regardless of the validity of the adiabatic approximation.

13.2 One-Electron Diatomic Molecules

Just as it was wise to study the hydrogen-like atom before many-electron atoms, so it is wise to begin the study of diatomic molecules with the one-electron case. We consider, therefore, the motion of a single electron in the Coulomb fields of two fixed nuclei, A and B. The electronic Hamiltonian (13.4) becomes

$$\boxed{\widehat{H} = -\frac{1}{2}\nabla^2 - \frac{Z_a}{r_a} - \frac{Z_b}{r_b}} \tag{13.15}$$

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[3] C. J. Ballhausen and Aa. E. Hansen, Ann. Revs. Phys. Chem. **23**, 15 (1972).

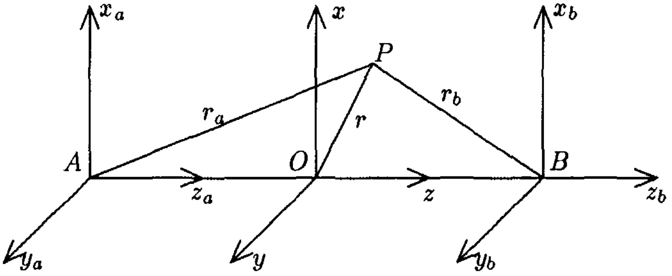

Figure 13.1: Coordinate systems for diatomic molecules. A and B are the atomic centers. $AO = OB = R/2$, where R is the internuclear distance. P is the field point of an electron.

where r_a and r_b are the distances from the electron to the nuclei A and B, respectively. We denote the internuclear distance by R and choose to describe the electronic wavefunction in a coordinate system whose z-axis coincides with the internuclear axis. Three ways of choosing such a system are shown in Fig. 13.1.

For the hydrogen-like atom it was possible to separate the variables in the Schrödinger equation by introducing spherical polar coordinates. Such a separation is, in fact, possible for any central-field problem (Sec. 8.2). The potential-energy part of the Hamiltonian (13.15) for our one-electron diatomic molecule is not of the central-field type, and hence we can no longer separate the variables in spherical polar coordinates. It turns out, however, that it is possible to separate the variables by introducing so-called *spheroidal coordinates* (also called ellipsoidal coordinates). They are defined as follows

$$\begin{cases} \mu = \dfrac{r_a + r_b}{R} & 1 \leq \mu \leq \infty, \\ \nu = \dfrac{r_a - r_b}{R} & -1 \leq \nu \leq 1, \\ \phi & 0 \leq \phi \leq 2\pi, \end{cases} \tag{13.16}$$

where ϕ has the same meaning as in spherical polar coordinates, i.e., ϕ is the angle from the xz-plane to the plane defined by r_a and r_b. The reverse relations can be shown to be

$$\begin{cases} x = \frac{R}{2}\left[\left(\mu^2-1\right)\left(1-\nu^2\right)\right]^{\frac{1}{2}}\cos\phi, \\ y = \frac{R}{2}\left[\left(\mu^2-1\right)\left(1-\nu^2\right)\right]^{\frac{1}{2}}\sin\phi, \\ z = \frac{R}{2}\mu\nu, \end{cases} \tag{13.17}$$

where x, y and z are measured from the midpoint of the $A - B$ bond, as in Fig. 13.1.

In the notation of Appendix C, the spheroidal coordinates define an orthogonal, curvilinear coordinate system. The expressions for the volume element and the Laplacian may therefore be evaluated from the general expressions (C.14) and (C.15) They are

$$dv = \left(\frac{R}{2}\right)^3 \left(\mu^2 - \nu^2\right) d\mu d\nu d\phi, \tag{13.18}$$

and

$$\nabla^2 = \left(\frac{2}{R}\right)^2 \frac{1}{\mu^2-\nu^2}\left\{\frac{\partial}{\partial\mu}\left[\left(\mu^2-1\right)\frac{\partial}{\partial\mu}\right] + \frac{\partial}{\partial\nu}\left[\left(1-\nu^2\right)\frac{\partial}{\partial\nu}\right] + \frac{\mu^2-\nu^2}{\left(\mu^2-1\right)\left(1-\nu^2\right)}\frac{\partial^2}{\partial\phi^2}\right\}. \tag{13.19}$$

We also get, from (13.16),

$$r_a = \frac{R}{2}(\mu+\nu), \qquad r_b = \frac{R}{2}(\mu-\nu). \tag{13.20}$$

By inserting the expressions (13.19) and (13.20) into (13.15) we get the electronic Hamiltonian in spheroidal coordinates, and hence the electronic Schrödinger equation

$$\widehat{H}\psi(\mu,\nu,\phi;R) = E(R)\psi(\mu,\nu,\phi;R). \tag{13.21}$$

As a first step towards solving this equation we note that the potential-energy part of the electronic Hamiltonian (13.15) is independent of the variable ϕ. Thus, the electronic Hamiltonian only depends on ϕ through the kinetic-energy operator, i. e., through the Laplacian ∇^2. From the explicit expression (13.19) for the Laplacian, it then follows that we may separate the variable ϕ from the variables μ and ν and write

$$\psi(\mu,\nu,\phi;R) = F(\mu,\nu;R)\Phi(\phi), \tag{13.22}$$

where $\Phi(\phi)$ satisfies the equation

$$\frac{d^2}{d\phi^2}\Phi(\phi) = -\lambda^2\Phi(\phi), \tag{13.23}$$

while $F(\mu,\nu;R)$ satisfies the equation

$$\begin{aligned} -\frac{1}{2}\left(\frac{2}{R}\right)^2 \frac{1}{\mu^2-\nu^2}\left\{\frac{\partial}{\partial\mu}\left[\left(\mu^2-1\right)\frac{\partial}{\partial\mu}\right]+\frac{\partial}{\partial\nu}\left[\left(1-\nu^2\right)\frac{\partial}{\partial\nu}\right]\right\}F(\mu,\nu;R) \\ +\frac{1}{2}\left(\frac{2}{R}\right)^2\frac{\lambda^2}{\left(\mu^2-1\right)\left(1-\nu^2\right)}F(\mu,\nu;R)+V(\mu,\nu;R)F(\mu,\nu;R) \\ = EF(\mu,\nu;R). \end{aligned} \tag{13.24}$$

$V(\mu,\nu;R)$ is the potential-energy part of the Hamiltonian,

$$V(\mu,\nu;R) = -\frac{Z_a}{r_a}-\frac{Z_b}{r_b} = -\frac{2Z_a}{R(\mu+\nu)}-\frac{2Z_b}{R(\mu-\nu)}, \tag{13.25}$$

and λ^2 is the separation constant. Writing the separation constant as λ^2 is, of course, dictated by hindsight, but it is really no limitation, for any constant may be written in this way (by allowing for complex values of λ).

Eq. (13.23) is familiar. It has the complete solution

$$\begin{aligned} \Phi(\phi) &= a_1\cos\lambda\phi + a_2\sin\lambda\phi \\ &= b_1e^{i\lambda\phi}+b_2e^{-i\lambda\phi}. \end{aligned} \tag{13.26}$$

We must require that $\Phi(\phi+2\pi) = \Phi(\phi)$, and hence that λ be an integer ($\lambda = 0,1,2,\ldots$). There are, however no restrictions on the values of the coefficients a_1, a_2 and b_1, b_2.

Having solved Eq. (13.23), we must solve Eq. (13.24). For each value of λ, this leads to a set of solutions which may be numbered by an integer $n = 1,2,3,\ldots$, such that the energy increases with n. Thus, we have the functions $F_{n\lambda}(\mu,\nu;R)$ and the corresponding energies $E_{n\lambda}$.

By combining the solutions of Eqs. (13.23) and (13.24), we obtain the solutions of the electronic Schrödinger equation (13.21) on the form

$$\boxed{\begin{array}{ll} \psi_{n\lambda\gamma}(\mu,\nu,\phi;R) = F_{n\lambda}(\mu,\nu;R)e^{\pm i\lambda\phi}, & \lambda = 0,1,2,\ldots \\ \text{or, equivalently,} & \\ \psi_{n\lambda\gamma}(\mu,\nu,\phi;R) = F_{n\lambda}(\mu,\nu;R)\left\{\begin{array}{l}\cos\lambda\phi, \\ \sin\lambda\phi,\end{array}\right. & \begin{array}{l}\lambda = 0,1,2,\ldots \\ \lambda = 1,2,\ldots\end{array} \end{array}} \tag{13.27}$$

The energy levels are doubly degenerate for $\lambda \neq 0$, and non-degenerate for $\lambda = 0$. For $\lambda \neq 0$, the two solutions may be distinguished by means of the index γ.

By analogy with the notation (9.5) used for atoms, one also introduces letter symbols for diatomic molecules:

$$\boxed{\begin{array}{c}\text{For the possible values of } \lambda,\\ \lambda = 0, 1, 2, 3, \ldots\\ \text{one often uses the letter symbols}\\ \sigma,\ \pi,\ \delta,\ \phi, \ldots\end{array}} \tag{13.28}$$

The physical meaning of λ is that it measures the *magnitude* of the angular momentum about the internuclear axis. Let us introduce the operators

$$\begin{cases} \hat{l}_z^2 = -\hbar^2 \dfrac{\partial^2}{\partial \phi^2}, \\ \hat{l}_z = -i\hbar \dfrac{\partial}{\partial \phi}, \\ \hat{\sigma}_{xz} \equiv \text{reflection in the } xz\text{-plane} \equiv \text{change sign of } \phi. \end{cases} \tag{13.29}$$

According to Eq. (8.44), $\hat{l}_z$ is the operator representing the angular momentum about the z-axis (the molecular axis). $\hat{l}_z^2$ is the square of this operator, and $\hat{\sigma}_{xz}$ is a *reflection operator*. From the expression (13.19), it is seen that these three operators all commute with the Hamiltonian $\widehat{H}$.

Further, it is obvious that $\hat{l}_z^2$ commutes with both $\hat{l}_z$ and $\hat{\sigma}_{xz}$. However, $\hat{l}_z$ and $\hat{\sigma}_{xz}$ do not commute with each other. We have, in fact, that

$$\hat{\sigma}_{xz}\hat{l}_z - \hat{l}_z\hat{\sigma}_{xz} = \hat{\sigma}_{xz}\left(-i\hbar\frac{\partial}{\partial\phi}\right) + i\hbar\frac{\partial}{\partial\phi}\hat{\sigma}_{xz} = 2i\hbar\frac{\partial}{\partial\phi}\hat{\sigma}_{xz}. \tag{13.30}$$

It follows that we have two sets of mutually commuting operators, namely, $(\widehat{H}, \hat{l}_z^2, \hat{l}_z)$ and $(\widehat{H}, \hat{l}_z^2, \sigma_{xz})$. The common eigenfunctions of the first of these sets are the complex functions given in (13.27), the eigenfunctions of the second set are the real functions. We have, in particular,

$$\hat{l}_z F_{n\lambda}(\mu, \nu; R) e^{\pm i\lambda\phi} = \pm\lambda\hbar F_{n\lambda}(\mu, \nu; R) e^{\pm i\lambda\phi}, \tag{13.31}$$

and

$$\sigma_{xz} F_{n\lambda}(\mu, \nu; R) \begin{cases} \cos\lambda\phi, \\ \sin\lambda\phi, \end{cases} = \pm F_{n\lambda}(\mu, \nu; R) \begin{cases} \cos\lambda\phi, \\ \sin\lambda\phi, \end{cases} \tag{13.32}$$

For any of the functions in (13.27) we have that

$$\hat{l}_z^2 \psi_{n\lambda\gamma}(\mu, \nu, \phi; R) = \lambda^2 \hbar^2 \psi_{n\lambda\gamma}(\mu, \nu, \phi; R), \tag{13.33}$$

in accordance with the statement presented above: the value of λ gives the *magnitude* of the angular momentum about the internuclear axis.

One should be careful to distinguish between the quantum number ℓ used for atoms and the quantum number λ used for diatomic molecules. In an atom, each component of the angular momentum commutes with the Hamiltonian. Hence, also the total angular momentum defines a good quantum number, and this is the quantum number ℓ. In a diatomic molecule, it is only the angular momentum about the internuclear axis that commutes with the Hamiltonian. The square of the total angular momentum cannot have a sharp value. In an atom, there are $2\ell + 1$ linearly independent functions for a given value of ℓ. In a diatomic molecule, there are just two linearly independent functions for a given value of λ, except for $\lambda = 0$, in which case there is only one function.

The conclusions we have arrived at are not only valid for the eigenfunctions of the Hamiltonian (13.15). They are valid for the eigenfunctions of any Hamiltonian of the form

$$\begin{aligned} \hat{H} &= -\frac{1}{2}\nabla^2 + V(r_a, r_b) \\ &= -\frac{1}{2}\nabla^2 + V(\mu, \nu). \end{aligned} \tag{13.34}$$

This is the Hamiltonian for an electron in an axial field. For a one-electron diatomic molecule it has the form (13.15). For a many-electron diatomic molecule, it may be taken to be the effective Hamiltonian for a single electron. The potential energy $V(r_a, r_b)$ is then the sum of the Coulomb fields from the two nuclei and an effective axial field from the other electrons. The eigenfunctions of such a Hamiltonian are the equivalents of the Hartree–Fock or Kohn–Sham orbitals for atoms introduced in Sec. 11.6. They have the form (13.27). As in Sec. 11.6 we shall stick to the language of Hartree–Fock theory and refer to the orbitals as molecular Hartree–Fock orbitals.

For the general axial potential, it is not possible to reduce the differential equation (13.24) further. But for a one-electron diatomic molecule the variables in the differential equation may be separated by writing

$$F_{n\lambda}(\mu, \nu; R) = X(\mu; R) Y(\nu; R), \tag{13.35}$$

and one obtains separate, albeit coupled, differential equations for $X(\mu; R)$ and $Y(\nu; R)$.

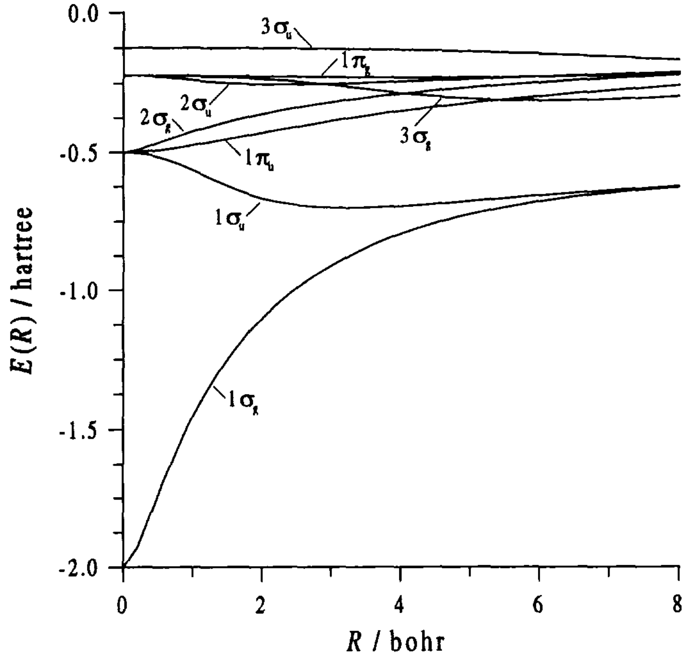

Figure 13.2: Lowest energy levels of H_2^+ as functions of internuclear distance. Internuclear repulsive energy not included.

In 1927, Øyvind Burrau studied the electronic Schrödinger equation for the hydrogen molecular ion H_2^+ (for which $Z_a = Z_b = 1$) in spheroidal coordinates. He proceeded by numerical integration and obtained the ground-state electronic energy as a function of R.[4] During the following years several attempts were made to solve the differential equations for $X(\mu)$ and $Y(\nu)$ analytically by means of power series expansions similar to those we have met for the harmonic oscillator (Chapter 7) and the hydrogen atom (Chapter 9). But the determination of the $X(\mu)$ function for large values of μ turned out to be a very difficult mathematical problem, and several erroneous conclusions were drawn in the literature. The problems were solved in 1933 by Jaffé for the homonuclear case $(Z_a = Z_b)$,[5] and in 1935 by Baber and Hassé for the general case.[6]

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[4] Ø. Burrau, Kgl. Danske Videnskab. Selskab Mat.-fys. Medd. **7**, No. 14 (1927).

[5] G. Jaffé, Z. Phys. **87**, 535 (1934).

[6] W. G. Baber and H. R. Hassé, Proc. Camb. Phil. Soc. **31**, 564 (1935).

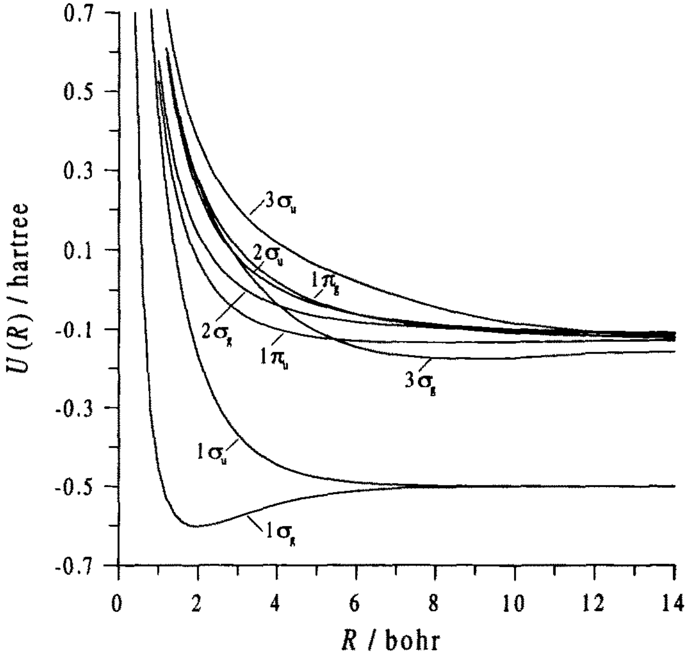

Figure 13.3: Lowest energy levels of H_2^+ as functions of internuclear distance. Internuclear repulsive energy included.

Exact wavefunctions for one-electron diatomics are now abundant in the literature. We refer, in particular, to two extensive reviews[7] and a general computer program for the calculation of energy eigenvalues.[8]

As we have already pointed out, the potential-energy surfaces discussed in Sec. 13.1 become potential-energy curves for diatomic molecules (the potential-energy functions depend only upon R). The general form of such curves is well illustrated by Figs. 13.2 and 13.3 which show the lowest potential-energy curves for the hydrogen molecular ion. Figure 13.2 shows the electronic energy curves $E_{n\lambda}(R)$, which are the solutions of Eq. (13.21). Figure 13.3 shows the

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[7] D. R. Bates, K. Ledsham and A. L. Stewart, Philos. Trans. Roy. Soc. A **246**, 215 (1953). E. Teller and H. L. Sahlin, in: H. Eyring, D. Henderson and W. Jost, *Physical Chemistry, an Advanced Treatment*, Vol. 5, Academic Press, New York, 1970.

[8] J. D. Power, Philos. Trans. Roy. Soc. A **274**, 663 (1973); Program OEDM (QCPE-233), available from Quantum Chemistry Program Exchange, Indiana University, Bloomington, Indiana 47405, U.S.A.

potential-energy curves $U_{n\lambda}(R)$ defined by expression (13.8), which now reads

$$\boxed{U_{n\lambda}(R) = E_{n\lambda}(R) + \frac{1}{R}} \tag{13.36}$$

The curves in Figs. 13.2 and 13.3 are labeled by the (n, λ)-values of the electronic wavefunctions. But in addition, they are labeled g or u. This additional labeling applies to all homonuclear molecules, i. e., molecules for which the atoms A and B are of the same type. In this case the electronic Hamiltonians (13.15) and (13.34) have a center of symmetry (the point O in Fig. 13.1), and as we already know from the discussion of the particle in a box and the harmonic oscilator, this causes the wavefunctions to be either even (label g) or odd (label u) under inversion in this center.

The spheroidal coordinates allow us to separate all three variables (μ, ν and ϕ) for the one-electron diatomic molecule. But as already pointed out, the variables μ and ν cannot be separated in many-electron diatomic molecules. Hence these coordinates are not much used in the description of many-electron diatomic molecules. They are, however, very useful for the evaluation of certain integrals as we shall show later.

We shall now turn to a very widely used representation of one-electron wavefunctions (orbitals) for molecules. This is the representation as linear combinations of atomic orbitals. Such a representation is useful both for one-electron molecules and for many-electron molecules in the Hartree-Fock description.

13.3 The LCAO Approximation

As first mentioned in Sec. 4.8, the term *orbital* means one-electron function, or rather one-electron spatial function. An orbital in an atom is called an *atomic orbital* (AO), an orbital in a molecule is called a *molecular orbital* (MO). With spin included (as in Sec. 10.2), an orbital becomes a *spin-orbital*, either an atomic spin-orbital (ASO) or a molecular spin-orbital (MSO).

It is often very convenient and useful to model an MO as a *linear combination of atomic orbitals* (LCAO). We may then speak of an LCAO-MO. The general form of an LCAO-MO is

$$\varphi(\boldsymbol{r}) = \sum_{s=1}^{m} c_s \chi_s(\boldsymbol{r}), \tag{13.37}$$

where $(\chi_1, \chi_2, \ldots, \chi_m)$ is a set of AO's. The way to determine the coefficients c_r is to apply the linear variational method that we described in Sec. 12.5. Let us see how this goes for the one-electron diatomic molecule.

To model the ground-state MO corresponding to the Hamiltonian (13.15), we introduce the normalized $1s$ atomic orbitals

$$\begin{cases} 1s_a = \left(\dfrac{\zeta_a^3}{\pi}\right)^{\frac{1}{2}} e^{-\zeta_a r_a}, \\ 1s_b = \left(\dfrac{\zeta_b^3}{\pi}\right)^{\frac{1}{2}} e^{-\zeta_b r_b}, \end{cases} \tag{13.38}$$

centered at the atomic sites A and B. They are Slater-type orbitals (STOs) of the type discussed in Sec. 11.7. When $\zeta_a = Z_a$ and $\zeta_b = Z_b$, they are eigenfunctions of the atomic Hamiltonians $-\frac{1}{2}\nabla^2 - Z_a/r_a$ and $-\frac{1}{2}\nabla^2 - Z_b/r_b$ which dominate the behavior of $\widehat{H}$ close to the nuclei A and B, respectively. If, therefore, we choose values for ζ_a and ζ_b close to Z_a and Z_b, then a function of the type

$$\varphi = c_1 1s_a + c_2 1s_b \tag{13.39}$$

must essentially have the correct behavior close to A and close to B. So it must be a decent approximation to the true ground state MO for not too small R. We therefore take it as our trial function.

The values of c_1 and c_2 are at our disposal. We must determine them such that the expectation value of $\widehat{H}$, viz.,

$$\mathcal{E} = \frac{\langle\varphi|\widehat{H}|\varphi\rangle}{\langle\varphi|\varphi\rangle} \tag{13.40}$$

becomes a minimum. This condition leads to the secular problem discussed in Sec. 12.5. It reads

$$\begin{pmatrix} H_{aa} - ES_{aa} & H_{ab} - ES_{ab} \\ H_{ba} - ES_{ba} & H_{bb} - ES_{bb} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \tag{13.41}$$

where

$$\begin{aligned} S_{aa} &= \langle 1s_a|1s_a\rangle = 1, \\ S_{bb} &= \langle 1s_b|1s_b\rangle = 1, \\ S_{ab} &= S_{ba} = \langle 1s_a|1s_b\rangle. \end{aligned} \tag{13.42}$$

We have used that the orbitals $1s_a$ and $1s_b$ are normalized to unity, and that $S_{ab} = S_{ba}$ because $1s_a$ and $1s_b$ are real. The matrix elements of $\widehat{H}$ are

$$\begin{aligned}
H_{aa} &= \langle 1s_a|\widehat{H}|1s_a\rangle \\
&= \left\langle 1s_a\left|-\frac{1}{2}\nabla^2\right|1s_a\right\rangle - \left\langle 1s_a\left|\frac{Z_a}{r_a}\right|1s_a\right\rangle - \left\langle 1s_a\left|\frac{Z_b}{r_b}\right|1s_a\right\rangle \\
&= \frac{1}{2}\zeta_a^2 - \zeta_a Z_a - \left\langle 1s_a\left|\frac{Z_b}{r_b}\right|1s_a\right\rangle, \qquad (13.43) \\
H_{bb} &= \langle 1s_b|\widehat{H}|1s_b\rangle \\
&= \left\langle 1s_b\left|-\frac{1}{2}\nabla^2\right|1s_b\right\rangle - \left\langle 1s_b\left|\frac{Z_b}{r_b}\right|1s_b\right\rangle - \left\langle 1s_b\left|\frac{Z_a}{r_a}\right|1s_b\right\rangle \\
&= \frac{1}{2}\zeta_b^2 - \zeta_b Z_b - \left\langle 1s_b\left|\frac{Z_a}{r_a}\right|1s_b\right\rangle, \qquad (13.44) \\
H_{ab} &= H_{ba} = \langle 1s_a|\widehat{H}|1s_b\rangle \\
&= \left\langle 1s_a\left|-\frac{1}{2}\nabla^2\right|1s_b\right\rangle - \left\langle 1s_a\left|\frac{Z_a}{r_a}\right|1s_b\right\rangle - \left\langle 1s_a\left|\frac{Z_b}{r_b}\right|1s_b\right\rangle. \qquad (13.45)
\end{aligned}$$

where we have inserted the values of the $1s$ one-center integrals that we already know from Eq. (12.17). That H_{ab} equals H_{ba} follows from the fact that H_{ab} is real and $\widehat{H}$ Hermitian ($H_{ba} = H_{ab}^*$).

To proceed, we must choose a particular molecule. We take this to be the singly charged hydrogen molecular ion H_2^+, so that we can make comparisons with the exact solution (Figs. 13.2 and 13.3).

13.4 The Homonuclear Case. Ground State of H_2^+

In the homonuclear case ($Z_a = Z_b$), the symmetry of the problem makes us choose the two orbital exponents ζ_a and ζ_b in (13.38) to be the same, so we put

$$\zeta = \zeta_a = \zeta_b. \qquad (13.46)$$

It is then obvious that also H_{aa} and H_{bb} become equal. Let us introduce the notation

$$\begin{aligned}
\alpha &= H_{aa} = H_{bb}, \\
\beta &= H_{ab} = H_{ba}, \qquad (13.47) \\
S &= S_{ab} = S_{ba}.
\end{aligned}$$

Eq. (13.41) becomes then

$$\begin{pmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}, \qquad (13.48)$$

where we have used that $S_{aa} = S_{bb} = 1$, because the orbitals (13.38) are normalized to unity.

To obtain the values of E for which Eq. (13.48) has solutions, we must solve the secular equation corresponding to Eq. (12.55), i. e.,

$$\begin{vmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{vmatrix} = 0, \qquad (13.49)$$

or,

$$(\alpha - E)^2 - (\beta - ES)^2 = 0. \qquad (13.50)$$

This equation has two solutions for E. One is obtained by putting $\alpha - E = -(\beta - ES)$ and is

$$\boxed{E_+ = \frac{\alpha + \beta}{1 + S}} \qquad (13.51)$$

The other solution corresponds to $\alpha - E = \beta - ES$ and is

$$\boxed{E_- = \frac{\alpha - \beta}{1 - S}} \qquad (13.52)$$

Having found the eigenvalues of the secular problem (13.48), we must determine the eigenvectors (c_1, c_2) and hence the LCAO-MOs $\varphi = c_1 1s_a + c_2 1s_b$. Inserting the value of E_+ into Eq. (13.48) gives

$$\begin{pmatrix} \frac{\alpha S - \beta}{1+S} & -\frac{\alpha S - \beta}{1+S} \\ -\frac{\alpha S - \beta}{1+S} & \frac{\alpha S - \beta}{1+S} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}, \qquad (13.53)$$

or,

$$\frac{\alpha S - \beta}{1 + S}(c_1 - c_2) = 0, \qquad (13.54)$$

which requires c_1 and c_2 to be equal. Hence, the LCAO-MO in question is

$$\varphi_+ = c(1s_a + 1s_b). \qquad (13.55)$$

In complete accordance with the discussion in Sec. 12.5, we have only been able to determine φ_+ to within a constant c. Let us determine the constant such that φ_+ is normalized to unity. The normalization integral is

$$\begin{aligned} \langle\varphi_+|\varphi_+\rangle &= c^*c\left(\langle 1s_a|1s_a\rangle + \langle 1s_b|1s_b\rangle + \langle 1s_a|1s_b\rangle + \langle 1s_b|1s_a\rangle\right) \\ &= 2c^*c(1+S). \end{aligned} \tag{13.56}$$

We choose c to be real and positive. The normalized LCAO-MO becomes then

$$\boxed{\varphi_+ = \sqrt{\frac{1}{2(1+S)}}\,(1s_a + 1s_b)} \tag{13.57}$$

By inserting the other value, i.e. the E_- of Eq. (13.52), into Eq. (13.48), we get in a similar way

$$\boxed{\varphi_- = \sqrt{\frac{1}{2(1-S)}}\,(1s_a - 1s_b)} \tag{13.58}$$

By evaluating $\langle\varphi_+|\varphi_-\rangle$ along the same lines as $\langle\varphi_+|\varphi_+\rangle$ was evaluated in Eq. (13.56), one finds the result zero. Thus, φ_+ and φ_- are orthogonal, in accordance with our general knowledge (Sec. 5.4) that functions corresponding to different eigenvalues of a Hermitian operator are orthogonal. (φ_+ and φ_- are, of course, not exact eigenfunctions of the Hamiltonian $\widehat{H}$, but the orthogonality property is equally valid for matrix problems involving only Hermitian matrices. This we shall not prove.)

With the purpose of obtaining numerical values for E_+ and E_-, we shall now discuss the evaluation of the two-center integrals in Eqs. (13.42)–(13.45). It is fairly obvious from these expressions that α and β must be negative. Hence, we find that $E_+ < E_-$. This implies that it is E_+ that approximates the ground state energy and φ_+ that models the ground state MO.

To evaluate the overlap integral $S = \langle 1s_a|1s_a\rangle$, we invoke the spheroidal coordinates of Sec. 13.2. First we get, from Eqs. (13.38), (13.46) and (13.16), that

$$1s_a 1s_b = \frac{\zeta^3}{\pi}e^{-\zeta(r_a+r_b)} = \frac{\zeta^3}{\pi}e^{-\zeta R\mu}. \tag{13.59}$$

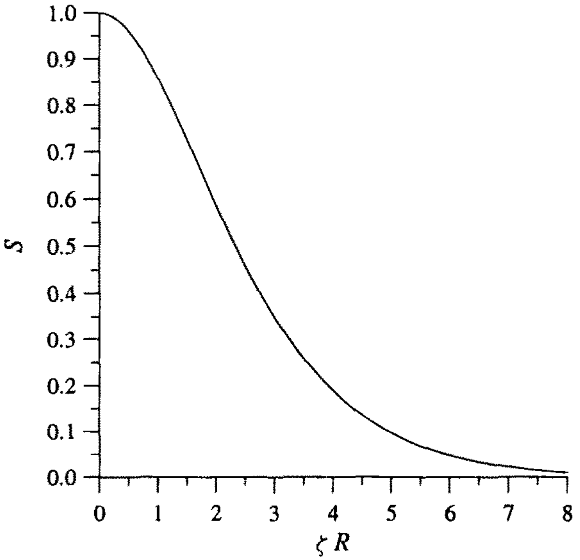

Figure 13.4: The $\langle 1s_a | 1s_b \rangle$ overlap as function of ζR. See Eq. (13.61).

Next we get, with the volume element from Eq. (13.18),

$$S = \frac{\zeta^3}{\pi} \left(\frac{R}{2} \right)^3 \int_{\mu=1}^{\infty} \int_{\nu=-1}^{1} \int_{\phi=0}^{2\pi} e^{-\zeta R \mu} \left(\mu^2 - \nu^2 \right) d\mu d\nu d\phi. \tag{13.60}$$

This expression involves only elementary integrations. Hence, we merely state the result

$$\boxed{S = e^{-\zeta R} \left(1 + \zeta R + \tfrac{1}{3} (\zeta R)^2 \right)} \tag{13.61}$$

Figure 13.4 shows a graph of S as a function of ζR, and hence as a function of R for a given ζ. We see that S equals 1 in the *united-atom limit* ($R = 0$), as it should because S becomes the scalar product of a normalized function with itself in this limit. Moreover, S is a decreasing function of R and tends to zero in the *separated-atoms limit* ($R \to \infty$).

The two-center integrals in Eqs. (13.43)–(13.45) may be evaluated in a similar fashion, by also invoking the relations (13.19) and (13.20). We find

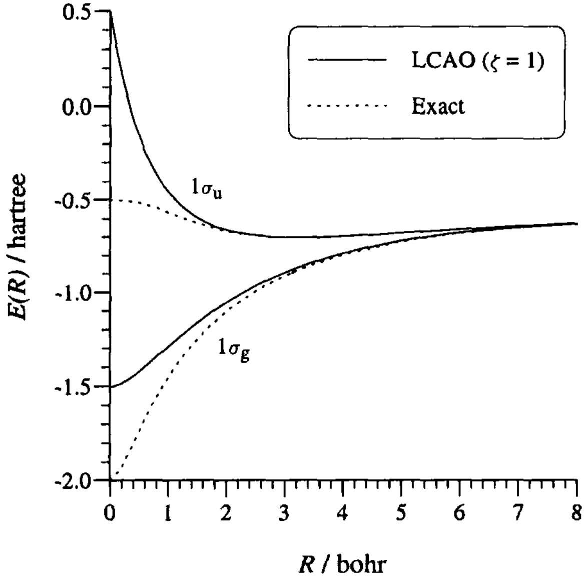

Figure 13.5: Electronic energies $E(R)$ of the ground state and lowest excited state of H_2^+.

first

$$\begin{aligned}\left\langle 1s_a \left| \frac{1}{r_b} \right| 1s_a \right\rangle &= \frac{1}{R}\left(1-(1+\zeta R)e^{-2\zeta R}\right),\\ \left\langle 1s_a \left| \frac{1}{r_a} \right| 1s_b \right\rangle &= \zeta(1+\zeta R)e^{-\zeta R},\\ \left\langle 1s_a \left| -\frac{1}{2}\nabla^2 \right| 1s_b \right\rangle &= \tfrac{1}{2}\zeta^2(1+\zeta R-\tfrac{1}{3}\zeta^2R^2)e^{-\zeta R}.\end{aligned} \tag{13.62}$$

and then, from (13.47) and (13.43)–(13.45),

$$\begin{aligned}\alpha &= \tfrac{1}{2}\zeta^2-\zeta Z-\tfrac{Z}{R}\left(1-(1+\zeta R)e^{-2\zeta R}\right),\\ \beta &= \tfrac{1}{2}\zeta^2((1+\zeta R-\tfrac{1}{3}\zeta^2R^2)e^{-\zeta R}-2\zeta Z(1+\zeta R)e^{-\zeta R}.\end{aligned} \tag{13.63}$$

By substituting the analytical expressions (13.61) and (13.63) for S, α and β into (13.51) and (13.52) we may calculate the energies E_+ and E_- as functions of R. The results of such a calculation are shown in Fig. 13.5 for the H_2^+ ion, for which $Z_a = Z_b = 1$. The orbital exponent ζ was assigned the

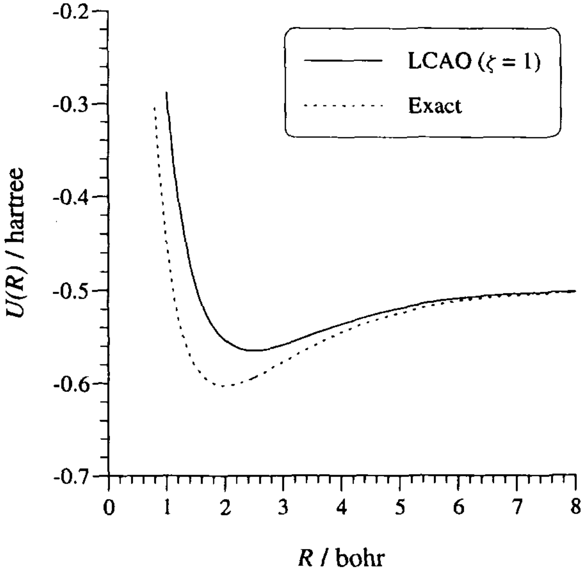

Figure 13.6: Exact and simple LCAO potential-energy curves $U(R)$ for the ground state of H_2^+.

value 1 for all R-values. The Figure also shows the exact energy curves of Fig. 13.2 that our LCAO calculation approximates. It is seen that the approximate curves lie above the exact ones for all R, in agreement with the remarks at the end of Sec. 12.5.

Next, we may add the nuclear repulsive energy $1/R$ to the curves of Fig. 13.5 to obtain the potential energy curves $U(R)$ defined by Eq. (13.23). Fig. 13.6 shows these curves for the ground state of H_2^+. The curve labeled *exact* is of course the same as the ground-state curve in Fig. 13.3.

The exact curve in Fig. 13.6 has its minimum at $R = R_e = 2.00$ bohr. The corresponding energy is $U(R_e) = -0.60263$ hartree. At the separated-atoms limit ($R \to \infty$, the dissociation limit) we have $U(\infty) = -0.50000$ hartree which is the energy of a free hydrogen atom. We introduce the *electronic dissociation energy* D_e by the definition

$$D_e = U(\infty) - U(R_e). \tag{13.64}$$

Its value is seen to be

$$D_e = 0.10263\,\text{hartree} = 2.79\,\text{eV}. \tag{13.65}$$

The LCAO curve in Fig. 13.6 has its minimum at $R = 2.49$ bohr. The corresponding value of $U(R_e)$ is -0.56483 hartree, which gives $D_e = 0.06483$ hartree $= 1.76$ eV. The agreement with the exact values is not spectacular. Qualitatively, we may understand the differences as follows.

The two $E(R)$ curves, i. e., the two lower curves in Fig. 13.5, come together in the separated-atoms limit. But for all finite distances, the LCAO curve lies above the exact curve. The difference between the two curves increases steadily as R diminishes, becoming very large in the united-atom limit. The slope of the LCAO curve is therefore smaller than the slope of the exact curve for all R. But since $U(R) = E(R) + 1/R$, the minimum of a $U(R)$ curve must occur where the derivative of the $E(R)$ curve cancels the derivative of the $1/R$ nuclear-repulsion curve, i. e. where the two derivatives have the same absolute value, but opposite signs. With the smaller slope of the LCAO curve this happens for a much larger R-value than for the exact curve.

Thus, we learn that the behavior of the potential-energy curve in the *valence region* is closely connected with the behavior of the electronic-energy curve for small and large R-values. This result is of general validity for the theory of molecular shapes and binding energies.

For the ground state of the H_2^+ ion, it is a fairly simple matter to improve the LCAO description so that it also describes the united-atom limit correctly. All that we need to do is to allow the orbital exponent ζ to vary with R. The way to do this is to treat ζ as a variational parameter for each value of R, that is, we must apply the variational method to the energy expression (13.51).[9] When we do this, we find that ζ varies with R as shown in Fig. 13.7. The figure also shows the ζ values that come from varying the energy expression (13.52) for the first excited state.[10]

Fig. 13.8 compares the electronic-energy curves obtained by varying ζ, with the exact energy curves. The improvement is seen to be dramatic. Adding the $1/R$ term to the ground-state's $E(R)$ curve produces a minimum at $R = 2.00$ bohr as for the exact curve. The electronic binding energy is found to be 0.08651 hartree $= 2.35$ eV, a substantial improvement over the simple LCAO result.

The reason behind the success of varying the ground-state ζ with R is that the description now becomes exact in both the separated-atoms limit and the united-atom limit. For in the separated-atoms limit the electron only senses a single nuclear charge, and the LCAO-MO (13.57) with $\zeta = 1$ becomes the exact MO. In the united-atom limit we have a He^+ ion. The exact ground-

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[9] B. N. Finkelstein and G. E. Horowitz, Z. Phys. **48**, 118, 448 (1928).

[10] C. A. Coulson, Trans. Faraday Soc. **33**, 1479 (1937).

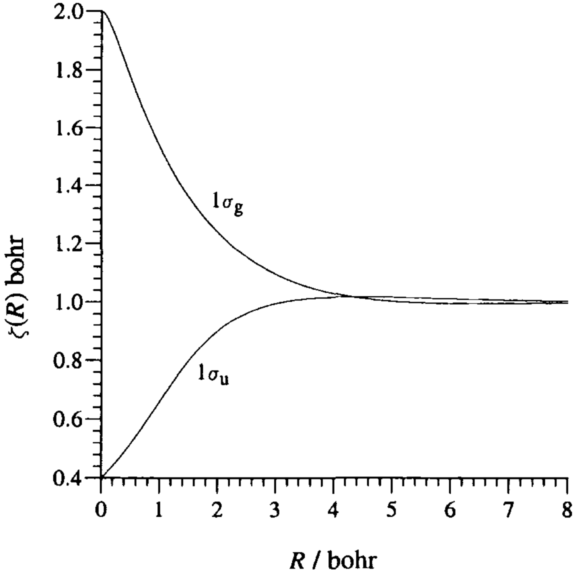


Figure 13.7: Variationally determined orbital exponents for the two lowest states of H_2^+.

state AO of this ion is a $\zeta = 2$ hydrogen-like orbital, and this is exactly the AO into which the LCAO-MO (13.57) merges when $R \to 0$.

We are somewhat less fortunate with the description of the lowest excited MO which we describe by the LCAO-MO (13.58). As with the ground-state LCAO-MO we do get the correct MO in the separated-atoms limit, but as the energy curve in Fig. 13.8 shows, things go wrong at the united-atom limit. The true MO becomes the $2p_z$ atomic orbital of He^+ in this limit. But although the limiting form of the function (13.58) is also found to be a p_z orbital, it turns out to be a p_z orbital with the wrong radial dependence (a $1p_z$ orbital).

Having seen how it is possible to give a decent description of the two lower states of the hydrogen molecular ion by the LCAO method, we shall now extend the description to other states. But first, a comment on notation is in order.

We have so far labeled the energy levels as in Fig. 13.2 and Fig. 13.8. The σ_g orbitals are numbered $1\sigma_g$, $2\sigma_g$, $3\sigma_g, \ldots$ in the order of increasing energy. Similarly, the σ_u orbitals are numbered $1\sigma_u$, $2\sigma_u$, $3\sigma_u, \ldots$ in the order of increasing energy. In another notation, usually referred to as the *united-atom notation*, the $1\sigma_g$ orbital is denoted $1s\sigma_g$ and the $1\sigma_u$ orbital is denoted $2p\sigma_u$,

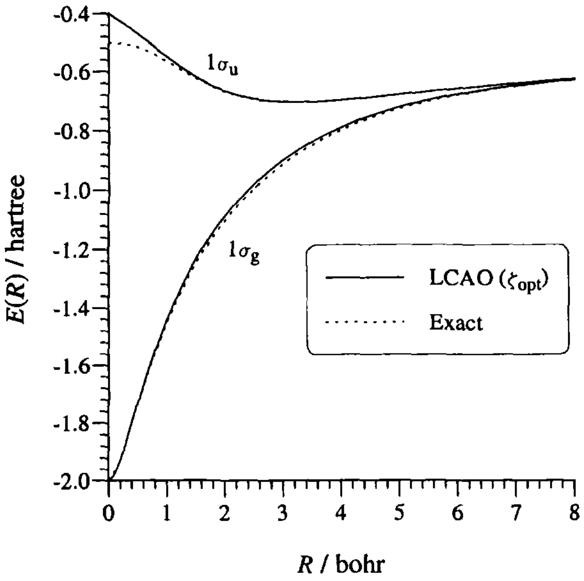


Figure 13.8: Exact and best ζ LCAO electronic-energy curves for the two lowest states of H_2^+.

because these orbitals become helium 1*s* and helium 2*p* orbitals, respectively, in the united-atom limit.

In yet another notation, the so-called *separated-atoms notation*, the $1\sigma_g$ orbital is denoted $\sigma_g 1s$, because the dissociated state obtained for very large values of R correlates with the 1*s* state of a hydrogen atom. The LCAO representation (13.57) is exact in the limit $R \to \infty$, with $\zeta = 1$. Similarly, the $1\sigma_u$ orbital is denoted $\sigma_u 1s$; it has the same dissociation limit as $\sigma_g 1s$, as Fig. 13.5 shows. Figure 13.3 shows that the $1\sigma_u$ state is a dissociative state: the potential-energy curve has no minimum. For this reason, the $1\sigma_u$ orbital is called an *antibonding orbital.* To emphasize the antibonding character of the orbital, it is often supplied with an asterix as superscript in the separated-atoms notation. Thus, one writes $\sigma_u^* 1s$. The $\sigma_g 1s$ orbital is called a *bonding orbital*, but no special symbol is introduced to indicate this.

Similar equivalent notations are used for other molecular orbitals of a homonuclear diatomic molecule.

The notation adapted in the following two sections will partially be the separated-atoms notation.

13.5 LCAO-MOs for Homonuclear Diatomics

The order of the H_2^+ energy levels in Fig. 13.2 is influenced by the high degeneracies of the levels in the united-atom and separated-atoms limits. This is the degeneracy exposed in Fig. 9.5: the energy of a hydrogen-like atom depends only on the principal quantum number n. In a many-electron atom, as described by the aufbau principle and Hartree-Fock theory (Secs. 11.3 and 11.6), this degeneracy is lifted, and we get a new energy ordering based on the $n + \ell$ rule. Thus, we have the level order $1s < 2s < 2p < \dots$ rather than $1s < 2s = 2p < \dots$.

The order of the energy levels in the free atoms influences the order of levels in the molecules formed from the atoms. To describe the new ordering for homonuclear diatomics with more than one electron, let us construct the following *elementary LCAO-MOs* which are generalizations of the functions φ_+ and φ_- given by (13.57) and (13.58),

$$\begin{aligned}
\varphi(\sigma_g 1s) &= \frac{1}{\sqrt{2(1+S)}}(1s_a + 1s_b)\,, & \varphi(\sigma_u 1s) &= \frac{1}{\sqrt{2(1-S)}}(1s_a - 1s_b)\,,\\
\varphi(\sigma_g 2s) &= \frac{1}{\sqrt{2(1+S)}}(2s_a + 2s_b)\,, & \varphi(\sigma_u 2s) &= \frac{1}{\sqrt{2(1-S)}}(2s_a - 2s_b)\,,\\
\varphi(\sigma_g 2p) &= \frac{1}{\sqrt{2(1+S)}}(2p_{za} + 2p_{zb})\,, & \varphi(\sigma_u 2p) &= \frac{1}{\sqrt{2(1-S)}}(2p_{za} - 2p_{zb})\,,\\
\varphi(\pi_u 2p_x) &= \frac{1}{\sqrt{2(1+S)}}(2p_{xa} + 2p_{xb})\,, & \varphi(\pi_g 2p_x) &= \frac{1}{\sqrt{2(1-S)}}(2p_{xa} - 2p_{xb})\,,\\
\varphi(\pi_u 2p_y) &= \frac{1}{\sqrt{2(1+S)}}(2p_{ya} + 2p_{yb})\,, & \varphi(\pi_g 2p_y) &= \frac{1}{\sqrt{2(1-S)}}(2p_{ya} - 2p_{yb})\,.
\end{aligned} \tag{13.66}$$

Here, S has a different meaning from one function to another, being the overlap integral between the two AOs with which it actually occurs in the list. Thus, $S = \langle 2p_{xa} | 2p_{xb} \rangle$ for each of the functions $\varphi(\pi_u 2p_x)$ and $\varphi(\pi_g 2p_x)$.

The LCAO-MOs in the above list are real-valued. They are eigenfunctions of $\hat{l}_z^2$, $\hat{\sigma}_v$ $(= \hat{\sigma}_{xz})$, and the inversion operator $\hat{I}$. However, they have been chosen so that they refer to a coordinate system slightly different from that of Fig. 13.1, in the sense that the z_a and z_b axes now are taken to point towards each other. Thus, the direction of z_b in Fig. 13.1 is supposed to be reversed, with the effect that the positive lobes of the $2p_{za}$ and $2p_{zb}$ orbitals become directed against each other and the overlap integral $\langle 2p_{za} | 2p_{zb} \rangle$ becomes positive.

The LCAOs in the list (13.66) are supposed to be reasonable first approximations to the molecular orbitals of homonuclear diatomic molecules and ions formed from first- and second-row atoms (H, He, Li, Be, B, C, N, O, F, Ne).

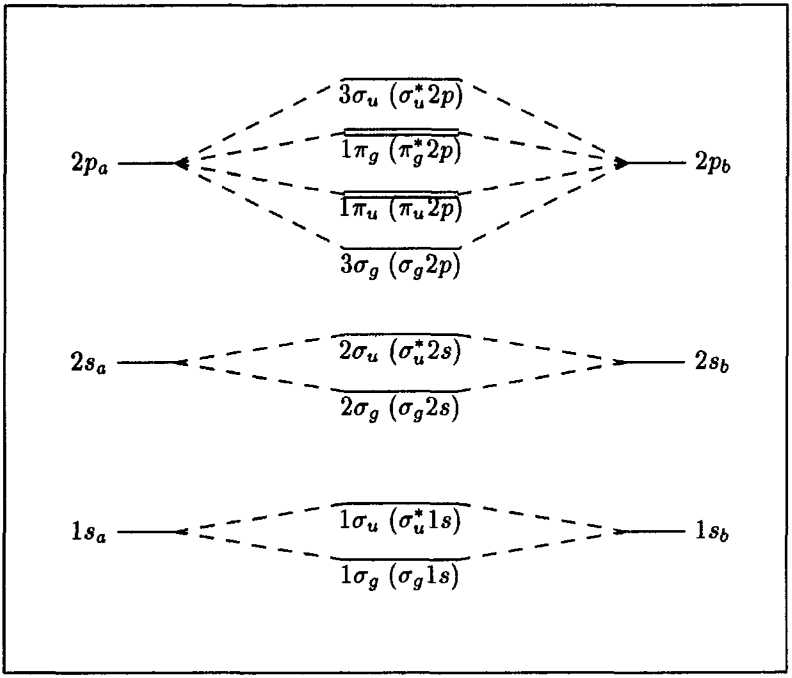


Figure 13.9: Homonuclear diatomic standard LCAO-MOs formed from $1s$, $2s$ and $2p$ AOs.

They are labeled by their symmetries and their composition. For each pair (for instance $\varphi(\sigma_g2p)$ and $\varphi(\sigma_u2p)$), energy expressions similar to those of Eqs. (13.51) and (13.52) hold, and an orbital to the left in the list will have a lower energy than the corresponding orbital to the right. They are *bonding* and *antibonding* orbitals, respectively. Note the degeneracy with respect to the x and y labels on the π orbitals. Like any level with $\lambda \neq 0$, a π level is always doubly degenerate. (Recall the discussion leading to Eq. (13.27).)

Figure 13.9 shows the order of all the orbitals in the list (13.66), the antibonding orbitals being marked with an asterix. Note, however, that the notation used for the orbitals is that referring to the exact molecular orbitals. The orbital $\varphi(\sigma_u2s)$ is, for instance, merely a first approximation to the exact orbital denoted $2\sigma_u$ or σ_u^*2s.

Figure 13.10 shows the form of the $\varphi(\sigma_g1s)$ and $\varphi(\sigma_u1s)$ LCAO-MOs for H_2^+ through contour diagrams.

Let us now improve on the description according to which the MOs for

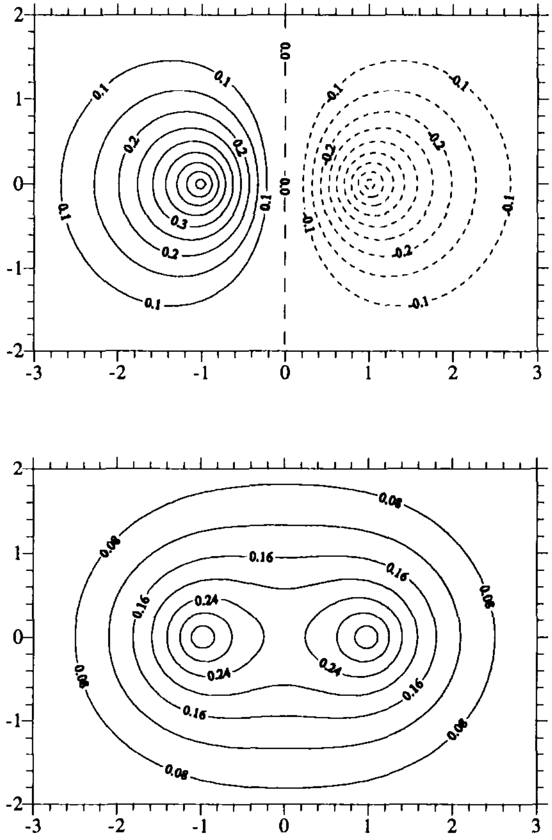


Figure 13.10: Contour curves in a plane through the internuclear axis for the $\varphi(\sigma_g 1s)$ (bottom) and $\varphi(\sigma_u 1s)$ (top) orbitals for H_2^+ at $R = 2$ bohr. $\zeta = 1$.

homonuclear diatomic molecules are given by the LCAO-MOs (13.66). To do so, we invoke the linear variational method and make the assumption that the MOs for molecules and ions formed from first- and second-row atoms can be represented as linear combinations of the form (13.37), with the sum including all $1s$, $2s$ and $2p$ AOs on the two centers A and B, i.e., ten AOs in all. The LCAOs are thus to be determined by solving a 10×10 matrix eigenvalue problem of the form (12.53). In this way, we find the optimal MOs within the 10-dimensional function space defined by the ten mentioned AOs.

The ten AOs form a basis for the function space, and expressing the molecular orbitals in the form (13.37) is tantamount to referring them to the basis formed by those ten AOs. Any set of ten linearly independent functions within the space may, however, equally well serve as a basis.

If the secular problem is set up in a new basis, the resulting LCAOs must become the same. So let us take the ten elementary LCAO-MOs (13.66) as a new basis. This is a so-called *symmetry-adapted basis*, because each basis function is an eigenfunction for a set of operators that commute with the one-electron Hamiltonian. They are the operators $\hat{l}_z^2$, $\hat{\sigma}_{xz}$ and $\hat{I}$.

Let us now recall the discussion of Sec. 12.6. It says effectively that only functions with the same set of eigenvalues for the mentioned operators, i.e. functions with the same symmetry characteristics, can combine in a linear variational calculation. This implies, first of all, that the separation into even and odd functions is exact. Next, we realize that the π orbitals are uniquely determined. But the three σ_g orbitals may "mix". Thus, we should really look for three better MOs of the form

$$\begin{aligned}(1\sigma_g, 2\sigma_g, 3\sigma_g) &\equiv (\sigma_g 1s, \sigma_g 2s, \sigma_g 2p)\\ &= (\varphi(\sigma_g 1s), \varphi(\sigma_g 2s), \varphi(\sigma_g 2p))\begin{pmatrix} a_{11} & a_{12} & a_{13}\\ a_{21} & a_{22} & a_{23}\\ a_{31} & a_{32} & a_{33}\end{pmatrix}\end{aligned} \tag{13.67}$$

and similarly for the odd σ orbitals,

$$\begin{aligned}(1\sigma_u, 2\sigma_u, 3\sigma_u) &\equiv (\sigma_u^* 1s, \sigma_u^* 2s, \sigma_u^* 2p)\\ &= (\varphi(\sigma_u 1s), \varphi(\sigma_u 2s), \varphi(\sigma_u 2p))\begin{pmatrix} b_{11} & b_{12} & b_{13}\\ b_{21} & b_{22} & b_{23}\\ b_{31} & b_{32} & b_{33}\end{pmatrix}\end{aligned} \tag{13.68}$$

This gives us two 3×3 secular problems to solve.

But since a $1s$ AO is energetically well separated from the $2s$ and $2p$ AOs, we will always find that $\langle\sigma_g 1s|\widehat{H}|\sigma_g 1s\rangle$ is much more negative than $\langle\sigma_g 2s|\widehat{H}|\sigma_g 2s\rangle$ and $\langle\sigma_g 2p|\widehat{H}|\sigma_g 2p\rangle$. And as an elementary study of secular problems shows, this implies very little mixing between the $\sigma_g 1s$ orbital and the other two. Thus, we may safely conclude that $\varphi(\sigma_g 1s)$, and similarly $\varphi(\sigma_u 1s)$, are good LCAO-MOs. In other words, the coefficients $(a_{12}, a_{13}, a_{21}, a_{31})$ and $(b_{12}, b_{13}, b_{21}, b_{31})$ are very small. This leaves us with two 2×2 secular problems for the determination of orbitals of the form

$$(2\sigma_g, 3\sigma_g) \equiv (\sigma_g 2s, \sigma_g 2p) = (\varphi(\sigma_g 2s), \varphi(\sigma_g 2p))\begin{pmatrix} a_{22} & a_{23}\\ a_{32} & a_{33}\end{pmatrix} \tag{13.69}$$

and

$$(2\sigma_u, 3\sigma_u) \equiv (\sigma_u^* 2s, \sigma_u^* 2p) = (\varphi(\sigma_u 2s), \varphi(\sigma_u 2p)) \begin{pmatrix} b_{22} & b_{23} \\ b_{32} & b_{33} \end{pmatrix} \tag{13.70}$$

Here, the mixing may be appreciable, and may in fact cause the $\sigma_g 2p$ MO in the drawing of Fig. 13.9 to move above the $\pi_u 2p$ MO. This happens, for instance, in the diatomics built from the elements from the first half of the second row (see below). The kind of mixing occurring in (13.69) and (13.70) is called *hybridization*, because it effectively mixes the $2s$ and $2p$ AOs on the same center. That hybridization is more pronounced in the beginning of a period, reflects the fact that the energy difference between the $2s$ and $2p$ atomic orbitals increases toward the end of a period.

With hybridization included, we may safely assume that the LCAO-MO picture given in this section is a reasonable one. We may therefore use it to determine electron configurations and determinantal wavefunctions for diatomics, in a similar way as we determined electron configurations and many-electron wavefunctions for atoms in Chapter 11.

13.6 Electronic Structure of Homonuclear Di-atomics

We shall now give a brief overview of the electron configurations for first- and second-row homonuclear diatomics on the basis of the energy-level diagram in Fig. 13.9. We shall also consider the *bond order* of these molecules and ions. We define it by the expression

$$\boxed{\begin{array}{c}\text{Bond order} = \frac{1}{2}\times \\ \text{(number of electrons in bonding orbitals} \\ \text{minus number of electrons in antibonding orbitals)}\end{array}} \tag{13.71}$$

H_2 has the electron configuration $(\sigma_g 1s)^2$. The bond order is 1, corresponding to a single bond between the hydrogen atoms.

He_2 has the electron configuration $(\sigma_g 1s)^2(\sigma_u^* 1s)^2$. The bond order is 0: He_2 is an unstable molecule. But He_2^+, with the electron configuration $(\sigma_g 1s)^2(\sigma_u^* 1s)^1$, has a bond order of $\frac{1}{2}$ just like H_2^+, and is a stable ion.

Li_2 has the electron configuration $(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 2s)^2$, which we shall write in the condensed form $[He_2](\sigma_g 2s)^2$. The bond order is 1. In accordance with this, Li_2 is found to be a stable species.

Be_2 has the electron configuration $[He_2](\sigma_g 2s)^2(\sigma_u^* 2s)^2$ and a bond order of 0. It is not a stable molecule.

In B_2, C_2 and N_2, the $\pi_u 2p$ MO lies below the $\sigma_g 2p$ MO as discussed above. Thus, B_2 has the electron configuration $[He_2](\sigma_g 2s)^2(\sigma_u^* 2s)^2(\pi_u 2p)^2$ which we shall also write as $[Be_2](\pi_u 2p)^2$. The bond order is 1.

There are two $\pi_u 2p$ orbitals: the $\pi_u 2p$ shell may contain four electrons. The electron configuration of C_2 is therefore $[Be_2](\pi_u 2p)^4$, and the bond in C_2 is a double bond, the bond order being 2.

For N_2 we get the electron configuration $[Be_2](\pi_u 2p)^4(\sigma_g 2p)^2$. The bond in N_2 is a triple bond.

O_2 has the electron configuration $[Be_2](\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g^* 2p)^2$. The bond order is 2. Now the $\sigma_g 2p$ MO lies below the $\pi_u 2p$ MO, but this has no effect on the electron configuration, since both orbital sets are fully occupied by electrons. It concerns the relative binding energies and hence the relative ionization energies associated with the orbitals.

For F_2 we get the configuration $[Be_2](\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g^* 2p)^4$, so the bond in F_2 is a single bond.

Finally, we get that Ne_2 is $[Be_2](\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g^* 2p)^4(\sigma_u^* 2p)^2$, with no bonding.

Thus we see that simple molecular orbital theory is able to give a chemically correct description of the bond orders. This also allows us to explain other important features. It is found, for instance, that O_2^+ has a shorter bond length than O_2, whereas the bond in O_2^- is longer than in O_2. This is in accordance with the respective bond orders $2\frac{1}{2}$, 2 and $1\frac{1}{2}$ for these species.

Thus, several molecular properties may be accounted for by referring to the electron configuration. But, in the same way as for atoms, the electron configuration is not the whole story. The properties of a molecule is tied to the wavefunction, toward the setup of which the electron configuration is merely the first step. To go from the electron configuration to the wavefunction, the molecular orbitals must be combined with α and β spin functions to give spin-orbitals. These spin-orbitals are then used in the construction of antisymmetric many-electron wavefunctions, the antisymmetry being conveniently achieved through the construction of Slater determinants.

An interesting case is the O_2 molecule for which the ground configuration is an open-shell configuration, $[Be_2](\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g^* 2p)^2$. This implies that the configuration gives rise to several Slater determinants. A detailed analysis shows that there results three distinct electronic states with different energies. Calculations show that the ground state is degenerate, with the spins of the two $\pi_g^* 2p$ electrons being parallel. Thus, we predict that O_2 should be a paramagnetic molecule which is in fact what one finds experimentally. The ability of molecular-orbital theory to give a straightforward explanation of this observation was one of the early successes of the theory.

An outstanding property of a Slater determinant is worthwhile noticing at this place, namely, its invariance up to a factor under linear transformations of the defining spin-orbitals. To verify this property, consider the determinantal wavefunction (11.40), defined in terms of the spin-orbitals $\psi_1, \psi_2, \ldots, \psi_N$. By a linear substitution we introduce N new spin-orbitals $\psi'_1, \psi'_2, \ldots, \psi'_N$, such that

$$\psi_i = \sum_{k=1}^{N} a_{ik}\psi'_k. \tag{13.72}$$

The $(i, j)^{th}$ element in the determinant (11.40) is then

$$\psi_i(x_j) = \sum_{k=1}^{N} a_{ik}\psi'_k(x_j). \tag{13.73}$$

But determinants multiply together in the same way as matrices do. We see, therefore, that $\psi_i(x_j)$ is the $(i, j)^{th}$ element in the determinant obtained by multiplying $\det\{a_{ik}\}$ by $\det\{\psi'_k(x_j)\}$. Thus,

$$\begin{vmatrix} \psi_1(x_1) & \psi_1(x_2) & \ldots & \psi_1(x_N) \\ \psi_2(x_1) & \psi_2(x_2) & \ldots & \psi_2(x_N) \\ \ldots & \ldots & \ldots & \ldots \\ \psi_N(x_1) & \psi_N(x_2) & \ldots & \psi_N(x_N) \end{vmatrix} = A \begin{vmatrix} \psi'_1(x_1) & \psi'_1(x_2) & \ldots & \psi'_1(x_N) \\ \psi'_2(x_1) & \psi'_2(x_2) & \ldots & \psi'_2(x_N) \\ \ldots & \ldots & \ldots & \ldots \\ \psi'_N(x_1) & \psi'_N(x_2) & \ldots & \psi'_N(x_N) \end{vmatrix} \tag{13.74}$$

where

$$A = \begin{vmatrix} a_{11} & a_{12} & \ldots & a_{1N} \\ a_{21} & a_{22} & \ldots & a_{2N} \\ \ldots & \ldots & \ldots & \ldots \\ a_{N1} & a_{N2} & \ldots & a_{NN} \end{vmatrix}. \tag{13.75}$$

Hence, a linear transformation of the type (13.72) merely leads to the multiplication of the determinantal wavefunction with a constant, namely, the value of the determinant $\det\{a_{ik}\}$. In the notation of Eq. (11.40) we may also write,

$$|\psi_1\psi_2\ldots\psi_N| = A|\psi'_1\psi'_2\ldots\psi'_N|. \tag{13.76}$$

The effect of the constant A is to ensure that the wavefunction remains normalized.

As an application of this result, let us construct the Slater determinant corresponding to the He_2 electron configuration $(\sigma_g 1s)^2(\sigma_u^* 1s)^2$. As discussed above, the $\sigma_g 1s$ and $\sigma_u^* 1s$ orbitals are well represented by the elementary LCAO-MOs in the first line of the list (13.66). Hence, we get

$$|\, \overset{+}{\sigma_g} 1s\ \overset{-}{\sigma_g} 1s\ \overset{+}{\sigma_u^*} 1s\ \overset{-}{\sigma_u^*} 1s \,| = A|\, \overset{+}{1s_a} \overset{-}{1s_a} \overset{+}{1s_b} \overset{-}{1s_b} \,| \tag{13.77}$$

where, as usual, + and - refer to *the α and β spin functions, respectively.* This result shows that, whenever *all* LCAO's that may be formed from a set of atomic orbitals are occupied by electrons, then the Slater determinant defined by the LCAO's is the same as the Slater determinant defined by the original atomic orbitals, apart from a constant factor. Hence, the construction of LCAO's is arbitrary in this case.

When only some of the LCAO's that may be formed from a set of atomic orbitals are occupied by electrons, as is usually the case, then the only linear transformations that leave the Slater determinant unchanged, are transformations between the occupied orbitals. Performing such transformations lead to more or less localized molecular orbitals and they are often used, especially for polyatomic molecules. We shall not consider them further here.

Supplementary Reading

The bibliography, [26], [29] and [30].

Problems

13.1. Study the contour diagrams in Fig. 13.10, and then consider the values of the orbitals along the bond axis ($x = 0, y = 0, -\infty < z < \infty$).

a. Draw a graph of $\varphi_+(\boldsymbol{r})$ along the bond axis. Similarly, draw a graph of $\varphi_-(\boldsymbol{r})$. (Use the expressions (13.57) and (13.58).)

b. Also draw graphs of the electron densities φ_+^2, φ_-^2 and $\frac{1}{2}(1s_a^2 + 1s_b^2)$.

c. Sketch the *deformation densities*

$$\varphi_+^2 - \tfrac{1}{2}(1s_a^2 + 1s_b^2) \quad \text{and} \quad \varphi_-^2 - \tfrac{1}{2}(1s_a^2 + 1s_b^2),$$

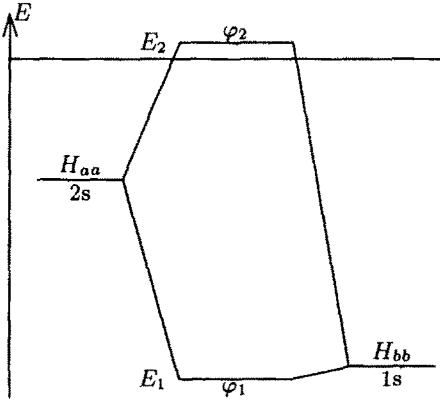
to illustrate the electron displacements caused by the bond formation.

13.2. Specify the electronic structure and bond orders in the following groups of diatomic molecules and ions:

$$(N_2^+,\ N_2,\ N_2^-),\quad (S_2^+,\ S_2,\ S_2^-),\quad (Na_2^+,\ Na_2,\ Na_2^-),$$

and discuss on this basis the relative bond lengths within each group.

13.3. In this exercise, we perform a simplified molecular-orbital calculation for LiH.



The molecular bond is supposed to be established between the $2s$ orbital, χ_a, of the Li atom and the $1s$ orbital, χ_b, of the H atom. Thus, the electron configuration of the LiH molecule becomes $1s^2_{\mathrm{Li}}\varphi_1^2$, where the bonding orbital φ_1 has the form

$$\varphi_1 = c_a\chi_a + c_b\chi_b.$$

The corresponding antibonding orbital is

$$\varphi_2 = c'_a\chi_a + c'_b\chi_b.$$

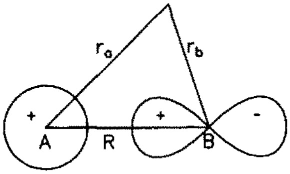
a. Determine the molecular-orbital energies, E_1 and E_2, and calculate the values of the coefficients (c_a, c_b) and (c'_a, c'_b). Use the following set of semiempirical values and approximations:

$$H_{aa} = -5.40\,\mathrm{eV},\quad H_{bb} = -13.60\,\mathrm{eV},\quad H_{ab} = (H_{aa} + H_{bb})S_{ab},$$
$$S_{ab} = 0.475 \quad \text{(at the equilibrium distance)}.$$

b. Check that φ_1 and φ_2 are mutually orthogonal.

13.4. The electron configurations of boron (B) and aluminum (Al) are, respectively, $1s^22s^22p^1$ and $[\mathrm{Ne}]3s^23p^1$.

a. Determine the orbital exponent ζ_{2p} for B and the orbital exponent ζ_{3p} for Al by applying Slater's rules.



Next, consider the molecule BH with the electron configuration $1s^2 2s^2 \varphi^2$, where $1s$ and $2s$ are the same orbitals as in the free boron atom, while the molecular orbital φ has the form:

$$\varphi = c_a \chi_a + c_b \chi_b.$$

χ_a is the $1s$ orbital of the hydrogen atom and χ_b is the $2p_z$ orbital of the boron atom. The relative positions of the atoms and the orbitals are shown on the figure.

b. Determine the energy E of the orbital φ by assuming that

$$H_{aa} = -13.61 \text{ eV}, \quad H_{bb} = -8.30 \text{ eV}, \quad H_{ab} = -2.35 \text{ eV}.$$

Further, assume that χ_a and χ_b are normalized atomic orbitals, and neglect the overlap between them

$$S_{aa} = 1, \quad S_{bb} = 1, \quad S_{ab} = 0.$$

c. Determine the coefficients c_a and c_b, requiring that the molecular orbital φ be normalized to 1.

d. Corresponding to the bonding orbital φ there is an antibonding orbital,

$$\varphi' = c'_a \chi_a + c'_b \chi_b.$$

Determine c'_a and c'_b, requiring that φ' be properly normalized.

e. In a more precise description, one would write the bonding molecular orbital on the form

$$\varphi = c_1 \chi_a + c_2 \chi_b + c_3 1s + c_4 2s,$$

where $1s$ and $2s$ again are orbitals of the free boron atom. Make a qualified guess concerning the magnitudes of c_3 and c_4.

Chapter 14

Vibration and Rotation of Diatomic Molecules

Contents

14.1 Introduction

As a natural continuation of the previous chapter, let us now consider the vibration and rotation of a diatomic molecule in the adiabatic approximation. The point of departure is Eq. (13.10), which for a diatomic system becomes

$$\left\{-\frac{1}{2M_A}\nabla_A^2 - \frac{1}{2M_B}\nabla_B^2 + U(r)\right\}\kappa(\boldsymbol{r}_A,\boldsymbol{r}_B) = E_{\text{mol}}\kappa(\boldsymbol{r}_A,\boldsymbol{r}_B), \qquad (14.1)$$

where $\boldsymbol{r}_A$ and $\boldsymbol{r}_B$ are the position vectors of nuclei A and B, respectively, and r is the internuclear distance (the same as R in Section 13.1). Eq. (14.1) is similar to Eq. (8.4) and may be treated in the same way.

In our work on atoms and molecules sofar, the zero of energy has been the energy of infinitely separated electrons and nuclei at rest. In the present context, it is convenient to measure energies relative to the total energy of the separated ground-state atoms instead. Calling this energy E_{atoms}, we write

$$E_{\text{mol}} = E_{\text{atoms}} + \widetilde{E}_{\text{mol}}, \qquad U(r) = E_{\text{atoms}} + \widetilde{U}(r). \tag{14.2}$$

With these substitutions, Eq. (14.1) becomes

$$\left\{-\frac{1}{2M_A}\nabla_A^2 - \frac{1}{2M_B}\nabla_B^2 + \widetilde{U}(r)\right\}\kappa(\boldsymbol{r}_A,\boldsymbol{r}_B) = \widetilde{E}_{\text{mol}}\kappa(\boldsymbol{r}_A,\boldsymbol{r}_B). \tag{14.3}$$

Obviously, Eq. (14.3) also has the same structure as Eq. (8.4).

In the following, we shall assume that we are dealing with a diatomic molecule in its electronic ground state. The potential-energy function $\widetilde{U}(r)$ is supposed to have a minimum at a certain internuclear distance, r_e. This distance is referred to as the equilibrium bond length of the molecule, and the requirement that it is associated with a minimum of $\widetilde{U}(r)$ implies that

$$\widetilde{U}'(r_e) = 0 \quad \text{and} \quad \widetilde{U}''(r_e) > 0 \tag{14.4}$$

where the primes denote differentiations with respect to r.

As a typical example, Figure 14.1 shows the potential-energy function $\widetilde{U}(r)$ as calculated for the electronic ground state of the hydrogen molecule, H_2.[1] When r is very large we deal with two free hydrogen atoms, and $\widetilde{U}(r)$ is then zero. Bringing the atoms together leads to the formation of a chemical bond and hence to a lowering of the energy, i. e., to a decrease of $\widetilde{U}(r)$. This decrease continues until the point $r = r_e$ is reached, after which $\widetilde{U}(r)$ starts rising to infinity as a result of the strong repulsion between the nuclei for small values of r.

Were it not for the dynamics of the nuclei, then r would settle at the value r_e and the energy of the molecule would be $U(r_e)$. But the nuclei cannot be brought to rest, so the energy of the molecule will be $U(r_e)$ plus the energy associated with the nuclear motion.

The motion of the nuclei may be separated into translation, rotation, and vibration. Translation is the center-of-mass motion and rotation means rotation of the molecule about the center of mass, while vibration means oscillation of r about its equilibrium value r_e.

We begin with a direct attack on the vibrational problem and postpone the formal separation of variables until Section 14.3.

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[1] The graph is based upon the results of an extremely accurate calculation by W. Kolos and L. Wolniewicz, J. Chem. Phys. **43**, 2429(1965).

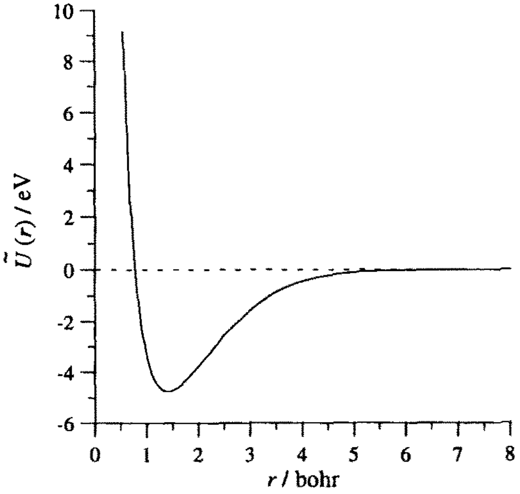

Figure 14.1: The ground-state potential-energy curve of the H_2 molecule, referred to the ground-state energy of two H atoms. The minimum defines the equilibrium bond length, $r_e = 1.401\,a_0 = 0.7414\,\text{Å}$, and the electronic dissociation energy $D_e = -\tilde{U}(r_e) = 4.7477\,\text{eV}$.

14.2 The Vibrational Motion

The vibrational position variable is the deviation of r from its equilibrium value. We denote this variable by x, i. e., we put

$$r = x + r_e. \tag{14.5}$$

The potential-energy function that the vibrator senses is the energy function $\tilde{U}(r)$ as measured from its minimum value $\tilde{U}(r_e)$. We call this function $V(x)$,

$$V(x) = \tilde{U}(r_e + x) - \tilde{U}(r_e). \tag{14.6}$$

For the hydrogen molecule, we show the function $V(x)$ in Figure 14.2 (solid curve). For negative values of x, it rises to infinity as x approaches the value $-r_e$, corresponding to the internuclear distance $r = 0$. For positive values of x, it approaches the value

$$D_e = -\tilde{U}(r_e) = |\tilde{U}(r_e)| \tag{14.7}$$

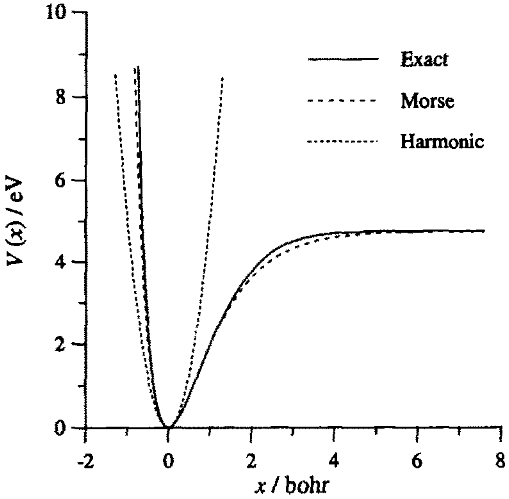

Figure 14.2: The exact potential-energy function $V(x)$ for the H_2 molecule and its approximation by a harmonic potential and a Morse potential.

which is the *electronic dissociation energy*. D_e is also called the *well depth*, for obvious reasons. The two other curves in Figure 14.2 will be explained at the end of this section.

We are now ready to present the Schrödinger equation for the vibrational motion. It has the form

$$\boxed{-\frac{\hbar^2}{2\mu}\frac{d^2\psi(x)}{dx^2}+V(x)\psi(x)=E\psi(x), \qquad -r_e < x < \infty} \tag{14.8}$$

where $\psi(x)$ is the vibrational wavefunction and E the vibrational energy. The effective mass of the oscillator is the *reduced mass*,

$$\boxed{\mu=\frac{M_A M_B}{M_A+M_B} \qquad \text{or} \qquad \frac{1}{\mu}=\frac{1}{M_A}+\frac{1}{M_B}} \tag{14.9}$$

We note that if $M_A \leq M_B$ then μ varies between $\frac{1}{2}M_A$ (when $M_A = M_B$) and M_A (when $M_B \to \infty$). As we know, the reduced mass emerges in a natural way when the center-of- mass motion is eliminated.

The form of $V(x)$, as exemplified by Figure 14.2, indicates that the spectrum of E will be discrete for $E < D_e$ (bound states) and continuous for $E > D_e$ (dissociative states), and this is in fact what one finds by solving Eq. (14.8). In general, it is impossible to solve this equation analytically. Indeed, $V(x)$ is itself only known as a numerical function. There is nothing wrong with numerical functions, however, and both $\psi(x)$ and E may be determined with great accuracy by the methods of numerical analysis.

The physical accuracy is, however, never better than the accuracy with which the exact form of $V(x)$ is known, and the theoretical calculation of the finer details of $V(x)$ is for most molecules a formidable task. More often than not, one must therefore be content with reasonable approximations to $V(x)$. Now, one may very often obtain a first approximation without actually calculating $V(x)$ from first principles (which involves the solution of an electronic Schrödinger equation for each value of r). For if the spectrum of E has been well determined experimentally, then methods exist by means of which one may deduce the gross features of $V(x)$.

Such methods usually take their starting point in an expression for the spectrum of E of the form

$$\boxed{\begin{aligned} E_n &= \hbar\omega\left[(n+\tfrac{1}{2}) - x_e(n+\tfrac{1}{2})^2 + y_e(n+\tfrac{1}{2})^3\right], \\ \frac{E_n}{hc} &= \omega_e\left[(n+\tfrac{1}{2}) - x_e(n+\tfrac{1}{2})^2 + y_e(n+\tfrac{1}{2})^3\right], \\ n &= 0, 1, 2, \ldots, n_{\text{max}} \end{aligned}} \tag{14.10}$$

in which $\omega_e = \omega/2\pi c$, x_e and y_e are empirical parameters, such that x_e is considerably smaller than 1, and y_e is considerably smaller than x_e. It is found that an expression of this kind is able to give a very good representation for many diatomic molecules, at least when they reside in their electronic ground state. For the hydrogen molecule one finds

$$\text{H}_2: \quad \begin{cases} \omega_e = 4401.21\,\text{cm}^{-1}, \\ x_e = 0.027567, \qquad y_e = 0.0001635, \\ n_{\text{max}} = 14. \end{cases} \tag{14.11}$$

Thus the electronic ground state of the hydrogen molecule supports 15 vibrational states. For other molecules, n_{max} may be much smaller or much larger than this.[2]

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[2] The vibrational parameters for a very large number of diatomic molecules is given in: K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules*, Van Nostrand Reinhold, New York, 1979.

There are various methods by means of which one may deduce the gross features of $V(x)$ from the energy spectrum, but we shall only consider the idea of using an approximating $V(x)$ of a particular analytical form, with built-in parameters, but such that the Schrödinger equation (14.8) may in fact be solved analytically. A large number of such functions have been discussed by Steele and Lippincott,[3] but we shall only consider the two most common ones.

The simplest approximating potential is the harmonic potential defined by Eq. (7.3), i. e.,

$$V^{\text{Harmonic}}(x) = \tfrac{1}{2}kx^2, \qquad -\infty < x < \infty. \tag{14.12}$$

We have studied the Schrödinger equation corresponding to this potential in great detail in Chapter 7. It leads to the well-known energy spectrum given by Eq. (7.41), and we note that this expression coincides with the expression of Eq. (14.10) when we put x_e and y_e equal to zero.

The energy spectrum of the harmonic oscillator differs from the vibrational energy spectrum of a real molecule in three important respects. Firstly, the energy levels are equally spaced. Secondly, there are infinitely many of them. And thirdly, the continuous spectrum is absent. Nevertheless, the lower part of the real spectrum is fairly well represented by the harmonic oscillator expression, provided the molecule considered has a large number of bound states. The harmonic-potential approximation is accordingly much used for lower n-values, also because the wavefunctions are simple and easy to work with. Note that in (14.12) the coordinate x is allowed to extend beyond its physical range, $-r_e < x < \infty$. Also for this reason, applications of the harmonic-oscillator description should be restricted to low values of n.

A much more realistic potential is the so-called Morse potential

$$V^{\text{Morse}}(x) = D_e\left(1 - e^{-bx}\right)^2, \qquad -\infty < x < \infty. \tag{14.13}$$

This potential goes so quickly to infinity for negative values of x that the motion of the particle is effectively limited to its physical range. It approaches the constant value D_e for large x. Thus, it has the same qualitative characteristics as a real vibrational potential with well depth D_e. The Schrödinger equation may again be solved analytically and the following expression obtained for the

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[3] D. Steele and E. R. Lippincott, Rev. Mod. Phys. **34**, 239 (1962).

energy levels [4]

$$\begin{cases} E_n^{\text{Morse}} = \hbar\omega\left[(n+\tfrac{1}{2}) - x_e(n+\tfrac{1}{2})^2\right], \\ \omega = \sqrt{\dfrac{2D_e b^2}{\mu}}, \\ x_e = \sqrt{\dfrac{b^2\hbar^2}{8\mu D_e}} = \dfrac{\hbar\omega}{4D_e}, \\ n_{\text{max}} = \text{largest integer smaller than } \lambda - \tfrac{1}{2}, \\ \lambda = \dfrac{1}{2x_e}. \end{cases} \tag{14.14}$$

A graph of the Morse potential and the associated energy spectrum is shown in Figure 14.3, in a dimensionless representation similar to the one defined by Eqs. (7.15) and (7.16) for the harmonic oscillator. Thus, the dimensionless coordinate Q is

$$Q = \sqrt{\frac{\mu\omega}{\hbar}}\, x, \tag{14.15}$$

where ω is defined in Eq. (14.14). The dimensionless energy E is the energy measured in units of $\hbar\omega$. The energy spectrum is very much like that of a real molecule.

Let us now compare the exact $V(x)$ for the hydrogen molecule with an approximating harmonic potential and an approximating Morse potential. This is done in Figure 14.2 which is based upon the criterion that the three potentials have the same curvature, $V''(0)$, at $x = 0$. This fixes the harmonic potential completely. For the Morse potential a second criterion has been used, namely, that it have the same well depth as the exact potential. The Morse curve is then also completely determined.

We see from the figure that the Morse potential approximates the exact potential quite well. The minor differences between the two potentials can, however, not be neglected. We find, for instance, that the Morse potential for H_2 supports two more vibrational bound states than does the exact potential.

It is important to note that the approximating harmonic potential and the approximating Morse potential define the same angular frequency ω. For we have required that the two potentials have the same curvature, V'', at $x = 0$, namely, the curvature of the true potential. Differentiating the expressions

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[4] For an overview see, for example, J. P. Dahl and M. Springborg, J. Chem. Phys. **88**, 4535 (1988).

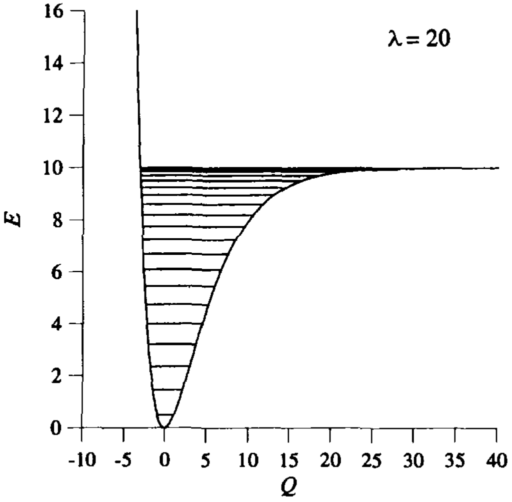

Figure 14.3: The potential-energy function and the energy levels for a Morse oscillator with 20 bound states. Dimensionless units as described in the text.

(14.12) and (14.13) twice gives therefore

$$k = 2D_e b^2. \tag{14.16}$$

The ω's defined by the harmonic-oscillator expression (7.5) and the Morse-oscillator expression (14.14) are accordingly the same, as claimed.

Let us now calculate the value of ω for the electronic ground state of the hydrogen molecule. From the data in the reference of Footnote 1 one finds

$$k = V''(0) = 10.0660\,\mathrm{eV}\,a_0^{-2} = 575.97\,\mathrm{N\,m^{-1}}. \tag{14.17}$$

Furthermore, the mass of a hydrogen atom is

$$m_{\mathrm{H}} = m_e + m_p = 1.67353 \times 10^{-27}\,\mathrm{kg}, \tag{14.18}$$

where we have inserted the values of m_e and m_p from Eqs. (1.11) and (1.16) respectively. In calculating the reduced mass of the oscillator by Eq. (14.9) we must put $M_A = M_B = m_{\mathrm{H}}$. This gives

$$\mu = \tfrac{1}{2} m_{\mathrm{H}} = 8.36767 \times 10^{-28}\,\mathrm{kg}. \tag{14.19}$$

Hence, we get

$$\omega = \sqrt{\frac{k}{\mu}} = 8.29655 \times 10^{14}\,\mathrm{s}^{-1}, \tag{14.20}$$

and therefore also

$$\omega_e = \frac{\hbar\omega}{hc} = 4404\,\mathrm{cm}^{-1}. \tag{14.21}$$

This value compares very favorably with the experimental value given in Eq. (14.11).

In the above calculation we have explicitly used that the hydrogen nucleus consists of a single proton. The only thing that is used when the theoretical potential curve is determined from first principles is, however, that the charge of the nucleus is $+e$. Hence we get the same curve for say HD and D_2, where D is deuterium. Deuterium has the mass

$$m_{\mathrm{D}} = m_e + m_d = 3.34450 \times 10^{-27}\,\mathrm{kg} \tag{14.22}$$

where we have used that the deuteron mass is

$$m_d = 3.34358 \times 10^{-27}\,\mathrm{kg}. \tag{14.23}$$

The different mass of deuterium causes $\omega_e(\mathrm{H_2})$, $\omega_e(\mathrm{HD})$ and $\omega_e(\mathrm{D_2})$ to be substantially different. Accordingly, the vibrational spectrum shows a pronounced *isotope effect.*

Using the definition (14.9) we find in fact that

$$\left\{ \begin{array}{l} \mu(\mathrm{HD}) = 1.11540 \times 10^{-27}\,\mathrm{kg}, \\ \mu(\mathrm{D_2}) = 1.67225 \times 10^{-27}\,\mathrm{kg}. \end{array} \right. \tag{14.24}$$

Hence we get, by using the same value of k as before,

$$\left\{ \begin{array}{l} \omega_e(\mathrm{HD}) = 3815\,\mathrm{cm}^{-1}, \\ \omega_e(\mathrm{D_2}) = 3116\,\mathrm{cm}^{-1}. \end{array} \right. \tag{14.25}$$

The experimental values are $3813\,\mathrm{cm}^{-1}$ and $3116\,\mathrm{cm}^{-1}$, respectively.

Table 14.1 gives some spectroscopically determined constants for a selected series of diatomic molecules. The quantity D_0 is the experimental, or *chemical dissociation energy*, which differs from the electronic dissociation energy D_e by the vibrational zero-point energy. The rotational constant B_e is defined in Section 14.4. The parameter y_e of Eq. (14.10) is not given in the table. For

Molecule	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	B_e (cm^{-1})	r_e (AA)	D_0 (eV)
$^1\mathrm{H}_2$	4401.21_3	121.33_6	60.853_0	0.74144	4.4781_3
$^1\mathrm{H}^2\mathrm{H}$	3813.1_5	91.65	45.655	0.74142	4.5138_3
$^2\mathrm{H}_2$	3115.50	61.82	30.443_6	0.74152	
$^1\mathrm{H}_2^+$	$2321._7$	66.2	30.2_1	1.052	2.6507_8
$^1\mathrm{H}^{35}\mathrm{Cl}$	2990.946_3	52.8186	10.59341_6	1.27455_2	4.433_6
$^1\mathrm{H}^{19}\mathrm{F}$	4138.32	89.88	20.9557	0.91680_8	5.869
$^{12}\mathrm{C}^1\mathrm{H}$	2858.5	63.0_2	14.457	1.1199	3.46_5
$^{14}\mathrm{N}_2$	2358.57	14.324	1.99824	1.09768_5	9.759_4
$^{23}\mathrm{Na}_2$	159.124_5	0.7254_7	0.154707	3.0788_7	0.720
$^{69}\mathrm{Ga}^{35}\mathrm{Cl}$	365.3	1.2	0.1499045	2.201690	4.92
$^{197}\mathrm{Au}_2$	190.7	0.420	0.028013	2.4719	2.30
$^{84}\mathrm{Kr}_2$	24.1_8	1.34		4.0_3	(0.0157)

Table 14.1: Constants of diatomic molecules.

(Extracted from the reference of footnote 2.)
ω_e and x_e are defined by Eq. (14.10).
B_e is defined in Section 14.4.
r_e is the equilibrium bond length.
$D_0 = D_e - E_0^{\mathrm{vib}}$ where D_e is the electronic dissociation energy, and E_0^{vib} is the vibrational zero-point energy.

most molecules it has not been determined, or it has not been determined with sufficient accuracy.

It is obvious from the table that the quality of the spectroscopic information about potential energy surfaces varies from molecule to molecule. The experimental recording of a spectrum may indeed be a very difficult undertaking, especially for molecules that only exist in low concentrations or at very low temperatures.

The quantum-mechanical calculation of good potential-energy functions from first principles is not an easy task either. But it is today an important alternative or supplement to spectroscopic measurements, and much progress in the study of molecules is due to a fruitful interaction between quantum-chemical calculations and spectroscopic experiments.

We have so far treated the vibrational problem in a very direct way. Let us now go back to Eq. (14.3) and derive both the vibrational and the rotational problem from that equation. In light of the discussions in Chapter 8 this is a simple task, for as already said, Eq. (14.3) has the same structure as Eq. (8.4).

14.3 The Vibrating Rotator

Proceeding as in Section 8.1, we begin by eliminating the center-of-mass motion and write

$$\boxed{\widetilde{E}_{\mathrm{mol}} = E^{\mathrm{trans}} + E^{\mathrm{rel}}} \tag{14.26}$$

where E^{trans} is the translational energy, and E^{rel} is the energy of the relative, or internal motion. As in Section 8.1, we need not consider the center-of-mass motion further. Let the wavefunction representing the relative motion be $\psi^{\mathrm{rel}}(\boldsymbol{r})$. We have, then, the Schrödinger equation

$$\boxed{-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi^{\mathrm{rel}}(\boldsymbol{r}) + \widetilde{U}(r)\psi^{\mathrm{rel}}(\boldsymbol{r}) = E^{\mathrm{rel}}\psi^{\mathrm{rel}}(\boldsymbol{r})} \tag{14.27}$$

The problem defined by Eq. (14.27) is that of a particle with mass μ moving in a central field, i. e., a potential-energy field which only depends upon the distance to the origin. We have given a thorough discussion of the central-field problem in Chapter 8. We know, therefore, that if we introduce spherical polar coordinates, then $\psi^{\mathrm{rel}}(\boldsymbol{r})$ may be factorized into the product of a surface spherical harmonic, depending on the angular coordinates (θ, ϕ), and a radial function of the variable r,

$$\psi^{\mathrm{rel}}(\boldsymbol{r}) = R(r)Y_{J\gamma_J}(\theta,\phi) = \frac{1}{r}P(r)Y_{J\gamma_J}(\theta,\phi). \tag{14.28}$$

$Y_{J\gamma_J}(\theta,\phi)$ is a surface spherical harmonic, but we have used J rather than ℓ for the angular-momentum quantum number, to conform to ordinary pratice. The allowed values for J are the integers 0, 1, 2, ... The index γ_J takes on $2J+1$ values for a given value of J, in accordance with the discussion following Eq. (8.94).

$Y_{J\gamma_J}(\theta,\phi)$ is the *rotational wavefunction*. For a given J-value, the radial function $P(r) = rR(r)$ must be determined by solving the analog of Eq. (8.100), i. e.,

$$-\frac{\hbar^2}{2\mu}\frac{d^2P(r)}{dr^2} + \frac{J(J+1)\hbar^2}{2\mu r^2}P(r) + \widetilde{U}(r)P(r) = E^{\mathrm{rel}}P(r). \tag{14.29}$$

Let us now assume that the potential-energy function $\widetilde{U}(r)$ is of the type described in Section 14.1. It has a minimum for $r = r_e$. Instead of the variable

r, we may then introduce the variable x which is the deviation of r from its equilibrium value r_e. (The definition of x is given in Eq. (14.5)). We may also introduce the function $V(x)$ which measures the potential energy from its minimum value according to Eq. (14.6). We see from Eq. (14.5) that $dr = dx$, and Eq. (14.29) may therefore be replaced by the following differential equation in x

$$-\frac{\hbar^2}{2\mu}\frac{d^2\psi(x)}{dx^2} + \frac{J(J+1)\hbar^2}{2\mu(r_e+x)^2}\psi(x) + V(x)\psi(x) = [E^{\text{rel}} - \widetilde{U}(r_e)]\psi(x), \quad (14.30)$$

where

$$\psi(x) = P(r). \quad (14.31)$$

$E^{\text{rel}} - \widetilde{U}(r_e)$ is the energy of the relative motion, referred to the potential-energy minimum $\widetilde{U}(r_e)$. $\psi(x)$ is the *vibrational wavefunction.*

Solving Eq. (14.30) is a fairly complicated matter. We have a separate equation for each value of J, so the vibrational wavefunctions will be different for different J-values. An immense simplification is, however, obtained if we approximate the denominator $2\mu(r_e + x)^2$ in the second term by $2\mu r_e^2$, for the equation may then be written

$$-\frac{\hbar^2}{2\mu}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = \left(E^{\text{rel}} - \widetilde{U}(r_e) - \frac{J(J+1)\hbar^2}{2\mu r_e^2}\right)\psi(x). \quad (14.32)$$

The factor in front of the wavefunction on the right-hand side of this equation is independent of r. Let us write

$$E^{\text{rel}} = \widetilde{U}(r_e) + \frac{J(J+1)\hbar^2}{2\mu r_e^2} + E^{\text{vib}}. \quad (14.33)$$

Eq. (14.32) becomes then

$$-\frac{\hbar^2}{2\mu}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E^{\text{vib}}\psi(x). \quad (14.34)$$

Thus, we have obtained an equation which is independent of the rotational state.

Apart from the notation for the eigenvalue, Eq. (14.34) is the same as Eq. (14.8) which is the Schrödinger equation for the vibrational problem discussed in Section 14.2. Thus, the solutions of Eq. (14.34) may be labeled by a vibrational quantum number n, with the values 0, 1, 2, ... The wavefunctions obtained by solving Eq. (14.34) are ψ_n, and the corresponding energy values are E_n^{vib}.

Combining the rotational and vibrational wavefunctions gives us the total wavefunction for the relative motion of the two atoms. It takes the form

$$\psi^{\text{rel}}(r) = \frac{1}{r}\psi_n(x)Y_{J\gamma_J}(\theta,\phi). \tag{14.35}$$

The degeneracy of an energy level is $2J+1$. Eq. (14.33) gives the expression for the energy, namely,

$$\boxed{E^{\text{rel}} = \widetilde{U}(r_e) + E_J^{\text{rot}} + E_n^{\text{vib}}} \tag{14.36}$$

where E_J^{rot} is the energy of rotation, and E_n^{vib} is the energy of vibration.

The energy of vibration may to a good approximation be written on the form (14.10). The energy of rotation is the second term on the right-hand side of Eq. (14.33),

$$\boxed{E_J^{\text{rot}} = \frac{J(J+1)\hbar^2}{2\mu r_e^2} = \frac{J(J+1)\hbar^2}{2I}} \tag{14.37}$$

The quantity

$$I = \mu r_e^2 \tag{14.38}$$

is the *moment of inertia*. We may also write

$$\boxed{E_J^{\text{rot}} = hcB_eJ(J+1), \qquad B_e = \frac{h}{8\pi^2 Ic}} \tag{14.39}$$

The constant B_e has the unit of wavenumbers and is called the *rotational constant*. The value of B_e is part of the experimental information given for a series of selected molecules in Table 14.1.

Thus, the approximation introduced in going from Eq. (14.30) to Eq. (14.32) leads to a very simple picture of the relative motion of the two atoms in a diatomic molecule. The energy is the sum of three terms: the electronic energy $\widetilde{U}(r_e)$ which binds the atoms together, the vibrational energy E_n^{vib}, and the rotational energy E_J^{rot}. The wavefunction is the product of a vibrational wavefunction $\psi_n(x)$ and a rotational wavefunction $Y_{J\gamma_J}(\theta,\phi)$. The vibrational and rotational motions are completely uncoupled in this picture.

The factor $1/r$ in the wavefunction (14.35) may to a good approximation be put equal to $1/r_e$ and assimilated in the normalization constant of the wavefunction. Doing so is, in fact, consistent with the approximation made in going from Eq. (14.30) to Eq. (14.32). The wavefunction becomes then

$$\boxed{\psi^{\mathrm{rel}} = \psi_n^{\mathrm{vib}}(x) Y_{J\gamma_J}(\theta,\phi)} \tag{14.40}$$

It is often convenient to consider ψ^{rel} as the eigenfunction of a *model Hamiltonian*

$$\widehat{H}^{\mathrm{vr}} = \widehat{H}^{\mathrm{vib}} + \widehat{H}^{\mathrm{rot}}, \tag{14.41}$$

where

$$\boxed{\widehat{H}^{\mathrm{vib}} = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + V(x)} \tag{14.42}$$

is the *vibrational Hamiltonian*, and

$$\boxed{\widehat{H}^{\mathrm{rot}} = \frac{\hbar^2 \hat{J}^2}{2I}} \tag{14.43}$$

is the *rotational Hamiltonian.*

The vibrational Hamiltonian defines the Schrödinger equation (14.8) which we studied in Section 14.2. The Schrödinger equation defined by the rotational Hamiltonian is the differential equation for the surface spherical harmonics which we studied in Section 8.3. The Hamiltonian (14.42) is said to describe a *vibrator*. The Hamiltonian (14.43) is said to describe a *rigid rotator*. The relative motion of the two atoms of our diatomic molecule is accordingly said to be described by a *vibrating rotator*. (Since the description does allow the molecule to vibrate while it rotates, it is better not to talk about a vibrating rigid rotator.)

The energy levels of a typical vibrator are shown in Fig. 14.3. The energy levels of the rigid rotator (Eq. (14.39)) are shown in Fig. 14.4.

This is as far as we shall take the description of the diatomic molecule. The simple picture based upon the approximation introduced in going from

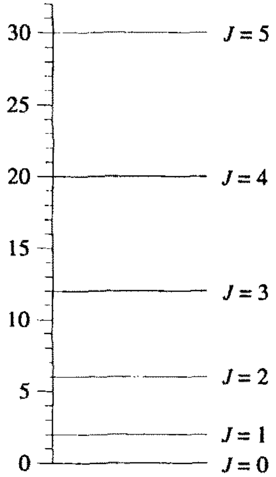

Figure 14.4: Energy level diagram for the rigid rotator. Energies in units of hcB_e.

Eq. (14.30) to Eq. (14.32) goes a long way and is very useful for the interpretation of rotational and vibrational spectra. But the picture is, of course, an approximation, and in detailed work it is necessary to go beyond it.

14.4 On Rotational and Vibrational Spectra

Since we have not studied the formal description of the interaction between molecules and photons, we are not prepared to discuss the rotational and vibrational spectra of diatomic molecules. A few remarks are, however, appropriate.

In order that a photon may cause a transition from one energy level to another, its associated frequency must satisfy Bohr's energy-frequency condition (2.54), i. e.,

$$\Delta E = h\nu. \tag{14.44}$$

But in addition there are selection rules on Δn, the change in vibrational quantum number, and ΔJ, the change in rotational quantum number. These rules are

$$\Delta n = 0, \pm 1, \pm 2, \ldots, \qquad \Delta J = \pm 1. \tag{14.45}$$

If the vibrator is harmonic, then the vibrational selection rule becomes $\Delta n = 0, \pm 1$.

Transitions for which $\Delta n = 0$, generate pure rotational spectra which are observed as microwave spectra. Transitions for which $\Delta n \neq 0$, generate vibrational-rotational spectra which are observed as infrared spectra.

Note that the rotational energy levels E_J^{rot}, measured in wavenumbers, according to Eq. (14.39) come at the values

$$0, 2B_e, 6B_e, 12B_e, 20B_e, \ldots$$

so that the difference between neighboring levels increases with J as

$$2B_e, 4B_e, 6B_e, 8B_e. \ldots$$

This implies that if we consider transitions corresponding to $\Delta n = 0$ or to a definite change $n_1 \to n_2$ in the vibrational quantum number, then the rotational contribution will lead to a series of equidistant spectral lines, correponding to the just listed series of differences between neighboring rotational levels (provided of course that a number of rotational levels are populated, and this is always the case at room temperature). The distance between neighboring lines is $2B_e$. By observing this difference, we may calculate the moment of inertia of the diatomic molecule from Eq. (14.39), and hence determine the internuclear equilibrium distance from Eq. (14.38). The formulae show, in fact, that

$$r_e = \sqrt{\frac{h}{8\pi^2 c\mu B_e}}. \tag{14.46}$$

As an example, Table 14.1 shows that the B_e value for the hydrogen molecule is 60.853 cm^{-1} = 6058.3 m^{-1}. The reduced mass, μ, is given by Eq. (14.19). Hence, we calculate r_e to be 0.74144×10^{-10} m = 0.74144 Å. This value is also given in Table 14.1. It agrees with the theoretical value listed in the caption of Fig. 14.1.

It is important to note that spectra may be absent even though the conditions (14.44) and (14.45) are satisfied. A homonuclear diatomic molecule must, in fact, have a permanent dipole moment in order that microwave and infrared spectra be observed. Homonuclear diatomics without a dipole moment may be observed through their so-called Raman spectra (with selection rules different from those given above). For instance, the B_e value for the hydrogen molecule must be determined from a Raman spectrum.

Supplementary Reading

The bibliography, entries [4], [8], [11], [18], and [31].

Problems

14.1. Table 14.1 has 6 columns. Add, for some selected molecules, a new set of columns according to the following instructions

Column **7**. Determine the zero-point energy E_0 in the harmonic approximation (cm^{-1}).

Column **8**. Determine E_0 in the Morse approximation (cm^{-1}).

Column **9**. Determine the reduced mass μ in u (use the table of isotope masses given below).

Column **10**. Calculate the force constant k (Nm^{-1}).

Column **11**. Calculate the electronic dissociation energy D_e (in eV) with E_0 determined by the harmonic approximation.

Column **12**. Calculate D_e (in eV) with E_0 determined by the Morse approximation.

Column **13**. Determine $n_{\max}$ from the expression (14.14).

Column **14**. Calculate $E_{n_{\max}}^{\mathrm{Morse}}$ and compare the result with the D_e value calculated in Column 12.

Finally, calculate ω_e for $^{12}\mathrm{C}^2\mathrm{H}$.

Isotope masses (u) (1 u = 1.66054×10^{-27} kg)

^{1}H	^{2}H	^{12}C	^{14}N	^{19}F	^{23}Na	^{35}Cl	^{69}Ga
1.008	2.014	12.000	14.003	18.998	22.990	34.969	68.926
^{84}Kr	^{197}Au						
83.912	196.967						

Note that the values given in Table 14.1 have been determined experimentally, by interpreting spectra by means of expressions like (14.10), (14.39) and (14.43). The dissociation energy has, however, sometimes been determined by different means. In some cases, the number of spectral lines available has been small. The purpose of the present exercise is to extract further information from the experimental results by means of the theoretical expressions in the present chapter. Some of the results, in particular the values determined for $n_{\max}$, must however be viewed with reservations. After all, our theory is a simplified one, and some experimental values, in particular the $\omega_e x_e$ values, may be quite uncertain.

Chapter 15

Atomic Term Symbols

Contents

In Chapters 11 and 13 we discussed the construction of many-electron wavefunctions for atoms and molecules in terms of Slater determinants built from atomic and molecular spin-orbitals. The discussion was, however, quite qualitative. It merely referred to the concept of electron configurations. In the present chapter, we shall extend the discussion so that also atomic term symbols, like those of Tables 11.2–11.4, may be included.

Term symbols refer to total angular momentum quantum numbers. The values of these quantum numbers may be accounted for by the theory of angular-momentum coupling, in particular the coupling of two angular momenta referring to different degrees of freedom. These two angular momenta might, for instance, be the orbital angular momenta of two separate electrons in an atom, or it might be the spins of two separate electrons, or the orbital angular momentum and the spin of a single electron or a group of electrons. But the two subsystems involved might also be of a more complex nature.

In the present chapter we discuss the types of angular momentum coupling that are implicit in the term symbols of Tables 11.2–11.4. We also discuss the coupling between the total electronic angular momentum and the angular momentum of the nucleus, and outline the connection between an atom's total angular momentum and the possibility of forming Bose–Einstein condensates.

Angular-momentum coupling involves a change of basis in the function space for the composite system, from an uncoupled representation to a coupled representation. The change of basis is described by a unitary matrix, the elements of which are known as coupling coefficients. As a useful preliminary, we shall therefore begin with a general section on basis changes and unitary matrices. This section attaches naturally to the earlier Sec. 5.10 on matrix algebra.

15.1 Orthonormal Bases and Unitary Matrices

Let us consider a linear function space $\mathcal{V}$ of dimension m and introduce two different orthonormal bases in $\mathcal{V}$,

$$\{\Phi_r\} = \Phi_1, \Phi_2, \dots, \Phi_m, \qquad \langle \Phi_r | \Phi_s \rangle = \delta_{rs}, \tag{15.1}$$

and

$$\{\tilde{\Phi}_r\} = \tilde{\Phi}_1, \tilde{\Phi}_2, \dots, \tilde{\Phi}_m, \qquad \langle \tilde{\Phi}_r | \tilde{\Phi}_s \rangle = \delta_{rs}. \tag{15.2}$$

The connection between the two bases may be expressed by means of a matrix $\boldsymbol{U}$:

$$\left(\tilde{\Phi}_1 \tilde{\Phi}_2 \dots \tilde{\Phi}_m\right) = (\Phi_1 \Phi_2 \dots \Phi_m) \begin{pmatrix} U_{11} & U_{12} & \cdots & U_{1m} \\ U_{21} & U_{22} & \cdots & U_{2m} \\ \dots & \dots & \dots & \dots \\ U_{m1} & U_{m2} & \cdots & U_{mm} \end{pmatrix}, \tag{15.3}$$

that is,

$$\tilde{\Phi}_i = \sum_{r=1}^{m} \Phi_r U_{ri}, \quad i = 1, 2, \ldots, m. \tag{15.4}$$

We get then, that

$$\langle \tilde{\Phi}_i | \tilde{\Phi}_j \rangle = \sum_{r=1}^{m} \sum_{s=1}^{m} \langle \Phi_r | \Phi_s \rangle U^*_{ri} U_{sj} = \sum_{r=1}^{m} \sum_{s=1}^{m} \delta_{rs} U^*_{ri} U_{sj} = \sum_{r=1}^{m} U^*_{ri} U_{rj}, \tag{15.5}$$

where we have used that the basis $\Phi_1, \Phi_2, \ldots, \Phi_m$ is orthonormal. Equation (15.5) shows, that the condition that also the basis $\tilde{\Phi}_1, \tilde{\Phi}_2, \ldots, \tilde{\Phi}_m$ be orthonormal becomes

$$\sum_{r=1}^{m} U^*_{ri} U_{rj} = \delta_{ij}. \tag{15.6}$$

By introducing the Hermitian conjugate matrix $\boldsymbol{U}^\dagger$, with elements $U^\dagger_{ir} = U^*_{ri}$, we may write the condition (15.6) in the form

$$\boldsymbol{U}^\dagger \boldsymbol{U} = \boldsymbol{E} \tag{15.7}$$

where $\boldsymbol{E}$ is the $m \times m$ unit matrix. Left multiplication by $\boldsymbol{U}$ and right multiplication by $\boldsymbol{U}^{-1}$ gives

$$\boldsymbol{U}\boldsymbol{U}^\dagger \boldsymbol{U}\boldsymbol{U}^{-1} = \boldsymbol{U}\boldsymbol{U}^{-1}, \tag{15.8}$$

or,

$$\boldsymbol{U}\boldsymbol{U}^\dagger = \boldsymbol{E}. \tag{15.9}$$

That $\boldsymbol{U}^{-1}$ actually exists follows from the fact that the relation (15.3) may be inverted. Combining Eqs. (15.7) and (15.9) gives

$$\boxed{\boldsymbol{U}\boldsymbol{U}^\dagger = \boldsymbol{U}^\dagger \boldsymbol{U} = \boldsymbol{E}} \tag{15.10}$$

This is the condition for $\boldsymbol{U}$ to be a *unitary matrix*. Thus, we have arrived at the very important conclusion

$$\boxed{\text{Orthonormal bases are connected by unitary matrices.}} \tag{15.11}$$

Note that Eq. (15.10) also shows that the inverse of a unitary matrix is the same as the Hermitian conjugate of the matrix.

In terms of matrix elements, Eq. (15.10) becomes

$$\boxed{\begin{aligned} &\sum_{r=1}^{m} U_{ir}U^*_{jr} = \delta_{ij}, \quad i,j = 1,2,\ldots,m \\ &\sum_{r=1}^{m} U^*_{ri}U_{rj} = \delta_{ij}, \quad i,j = 1,2,\ldots,m \end{aligned}} \tag{15.12}$$

These relations, which include Eq. (15.6), are a set of orthonormality relations for the rows and the columns of $\boldsymbol{U}$.

By multiplying Eq. (15.3) from the right with $\boldsymbol{U}^\dagger$ and using Eq. (15.10), we note that the transformation from the basis $\tilde{\Phi}_1, \tilde{\Phi}_2, \ldots, \tilde{\Phi}_m$ to the basis $\Phi_1, \Phi_2, \ldots, \Phi_m$ may be written

$$(\Phi_1\Phi_2\ldots\Phi_m) = \left(\tilde{\Phi}_1\tilde{\Phi}_2\ldots\tilde{\Phi}_m\right)\begin{pmatrix} U^\dagger_{11} & U^\dagger_{12} & \cdots & U^\dagger_{1m} \\ U^\dagger_{21} & U^\dagger_{22} & \cdots & U^\dagger_{2m} \\ \cdots & \cdots & \cdots & \cdots \\ U^\dagger_{m1} & U^\dagger_{m2} & \cdots & U^\dagger_{mm} \end{pmatrix}. \tag{15.13}$$

Thus, the matrices $\boldsymbol{U}$ and $\boldsymbol{U}^\dagger$ play symmetrical roles with respect to the two bases the connect.

Note that the elements of the matrices $\boldsymbol{U}$ and $\boldsymbol{U}^\dagger$ are nothing but the overlap integrals between the elements of the two bases. We have, in fact, that

$$\boxed{U_{rs} = \langle\Phi_r|\tilde{\Phi}_s\rangle, \quad \tilde{U}^\dagger_{sr} = \langle\tilde{\Phi}_s|\Phi_r\rangle = U^*_{rs}} \tag{15.14}$$

To obtain the first of these relations, take the scalar product with Φ_s on both sides of Eq. (15.4). This gives $\langle\Phi_s|\tilde{\Phi}_i\rangle = U_{si}$, or $\langle\Phi_r|\tilde{\Phi}_s\rangle = U_{rs}$. The second relation is obtained from the expression (15.13) in a similar way.

As a simple illustration of the above relations, let us consider the $\ell = 1$ functions of Tables 8.1 and 8.2. We get easily:

$$(Y_{1-1}Y_{11}Y_{10}) = (Y_xY_yY_z)\begin{pmatrix} \sqrt{\frac{1}{2}} & -\sqrt{\frac{1}{2}} & 0 \\ -i\sqrt{\frac{1}{2}} & -i\sqrt{\frac{1}{2}} & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{15.15}$$

and

$$(Y_xY_yY_z) = (Y_{1-1}Y_{11}Y_{10})\begin{pmatrix} \sqrt{\frac{1}{2}} & i\sqrt{\frac{1}{2}} & 0 \\ -\sqrt{\frac{1}{2}} & i\sqrt{\frac{1}{2}} & 0 \\ 0 & 0 & 1 \end{pmatrix}. \tag{15.16}$$

We see that the two transformation matrices are unitary and, in accordance with the general relations (15.3) and (15.13), they are also the Hermitian conjugates of each other.

15.2 Coupling of Two Angular Momenta

We shall now apply the concepts of the previous section to the problem of coupling of two angular momenta. We shall draw heavily on the discussion in Chapters 8 and 10 where we gave a fairly comprehensive treatment of the basic theory of angular momentum, and discussed its use in the description of the orbital angular momentum and the spin of a single particle.

We begin by specifying the uncoupled representation referred to in the introductory remarks.

15.2.1 The Uncoupled Representation

Let us consider some particular angular momentum

$$\hat{\boldsymbol{J}}_1 = (\hat{J}_{1x}, \hat{J}_{1y}, \hat{J}_{1z}) \tag{15.17}$$

which may, for instance, be thought of as an orbital angular momentum or a spin angular momentum, but which may also be more general. The common eigenfunctions of $\hat{J}_1^2$ and $\hat{J}_{1z}$ are denoted $|J_1M_1\rangle$. We shall consider the $2J_1+1$ dimensional function space $\mathcal{V}(J_1)$ spanned by the $2J_1+1$ functions corresponding to $M_1 = J_1, J_1-1, \ldots, -J_1$, for a fixed value of J_1. This function space is invariant under any operator built from the operators $\hat{J}_{1x}$, $\hat{J}_{1y}$ and $\hat{J}_{1z}$, that is, whenever such an operator acts on a function belonging to $\mathcal{V}(J_1)$, then the result also belongs to $\mathcal{V}(J_1)$.

Together with $\hat{\boldsymbol{J}}_1$, let us also consider another angular momentum

$$\hat{\boldsymbol{J}}_2 = (\hat{J}_{2x}, \hat{J}_{2y}, \hat{J}_{2z}), \tag{15.18}$$

and a function space $\mathcal{V}(J_2)$ spanned by the $2J_2+1$ functions $|J_2M_2\rangle$, for a fixed value of J_2. We assume that the two angular momenta considered refer to different degrees of freedom. This implies that each operator in the set (15.17) commutes with each operator in the set (15.18) whenever the operators work on functions that depend on both q_1 and q_2, where q_1 and q_2 are the variable sets associated with the two independent degrees of freedom.

We consider now a function space which is invariant under all the angular momentum operators involved, i.e., both those of Eq. (15.17) and those of Eq. (15.18), and hence also any combination of them. The simplest type of such a space is the *direct-product space*

$$\mathcal{V}(J_1, J_2) = \mathcal{V}(J_1) \times \mathcal{V}(J_2). \tag{15.19}$$

By definition of a direct-product space, $\mathcal{V}(J_1, J_2)$ consists of all functions of the form

$$|\Psi\rangle = \sum_{M_1} \sum_{M_2} |J_1 M_1\rangle |J_2 M_2\rangle a_{M_1 M_2}, \tag{15.20}$$

with arbitrary complex coefficients $a_{M_1 M_2}$. Its dimension is $(2J_1 + 1)(2J_2 + 1)$, and the product functions $|J_1 M_1\rangle |J_2 M_2\rangle$ form a natural orthonormal basis.

We note that

$$\begin{cases} \hat{J}_1^2 |J_1 M_1\rangle |J_2 M_2\rangle = J_1(J_1 + 1)\hbar^2 |J_1 M_1\rangle |J_2 M_2\rangle, \\ \hat{J}_2^2 |J_1 M_1\rangle |J_2 M_2\rangle = J_2(J_2 + 1)\hbar^2 |J_1 M_1\rangle |J_2 M_2\rangle, \end{cases} \tag{15.21}$$

for all values of M_1 and M_2. This implies that

$$\hat{J}_1^2 |\Psi\rangle = J_1(J_1 + 1)\hbar^2 |\Psi\rangle, \quad \hat{J}_2^2 |\Psi\rangle = J_2(J_2 + 1)\hbar^2 |\Psi\rangle, \tag{15.22}$$

for arbitrary values of $a_{M_1 M_2}$. Any function in $\mathcal{V}(J_1, J_2)$ is accordingly an eigenfunction of both $\hat{J}_1^2$ and $\hat{J}_2^2$, with the respective eigenvalues $J_1(J_1 + 1)\hbar^2$ and $J_2(J_2 + 1)\hbar^2$. This is, of course, the justification for calling the function space $\mathcal{V}(J_1, J_2)$.

Apart from this, the basis functions $|J_1 M_1\rangle |J_2 M_2\rangle$ are eigenfunctions of the operators $\hat{J}_{1z}$ and $\hat{J}_{2z}$,

$$\begin{cases} \hat{J}_{1z} |J_1 M_1\rangle |J_2 M_2\rangle = M_1 \hbar |J_1 M_1\rangle |J_2 M_2\rangle, \\ \hat{J}_{2z} |J_1 M_1\rangle |J_2 M_2\rangle = M_2 \hbar |J_1 M_1\rangle |J_2 M_2\rangle. \end{cases} \tag{15.23}$$

This is in keeping with the fact that $\hat{J}_1^2, \hat{J}_{1z}, \hat{J}_2^2, \hat{J}_{2z}$ is a set of mutually commuting operators,

> The orthonormal basis $|J_1 M_1\rangle |J_2 M_2\rangle$ is called the *uncoupled representation*. It is determined by the independent, commuting operators $\hat{J}_1^2, \hat{J}_{1z}, \hat{J}_2^2, \hat{J}_{2z}$. (15.24)

In addition to the separate angular momenta $\hat{\boldsymbol{J}}_1$ and $\hat{\boldsymbol{J}}_2$, we shall now consider the total angular momentum obtained by vector addition of $\hat{\boldsymbol{J}}_1$ and $\hat{\boldsymbol{J}}_2$,

$$\hat{\boldsymbol{J}} = \hat{\boldsymbol{J}}_1 + \hat{\boldsymbol{J}}_2 = (\hat{J}_{1x} + \hat{J}_{2x}, \hat{J}_{1y} + \hat{J}_{2y}, \hat{J}_{1z} + \hat{J}_{2z}). \tag{15.25}$$

A simple analysis, similar to the one represented by Eq. (10.10), shows that $\hat{J}_x, \hat{J}_y, \hat{J}_z$ satisfy the usual angular-momentum commutation relations. Hence, $\hat{\boldsymbol{J}}$ is a proper angular-momentum vector. We shall now consider the transformation from the basis $|J_1M_1\rangle|J_2M_2\rangle$ to a basis determined by the total angular momentum. The physical significance of such a transformation is the following.

Assume that the Hamiltonian $\hat{H}$ of our system commutes with all the operators listed in Eqs. (15.17) and (15.18). It will then also commute with the step-up and step-down operators $\hat{J}_{1+}, \hat{J}_{1-}, \hat{J}_{2+}, \hat{J}_{2-}$. But the basis functions $|J_1M_1\rangle|J_2M_2\rangle$ will successively be transformed into each other by these operators. So if one of them is an eigenfunction of $\hat{H}$ with energy E, they will all be, and the energy level will in fact have a high degeneracy, namely $(2J_1+1)(2J_2+1)$. This follows from an argument similar to the one applied in Secs. 4.5 and 4.7 for a general symmetry operator. Let us repeat the argument here.

Assume that $\hat{H}\Psi = E\Psi$ for some Ψ, and that the operator $\hat{\Omega}$ commutes with $\hat{H}$. We get then

$$\hat{H}\hat{\Omega}\Psi = \hat{\Omega}\hat{H}\Psi = \hat{\Omega}E\Psi = E\hat{\Omega}\Psi. \tag{15.26}$$

But this equation shows exactly what we claimed, namely, that $\hat{\Omega}\Psi$ is an eigenfunction of $\hat{H}$ with energy E whenever Ψ is.

Most often, the Hamiltonian will not commute with all the operators listed in Eqs. (15.17) and (15.18). But it will often commute with $\hat{J}_1^2$, $\hat{J}_2^2$ and the components (and hence also the square) of the total angular momentum $\hat{\boldsymbol{J}}$. In other words, the Hamiltonian may not commute with the x, y and z components of the individual angular momenta, but only with the x, y and z components of the total angular momentum. States with different values of the total angular momentum may therefore well have different energies. Accordingly, it is of great physical interest to consider the transformation from the uncoupled representation (15.24) to the so-called *coupled representation*, in which the basis is determined by the total angular momentum of the system. That such a transformation exists, follows from the fact that $\mathcal{V}(J_1, J_2)$ is invariant under the operators (15.25), so that we may determine common eigenfunctions of $\hat{J}^2$ and one of its components, say $\hat{J}_z$.

15.2.2 The Coupled Representation

The square of the total angular momentum (15.25) may be written

$$\begin{aligned}\hat{J}^2 &= (\hat{J}_{1x} + \hat{J}_{2x})^2 + (\hat{J}_{1y} + \hat{J}_{2y})^2 + (\hat{J}_{1z} + \hat{J}_{2z})^2 \\ &= \hat{J}_1^2 + \hat{J}_2^2 + \hat{\boldsymbol{J}}_1 \cdot \hat{\boldsymbol{J}}_2 + \hat{\boldsymbol{J}}_2 \cdot \hat{\boldsymbol{J}}_1 \\ &= \hat{J}_1^2 + \hat{J}_2^2 + 2\hat{\boldsymbol{J}}_1 \cdot \hat{\boldsymbol{J}}_2,\end{aligned} \tag{15.27}$$

where we have used that $\hat{\boldsymbol{J}}_1 \cdot \hat{\boldsymbol{J}}_2 = \hat{\boldsymbol{J}}_2 \cdot \hat{\boldsymbol{J}}_1$, which is true because operators referring to different degrees of freedom commute.

Since $\hat{J}_1^2$ and $\hat{J}_2^2$ commute with all the components of $\hat{\boldsymbol{J}}_1$ and $\hat{\boldsymbol{J}}_2$ they also commute with $\hat{J}_z = \hat{J}_{1z} + \hat{J}_{2z}$. For the same reason they also commute with $\hat{\boldsymbol{J}}_1 \cdot \hat{\boldsymbol{J}}_2$ and hence with $\hat{J}^2$ (Use the last expression for $\hat{J}^2$ in Eq. (15.27)). The eigenfunctions of $\hat{J}^2$ and $\hat{J}_z$ that we want to determine will accordingly also be eigenfunctions of $\hat{J}_1^2$ and $\hat{J}_2^2$. This is really not surprising, for any function in $\mathcal{V}(J_1, J_2)$ is.

Thus, our alternative set of mutually commuting operators is $\hat{J}_1^2, \hat{J}_2^2, \hat{J}^2, \hat{J}_z$. The common eigenfunctions of these operators determine our new basis for $\mathcal{V}(J_1, J_2)$. We shall denote the new eigenfunctions by $|J_1 J_2 J M\rangle$:

> The orthonormal basis $|J_1 J_2 J M\rangle$ is called the *coupled representation.* It is determined by the independent, commuting operators $\hat{J}_1^2, \hat{J}_2^2, \hat{J}^2, \hat{J}_z$. (15.28)

Our problem is to determine which values of J that occur in $\mathcal{V}(J_1, J_2)$, and then to represent the basis functions of the coupled representation in terms of those of the uncoupled representation, that is, to determine the coefficients in the expansion

$$|J_1 J_2 J M\rangle = \sum_{M_1} \sum_{M_2} |J_1 M_1 J_2 M_2\rangle C_{M_1 M_2}, \tag{15.29}$$

where we have written $|J_1 M_1 J_2 M_2\rangle$ instead of $|J_1 M_1\rangle |J_2 M_2\rangle$ to simplify the notation,

$$|J_1 M_1 J_2 M_2\rangle = |J_1 M_1\rangle |J_2 M_2\rangle. \tag{15.30}$$

From the discussion of Sec. 15.1, it follows that the coefficients $C_{M_1 M_2}$ are the elements of a unitary matrix, and also that their values are the scalar products between the old and the new basis functions. Thus we have:

$$C_{M_1 M_2} = \langle J_1 M_1 J_2 M_2 | J_1 J_2 J M\rangle, \tag{15.31}$$

and Eq. (15.29) becomes

$$|J_1J_2JM\rangle = \sum_{M_1}\sum_{M_2} |J_1M_1J_2M_2\rangle\langle J_1M_1J_2M_2|J_1J_2JM\rangle. \tag{15.32}$$

At this stage we note that addition of the two relations of Eq. (15.23) gives

$$\hat{J}_z|J_1M_1J_2M_2\rangle = (M_1 + M_2)\hbar|J_1M_1J_2M_2\rangle \tag{15.33}$$

which shows that the basis functions of the uncoupled representation are, in fact, already eigenfunctions of $\hat{J}_z$. But eigenfunctions corresponding to different eigenvalues of the same Hermitian operator are known to be orthogonal (See Sec. 5.4). The scalar products $\langle J_1M_1J_2M_2|J_1J_2JM\rangle$ are consequently zero, unless $M = M_1 + M_2$. Thus, Eq. (15.32) takes the simpler form

$$|J_1J_2JM\rangle = \sum_{M_1} |J_1M_1J_2M - M_1\rangle\langle J_1M_1J_2M - M_1|J_1J_2JM\rangle. \tag{15.34}$$

For a given M-value, the number of terms in Eq. (15.34) is restricted by the requirement that $M - M_1$ lie within the range of M_2, i. e., $-J_2 \le M - M_1 \le J_2$. In addition, we have of course that $-J_1 \le M_1 \le J_1$. Thus, M_1 must satisfy the conditions

$$-J_1 \le M_1 \le J_1 \quad \text{and} \quad M - J_2 \le M_1 \le M + J_2. \tag{15.35}$$

According to the first of these conditions, M_1 can at most take $2J_1 + 1$ values, according to the second it can take at most $2J_2 + 1$ values. The number of terms in the sum of Eq. (15.34) can accordingly never exceed the smaller of the two numbers $2J_1 + 1$ and $2J_2 + 1$.

Let us, without loss of generality, assume that $J_2 \le J_1$. The maximum number of terms in the sum of Eq. (15.34) is then $2J_2 + 1$. The value of M will of course lie between $J_1 + J_2$ and $-(J_1 + J_2)$.

The connection between the values of M_1 and M, and hence the number of terms in the sum of Eq. (15.34), is easily derived from the conditions (15.35). The result is shown in Table 15.1.

The number of terms in the sum of Eq. (15.34) is equal to the number of linearly independent functions $|J_1J_2JM\rangle$ that we may construct for a given M-value. Let us therefore imagine that we replace the word term(s) in Table 15.1 by the word function(s). Then the table gives the number of functions with given M-values in the coupled representation.

Let us now realize that each J-value in the coupled representation must be accompanied by the $2J + 1$ M-values $J, J - 1, \ldots, -J$. Then the scheme

Table 15.1: Number, ν, of terms in the sum of Eq. (15.34)

M	M_1	ν
$J_1 + J_2$	J_1	1
$J_1 + J_2 - 1$	$J_1, J_1 - 1$	2
$J_1 + J_2 - 2$	$J_1, J_1 - 1, J_1 - 2$	3
$\dots$	$\dots\dots$	$\dots$
$J_1 - J_2$	$J_1, J_1 - 1, \dots, J_1 - 2J_2$	$2J_2 + 1$
$\dots$	$\dots\dots$	$2J_2 + 1$
$-(J_1 - J_2)$	$-(J_1, J_1 - 1, \dots, J_1 - 2J_2)$	$2J_2 + 1$
$\dots$	$\dots\dots$	$\dots$
$-(J_1 + J_2 - 2)$	$-(J_1, J_1 - 1, J_1 - 2)$	3
$-(J_1 + J_2 - 1)$	$-(J_1, J_1 - 1)$	2
$-(J_1 + J_2)$	$-J_1$	1

predicts that there are $2J_2 + 1$ possible values of J, namely,

$$J = J_1 + J_2, J_1 + J_2 - 1, J_1 + J_2 - 2, \dots, J_1 - J_2 \tag{15.36}$$

and that each of these J-values occur just once. For $J = J_1 + J_2$ seizes one function in each row of Table 15.1. $J = J_1 + J_2 - 1$ seizes one functions in each row apart from the top and bottom rows. $J = J_1 + J_2 - 2$ seizes a function in each row apart from the two uppermost and the two lowest rows, etc. By the time $J = J_1 - J_2$ has seized its functions, all functions are gone. This, then, proves the correctness of the series (15.36).

In the above analysis, we assumed that $J_2 \leq J_1$. We can obviously remove this assumption by replacing the term $J_1 - J_2$ in Eq. (15.36) by $|J_1 - J_2|$. Thus we get the celebrated

$$\boxed{\begin{array}{c}\text{Clebsch–Gordan series:}\\ J = J_1 + J_2, J_1 + J_2 - 1, J_1 + J_2 - 2, \dots, |J_1 - J_2|\end{array}} \tag{15.37}$$

As an interesting exercise, let us count the number of basis functions directly from the Clebsch–Gordan series, under the assumption that $J_2 \leq J_1$. The number of J-values is then $2J_2 + 1$. The total number of M-values is the sum of $2J + 1$ over these J-values. The sum is an arithmetic progression with $2J_2 + 1$ terms, and with the first and last terms being $2(J_1 + J_2) + 1$ and $2(J_1 - J_2) + 1$, respectively. The total number of M-values is therefore

$$\tfrac{1}{2}(2J_2 + 1)\left\{2(J_1 + J_2) + 1 + 2(J_1 - J_2) + 1\right\} = (2J_1 + 1)(2J_2 + 1). \tag{15.38}$$

If $J_1 < J_2$ we would evidently get the same result. But this is exactly the dimension of $\mathcal{V}(J_1, J_2)$, as it should be.

The values of J, as given by the Clebsch–Gordan series, are often said to be given by the *vector-coupling method*. One can represent the result pictorially by thinking of vectors of length J_1 and J_2 added vectorially, starting with the parallel case which gives the resultant $J_1 + J_2$, and taking all possible values differing from this by integers down to $|J_1 - J_2|$ for the antiparallel case.

The coefficients $\langle J_1 M_1 J_2 M_2 | J_1 J_2 J M\rangle$ in Eq. (15.32), i. e., the elements of the unitary matrix which connects the coupled with the uncoupled representation, are known as the *Clebsch–Gordan coefficients* or *Wigner coefficients*, or simply *vector-coupling coefficients*. We shall now see how they can be easily evaluated in some simple cases.

15.3 Vector-Coupling Coefficients by the Construction Method

Because the Clebsch–Gordan series (15.37) contains no J-value more than once, it is possible to perform the transformation from the uncoupled to the coupled representation solely from the step-up and step-down relations (10.6) and the orthonormality relations (15.12). For angular momenta of low order this is a very practical method. We shall call it the construction method.

To determine the functions $|J_1 J_2 J M\rangle$ by this method, one begins by constructing the $2(J_1+J_2)+1$ functions with J equal to J_1+J_2. There is one such function for each of the rows in Table 15.1. And since there is only a single function in the table with $M = J_1 + J_2$, this must be $|J_1 J_2, J_1 + J_2, J_1 + J_2\rangle$, i. e.,

$$|J_1 J_2, J_1 + J_2, J_1 + J_2\rangle = |J_1 J_1; J_2 J_2\rangle. \tag{15.39}$$

To avoid cluttering, we have inserted a semicolon between the two angular momenta that are being added. We have also inserted optional commas.

From the function of Eq. (15.39), we may determine all the functions $|J_1 J_2, J_1 + J_2, M\rangle$ by using the step-down relation of Eq. (10.6), in a similar way as we used the step-up relation in Sec. 8.3.6.[1] Let us, for simplicity,

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[1] We used the step-up operator in Sec. 8.3.6, in order to get the standard distribution of signs in Table 8.1. Here, the generally accepted distribution of signs emerges when using the step-down operator instead.

put $\hbar = 1$ and thus measure angular momenta in units of $\hbar$. We get then

$$|JM-1\rangle = 1/\sqrt{(J+M)(J-M+1)}\hat{J}_-|JM\rangle, \tag{15.40}$$

with $\hat{J}_- = \hat{J}_{1-} + \hat{J}_{2-}$. This gives, with $M = J$,

$$\begin{aligned}|J_1J_2, J_1+J_2, J_1+J_2-1\rangle &= 1/\sqrt{2(J_1+J_2)}(\hat{J}_{2-}+\hat{J}_{1-})|J_1J_1; J_2J_2\rangle \\ &= 1/\sqrt{2(J_1+J_2)}\left(\sqrt{2J_2}|J_1J_1; J_2J_2-1\rangle + \sqrt{2J_1}|J_1J_1-1; J_2J_2\rangle\right), \end{aligned} \tag{15.41}$$

et cetera.

Having determined the functions with $J = J_1 + J_2$, we may proceed to determine those with $J = J_1 + J_2 - 1$ The function with $M = J_1 + J_2 - 1$ must be composed of the same functions as $|J_1J_2, J_1+J_2, J_1+J_2-1\rangle$, but be orthogonal to it. This gives

$$\begin{aligned}&|J_1J_2, J_1+J_2-1, J_1+J_2-1\rangle \\ &= 1/\sqrt{2(J_1+J_2)}\left(\sqrt{2J_1}|J_1J_1; J_2J_2-1\rangle - \sqrt{2J_2}|J_1J_1-1; J_2J_2\rangle\right). \end{aligned} \tag{15.42}$$

Successive operation with $\hat{J}_-$ will generate the remaining functions with $J = J_1 + J_2 - 1$.

In the process of constructing all the functions with $J = J_1 + J_2$ and $J = J_1 + J_2 - 1$, we construct two functions with $M = J_1 + J_2 - 2$. But according to the third row of Table 15.1, a third function with this M-value exists. This is the function $|J_1J_2, J_1+J_2-2, J_1+J_2-2\rangle$, and we construct it by the requirement that it be orthogonal to the two functions we already know. Having constructed the new function, we may again start operating with $\hat{J}_-$, and so on, until all functions of the coupled representation have been generated.

This is a straightforward procedure, but we must be aware that it involves some phase choices beyond the Condon-Shortley convention which we described in Sec. 8.3.5: The first phase choice was made in Eq. (15.39), by not inserting a minus sign or a complex phase factor on the right-hand side of that equation. The second phase choice was made in writing down Eq. (15.42). The sign on the right-hand side was here implicitly chosen such that the matrix element of $\hat{J}_{1z}$ between this function and the function with the same M, but a J-value higher by one unit, became real and positive. A similar criterion should be used to fix the phase of the function $|J_1J_2, J_1+J_2-2, J_1+J_2-2\rangle$, etc. With these additional phase conventions, the functions in the coupled representation are uniquely determined, and we note that all the vector-coupling coefficients become real, by construction. This implies, in turn, that the unitary matrix which they form becomes orthogonal. It may thus be inverted by *a simple reflection in the main diagonal.*

For higher J-values, the direct construction method becomes cumbersome. But then other and more specialized methods based upon recursion relations and series expansions exist. The theory of vector-coupling coefficients is surprisingly rich, and far too extensive to be covered here in further detail.[2] Suffice it to say that the coefficients possess a number of symmetry properties with respect to interchange of quantum numbers. These symmetry properties stand out clearer when one introduces the so-called 3-j symbol, as defined by the relation

$$\begin{pmatrix} J_1 & J_2 & J \\ M_1 & M_2 & M \end{pmatrix} = \frac{(-1)^{J_1-J_2-M}}{\sqrt{2J+1}} \langle J_1 M_1 J_2 M_2 | J_1 J_2 J - M \rangle . \tag{15.43}$$

Much of the literature on vector-coupling coefficients is accordingly a literature on 3-j symbols.

But let us now determine a few Clebsch–Gordan coefficients by the construction method. The values of the Clebsch–Gordan coefficients depend, of course, only on the angular-momentum quantum numbers involved, not on the kind of physical system that the angular momenta might represent. It is accordingly in order to evaluate the coefficients by using the angular momenta with which one is most familiar, and that is the procedure we shall follow.

15.3.1 Coupling of Two Spin $\frac{1}{2}$ Particles

This is the simplest example of angular-momentum coupling, yet a very important one. Let us think of two electrons and use the notation of Sec. 10.2. Thus, we write

$$|\tfrac{1}{2}\tfrac{1}{2}\rangle = \alpha(\varsigma), \quad |\tfrac{1}{2} - \tfrac{1}{2}\rangle = \beta(\varsigma). \tag{15.44}$$

Let us even write $\alpha(1)$ instead of $\alpha(\varsigma_1)$, etc. The basis functions of the uncoupled representation are then

	$\alpha(1)\alpha(2)$	$\alpha(1)\beta(2)$	$\beta(1)\alpha(2)$	$\beta(1)\beta(2)$
$m_{s_1} + m_{s_2}$	1	0	0	-1

(15.45)

where we have also listed the value of $m_{s_1} + m_{s_2}$ for each basis function.

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[2] See, for instance, the bibliography, entries [16], [32] and [33].

Let us denote the two-electron spin functions in the coupled representation by $\Theta_{SM_S}(\varsigma_1, \varsigma_2)$, or just $\Theta_{SM_S}(1,2)$. We have, of course, that $M_S = m_{s_1} + m_{s_2}$. According to the Clebsch–Gordan series (15.37), the total spin quantum number S may take two values, namely $\frac{1}{2} + \frac{1}{2} = 1$ and $\frac{1}{2} - \frac{1}{2} = 0$. The spin functions corresponding to S = 1 are $\Theta_{11}(1,2)$, $\Theta_{10}(1,2)$ and $\Theta_{1-1}(1,2)$. They are said to define a *triplet* state. The spin function corresponding to $S = 0$ is $\Theta_{00}(1,2)$. It defines a *singlet* state.

By the method of the preceding section we get immediately

$$\Theta_{11}(1,2) = \alpha(1)\alpha(2), \tag{15.46}$$

and then, still with $\hbar$ put equal to 1,

$$\begin{aligned} \Theta_{10}(1,2) &= 1/\sqrt{2}\hat{S}_-\Theta_{11}(1,2) = 1/\sqrt{2}(\hat{s}_{2-} + \hat{s}_{1-})\alpha(1)\alpha(2) \\ &= \sqrt{\tfrac{1}{2}}\left\{\alpha(1)\beta(2) + \beta(1)\alpha(2)\right\}. \end{aligned} \tag{15.47}$$

Operating once more with $\hat{S}_-$ gives

$$\begin{aligned} \Theta_{1-1}(1,2) &= 1/\sqrt{2}\hat{S}_-\Theta_{10}(1,2) \\ &= 1/\sqrt{2}(\hat{s}_{2-} + \hat{s}_{1-})\sqrt{\tfrac{1}{2}}\left\{\alpha(1)\beta(2) + \beta(1)\alpha(2)\right\} \\ &= \beta(1)\beta(2). \end{aligned} \tag{15.48}$$

We have now found the three components of the triplet. The singlet spin function may then be determined as that paticular normalized linear combination of $\alpha(1)\beta(2)$ and $\beta(1)\alpha(2)$ which is orthogonal to the triplet function $\Theta_{10}(1,2)$. We get immediately

$$\Theta_{00}(1,2) = \sqrt{\tfrac{1}{2}}\left\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\right\}. \tag{15.49}$$

To summarize, we have found that

The coupling of two spin $\frac{1}{2}$ particles leads to a triplet state with the spin functions

$$\begin{aligned}\Theta_{11}(1,2) &= \alpha(1)\alpha(2),\\ \Theta_{10}(1,2) &= \sqrt{\tfrac{1}{2}}\left\{\alpha(1)\beta(2)+\beta(1)\alpha(2)\right\},\\ \Theta_{1-1}(1,2) &= \beta(1)\beta(2),\end{aligned} \tag{15.50}$$

and a singlet state with the spin function

$$\Theta_{00}(1,2)=\sqrt{\tfrac{1}{2}}\left\{\alpha(1)\beta(2)-\beta(1)\alpha(2)\right\}.$$

We note that we have encountered the singlet spin function before, namely, as the spin part of the wavefunction for the electronic ground state of the helium atom (Eq. (11.42)).

The coefficients in the functions (15.50) are, of course, Clebsch–Gordan coefficients. They are tabulated in matrix form in Table 15.2.

15.3.2 Coupling of Spin and Orbital Angular Momentum

As our second example, let us consider the coupling of an electron's spin, $s=\frac{1}{2}$, with its orbital angular momentum, as described by the quantum number ℓ. The resulting total angular momentum quantum numbers are denoted by j and m. The possible values of j are $\ell+\frac{1}{2}$ and $\ell-\frac{1}{2}$. We designate the basis functions of the coupled representation $\mathcal{Y}^m_{j\ell}$.

Let us first consider the $\ell=1$ case. We represent the orbital functions by the surface spherical harmonics Y_{11}, Y_{10} and Y_{1-1} of Sec. 8.3.6. The basis functions of the uncoupled representation are then

	$Y_{11}\alpha$	$Y_{11}\beta$	$Y_{10}\alpha$	$Y_{10}\beta$	$Y_{1-1}\alpha$	$Y_{1-1}\beta$
$m_\ell+m_s$	$\frac{3}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{3}{2}$

(15.51)

We get immediately that

$$\mathcal{Y}^{\frac{3}{2}}_{\frac{3}{2}1}=Y_{11}\alpha, \tag{15.52}$$

and then,

$$\mathcal{Y}^{\frac{1}{2}}_{\frac{3}{2}1}=1/\sqrt{3}(\hat{s}_-+\hat{\ell}_-)Y_{11}\alpha=\sqrt{\tfrac{1}{3}}(Y_{11}\beta+\sqrt{2}Y_{10}\alpha), \tag{15.53}$$

and

$$\mathcal{Y}_{\frac{1}{2}1}^{\frac{1}{2}} = \sqrt{\tfrac{1}{3}}(\sqrt{2}Y_{11}\beta - Y_{10}\alpha). \tag{15.54}$$

Successive application of $\hat{s}_- + \hat{\ell}_-$ to these functions gives

$$\mathcal{Y}_{\frac{3}{2}1}^{-\frac{1}{2}} = \sqrt{\tfrac{1}{3}}(\sqrt{2}Y_{10}\beta + Y_{1-1}\alpha), \quad \mathcal{Y}_{\frac{3}{2}1}^{-\frac{3}{2}} = Y_{1-1}\beta, \tag{15.55}$$

and

$$\mathcal{Y}_{\frac{1}{2}1}^{-\frac{1}{2}} = \sqrt{\tfrac{1}{3}}(Y_{10}\beta - \sqrt{2}Y_{1-1}\alpha). \tag{15.56}$$

The Clebsch–Gordan coefficients that may be read off the above expressions are again tabulated in Table 15.2.

For a general ℓ-value, we combine the $2\ell + 1$ surface spherical harmonics $Y_{lm_\ell}(\theta, \phi)$ with the α and β spin functions. We get then, after some algebra,

$$\begin{aligned} \mathcal{Y}_{\ell+\frac{1}{2},\ell}^{m} &= \sqrt{\frac{\ell + m + \frac{1}{2}}{2\ell + 1}}Y_{\ell,m-\frac{1}{2}}\alpha + \sqrt{\frac{\ell - m + \frac{1}{2}}{2\ell + 1}}Y_{\ell,m+\frac{1}{2}}\beta, \\ \mathcal{Y}_{\ell-\frac{1}{2},\ell}^{m} &= -\sqrt{\frac{\ell - m + \frac{1}{2}}{2\ell + 1}}Y_{\ell,m-\frac{1}{2}}\alpha + \sqrt{\frac{\ell + m + \frac{1}{2}}{2\ell + 1}}Y_{\ell,m+\frac{1}{2}}\beta. \end{aligned} \tag{15.57}$$

The Clebsch–Gordan coefficients that may be read off these expressions are not reproduced in Table 15.2. The table includes, on the other hand, the coefficients that one obtains by coupling two angular momenta with J_1 and J_2 both equal to 1.

15.4 Angular Momenta in Many-Electron Atoms

Having studied the rules for coupling of two angular momenta, let us now proceed to the study of angular momenta in many-electron atoms. The problem is to determine a complete set of angular momentum operators that commute with the Hamiltonian and with each other, so that we may have common eigenfunctions of these operators and the Hamiltonian, in accordance with the general theorem (5.120). We continue to use atomic units.

15.4.1 The Total Orbital Angular Momentum

With the neglect of relativistic effects, the Hamiltonian for an N-electron atom has the form (11.12), which we reproduce here, for convenience:

$$\begin{aligned} \hat{H} &= \sum_{i=1}^{N} \hat{h}(i) + \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}{}' \frac{1}{r_{ij}}, \\ \hat{h}(i) &= -\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i}. \end{aligned} \tag{15.58}$$

The interpretation of the various terms in the Hamiltonian was given in Sec. 11.1. We shall now show that the total orbital angular momentum

$$\hat{\boldsymbol{L}} = \sum_{i=1}^{N} \hat{\boldsymbol{\ell}}_i, \tag{15.59}$$

already introduced in Eq. (10.8), commutes with $\hat{H}$. But the individual angular momenta, like $\hat{\boldsymbol{\ell}}_1$, do not.

From our discussion of the central field problem in Chapter 8 we know that $\hat{\boldsymbol{\ell}}_1$ commutes with $\hat{h}(1)$. It certainly also commutes with the operators $\hat{h}(2), \ldots, \hat{h}(N)$ which all refer to different particles. Hence, $\hat{\boldsymbol{\ell}}_1$ commutes with the first sum in the Hamiltonian.

With respect to the second part of the Hamiltonian, it is clear that $\hat{\boldsymbol{\ell}}_1$ commutes with those $1/r_{ij}$ terms for which both i and j are different from 1. Thus, we get

$$[\hat{H}, \hat{\boldsymbol{\ell}}_1] = \sum_{j=2}^{N} \left[\frac{1}{r_{1j}}, \hat{\boldsymbol{\ell}}_1\right]. \tag{15.60}$$

Exploiting the commutation relations of Sec. 5.2, and inserting an optional i, it is straightforward to show that this becomes

$$i[\hat{H}, \hat{\boldsymbol{\ell}}_1] = \boldsymbol{r}_1 \times \sum_{j=2}^{N} \boldsymbol{F}_1^{(j)} \tag{15.61}$$

where

$$\boldsymbol{F}_1^{(j)} = \frac{\boldsymbol{r}_1 - \boldsymbol{r}_j}{r_{1j}^3} \tag{15.62}$$

is the force that particle j exerts on particle 1. The right-hand side of Eq. (15.61) is the torque (moment of force) acting on electron 1, and Eq. (15.61) is, in fact, the quantum-mechanical counterpart of the classical relation

$$\frac{d\boldsymbol{\ell}_1}{dt} = \boldsymbol{r}_1 \times \sum_{j=2}^{N} \boldsymbol{F}_1^{(j)}. \tag{15.63}$$

We have now seen that the angular momentum of an individual electron fails to commute with $\widehat{H}$. Consider, however, the commutator

$$i\left[\frac{1}{r_{12}}, \hat{\boldsymbol{\ell}}_1 + \hat{\boldsymbol{\ell}}_2\right] = \boldsymbol{r}_1 \times \boldsymbol{F}_1^{(2)} + \boldsymbol{r}_2 \times \boldsymbol{F}_2^{(1)} = (\boldsymbol{r}_1 - \boldsymbol{r}_2) \times \boldsymbol{F}_1^{(2)}. \tag{15.64}$$

This commutator is zero, because $\boldsymbol{F}_1^{(2)}$ is directed along the axis between electrons 1 and 2. Thus, $\hat{\boldsymbol{\ell}}_1 + \hat{\boldsymbol{\ell}}_2$ commutes with $1/r_{12}$. In a similar way we can show that $\hat{\boldsymbol{\ell}}_1 + \hat{\boldsymbol{\ell}}_3$ commutes with $1/r_{13}$, etc., and we arrive at the anticipated result:

$$[\widehat{H}, \hat{\boldsymbol{L}}] = 0. \tag{15.65}$$

The relation (15.65) implies that we may look for eigenfunctions of $\widehat{H}$ that are also eigenfunctions of $\hat{L}^2$ and, say $\hat{L}_z$. Such eigenfunctions will not only satisfy the atomic Schrödinger equation

$$\widehat{H}\Psi = E\Psi, \tag{15.66}$$

but also the eigenvalue equations

$$\left\{\begin{array}{ll} \hat{L}^2\Psi = L(L+1)\Psi, & L = 0, 1, 2, \ldots \\ \hat{L}_z\Psi = M_L\Psi, & M_L = L, L-1, \ldots, -L. \end{array}\right. \tag{15.67}$$

One often uses the colloquial expression that L and M_L are *good quantum numbers*.

15.4.2 The Total Spin Angular Momentum

We must now recall (Sec. 11.4) that not every solution of Eq. (15.66) gives an acceptable wavefunction. According to the fumdamental symmetry principle (11.37), Nature only allows the antisymmetric solutions to come into play, i.e., solutions for which

$$\hat{P}_{ij}\Psi = -\Psi \tag{15.68}$$

for all (i,j)-pairs. $\hat{P}_{ij}$ is the operator that interchanges electron i and j,

$$\hat{P}_{ij}\Psi(x_1,\ldots,x_i,\ldots,x_j,\ldots,x_N)=\Psi(x_1,\ldots,x_j,\ldots,x_i,\ldots,x_N). \tag{15.69}$$

Any permutation $\hat{P}$ of the N electrons can be written as a product of transpositions (interchanges of two electrons). If p is the number of transpositions required to generate $\hat{P}$, then Eq. (15.68) is seen to imply that

$$\boxed{\hat{P}\Psi=(-1)^p\Psi} \tag{15.70}$$

which is a very convenient formulation of the antisymmetry requirement.

Now, let $\hat{B}(1,2,\ldots,N)$ be an arbitrary operator for our N-electron system. We get then that

$$\hat{P}\hat{B}(1,2,\ldots,N)=\hat{B}(P1,P2,\ldots,PN)\hat{P} \tag{15.71}$$

where $P1,P2,\ldots,PN$ is the permutation defined by $\hat{P}$. Obviously $\hat{B}$ fails to commute with $\hat{P}$ unless it is an operator that is symmetric in all electrons, such that $\hat{B}(P1,P2,\ldots,PN)=\hat{B}(1,2,\ldots,N)$.

The operators $\widehat{H}$, $\hat{L}^2$ and $\hat{L}_z$ are symmetric operators. Thus they commute with every $\hat{P}$, and the eigenvalue equations (15.66) and (15.67) can be satisfied together with the eigenvalue equation (15.70).

Since $\widehat{H}$ does not contain any spin terms, any spin operator commutes with $\widehat{H}$. But it is only symmetric spin operators that commute with every $\hat{P}$. Thus only the total spin

$$\hat{\boldsymbol{S}}=\sum_{i=1}^{N}\hat{\boldsymbol{s}}_i \tag{15.72}$$

is of interest in the search for good quantum numbers. Obviously, $\widehat{H}$ commutes with $\hat{\boldsymbol{S}}$. We may accordingly take Ψ to satisfy the eigenvalue equations

$$\begin{cases}\hat{S}^2\Psi=S(S+1)\Psi, & \\ \hat{S}_z\Psi=M_S\Psi, & M_S=S,S-1,\ldots,-S.\end{cases} \tag{15.73}$$

as a supplement to the eigenvalue equations (15.66) and (15.67). As one sees by repeated reference to the Clebsch–Gordan series (15.37), the possible values of S are $(S=\frac{1}{2},\frac{3}{2},\ldots,\frac{N}{2})$ when N is odd, and $(S=0,1,\ldots,\frac{N}{2})$ when N is even.

15.4.3 L-S Coupling

For given values of L and S, the eigenvalue equations (15.66), (15.67) and (15.73) define a set of $(2L+1)(2S+1)$ wavefunctions which, by arguments similar to those around Eqs. (15.25) and (15.26),are all degenerate. They are said to define an *electronic term.*

Electronic terms are labeled by symbols of the type ${}^{2S+1}L$, where S is the spin quantum number in Eq. (15.73) and L the orbital angular momentum quantum number in Eq. (15.67). L-values are specified by letter symbols equivalent to those used for atomic orbitals, the only difference being that one always uses capital letters for terms. A list of the letter symbols in question was given in Chap. 9 (See the scheme (9.5)). The value of $2S+1$ is referred to as the *multiplicity* of the term.

Thus, a term with $L=2$ and $S=1$ is denoted ${}^3D$, a term with $L=3$ and $S=3/2$ is denoted ${}^4F$, etc

That the $(2L+1)(2S+1)$ wavefunctions describing a given term all have the same energy is an exact statement as long as the Hamiltonian (15.58) is the exact Hamiltonian. But it never is. In the true Hamiltonian, there are additional terms, which are of relativistic origin, as discussed in Sec. 10.4.3 for the one-electron atom. A prominent term is the spin-orbit coupling term,

$$\widehat{H}_{so} = \sum_{i=1}^{N} \xi(r_i)\hat{s}_i \cdot \hat{\ell}_i, \tag{15.74}$$

with $\xi(r)$ as given by Eq. (10.74).

It is readily seen that the spin-orbit coupling term (15.74) fails to commute with the Hamiltonian (15.58), to which it is an amendment. It is also easy to see that neither $\hat{L}$ nor $\hat{S}$ commutes with $\widehat{H}_{so}$. Thus, L and S cease to be good quantum numbers. However, the vector sum

$$\hat{J} = \hat{L} + \hat{S} \tag{15.75}$$

does commute with $\widehat{H}_{so}$. Consequently, J and M will serve as good angular-momentum quantum numbers in the presence of spin-orbit coupling.

As already mentioned in Sec. 10.4.3, spin-orbit coupling effects are found to be quite small for light atoms, whereas they become appreciable for heavier atoms. Let us continue under the assumption that they are small. It is then possible to preserve the quantum numbers L and S, albeit not M_L and M_S, by replacing $\widehat{H}_{so}$ by an *effective operator* of the form

$$\widehat{H}'_{so} = \lambda \hat{S} \cdot \hat{L}, \tag{15.76}$$

where λ is a parameter. This operator commutes with the Hamiltonian (15.58) and with the operators $\hat{L}^2$ and $\hat{S}^2$, but not with the components of $\hat{\boldsymbol{L}}$ and $\hat{\boldsymbol{S}}$. It also commutes with $\hat{J}^2$ and the components of $\hat{\boldsymbol{J}}$.

The effect of the operator $\widehat{H}'_{so}$ is, consequently, to split a given ${}^{2S+1}L$ term into a *multiplet* of *levels* characterized by the J-values $L+S, L+S-1, \ldots, |L-S|$, in accordance with the Clebsch-Gordan series (15.37). The resulting levels are designated ${}^{2S+1}L_J$. The number of levels in the multiplet equals the smaller of the numbers $2S+1$ and $2L+1$.

As an example, a ${}^3D$ term becomes a multiplet characterized by the levels ${}^3D_3$, ${}^3D_2$ and ${}^3D_1$. A ${}^4F$ term splits into the levels ${}^4F_{9/2}$, ${}^4F_{7/2}$, ${}^4F_{5/2}$, and ${}^4F_{3/2}$.

The process of replacing the operator $\widehat{H}_{so}$ by the effective operator $\widehat{H}'_{so}$ requires, of course, a few additional comments. It builds, first, on the assumption that the matrix representing the operator $\widehat{H}_{so}$ along the lines of Sec. 5.10 factorizes, that is, all matrix elements connecting functions belonging to different terms are neglected. We have, then, a situation like the one described in Sec. 12.6, and we may diagonalize the spin-orbit operator separately within each term's $(2L+1)(2S+1)$ dimensional function space. Next, it may be shown that the matrix elements of the operator $\widehat{H}_{so}$ within a given term are proportional to the matrix elements of $\hat{\boldsymbol{S}} \cdot \hat{\boldsymbol{L}}$, with a constant of proportionality that varies from term to term. This is a result of the so-called Wigner–Eckart theorem which one encounters in more advanced presentations of angular-momentum theory.[3] The constant of proportionality is the parameter λ in the effective operator $\widehat{H}'_{so}$. Not only its magnitude, but also its sign, may vary from term to term. Its value may, of course, be calculated if proper wavefunctions are available for a given term. Alternatively, it may be treated as a semiempirical parameter to be determined by comparison with experimental atomic spectra.

The multiplet structure generated by the spin-orbit coupling is referred to as atomic *fine structure*. The way it is accounted for by applying the Clebsch–Gordan series to the L and S quantum numbers of separate terms is known as L-S coupling, or Russell–Saunders coupling. By applying the operator identity

$$J^2 = (\hat{\boldsymbol{L}} + \hat{\boldsymbol{S}})^2 = L^2 + S^2 + 2\hat{\boldsymbol{L}} \cdot \hat{\boldsymbol{S}}, \tag{15.77}$$

we get the following expression for the relative energies of a given multiplet

$$E(J) = \tfrac{1}{2}\lambda[J(J+1) - L(L+1) - S(S+1)]. \tag{15.78}$$

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[3] See, for instance, the bibliography, entry [16].

The energy difference between neighboring levels becomes

$$E(J) - E(J-1) = \lambda J. \tag{15.79}$$

The observation that the separation between two adjacent levels of a multiplet is proportional to the higher J-value is known as the Landé *interval rule*. The multiplet is called *normal* when the energy increases with J (positive λ). When the lowest energy occurs for the highest J-value (negative λ), the multiplet is said to be *inverted*.

In the following chapter we shall establish the connection between the electron configuration of an atom and its term structure. We shall see how to construct the atomic wavefunctions associated with a term, and also discuss how to write down proper expressions for the electronic energy corresponding to these wavefunctions. We close the present chapter with some remarks on the coupling of electronic and nuclear angular momenta.

15.4.4 Adding the Nuclear Angular Momentum. Bose–Einstein Condensates

As emphasized in Sec. 1.7, the atomic nucleus is composed of protons and neutrons. Like the electron, these nucleons are spin $\frac{1}{2}$ particles. The spins of the nucleons add together to form the total nuclear spin, described by the angular-momentum operator $\hat{I}$. The corresponding quantum numbers are I and M_I. Nuclear energy separations are usually much larger than energy separations between the electronic states of an atom, so for our studies we may safely assume that the nucleus is found in its quantum-mechanical ground state. Hence, we may also assume that the quantum number I refers to this state.

It is, of course, the electric charge of the nucleus which, through the Coulomb force, determines the number of electrons that may bind to the nucleus. But other properties of the nucleus have very little influence on the electronic structure of an atom. The finite size of the nucleus, the nuclear electric quadrupole moment and the nuclear angular momenta all play very minor roles in this respect. They are not entirely negligible, though, and they give rise to effects that have analytical significance in, for instance, electron spin resonance experiments on molecular radicals. The detailed form of the interaction terms is quite complicated,[4] and we shall not consider it here. But it is of importance to note that the primary effect of the nuclear angular momentum

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[4] See, for instance, the bibliography entries [8] and [34]

may be represented by a spin-orbit like contribution to the Hamiltonian of the form

$$\hat{H}_{hf} = a\hat{\boldsymbol{I}} \cdot \hat{\boldsymbol{J}}. \tag{15.80}$$

The angular momentum vector

$$\hat{\boldsymbol{F}} = \hat{\boldsymbol{I}} + \hat{\boldsymbol{J}} \tag{15.81}$$

will accordingly commute with the Hamiltonian obtained by including the new interaction, and the quantum number F, with the values

$$F = I + J, I + J - 1, \ldots, |I - J|, \tag{15.82}$$

will be a good quantum number. Thus, a J-level will be split into $2I + 1$ or $2J + 1$ sublevels, with relative energies

$$E(F) = \tfrac{1}{2}a[F(F+1) - I(I+1) - J(J+1)]. \tag{15.83}$$

The parameter a is called the *hyperfine constant*, and the extra structure added to the elctronic levels is referred to as *hyperfine structure*. The value of a is usually much smaller than the spin-orbit parameter λ, typically a few thousandths of a wavenumber (cm^{-1}).

The smallness of a implies that all sublevels will be populated unless the temperature is very small. As in Sec. 2.4, energy differences should be compared with the magnitude of kT. The value of kT corresponding to an energy equivalent of 1 cm^{-1} is

$$T = \frac{hc}{k}(100\,\mathrm{m}^{-1}) = 1.4388\,\mathrm{K}. \tag{15.84}$$

To selectively populate a chosen hyperfine sublevel, one must accordingly work in the milli-Kelvin region or below.

A very important qualitative consequence of the hyperfine coupling should be noted. Let us, for instance, consider the neutral Li atom, with its three bound electrons. As shown in Table 11.2, its electronic ground state is a ${}^2S_{\frac{1}{2}}$ level, so $J = \frac{1}{2}$. The naturally occurring isotopes of Li are ^{6}Li (7.59 %) and ^{7}Li (92.41 %). The former isotope has a nuclear spin of 1, and the latter a nuclear spin of $\frac{3}{2}$. Thus, the hyperfine structure of a ^{6}Li atom is characterized by $(F = \frac{3}{2}, \frac{1}{2})$, whereas the hyperfine structure of a ^{7}Li atom is characterized by $(F = 2, 1)$. But this implies that the ^{6}Li atom is a fermion while the ^{7}Li atom is a boson. The behavior of a cloud of Li atoms at extremely low temperatures is therefore very dependent on the kind of isotope that is involved.

As discussed in Sec. 11.4, a system of fermions must be described by an antisymmetric wavefunction and a system of bosons by a symmetric wavefunction. An antisymmetric wavefunction $\Psi(1, 2, \ldots, N)$ keeps particles out of each other's way because Ψ becomes zero when the general coordinates of two identical particles become the same. There is no such exclusion principle for bosons. In accordance with this, it should be possible to make a cloud of bosons form a so-called Bose–Einstein condensate, in which all atoms of the gas may be said to occupy a single energy level. This possibility has quite recently been realized, by confining the atoms in suitable magnetic fields while cooling them to temperatures in the micro-Kelvin or nano-Kelvin region, primarily by means of laser beams. Bose–Einstein condensates are at the basis of a rapidly developing new branch of physics, but here we must refer the reader to current review articles.[5]

Examples of atoms for which Bose–Einstein condensates have been made are ^{7}Li, ^{23}Na, ^{87}Rb, and ^{1}H. These atoms all have a $^2S_{\frac{1}{2}}$ electronic ground state. The nuclear spin of the first three atoms is $\frac{3}{2}$. The nuclear spin of ^{1}H is $\frac{1}{2}$.

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[5] See, for instance: W. Ketterle, Physics Today **52**, No. 12, (1999), p.30; and K. Burnett, M. Edwards and C. W. Clark, *ibid.* p. 37

Table 15.2: Vector-Coupling Coefficients

$J_1 = J_2 = \frac{1}{2}$

M_1	M_2	$\vert 11\rangle$	$\vert 10\rangle$	$\vert 00\rangle$	$\vert 1-1\rangle$
$\frac{1}{2}$	$\frac{1}{2}$	1			
$\frac{1}{2}$	$-\frac{1}{2}$		$\sqrt{\frac{1}{2}}$	$\sqrt{\frac{1}{2}}$	
$-\frac{1}{2}$	$\frac{1}{2}$		$\sqrt{\frac{1}{2}}$	$-\sqrt{\frac{1}{2}}$	
$-\frac{1}{2}$	$-\frac{1}{2}$				1

$J_1 = 1, J_2 = \frac{1}{2}$

M_1	M_2	$\vert\frac{3}{2}\frac{3}{2}\rangle$	$\vert\frac{3}{2}\frac{1}{2}\rangle$	$\vert\frac{1}{2}\frac{1}{2}\rangle$	$\vert\frac{3}{2}-\frac{1}{2}\rangle$	$\vert\frac{1}{2}-\frac{1}{2}\rangle$	$\vert\frac{3}{2}-\frac{3}{2}\rangle$
1	$\frac{1}{2}$	1					
1	$-\frac{1}{2}$		$\sqrt{\frac{1}{3}}$	$\sqrt{\frac{2}{3}}$			
0	$\frac{1}{2}$		$\sqrt{\frac{2}{3}}$	$-\sqrt{\frac{1}{3}}$			
0	$-\frac{1}{2}$				$\sqrt{\frac{2}{3}}$	$\sqrt{\frac{1}{3}}$	
-1	$\frac{1}{2}$				$\sqrt{\frac{1}{3}}$	$-\sqrt{\frac{2}{3}}$	
-1	$-\frac{1}{2}$						1

$J_1 = 1, J_2 = 1$

M_1	M_2	$\vert 22\rangle$	$\vert 21\rangle$	$\vert 11\rangle$	$\vert 20\rangle$	$\vert 10\rangle$	$\vert 00\rangle$	$\vert 2-1\rangle$	$\vert 1-1\rangle$	$\vert 2-2\rangle$
1	1	1								
1	0		$\sqrt{\frac{1}{2}}$	$\sqrt{\frac{1}{2}}$						
0	1		$\sqrt{\frac{1}{2}}$	$-\sqrt{\frac{1}{2}}$						
1	-1				$\sqrt{\frac{1}{6}}$	$\sqrt{\frac{1}{2}}$	$\sqrt{\frac{1}{3}}$			
0	0				$\sqrt{\frac{2}{3}}$	0	$-\sqrt{\frac{1}{3}}$			
-1	1				$\sqrt{\frac{1}{6}}$	$-\sqrt{\frac{1}{2}}$	$\sqrt{\frac{1}{3}}$			
-1	0							$\sqrt{\frac{1}{2}}$	$-\sqrt{\frac{1}{2}}$	
0	-1							$\sqrt{\frac{1}{2}}$	$\sqrt{\frac{1}{2}}$	
-1	-1									1

Supplementary Reading

The bibliography, entries [15], [16], [32], [33], [34], [8].

Problems

15.1. In the present exercise, we consider the total spin states of a system of three spin $\frac{1}{2}$ particles, that is, we want to construct eigenfunctions of $\hat{S}^2$ and $\hat{S}_z$, where

$$\hat{S} = \hat{s}_1 + \hat{s}_2 + \hat{s}_3$$

is the total spin of the three particles.

a. Write down the eight spin functions of the uncoupled representation, i. e.,

$$\alpha(1)\alpha(2)\alpha(3), \alpha(1)\alpha(2)\beta(3), \ldots$$

Collect the functions in a scheme similar to the scheme (15.45) and show that the possible values of S are $\frac{3}{2}$ and $\frac{1}{2}$. Show that $S = \frac{3}{2}$ only occurs once, whereas $S = \frac{1}{2}$ occurs twice. Distinguish the two $S = \frac{1}{2}$ cases by indices a and b.

b. Starting from the last function in the setup (15.50), together with the spin functions $\alpha(3)$ and $\beta(3)$, write down the spin $S = \frac{1}{2}$ functions $|\frac{1}{2}\frac{1}{2}\rangle_a$ and $|\frac{1}{2} - \frac{1}{2}\rangle_a$.

c. Next, start from the three first functions in the setup (15.50) and add the spin functions $\alpha(3)$ and $\beta(3)$, by exploiting the vector-coupling coefficients of Table 15.2. Write down the form of the resulting functions

$$|\frac{3}{2}\frac{3}{2}\rangle, \quad |\frac{3}{2}\frac{1}{2}\rangle, \quad |\frac{3}{2} - \frac{1}{2}\rangle, \quad |\frac{3}{2} - \frac{3}{2}\rangle$$

and

$$|\frac{1}{2}\frac{1}{2}\rangle_b, \quad |\frac{1}{2} - \frac{1}{2}\rangle_b.$$

d. Show that the two sets of functions

$$|\frac{1}{2}\frac{1}{2}\rangle_a, \quad |\frac{1}{2} - \frac{1}{2}\rangle_a$$

and

$$|\frac{1}{2}\frac{1}{2}\rangle_b, \quad |\frac{1}{2} - \frac{1}{2}\rangle_b$$

are linearly independent, and in fact mutually orthogonal.

d. Which differences would occur in the form of the total spinfunctions if we had first coupled particles 1 and 3 according to the setup (15.50) and then added particle 3 afterwards?

Chapter 16

Atomic Terms. Wavefunctions and Energies

Contents

In this chapter we shall establish the connection between the electron configuration of an atom and its term structure, by combining the conclusions of

Chapters 11 and 15. We do this by directing our attention to specific atoms, in particular the helium atom and the carbon atom.

In the first section, we develop some useful rules concerning the action of operators on Slater determinants. We then discuss the problem of constructing proper term wavefunctions from the set of determinants that are compatible with a given electron configuration.

Next, we develop a set of rules for evaluating matrix elements between Slater determinants, and use these rules to relate the term energies to atomic one- and two-electron integrals. Finally, we discuss how the ground level of an atom may be determined by exploiting the celebrated Hund's rules. We also discuss the theoretical interpretation of Hund's rules.

16.1 Operating on Slater Determinants

As pointed out in Secs. 11.5 and 11.6, a fundamental building block in the construction of many-electron wavefunctions is the Slater determinant. It was introduced by Eqs. (11.39) and (11.40). Its general form is

$$D = |\psi_1\psi_2\ldots\psi_N| = \sqrt{\frac{1}{N!}}\begin{vmatrix} \psi_1(x_1) & \psi_1(x_2) & \ldots & \psi_1(x_N) \\ \psi_2(x_1) & \psi_2(x_2) & \ldots & \psi_2(x_N) \\ \ldots & \ldots & \ldots & \ldots \\ \psi_N(x_1) & \psi_N(x_2) & \ldots & \psi_N(x_N) \end{vmatrix} . \tag{16.1}$$

where $\psi_1, \psi_2, \ldots, \psi_N$ are N linearly independent spin-orbitals. We may assume that they form an orthonormal set, i. e.,

$$\langle\psi_i|\psi_j\rangle = \delta_{ij}. \tag{16.2}$$

The determinant (16.1) is then normalized to unity.

By expanding the determinant we get:

$$D = |\psi_1\psi_2\cdots\psi_N| = \sqrt{\frac{1}{N!}}\sum_P (-1)^p \hat{P}\psi_1(x_1)\psi_2(x_2)\cdots\psi_N(x_N) \tag{16.3}$$

where the sum is over all $N!$ permutations of the N electrons, and where it is understood that

$$\hat{P}\psi_1(x_1)\psi_2(x_2)\cdots\psi_N(x_N) = \psi_1(Px_1)\psi_2(Px_2)\cdots\psi_N(Px_N). \tag{16.4}$$

As in Eq. (15.70), p is the number of transpositions required to generate the permutation defined by $\hat{P}$.

It is expedient to define the so-called *antisymmetrizer*

$$\hat{A} = \sqrt{\frac{1}{N!}} \sum_P (-1)^p \hat{P}. \tag{16.5}$$

We may then write Eq. (16.3) as

$$D = \hat{A}\Phi, \tag{16.6}$$

where

$$\Phi = \psi_1(x_1)\psi_2(x_2)\cdots\psi_N(x_N). \tag{16.7}$$

Φ is often called a *Hartree product*, in honor of the English physicist Douglas Rayner Hartree, who was an early pioneer in the calculation of atomic structure. A Slater determinant may, accordingly, be called an antisymmetrized Hartree product.

Let us now introduce an operator $\hat{B}$ which is symmetric in all N electrons. $\hat{B}$ will then commute with every $\hat{P}$ and hence also with $\hat{A}$,

$$[\hat{B}, \hat{A}] = 0. \tag{16.8}$$

We get therefore

$$\hat{B}|\psi_1\psi_2\ldots\psi_N| = \hat{B}\hat{A}\Phi = \hat{A}\hat{B}\Phi. \tag{16.9}$$

As an important example, let us consider the case where $\hat{B}$ is a symmetric sum of one-electron operators,

$$\hat{B} = \sum_{i=1}^{N} \hat{b}(i). \tag{16.10}$$

$\hat{B}\Phi$ will then be the sum of N new Hartree products. The first of these is obtained from Eq. (16.7) by replacing ψ_1 by $\hat{b}\psi_1$, the second by replacing ψ_2 by $\hat{b}\psi_2$, and so on. Eq. (16.9) becomes therefore

$$\boxed{\begin{aligned}\hat{B}|\psi_1\psi_2\ldots\psi_N| = {}&|(\hat{b}\psi_1)\psi_2\ldots\psi_N| + |\psi_1(\hat{b}\psi_2)\ldots\psi_N|\\ &+\ldots+|\psi_1\psi_2\ldots(\hat{b}\psi_N)|\end{aligned}} \tag{16.11}$$

As an application of this result, consider the case where each ψ_i is an eigenfunction of $\hat{b}$, i. e.,

$$\hat{b}\psi_i = b_i\psi_i. \tag{16.12}$$

Eq. (16.11) shows then that

$$\hat{B}|\psi_1\psi_2\ldots\psi_N| = B|\psi_1\psi_2\ldots\psi_N| \tag{16.13}$$

where

$$B = \sum_{i=1}^{N} b_i. \tag{16.14}$$

The spin-orbitals used in the description of atoms are usually of the form (11.41), viz.,

$$\psi_{n\ell\gamma_\ell m_s}(x) = R_{n\ell}(r)Y_{\ell\gamma_\ell}(\theta,\phi)\left\{\begin{array}{c}\alpha(\varsigma)\\ \beta(\varsigma)\end{array}\right. . \tag{16.15}$$

Let us choose to let γ_ℓ mean m_ℓ. The spin-orbitals are then

$$\psi_{n\ell m_\ell m_s}(x) = R_{n\ell}(r)Y_{\ell m_\ell}(\theta,\phi)\left\{\begin{array}{c}\alpha(\varsigma)\\ \beta(\varsigma)\end{array}\right. . \tag{16.16}$$

These spin-orbitals are eigenfunctions of $\hat{\ell}_z$ and $\hat{s}_z$. Any Slater determinant built from them will accordingly be an eigenfunction of $\hat{L}_z$ and $\hat{S}_z$, with eigenvalues M_L and M_S, which are the sums of the m_ℓ and m_s quantum numbers for the individual spin-orbitals that define the determinant.

In the following we shall draw on these results in our analysis of electronic terms.

16.2 Term Wavefunctions

16.2.1 The Helium Atom

We have discussed the ground state of the helium atom in Secs. 11.5 and 12.4. The electron configuration is $1s^2$, and the only Slater determinant that can be constructed from this configuration is

$$\begin{aligned}\Psi &= |\overset{+}{1}s\,\overset{-}{1}s| = |\overset{+}{\varphi}_{1s}\bar{\varphi}_{1s}| \\ &= \sqrt{\tfrac{1}{2}}\begin{vmatrix}\varphi_{1s}(\boldsymbol{r}_1)\alpha(\varsigma_1) & \varphi_{1s}(\boldsymbol{r}_2)\alpha(\varsigma_2)\\ \varphi_{1s}(\boldsymbol{r}_1)\beta(\varsigma_1) & \varphi_{1s}(\boldsymbol{r}_2)\beta(\varsigma_1)\end{vmatrix} .\end{aligned} \tag{16.17}$$

As indicated, we shall freely write $1s$ etc. for atomic orbitals instead of φ_{1s} etc., a practise we already introduced by Eq. (13.38). Often, we shall also write, for instance, $1s(2)$ instead of $1s(\boldsymbol{r}_2)$, in analogy with a similar practice introduced for spin functions in Sec. 15.3.1. Finally, we shall freely avoid writing (x_i) or $(\boldsymbol{r}_i, \varsigma_i)$ and just write (i) instead.

In Sec. 11.5, Eq. (11.42), we took the $1s$ orbital to be a hydrogen-like orbital with $Z = 2$. In Sec. 12.4, Eq. (12.24), we took it to be a similar orbital, a so-called Slater orbital, where Z was replaced by the orbital exponent $\zeta = 27/16$. The best $1s$ orbital (the Hartree-Fock orbital) is more complicated than this, but is still spherically symmetrical. We may assume that the $1s$ orbital in Eq. (16.17) is the best possible orbital we can get.

By applying the results of the previous section we see immediately that $|\overset{+}{1}s\overset{-}{1}s|$ is an eigenfunction of $\hat{L}_z$ and $\hat{S}_z$, in both cases with the eigenvalue 0. In other words, both M_L and M_S are 0. The wavefunction describes a ^1S term:

> The ground configuration of the helium atom is $1s^2$.
> It gives rise to a ^1S term, with $\Psi = |\overset{+}{1}s\overset{-}{1}s|$. (16.18)

The same conclusion may easily be arrived at by expanding the determinant (16.17), in the same way as in Eq. (11.42):

$$\Psi = \varphi_{1s}(\boldsymbol{r}_1)\varphi_{1s}(\boldsymbol{r}_2)\sqrt{\tfrac{1}{2}}\left\{\alpha(\varsigma_1)\beta(\varsigma_2) - \beta(\varsigma_1)\alpha(\varsigma_2)\right\}. \tag{16.19}$$

Here, Ψ appears as the product of a two-electron spatial function with L and M_L equal to zero, and a two-electron spin function. The spin function is identical with the singlet spin function $\Theta_{00}(1,2)$ of Eq. (15.50).

By L-S coupling, the quantum numbers $L = 0$ and $S = 0$ give $J = 0$. The complete designation for the ground state of the helium atom is therefore $^1S_0$, in accordance with Table 11.2.

By exciting an electron from the $1s$ shell to the $2s$ shell we arrive at the electron configuration $1s^1 2s^1$.[1] It gives rise to four determinants, all with $M_L = 0$, and with M_S-values as indicated in the following scheme

	$\vert\overset{+}{1}s\,\overset{+}{2}s\vert$	$\vert\overset{+}{1}s\,\overset{-}{2}s\vert$	$\vert\overset{-}{1}s\,\overset{+}{2}s\vert$	$\vert\overset{-}{1}s\,\overset{-}{2}s\vert$
M_S	1	0	0	-1

(16.20)

---

[1] As in Problem 11.2, the orbitals should be optimized for the electron configuration in question. In Problem 11.2, the $2s$ orbital was chosen as a simple Slater orbital which overlapped with the $1s$ orbital. Here, we assume that the two orbitals are the best possible ones, and that they are mutually orthogonal.

This scheme is similar to the scheme (15.45), and we conclude that the configuration gives rise to a triplet state ($S = 1$) and a singlet state ($S = 0$). And since L must be zero, both of these states must be S states. Thus we get

$$\boxed{\text{The configuration } 1s^1 2s^1 \text{ gives rise to a } {}^3S \text{ term and a } {}^1S \text{ term.}} \tag{16.21}$$

The associated wavefunctions may be found by the standard methods of angular momentum theory. The operator $\hat{S}_- = \hat{s}_{1-} + \hat{s}_{2-}$ is of the type (16.10), and its application to a Slater determinant follows the rule (16.11). Thus we get, in a self-explanatory notation

$$\begin{cases} {}^3\Psi(M_S = 1) = |\overset{+}{1s}\,\overset{+}{2s}|, \\ {}^3\Psi(M_S = 0) = \sqrt{\tfrac{1}{2}}\hat{S}_-|\overset{+}{1s}\,\overset{+}{2s}| = \sqrt{\tfrac{1}{2}}\left\{|\overset{+}{1s}\,\overset{-}{2s}| + |\overset{-}{1s}\,\overset{+}{2s}|\right\}, \\ {}^3\Psi(M_S = -1) = |\overset{-}{1s}\,\overset{-}{2s}|, \end{cases} \tag{16.22}$$

and

$${}^1\Psi = \sqrt{\tfrac{1}{2}}\left\{|\overset{+}{1s}\,\overset{-}{2s}| - |\overset{-}{1s}\,\overset{+}{2s}|\right\}. \tag{16.23}$$

The wavefunction ${}^1\Psi$ has been obtained by requiring that it be orthogonal to the wavefunction ${}^3\Psi(M_S = 0)$. In so doing, we have used that the Slater determinants formed from an orthonormal set of spin-orbitals form themselves an orthonormal set. This result will be proved in Sec. 16.3, as the lemma (16.40).

By expanding the above determinants we also get

$$\begin{cases} {}^3\Psi(M_S = 1) = \sqrt{\tfrac{1}{2}}\,\{1s(1)2s(2) - 2s(1)1s(2)\}\,\alpha(1)\alpha(2), \\ {}^3\Psi(M_S = 0) = \tfrac{1}{2}\,\{1s(1)2s(2) - 2s(1)1s(2)\}\,\{\alpha(1)\beta(2) + \beta(1)\alpha(2)\}, \\ {}^3\Psi(M_S = -1) = \sqrt{\tfrac{1}{2}}\,\{1s(1)2s(2) - 2s(1)1s(2)\}\,\beta(1)\beta(2), \end{cases} \tag{16.24}$$

and

$${}^1\Psi = \tfrac{1}{2}\,\{1s(1)2s(2) + 2s(1)1s(2)\}\,\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}. \tag{16.25}$$

Thus, each wavefunction factors into the product of a two-electron spatial function and a two-electron spin function in a similar way as the ground-state wavefunction does (See Eq. (16.19)). A symmetric spatial function goes with an antisymmetric spin function and vice versa. The spin functions are recognized to be the same as the two-electron spin functions in the setup (15.50), as they must be.

Having determined the wavefunctions of the two terms that originate from the $1s^1 2s^1$ configuration we must also worry about the term energies. We shall, however, postpone the problem of evaluating these energies. It is found that the triplet state lies below the singlet state.

Other excited configurations of the helium atom may be analyzed in a similar way as the $1s^1 2s^1$ configuration. The states of the helium atom fall in two groups, singlets and triplets. Experimentally, one observes spectral transitions within the group of singlet states and spectral transitions within the group of triplet states, but only extremely weak transitions (intercombinations) between the two groups of states. It looks in fact as if two different kinds of atoms were involved. For this reason one often refers to the singlet states as *parahelium* and to the triplet states as *orthohelium*.

16.2.2 The Carbon Atom

In this section we shall consider the terms that arise from the ground configuration $1s^2 2s^2 2p^2$ of the carbon atom. The three $2p$ orbitals give rise to six spin-orbitals, and the number of Slater determinants that we may construct is $\binom{6}{2} = 15$. They are listed below together with their M_L- and M_S-values. For simplicity, we write $|\overset{+}{1}\ \overset{+}{0}\,|$ instead of $|\overset{+}{1s}\,\overset{-}{1s}\,\overset{+}{2s}\,\overset{-}{2s}\,\overset{+}{2p_1}\,\overset{-}{2p_0}|$, etc. This is motivated by the observation that closed shells donot contribute to the total values of M_L and M_S (the shell sums over m_s and m_ℓ are both zero).

$M_L \backslash M_S$	1	0	-1
2		$\lvert\overset{+}{1}\ \overset{-}{1}\rvert$	
1	$\lvert\overset{+}{1}\ \overset{+}{0}\rvert$	$\lvert\overset{+}{1}\ \overset{-}{0}\rvert \quad \lvert\overset{-}{1}\ \overset{+}{0}\rvert$	$\lvert\overset{-}{1}\ \overset{-}{0}\rvert$
0	$\lvert\overset{+}{1}\ \overset{+}{-1}\rvert$	$\lvert\overset{+}{1}\ \overset{-}{-1}\rvert \quad \lvert\overset{+}{0}\ \overset{-}{0}\rvert \quad \lvert\overset{-}{1}\ \overset{+}{-1}\rvert$	$\lvert\overset{-}{1}\ \overset{-}{-1}\rvert$
-1	$\lvert\overset{+}{0}\ \overset{+}{-1}\rvert$	$\lvert\overset{-}{0}\ \overset{+}{-1}\rvert \quad \lvert\overset{+}{0}\ \overset{-}{-1}\rvert$	$\lvert\overset{-}{0}\ \overset{-}{-1}\rvert$
-2		$\lvert\overset{+}{-1}\ \overset{-}{-1}\rvert$	

(16.26)

From the structure of this table we deduce that

The configuration $1s^2 2s^2 2p^2$ gives rise to three terms: ${}^3P$, ${}^1D$ and ${}^1S$. (16.27)

The proper linear combinations of determinants which describe the wavefunctions of the three terms are shown in Table 16.1. They are readily constructed by means of the $\hat{L}_-$ and $\hat{S}_-$ operators. Thus, we can construct all functions belonging to the ${}^1D$ term from $|\overset{+}{1}\,\overset{-}{1}|$ by means of $\hat{L}_-$, and all functions belonging to the ${}^3P$ term may be constructed from $|\overset{+}{1}\,\overset{+}{0}|$ by means of $\hat{L}_-$ and $\hat{S}_-$. Finally, the wavefunction for the ${}^1S$ term may be constructed as a linear combination of the three determinants with $M_L = M_S = 0$, and such that it is orthogonal to the corresponding components of the ${}^1D$ and ${}^3P$ terms.

The order of the term energies are found to be

$$E({}^3P) < E({}^1D) < E({}^1S). \tag{16.28}$$

Our next task is to find theoretical expressions for such term energies. To do so requires a set of rules for evaluating matrix elements between Slater determinants. We insert, therefore, a section on this problem.

We continue to use the notation developed between Eqs. (10.21) and (10.25) of Sec. 10.2.

16.3 Matrix Elements Between Slater Determinants

Consider a set of spin-orbitals

$$\psi_1, \psi_2, \ldots, \psi_i, \ldots \tag{16.29}$$

which is assumed to be orthonormal,

$$\langle \psi_i | \psi_j \rangle = \int \psi_i^*(x_1)\psi_j(x_1)dx_1 = \delta_{ij}. \tag{16.30}$$

We shall derive rules for evaluating the matrix element

$$\langle \Psi | \hat{F} | \Psi' \rangle = \int |\psi_1\psi_2 \ldots \psi_N|^* \hat{F} |\psi_1'\psi_2' \ldots \psi_N'| dx \tag{16.31}$$

Table 16.1: Terms and wavefunctions for the p^2 configuration

	M_L	M_S	Ψ
^3P	1	1	$\lvert\overset{+}{1}\,\overset{+}{0}\rvert$
	0	1	$\lvert\overset{+}{1}\;\overset{+}{-1}\rvert$
	-1	1	$\lvert\overset{+}{0}\;\overset{+}{-1}\rvert$
	1	0	$\sqrt{\frac{1}{2}}\left(\lvert\overset{-}{1}\,\overset{+}{0}\rvert+\lvert\overset{+}{1}\,\overset{-}{0}\rvert\right)$
	0	0	$\sqrt{\frac{1}{2}}\left(\lvert\overset{-}{1}\;\overset{+}{-1}\rvert+\lvert\overset{+}{1}\;\overset{-}{-1}\rvert\right)$
	-1	0	$\sqrt{\frac{1}{2}}\left(\lvert\overset{-}{0}\;\overset{+}{-1}\rvert+\lvert\overset{+}{0}\;\overset{-}{-1}\rvert\right)$
	1	-1	$\lvert\overset{-}{1}\,\overset{-}{0}\rvert$
	0	-1	$\lvert\overset{-}{1}\;\overset{-}{-1}\rvert$
	-1	-1	$\lvert\overset{-}{0}\;\overset{-}{-1}\rvert$
^1D	2	0	$\lvert\overset{+}{1}\,\overset{-}{1}\rvert$
	1	0	$\sqrt{\frac{1}{2}}\left(\lvert\overset{+}{1}\,\overset{-}{0}\rvert-\lvert\overset{-}{1}\,\overset{+}{0}\rvert\right)$
	0	0	$\sqrt{\frac{1}{6}}\left(\lvert\overset{+}{1}\;\overset{-}{-1}\rvert+2\lvert\overset{+}{0}\,\overset{-}{0}\rvert-\lvert\overset{-}{1}\;\overset{+}{-1}\rvert\right)$
	-1	0	$\sqrt{\frac{1}{2}}\left(\lvert\overset{+}{0}\;\overset{-}{-1}\rvert-\lvert\overset{-}{0}\;\overset{+}{-1}\rvert\right)$
	-2	0	$\lvert\overset{+}{-1}\;\overset{-}{-1}\rvert$
^1S	0	0	$\sqrt{\frac{1}{3}}\left(\lvert\overset{+}{1}\;\overset{-}{-1}\rvert-\lvert\overset{+}{0}\,\overset{-}{0}\rvert-\lvert\overset{-}{1}\;\overset{+}{-1}\rvert\right)$

where Ψ and Ψ' are Slater determinants constructed from the set (16.29), and $\hat{F}$ is an operator which is symmetric in the N particles, for instance the Hamiltonian set up by Eq. (11.12), and repeated as Eq. (15.58).

When we expand the determinant to the left in (16.31) by using the expressions (16.3) and (16.4), we get a sum of $N!$ terms. The diagonal of the determinant gives the contribution

$$\frac{1}{N!}\int \psi_1^*(x_1)\psi_2^*(x_2)\cdots\psi_N^*(x_N)\hat{F}\begin{vmatrix}\psi_1'(x_1) & \dots & \psi_1'(x_N)\\ \dots & \dots & \dots\\ \psi_N'(x_1) & \dots & \psi_N'(x_N)\end{vmatrix} dx \tag{16.32}$$

where

$$dx = dx_1 dx_2 \cdots dx_N. \tag{16.33}$$

A general term in the sum is

$$(-1)^p\frac{1}{N!}\int \psi_1^*(Px_1)\psi_2^*(Px_2)\cdots\psi_N^*(Px_N)\hat{F}\begin{vmatrix}\psi_1'(x_1) & \dots & \psi_1'(x_N)\\ \dots & \dots & \dots\\ \psi_N'(x_1) & \dots & \psi_N'(x_N)\end{vmatrix} dx. \tag{16.34}$$

By permuting columns in the determinant to the right of $\hat{F}$, we get

$$\begin{vmatrix}\psi_1'(x_1) & \dots & \psi_1'(x_N)\\ \dots & \dots & \dots\\ \psi_N'(x_1) & \dots & \psi_N'(x_N)\end{vmatrix} = (-1)^p\begin{vmatrix}\psi_1'(Px_1) & \dots & \psi_1'(Px_N)\\ \dots & \dots & \dots\\ \psi_N'(Px_1) & \dots & \psi_N'(Px_N)\end{vmatrix}. \tag{16.35}$$

When we substitute this result in (16.34), the factor $(-1)^p$ cancels. Furthermore, $x_1, x_2, \dots, x_N$ are dummy variables over which we integrate. We may therefore interchange the meaning of x_1 and Px_1, of x_2 and Px_2, etc. When we do this, and use that $\hat{F}$ is symmetric, the integral (16.34) is transformed into the integral (16.32). Hence, by adding $N!$ identical terms, we obtain the general result

$$\langle\Psi|\hat{F}|\Psi'\rangle = \int \psi_1^*(x_1)\psi_2^*(x_2)\cdots\psi_N^*(x_N)\hat{F}\begin{vmatrix}\psi_1'(x_1) & \dots & \psi_1'(x_N)\\ \dots & \dots & \dots\\ \psi_N'(x_1) & \dots & \psi_N'(x_N)\end{vmatrix} dx. \tag{16.36}$$

While Eq. (16.31) involves a double summation over $N!$ terms, Eq. (16.36) only involves a single summation.

We shall now evaluate the integral in Eq. (16.36) for different choices of the operator $\hat{F}$. First, we treat

Case 1.
$\hat{F} = F_0$, independent of electron coordinates.
$\langle\Psi|\hat{F}|\Psi'\rangle = F_0$ if the sets $\psi_1, \psi_2, \ldots, \psi_N$ and $\psi'_1, \psi'_2, \ldots, \psi'_N$ are identical. Otherwise, the integral vanishes. (16.37)

This, and also the following results, are most easily obtained when we permute function indices instead of function arguments in evaluating the determinant in (16.36). The result is the same, for the function indices are the row indices of the determinant, while the function arguments serve as column indices; and a determinant and its transpose are known to have the same value. We get

$$\begin{vmatrix} \psi'_1(x_1) & \ldots & \psi'_1(x_N) \\ \ldots & \ldots & \ldots \\ \psi'_N(x_1) & \ldots & \psi'_N(x_N) \end{vmatrix} = \sum_P (-1)^p \psi'_{P1}(x_1)\psi'_{P2}(x_2)\cdots\psi'_{PN}(x_N), \quad (16.38)$$

and thus

$$\langle\Psi|F_0|\Psi'\rangle =$$
$$F_0 \sum_P (-1)^p \int \psi_1^*(x_1)\psi_2^*(x_2)\cdots\psi_N^*(x_N)\psi'_{P1}(x_1)\psi'_{P2}(x_2)\cdots\psi'_{PN}(x_N)dx$$
$$= F_0 \sum_P (-1)^p \langle\psi_1|\psi'_{P1}\rangle\langle\psi_2|\psi'_{P2}\rangle\cdots\langle\psi_N|\psi'_{PN}\rangle. \quad (16.39)$$

Because of the orthonormality condition (16.30) we get zero unless $\psi'_{Pi} = \psi_i$ for all i, that is, the two determinants must be identical. When this is the case, only the identity permutation contributes. We have thus proved the lemma (16.37).

By setting $F_0 = 1$, we obtain the result that the Slater determinant (16.1) is normalized to unity, a result we already derived in Sec. 11.5. More specifically, we have shown that

The Slater determinants formed from the set (16.29) form themselves an orthonormal set. (16.40)

Next, we shall treat the case where $\hat{F}$ is a sum of one-electron operators. Examples are the first term in the Hamiltonian (15.58) and the spin-orbit operator (15.74).The usual angular-momentum operators $\hat{\boldsymbol{L}}$, $\hat{\boldsymbol{S}}$ and $\hat{\boldsymbol{J}}$ are also of this type—but $\hat{L}^2$, $\hat{S}^2$ and $\hat{J}^2$ are not. We get

Case 2.

$\hat{F} = \sum_{i=1}^{N} \hat{f}(x_i)$, a sum of one-electron operators.

a. $\langle \Psi | \hat{F} | \Psi' \rangle = 0$ if Ψ and Ψ' differ in more than one spin-orbital.

b. $\langle \Psi | \hat{F} | \Psi' \rangle = \langle \psi_k | \hat{f} | \psi'_k \rangle$ if Ψ' may be obtained from Ψ by replacing ψ_k with ψ'_k, all other orbitals the same.

c. $\langle \Psi | \hat{F} | \Psi \rangle = \sum_{i=1}^{N} \langle \psi_i | \hat{f} | \psi_i \rangle$.

(16.41)

From Eqs. (16.36) and (16.38) we see that the contribution of $\hat{f}(x_1)$ to the matrix element $\langle \Psi | \hat{F} | \Psi' \rangle$ is

$$\sum_{P} (-1)^p \langle \psi_1 | \hat{f} | \psi'_{P1} \rangle \langle \psi_2 | \psi'_{P2} \rangle \cdots \langle \psi_N | \psi'_{PN} \rangle . \tag{16.42}$$

Due to orthogonality, this contribution is zero unless

$$\psi'_{P2} = \psi_2, \ldots, \psi'_{PN} = \psi_N, \tag{16.43}$$

which implies that at least $N-1$ spin-orbitals are identical. A similar conclusion may be drawn when the operators $\hat{f}(x_2), \hat{f}(x_3), \ldots, \hat{f}(x_N)$ are considered. We have thus proved the first part of (16.41).

Let us then consider the case where

$$\begin{aligned} \Psi &= |\psi_1 \psi_2 \ldots \psi_{k-1} \psi_k \psi_{k+1} \ldots \psi_N|, \\ \Psi' &= |\psi_1 \psi_2 \ldots \psi_{k-1} \psi'_k \psi_{k+1} \ldots \psi_N|. \end{aligned} \tag{16.44}$$

Because a determinant changes sign when two of the defining functions are interchanged, the order of the orbitals is of importance here. We follow the convention of placing ψ_k and ψ'_k in identical positions. If this order is not present from the outset it is easily achieved by row transpositions in the determinant. However, each transposition implies a change of sign, so a factor of -1 may have to be multiplied onto the result.

When the k in Eq. (16.44) is different from 1, it is obvious that (16.43) cannot be fulfilled for any permutation, and the sum (16.42) must vanish. Only $\hat{f}(x_k)$ can contribute to the integral (16.36). The contribution is

$$\sum_P (-1)^p \langle \psi_1 | \psi'_{P1} \rangle \cdots \langle \psi_k | \hat{f} | \psi'_{Pk} \rangle \cdots \langle \psi_N | \psi'_{PN} \rangle . \tag{16.45}$$

Due to orthogonality, only the identity permutation can contribute. It gives the contribution $\langle \psi_k | \hat{f} | \psi'_k \rangle$ which, then, is the value of $\langle \Psi | \hat{F} | \Psi' \rangle$, as stated in (16.41).

When we finally consider the diagonal element $\langle \Psi | \hat{F} | \Psi \rangle$, the expression (16.42) gives the contribution $\langle \psi_1 | \hat{f} | \psi_1 \rangle$, since the condition (16.43) is fulfilled for the identity permutation. Similarly, the contribution of $\hat{f}(x_2)$ to the matrix element $\langle \Psi | \hat{F} | \Psi' \rangle$ is $\langle \psi_2 | \hat{f} | \psi_2 \rangle$, etc. This proves the last part of the lemma (16.41).

The last case to be studied is

Case 3.

$\hat{F} = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N}{}' \hat{g}(x_i, x_j) = \sum_{i<j} \hat{g}(x_i, x_j)$, a sum of two-electron operators.

a. $\langle \Psi | \hat{F} | \Psi' \rangle = 0$, if Ψ and Ψ' differ in more than two spin-orbitals.

b. $\langle \Psi | \hat{F} | \Psi' \rangle = \langle \psi_k \psi_l | \hat{g} | \psi'_k \psi'_l \rangle - \langle \psi_k \psi_l | \hat{g} | \psi'_l \psi'_k \rangle$, if Ψ and Ψ' differ in just two spin-orbitals such that ψ'_k and ψ'_l have replacced ψ_k and ψ_l, respectively.

c. $\langle \Psi | \hat{F} | \Psi' \rangle = \sum_{l \neq k} \{ \langle \psi_k \psi_l | \hat{g} | \psi'_k \psi_l \rangle - \langle \psi_k \psi_l | \hat{g} | \psi_l \psi'_k \rangle \}$, if Ψ and Ψ' differ in just one spin-orbital such that ψ'_k has replaced ψ_k.

d. $\langle \Psi | \hat{F} | \Psi \rangle = \frac{1}{2} \sum_{k=1}^{N} \sum_{l=1}^{N}{}' \{ \langle \psi_k \psi_l | \hat{g} | \psi_k \psi_l \rangle - \langle \psi_k \psi_l | \hat{g} | \psi_l \psi_k \rangle \}$.

Per definition:
$\langle \psi_k \psi_l | \hat{g} | \psi_s \psi_t \rangle = \int \int \psi_k^*(x_1) \psi_l^*(x_2) \hat{g}(x_1, x_2) \psi_s(x_1) \psi_t(x_2) dx_1 dx_2$.

(16.46)

When applying (16.46), it is again important to note that a standard order, similar to that in (16.44), has been presupposed.

To derive the results in (16.46), we proceed in a similar manner as when the results in (16.41) were derived. The operator $\hat{g}(x_1, x_2)$ gived the following contribution to the matrix element $\langle\Psi|\hat{F}|\Psi'\rangle$,

$$\sum_P (-1)^p \langle\psi_1\psi_2|\hat{g}|\psi'_{P1}\psi'_{P2}\rangle\langle\psi_3|\psi'_{P3}\rangle\cdots\langle\psi_N|\psi'_{PN}\rangle. \tag{16.47}$$

Due to orthogonality, the contribution is zero unless

$$\psi'_{P3} = \psi_3, \dots, \psi'_{PN} = \psi_N, \tag{16.48}$$

which implies that at least $N-2$ spin-orbitals are identical. Hence, the first result in (16.46) follows. It is a straightforward exercise to go through the derivation of the remaining results, and we shall skip it here.

An example of an operator of the type $\hat{F}$ in (16.46) is the electron-electron repulsion term in the Hamiltonian (15.58).

This completes our derivation of rules for evaluating matrix elements between Slater determinants. We stress that the rules we have derived only hold when the spin-orbitals (16.29) defining the determinants are mutually orthogonal. Rules have, however, also been derived for determinants built of non-orthogonal orbitals, but we shall not consider them here.[2]

16.4 Energies of Atomic Terms

We shall now derive expressions for the energies of a few atomic terms, under the assumption that the Hamiltonian is given by the expression (15.58), and that the term wavefunctions may be represented by means of Slater determinants in the way described in the previous section. We assume that all spin-orbitals are of the form (10.21), so that the i^{th} spin-orbital may be written as either $\varphi_i(\boldsymbol{r})\alpha(\varsigma)$ or $\varphi_i(\boldsymbol{r})\beta(\varsigma)$. Thus, the spatial orbital going with the i^{th} spin-orbital is also given the index i.

We use the following nomenclature for one-and two-electron integrals:

$$h'_i = \langle\psi_i|\hat{h}|\psi_i\rangle, \quad h_i = \langle\varphi_i|\hat{h}|\varphi_i\rangle, \tag{16.49}$$

$$J'_{ij} = \langle\psi_i\psi_j|\tfrac{1}{r_{12}}|\psi_i\psi_j\rangle, \quad J_{ij} = \langle\varphi_i\varphi_j|\tfrac{1}{r_{12}}|\varphi_i\varphi_j\rangle, \tag{16.50}$$

$$K'_{ij} = \langle\psi_i\psi_j|\tfrac{1}{r_{12}}|\psi_j\psi_i\rangle, \quad K_{ij} = \langle\varphi_i\varphi_j|\tfrac{1}{r_{12}}|\varphi_j\varphi_i\rangle. \tag{16.51}$$

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[2] See, for instance, the bibliography, entrance [34].

We see that

$$h'_i = h_i, \quad J'_{ij} = J_{ij}, \quad K'_{ij} = K_{ij}\delta(m_{si}, m_{sj}), \tag{16.52}$$

where the quantum number m_{si} as usual is understood to be $\frac{1}{2}$ when the spin function associated with φ_i is $\alpha(\varsigma)$, and $-\frac{1}{2}$ when the spin function is $\beta(\varsigma)$. J'_{ij} and J_{ij} are called *Coulomb integrals*, while K'_{ij} and K_{ij} are called *exchange integrals*. Due to the orthogonality between the α and the β spin functions, the exchange integral K'_{ij}vanishes unless φ_i and φ_j have the same spin function associated with them, in which case it becomes K_{ij}.

The notation for general two-electron integrals is

$$\langle\psi_i\psi_j|\tfrac{1}{r_{12}}|\psi_k\psi_l\rangle = \int\int \psi_i^*(x_1)\psi_j^*(x_2)\tfrac{1}{r_{12}}\psi_k(x_1)\psi_l(x_2)dx_1dx_2, \tag{16.53}$$

in accordance with the last line of (16.46), and

$$\langle\varphi_i\varphi_j|\tfrac{1}{r_{12}}|\varphi_k\varphi_l\rangle = \int\int \varphi_i^*(r_1)\varphi_j^*(r_2)\tfrac{1}{r_{12}}\varphi_k(r_1)\varphi_l(r_2)dv_1dv_2. \tag{16.54}$$

Because, for instance, x_i and x_j are dummy indices over which we integrate, we have symmetry relations like

$$\langle\psi_i\psi_j|\tfrac{1}{r_{12}}|\psi_k\psi_l\rangle = \langle\psi_j\psi_i|\tfrac{1}{r_{12}}|\psi_l\psi_k\rangle = \langle\psi_k\psi_l|\tfrac{1}{r_{12}}|\psi_i\psi_j\rangle^* = \langle\psi_l\psi_k\tfrac{1}{r_{12}}|\psi_j\psi_i\rangle^*, \tag{16.55}$$

with similar relations for the integrals defined by (16.53). We see, in particular, that

$$J'_{ij} = J'_{ji}, \quad K'_{ij} = K'_{ji}, \quad J'_{ii} = K'_{ii}, \tag{16.56}$$

with similar relations between the unprimed integrals.

With the above definitions, it is a straightforward matter to derive expressions for atomic term energies, by applying the rules of the previous section for evaluating matrix elements between Slater determinants. First, we look for a general expression for $\langle D|\widehat{H}|D\rangle$ where D is a single Slater determinant of the form (16.1). We get immediately

$$\langle D|\widehat{H}|D\rangle = \sum_{i=1}^{N} h'_i + \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}{}' \left(J'_{ij} - K'_{ij}\right), \tag{16.57}$$

or, by using that $J'_{ii} = K'_{ii}$,

$$\langle D|\widehat{H}|D\rangle = \sum_{i=1}^{N} h'_i + \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N} \left(J'_{ij} - K'_{ij}\right). \tag{16.58}$$

The various terms in the sums may be interpreted as follows: $h'_i = h_i$ gives the kinetic energy of an electron in the orbital φ_i plus the electrostatic attraction energy between the charge ditribution $-\varphi_i^*\varphi_i$ and the atomic nucleus. $J'_{ij} = J_{ij}$ is the classical expression for the electrostatic repulsion energy between an electron with the charge distribution $\varphi_i^*\varphi_i$ and an electron with the charge distribution $\varphi_j^*\varphi_j$. The exchange integral K'_{ij} reduces this repulsion energy for two electrons with parallel spin.

It is interesting to note that the simple Hartree product (16.7) leads to the same energy expression as the determinant (16.1), apart from the contribution from the exchange integrals,

$$\langle D|\widehat{H}|D\rangle = \langle\Phi|\widehat{H}|\Phi\rangle - \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}{}' K'_{ij}. \tag{16.59}$$

Thus, we may say that the exchange terms originate as a result of the antisymmetrization (16.6).

By using the expression (16.57) and also the expressions for matrix elements of $\widehat{H}$ between different determinants, we arrive at the following results for a few selected atoms.

16.4.1 The Helium Atom

The energy of the ground state, as described by the wavefunction (16.17), is

$$E_0 = \langle\Psi|\widehat{H}|\Psi\rangle = 2h_{1s} + J_{1s,1s}. \tag{16.60}$$

We recognize the expression (12.30) of Sec. 12.4.

The excited configuration $1s^2 2s^2$ gives rise to a ^3S and a ^1S term. The wavefunctions associated with these terms were given in Eqs. (16.22) and (16.23). Using the $M_S = 1$ component of the ^3S term gives immediately

$$E(^3S) = h_{1s} + h_{2s} + J_{1s,2s} - K_{1s,2s}. \tag{16.61}$$

For the ^1S term we find

$$\begin{aligned}
E(^1S) &= \frac{1}{2}\Big\{ \int |\overset{+}{1}s\overset{-}{2}s|\widehat{H}|\overset{+}{1}s\overset{-}{2}s|dx + \int |\overset{-}{1}s\overset{+}{2}s|\widehat{H}|\overset{-}{1}s\overset{+}{2}s|dx \\
&\qquad - 2\int |\overset{+}{1}s\overset{-}{2}s|\widehat{H}|\overset{-}{1}s\overset{+}{2}s|dx\Big\} \\
&= \frac{1}{2}\Big\{ h_{1s} + h_{2s} + J_{1s,2s} + h_{1s} + h_{2s} + J_{1s,2s} \\
&\qquad - 2\left(\langle\overset{+}{1}s\overset{-}{2}s|\tfrac{1}{r_{12}}|\overset{-}{1}s\overset{+}{2}s\rangle - \langle\overset{+}{1}s\overset{-}{2}s|\tfrac{1}{r_{12}}|\overset{+}{2}s\overset{-}{1}s\rangle\right)\Big\} \\
&= h_{1s} + h_{2s} + J_{1s,2s} + K_{1s,2s}.
\end{aligned} \tag{16.62}$$

Thus, we get

$$\boxed{E(^1S) - E(^3S) = 2K_{1s,2s}} \tag{16.63}$$

It can be shown that an exchange integral is always non-negative. The triplet term is accordingly predicted to have a lower energy than the singlet term. This prediction is borne out by experiment. The experimental singlet-triplet separation is found to be 0.79 eV. The value calculated by Eq. (16.63) is somewhat larger than this. It depends on the actual form of the 1s and 2s radial functions.

It must, of course, always be remembered that simple wavefunctions, like those of Eqs. (16.22) and (16.23), only are approximations to the true wavefunctions. They are, however, good enough to give us a reasonable first description.

16.4.2 The Beryllium Atom

The ground state of the beryllium atom is described by the wavefunction (11.47), i. e.,

$$\Psi_{\mathrm{Be}} = |\overset{+}{1}s\overset{-}{1}s\overset{+}{2}s\overset{-}{2}s|. \tag{16.64}$$

It is obviously a ^1S state. Its energy is readily seen to be

$$E(\mathrm{Be}) = (2h_{1s} + J_{1s,1s}) + (2h_{2s} + J_{2s,2s}) + (4J_{1s,2s} - 2K_{1s,2s}). \tag{16.65}$$

It appears as the sum of three contributions: the energy of the 1s shell, the energy of the 2s shell, and the energy representing the interaction between the two shells.

A similar partition of the energy into intra-shell contributions and inter-shell contributions may be performed for other atoms.

16.4.3 The Carbon Atom

The ground electron configuration of the carbon atom, $1s^2 2s^2 2p^2$, corresponds to four electrons in the *closed* $1s$ and $2s$ shells and two electrons in the *open* $2p$ shell. The closed shells give an energy contribution of the same form as the expression (16.65), and it may be proved that the interaction between the closed shells and the $2p$ shell is the same for all the determinants in the setup (16.26) and for all states of Table 16.1. The term energies may consequently be written as a contribution, E_0, which is the same for all three terms, ^3P, ^1D and ^1S, plus a contribution which varies with the term, but may be evaluated by neglecting the $1s$ and $2s$ orbitals. We get, for example, from the $M_L = 1, M_S = 1$ wavefunction of Table 16.1,

$$E(^3P) = E_0 + 2h_{2p} + J_{10} - K_{10} \tag{16.66}$$

where the subscripts refer to the m_ℓ quantum numbers, as in Table 16.1, and we have used that the integral (16.49) is the same for each $2p$ orbital. Similar expressions may be written down for the other term energies, and when the involved two-electron integrals are actually evaluated one reproduces the experimentally observed order of Eq. (16.28). The calculated energies depend, of course, on the form of the radial function, $R_{2p}(r)$. The order of the terms may, however, be shown to be the same for all $R_{2p}(r)$. It is solely determined by the angular part of the two-electron integrals. One finds, in fact, the following expressions for the term energies

$$\begin{aligned} E(^1S) &= E_0 + 2h_{2p} + F_0 + 10F_2, \\ E(^1D) &= E_0 + 2h_{2p} + F_0 + F_2, \\ E(^3P) &= E_0 + 2h_{2p} + F_0 - 5F_2, \end{aligned} \tag{16.67}$$

where F_0 and F_2 are reduced two-electron radial integrals. Such integrals play a large role in atomic physics,[3] in particular in atomic spectroscopy where they often are treated as adjustable parameters. F_0 and F_2 are both positive quantities, so the expression (16.67) does actually confirm the order of terms presented by Eq. (16.28).

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[3] For a detailed discussion with many examples, see the bibliography, entries [6] and [15].

16.5 Hund's Rules

In the above examples, we found that the ground terms of the atoms He, Be and C are ^1S, ^1S and ^3P, respectively. This is in accordance with the information in Table 11.2 which, together with Tables 11.3 and 11.4, gives the ground states of the neutral atoms. But we still have to add the J-value. From the discussion in Sec. 15.4.3 it is obvious that the J-value for He and Be must be zero, but for the ^3P term of carbon we must choose between the multiplet levels $^3P_2$, $^3P_1$ and $^3P_0$. The proper choice turns out to be $^3P_0$. Thus, the multiplet is *normal*, in the sense discussed in connection with Eq. (15.79).

For the majority of the atoms of the periodic table, the ground state may be determined by a set of rules known as *Hund's rules*. The rules build upon the assumption that it is possible to define a dominant electron configuration for the ground state, with only one partly filled shell, and that the necessary information is contained in this configuration. To determine the ground state on this basis, proceed as follows:

1. From a term analysis like that of Sec. 16.2.2, choose the maximum value of S.
2. Choose the maximum value of L consistent with rule 1.
3. If the shell is less than half full, choose $J = J_{\text{min}} = |L - S|$. If the shell is more than half full, choose $J = J_{\text{max}} = |L + S|$.

With reference to the Landé interval rule (15.79), we may say that a less than half full shell leads to a normal multiplet, whereas a more than half full shell leads to an inverted multiplet.

As a closer study of Tables 11.2–11.4 will reveal, Hund's rules work extremely well. Sometimes the two first rules may even be used to determine the order of the lower excited states. This is, for instance, the case for the carbon atom, where the ^1D term is predicted to lie below the ^1S term because its L-value is higher, for the same S-value.

Energy expressions like those of Eq. (16.67) for the carbon atom, indicate that the mechanism behind Hund's two first rules is tied to the electron-electron repulsion energy. The popular argument has been the following.

An acceptable many-electron wavefunction, Ψ, must be antisymmetric. *Interchange the positions and the spins of two electrons*, and the value of Ψ must change sign. Therefore, Ψ must be zero for the situation of having two electrons with parallel spins occupy the same position in space. In other words, electrons with parallel spins are kept apart. As a result, the electron-electron repulsion energy is lowered. The term with the highest S-values have more parallel spins, and consequently the lowest energy. High L-values implies preferential orbital motion which also tends to keep electrons out of each other's way. The highest energy therefore corresponds to the lowest values of both S and L.

Unfortunately, it has turned out that this intuitive explanation of Hund's rules is wrong. It is now understood that the explanation is more subtle. It is, in fact, found that the electron-electron repulsion energy is highest when S is large. A new explanation that often works is the following: The fact that electrons are kept apart implies, in the language of screening (Sec. 11.7), that the effective nuclear charge seen by an electron becomes more positive. As a result, the electrons are pulled closer to the nucleus. This lowers the electron-nuclear attraction energy, but also increases the electron-electron repulsion. However, the electron-nuclear attraction effect dominates, and high-spin states are thus favored.

Energy expressions like those of Eq. (16.67) presuppose that the same orbitals, and hence the same radial functions, are used everywhere in a setup like that of Table 16.1. Obviously, the alternative explanation just given corresponds to relaxing this condition. But apart from this, the amount of configuration interaction (see Sec. 11.6) may vary from term to term.

This completes our discussion of the connection between the electron configuration of an atom and its term structure, as described by its wavefunctions and corresponding energies. In the following chapter, we shall extend the discussion to diatomic molecules.

Supplementary Reading

The bibliography, entries [6], [15], [28], [34], [35].

Problems

16.1. The electron configuration of the titanium atom is [Ar]$3d^2 4s^2$ (Table 11.2).

a. How many Slater determinants does this configuration give rise to?

b. Perform a term analysis for the titanium atom, similar to the one performed for the carbon atom in Sec. 16.2.2. Show that the number of terms is five, and write down the proper term designations.

c. By referring to Hund's rules, verify that the ground state of the titanium atom is a ${}^3F_2$ level, in accordance with Table 11.2.

16.2. The oxygen atom has the electron configuration $1s^2 2s^2 2p^4$. It is equivalent to the electron configuration of the carbon atom in the following sense: The carbon atom has 2 electrons in the $2p$ shell, the oxygen atom has two 'holes' in the same shell, that is, the number of electrons is two less than that of a filled $2p$ shell.

> **a.** Perform a term analysis for the oxygen atom, similar to the one performed for the carbon atom in Sec. 16.2.2. Show that the term structure is the same as for the carbon atom.
>
> **b.** By referring to Hund's rules, verify that the ground state of the oxygen atom is a $^3P_2$ level, in accordance with Table 11.2.
>
> **c.** The nickel atom is equivalent to the titanium atom by the same electron-hole criterion as used above. Compare the ground states of the nickel atom and the titanium atom on this basis, and compare again with Table 11.2.

Chapter 17

Electronic Terms of Diatomic Molecules

Contents

In Chapter 13 we discussed the classification of molecular orbitals for diatomic molecules. We shall now consider the construction of many-electron states deriving from configurations. We do this with the oxygen molecule as an example.

17.1 The Oxygen Molecule. Term Analysis

The problem is similar to the carbon atom problem treated in Chapter 16. The many-electron Hamiltonian (13.4) is independent of spin. Hence, S and M_S are good quantum numbers. But the spherical symmetry that characterized the atomic problem has now been broken, and the quantum number L is no longer relevant. Instead, we have the quantum number Λ, which corresponds to λ for the molecular orbitals and may take the same values. And in analogy with the nomenclature for orbitals, Eq. (13.28), we use the designations Σ, Π, Δ, Φ, $\Gamma, \ldots$ for states with $\Lambda = 0, 1, 2, 3, 4, \ldots$, respectively. The states of the oxygen molecule may also be classified as even (g) or odd (u) under inversion in the midpoint of the bond. In addition, we shall see that Σ states may be either even (superscript +) or odd (superscript -) under the reflection $\hat{\sigma}_v = \hat{\sigma}_{xz}$, defined as the reflection in the xz-plane, as in Secs. 13.2 and 13.5.

The ground configuration of oxygen is (See Sec. 13.6):

$$(\sigma_g 1s)^2 (\sigma_u^* 1s)^2 (\sigma_g 2s)^2 (\sigma_u^* 2s)^2 (\sigma_g 2p)^2 (\pi_u 2p)^4 (\pi_g^* 2p)^2. \tag{17.1}$$

It gives rise to 6 Slater determinants. In specifying these we discard the closed-shell orbitals $\sigma_g 1s, \ldots, \pi_u 2p$. We also choose to work with the complex $\pi_g^* 2p$ orbitals, and for simplicity we call these orbitals π_1 and π_{-1}, where the subscripts refer to the m_λ values. The definition of the complex orbitals is

$$\begin{aligned} \pi_1 &= \sqrt{\tfrac{1}{2}}(\pi_x + i\pi_y), \\ \pi_{-1} &= \sqrt{\tfrac{1}{2}}(\pi_x - i\pi_y), \end{aligned} \tag{17.2}$$

where π_x and π_y are the $\pi_g 2p_x$ and $\pi_g 2p_y$ orbitals discussed in Secs. 13.5 and 13.6. The inverse of Eq. (17.2) is

$$\begin{aligned} \pi_x &= \sqrt{\tfrac{1}{2}}(\pi_1 + \pi_{-1}), \\ \pi_y &= -i\sqrt{\tfrac{1}{2}}(\pi_1 - \pi_{-1}). \end{aligned} \tag{17.3}$$

The 6 Slater determinants arising from the above configuration are listed in the following table, together with the corresponding values of M_Λ and M_S:

	M_Λ	M_S
$\lvert\overset{+}{\pi}_1\,\overset{-}{\pi}_1\rvert$	2	0
$\lvert\overset{+}{\pi}_1\,\overset{+}{\pi}_{-1}\rvert$	0	1
$\lvert\overset{+}{\pi}_1\,\overset{-}{\pi}_{-1}\rvert$	0	0
$\lvert\overset{-}{\pi}_1\,\overset{+}{\pi}_{-1}\rvert$	0	0
$\lvert\overset{-}{\pi}_1\,\overset{-}{\pi}_{-1}\rvert$	0	-1
$\lvert\overset{+}{\pi}_{-1}\,\overset{-}{\pi}_{-1}\rvert$	-2	0

(17.4)

From the structure of this table we may deduce that

$$\boxed{\begin{array}{l}\text{The ground configuration of the oxygen molecule}\\ \text{gives rise to three terms: } {}^3\Sigma_g^-,\ {}^1\Delta_g \text{ and } {}^1\Sigma_g^+.\end{array}} \tag{17.5}$$

All terms are even (g), because an even number of odd orbitals are occupied.

To verify the statement (17.5), we note that the two entries with $M_\Lambda = \pm 2$ show the presence of a term with $\Lambda = 2$ and $S = 0$, i. e., a ${}^1\Delta_g$ term. The wavefunctions are

$$\boxed{{}^1\Delta_g : \quad \begin{cases} |\overset{+}{\pi}_1\,\bar{\pi}_1|, & M_\Lambda = 2 \\ |\overset{+}{\pi}_{-1}\,\bar{\pi}_{-1}|, & M_\Lambda = -2 \end{cases}} \tag{17.6}$$

Next, the two entries with $M_S = \pm 1$ show the presence of a term with $\Lambda = 0$ and $S = 1$, i. e., a ${}^3\Sigma_g$ term. The $M_S = 0$ component may be found by applying the $\hat{S}_-$ operator. Hence, we get the wavefunctions

$$\boxed{{}^3\Sigma_g^- : \quad \begin{cases} |\overset{+}{\pi}_1\,\overset{+}{\pi}_{-1}|, & M_S = 1 \\ \sqrt{\tfrac{1}{2}}\left(|\overset{+}{\pi}_1\,\bar{\pi}_{-1}| + |\bar{\pi}_1\,\overset{+}{\pi}_{-1}|\right), & M_S = 0 \\ |\bar{\pi}_1\,\bar{\pi}_{-1}|, & M_S = -1 \end{cases}} \tag{17.7}$$

Finally, we may construct a term with $\Lambda = 0$ and $S = 0$, i. e., a ${}^1\Sigma_g$ term, as the orthogonal complement to the $M_S = 0$ function of Eq. (17.7),

$$\boxed{{}^1\Sigma_g^+ : \quad \sqrt{\tfrac{1}{2}}\left(|\overset{+}{\pi}_1\,\bar{\pi}_{-1}| - |\bar{\pi}_1\,\overset{+}{\pi}_{-1}|\right)} \tag{17.8}$$

To verify the superscripts - and + in (17.7) and (17.8), respectively, remember that $\hat{\sigma}_{xz}$ turns π_1 into π_{-1} and vice versa. We get, for instance,

$$\hat{\sigma}_{xz}|\overset{+}{\pi}_1\,\overset{+}{\pi}_{-1}| = |\overset{+}{\pi}_{-1}\,\overset{+}{\pi}_1| = |\overset{+}{\pi}_1\,\overset{+}{\pi}_{-1}|. \tag{17.9}$$

We shall evaluate the term energies in Sec. 17.3 and show that the relative ordering is $E({}^3\Sigma_g^-) < E({}^1\Delta_g) < E({}^1\Sigma_g^+)$. The ${}^3\Sigma_g^-$ term is accordingly the ground term of the oxygen molecule.

17.2 The Oxygen Molecule. Real Wavefunctions

The determination of the wavefunctions just obtained was facilitated by working with the complex orbitals π_1 and π_{-1}. It may, however, sometimes be convenient to express the wavefunctions in terms of the real orbitals (17.3) instead.

Inserting the relations (17.2) into the wavefunctions (17.6) for the ${}^1\Delta_g$ term gives

$$\begin{aligned} |\overset{+}{\pi}_1\,\overset{-}{\pi}_1| &= \tfrac{1}{2}|(\overset{+}{\pi}_x + i\overset{+}{\pi}_y)(\overset{-}{\pi}_x + i\overset{-}{\pi}_y)| \\ &= \tfrac{1}{2}\left(|\overset{+}{\pi}_x\,\overset{-}{\pi}_x| - |\overset{+}{\pi}_y\,\overset{-}{\pi}_y| + i|\overset{+}{\pi}_x\,\overset{-}{\pi}_y| + i|\overset{+}{\pi}_y\,\overset{-}{\pi}_x|\right) \end{aligned} \tag{17.10}$$

and

$$|\overset{+}{\pi}_{-1}\,\overset{-}{\pi}_{-1}| = \tfrac{1}{2}\left(|\overset{+}{\pi}_x\,\overset{-}{\pi}_x| - |\overset{+}{\pi}_y\,\overset{-}{\pi}_y| - i|\overset{+}{\pi}_x\,\overset{-}{\pi}_y| - i|\overset{+}{\pi}_y\,\overset{-}{\pi}_x|\right). \tag{17.11}$$

These wavefunctions are complex, but in analogy with Eq. (17.3) we may obtain a real set by simple addition and subtraction:

$$\boxed{{}^1\Delta_g : \quad \begin{cases} \Psi^c = \sqrt{\tfrac{1}{2}}\left(|\overset{+}{\pi}_x\,\overset{-}{\pi}_x| - |\overset{+}{\pi}_y\,\overset{-}{\pi}_y|\right) \\ \Psi^s = \sqrt{\tfrac{1}{2}}\left(|\overset{+}{\pi}_x\,\overset{-}{\pi}_y| + |\overset{+}{\pi}_y\,\overset{-}{\pi}_x|\right) \end{cases}} \tag{17.12}$$

For the $M_S = 1$ component of the ${}^3\Sigma_g^-$ term, Eq. (17.7), we get

$$|\overset{+}{\pi}_1\,\overset{+}{\pi}_{-1}| = \tfrac{1}{2}|(\overset{+}{\pi}_x + i\overset{+}{\pi}_y)(\overset{+}{\pi}_x - i\overset{+}{\pi}_y)| = -i|\overset{+}{\pi}_x\,\overset{+}{\pi}_y|. \tag{17.13}$$

The phase factor $-i$ is of no physical significance, so we decide to represent the $M_S = 1$ component of the ${}^3\Sigma_g^-$ term by the determinant $|\overset{+}{\pi}_x\,\overset{+}{\pi}_y|$ without the factor $-i$. The $M_S = 0$ and $M_S = -1$ components may also be found by insertion, but it is easier to apply the $\hat{S}_-$ operator to the $M_S = 1$ component. All in all, we get

$$\boxed{{}^3\Sigma_g^- : \quad \begin{cases} |\overset{+}{\pi}_x\,\overset{+}{\pi}_y|, & M_S = 1 \\ \sqrt{\tfrac{1}{2}}\left(|\overset{+}{\pi}_x\,\overset{-}{\pi}_y| + |\overset{-}{\pi}_x\,\overset{+}{\pi}_y|\right), & M_S = 0 \\ |\overset{-}{\pi}_x\,\overset{-}{\pi}_y|, & M_S = -1 \end{cases}} \tag{17.14}$$

The ${}^1\Sigma_g^+$ wavefunction may be found from Eq. (17.8) by insertion, but it is simpler to note that orthogonality relations determines it as the orthogonal complement of the ${}^1\Delta_g$ function Ψ^c:

$$\boxed{{}^1\Sigma_g^+ : \quad \sqrt{\tfrac{1}{2}}\left(|\overset{+}{\pi}_x\, \bar{\pi}_x| + |\overset{+}{\pi}_y\, \bar{\pi}_y|\right)} \tag{17.15}$$

This completes the construction of the real oxygen wavefunctions.

17.3 The Oxygen Molecule. Term Energies

We shall now evaluate the energies of the ${}^3\Sigma_g^-$, ${}^1\Delta_g$ and ${}^1\Sigma_g^+$ terms, using the real wavefunctions of the previous section. As in Sec. 16.4.3 on the energies of the carbon atom, we may write the energies as the sum of a constant part

$$\mathcal{E}_0 = E_0 + 2h_\pi, \tag{17.16}$$

which is the same for all terms, and the electron-electron interaction energies as evaluated with the two-particle wavefunctions. The latter energies are combinations of two-electron integrals similar to those defined in Sec. 16.4. We shall, in particular, encounter the Coulomb integrals

$$\begin{aligned} J_{xx} &= \langle \pi_x \pi_x | \tfrac{1}{r_{12}} | \pi_x \pi_x \rangle, \\ J_{yy} &= \langle \pi_y \pi_y | \tfrac{1}{r_{12}} | \pi_y \pi_y \rangle, \end{aligned} \tag{17.17}$$

and

$$J_{xy} = \langle \pi_x \pi_y | \tfrac{1}{r_{12}} | \pi_x \pi_y \rangle. \tag{17.18}$$

The Coulomb integral J_{yy} is numerically equal to J_{xx} because the orbitals π_x and π_y only differ by their directions in space. We shall also meet the exchange integral

$$K_{xy} = \langle \pi_x \pi_y | \tfrac{1}{r_{12}} | \pi_y \pi_x \rangle. \tag{17.19}$$

The term energies are now easily written down, by drawing on the rules for evaluating matrix elements between Slater determinants (Sec. 16.3). Thus, the two wavefunctions of Eq. (17.12) give

$$\begin{aligned} E^c({}^1\Delta_g) &= \mathcal{E}_0 + \tfrac{1}{2}(J_{xx} + J_{yy} - 2K_{xy}) = \mathcal{E}_0 + J_{xx} - K_{xy}, \\ E^s({}^1\Delta_g) &= \mathcal{E}_0 + \tfrac{1}{2}(2J_{xy} + 2K_{xy}) = \mathcal{E}_0 + J_{xy} + K_{xy}. \end{aligned} \tag{17.20}$$

The two energy expressions must be equivalent, for the energy of a degenerate term cannot depend on the component wavefunction used to evaluate it. To show that the energy expressions are in fact equivalent, we focus on the exchange integral K_{xy} and use that its value must be independent of the coordinate system in which it is evaluated. Assume, therefore, that we decide to evaluate K_{xy} in a coordinate system obtained from the original one by rotating it clockwise about the z-axis, through an angle of $\pi/4$. The π_x orbital then becomes $\sqrt{\frac{1}{2}}(\pi_x + \pi_y)$, and the π_y orbital becomes $\sqrt{\frac{1}{2}}(-\pi_x + \pi_y)$. Inserting these expressions in the definition (17.19) gives

$$K_{xy} = \tfrac{1}{4}\langle(\pi_x + \pi_y)(-\pi_x + \pi_y)|\tfrac{1}{r_{12}}|(-\pi_x + \pi_y)(\pi_x + \pi_y)\rangle. \tag{17.21}$$

By expansion, we encounter the integrals of Eqs. (17.17)–(17.19), plus the integral $\langle\pi_x\pi_x|\frac{1}{r_{12}}|\pi_x\pi_y\rangle = \langle\pi_x\pi_y|\frac{1}{r_{12}}|\pi_y\pi_y\rangle$. However, the various contributions from the latter integral cancel out, so the final result becomes

$$K_{xy} = \tfrac{1}{4}(J_{xx} + J_{yy} - 2J_{xy}) = \tfrac{1}{2}(J_{xx} - J_{xy}). \tag{17.22}$$

Hence, we may write

$$J_{xy} = J_{xx} - 2K_{xy}. \tag{17.23}$$

By inserting this expression for J_{xy} into the second expression in Eq. (17.20), we see that the two expressions given in that equation are, in fact, equivalent. Thus, we may write

$$E(^1\Delta_g) = \mathcal{E}_0 + J_{xx} - K_{xy}. \tag{17.24}$$

Next we get, from any of the $^3\Sigma_g^-$ components in (17.14),

$$E(^3\Sigma_g^-) = \mathcal{E}_0 + J_{xy} - K_{xy}, \tag{17.25}$$

or, by inserting the expression (17.23) for J_{xy},

$$E(^3\Sigma_g^-) = \mathcal{E}_0 + J_{xx} - 3K_{xy}. \tag{17.26}$$

Finally, the $^1\Sigma_g^+$ term (17.15) gives

$$E(^1\Sigma_g^+) = \mathcal{E}_0 + \tfrac{1}{2}(J_{xx} + J_{yy} + 2K_{xy}) = \mathcal{E}_0 + J_{xx} + K_{xy}. \tag{17.27}$$

Summarizing the above results, we have found that

$$\boxed{\begin{aligned} E(^1\Sigma_g^+) &= \mathcal{E}_0 + J_{xx} + K_{xy} \\ E(^1\Delta_g) &= \mathcal{E}_0 + J_{xx} - K_{xy} \\ E(^3\Sigma_g^-) &= \mathcal{E}_0 + J_{xx} - 3K_{xy} \end{aligned}} \tag{17.28}$$

We have thus confirmed the ordering mentioned at the end of Sec. 17.1. But, more than this, we have derived transparent energy expressions for the three terms.

These expressions predict that the three terms be equally spaced, the energy difference between two neighboring terms being $2K_{xy}$. However, it is found experimentally that the ${}^1\Delta_g$ and ${}^1\Sigma_g^+$ terms lie 0.982 eV and 1.636 eV, respectively, above the ground state, ${}^3\Sigma_g^-$. The experimentally observed spacing (0.654 eV) between the ${}^1\Delta_g$ and ${}^1\Sigma_g^+$ terms is thus somewhat smaller than the experimentally observed spacing (0.982 eV) between the ${}^3\Sigma_g^-$ and ${}^1\Delta_g$ terms. But qualitatively, the theoretical description has done quite well.

As for atoms (Sec. 16.5), the theoretical result may be readily improved at two levels. Firstly, we realize that we have tacitly assumed that all occupied molecular orbitals, and hence also $\mathcal{E}_0$, J_{xx} and K_{xy}, are the same for all three terms of the oxygen molecule. This condition may be relaxed. The expressions (17.27) will then still be valid, but the values of $\mathcal{E}_0$, J_{xx} and K_{xy} will differ from one term to another, and the constant spacing between the terms will be destroyed.

The second level at which the theoretical result may be improved is the configuration interaction level. At this level, the wavefunctions are represented as linear combinations of several Slater determinants, referring to different electron configurations, with the coefficients of the linear combinations determined variationally.

The discussion of this chapter has been tied to a single diatomic molecule, namely, the oxygen molecule. Other diatomics may, however, be discussed along similar lines. And most often, the discussion will be simpler, for the ground term of most diatomic molecules is a ${}^1\Sigma^+$ term, for homonuclear diatomics a ${}^1\Sigma_g^+$ term.

As to the role of spin-orbit coupling, which we discussed in some detail for atoms in Sec. 15.4.3, it is of no less importance in molecules. Thus, it splits the various electronic terms into multiplets characterized by the eigenvalues of $\hat{L}_z + \hat{S}_z$. The situation is, however, more complicated than this because $\hat{\boldsymbol{L}}$ and $\hat{\boldsymbol{S}}$ also couple to the rotational motion of the molecule. Obviously, the overall effect depends on the relative strengths of the various couplings, and each molecule must accordingly be treated as a separate case. We refer the reader to the literature for a detailed discussion of this problem.[1]

Finally, it should be remembered that our discussion of molecules has been based on the adiabatic approximation which we discussed in Sec. 13.1. The

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[1] See the bibliography, entries [36], [37] and [38].

validity of this approximation is usually better for states of low energy than for higher energy states. But it is always an approximation. To go beyond it in a general way is a very complicated matter. Again, we must refer the reader to the literature.[2]

Supplementary Reading

The bibliography, entries [36], [37], [38].

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[2] See B. T. Sutcliffe, Adv. Chem. Phys. **114**, 1 (2000).

Chapter 18

The Hartree–Fock Method

Contents

We have now proceeded quite far in our understanding of the basic structure of atomic and molecular quantum mechanics. With the last chapter we have completed the discussion of the connection between the idea of electron configurations and electronic terms. As a result, we finally understand how to construct reasonable approximations to proper many-electron wavefunctions, starting from orbitals, that is, one-electron wavefunctions. We shall now direct our attention to the problem of actually determining the best possible orbitals within this picture.

This is a problem we have commented on at various occasions, for atoms primarily in Sec. 11.6, and for molecules in Sec. 13.2. We have also pointed out that the notion 'best possible orbitals' is ambigious. As discussed in Sec. 11.6, we may take it to mean either Hartree–Fock orbitals or Kohn–Sham orbitals.

In this chapter, we shall focus on the Hartree–Fock description. It is a description that has undergone many refinements during the years. It was originally introduced by the Russian physicist Vladimir Aleksandrovitj Fock[1] and J. C. Slater,[2] as a completion of the originally intuitive method developed by D. R. Hartree[3] on the basis of product functions like that of Eq. (16.7).

We first discuss the Hartree–Fock method for a single determinant. We then introduce spin and equivalence restrictions and reach what is known as the conventional Hartree–Fock method. Finally, we comment on the correlation problem, i. e., the problem of going beyond the Hartree–Fock description.

18.1 Hartree–Fock Method for a Single Determinant

In the Hartree–Fock method for a single determinant, one assumes that the N-electron state under study may be reasonably well described by a wavefunction of the form (16.1), i. e.,

$$D = |\psi_1\psi_2\ldots\psi_N| = \sqrt{\frac{1}{N!}}\begin{vmatrix} \psi_1(x_1) & \psi_1(x_2) & \ldots & \psi_1(x_N) \\ \psi_2(x_1) & \psi_2(x_2) & \ldots & \psi_2(x_N) \\ \ldots & \ldots & \ldots & \ldots \\ \psi_N(x_1) & \psi_N(x_2) & \ldots & \psi_N(x_N) \end{vmatrix}, \tag{18.1}$$

where $\psi_1, \psi_2, \ldots, \psi_N$ is an orthonormal set of N spin-orbitals,

$$\langle\psi_i|\psi_j\rangle = \delta_{ij}. \tag{18.2}$$

With reference to the variational theorem (12.12), the spin-orbitals should be chosen so as to make the expectation value of the Hamiltonian an absolute minimum. Those spin-orbitals are, per definition, the Hartree–Fock orbitals.

Because of the orthonormality relations (18.2), D is normalized to unity. Thus, the expectation value of the Hamiltonian simply becomes $\langle D|\widehat{H}|D\rangle$.

We write the electronic Hamiltonian as

$$\boxed{\begin{aligned} \widehat{H} &= \sum_{i=1}^{N}\hat{h}(i) + \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}{}' \frac{1}{r_{ij}}, \\ \hat{h}(i) &= -\frac{1}{2}\nabla_i^2 - \sum_{g=1}^{K}\frac{Z_g}{r_{ig}}. \end{aligned}} \tag{18.3}$$

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[1] V. Fock, Z. Phys. **61**, 126 (1930).

[2] J. C. Slater, Phys. Rev. **35**, 210 (1930).

[3] D. R. Hartree, Proc. Cambridge Phil. Soc. **24** (1928).

For a molecule, the Hamiltonian agrees with that of Eq. (13.4) which is the electronic Hamiltonian for a fixed configuration of K nuclei. For an atom, where $K = 1$, we recognize the Hamiltonian (16.58).

The expectation value $\langle D|\widehat{H}|D\rangle$ may be written as in Eq. (16.58),

$$\langle D|\widehat{H}|D\rangle = \sum_{i=1}^{N} h_i' + \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\left(J_{ij}' - K_{ij}'\right). \tag{18.4}$$

The quantities in the expression for $\langle D|\widehat{H}|D\rangle$ have the same meaning as in Sec. 16.4, except that h_i' now honors the presence of K nuclei, that is, h_i' gives the kinetic energy of an electron in the spin-orbital ψ_i plus the energy of this electron in the field of K fixed nuclei.

As said above, the spin-orbitals $\psi_1, \psi_2, \ldots, \psi_N$ should be determined such that $\langle D|\widehat{H}|D\rangle$ becomes an absolute minimum. This implies that the variation $\delta\langle D|\widehat{H}|D\rangle$ should be zero. The expression for the variation is obtained as the first-order term in the expression (18.4) when each ψ_i and ψ_j therein are replaced by $\psi_i + \delta\psi_i$ and $\psi_i + \delta\psi_i$. The result is

$$\begin{aligned}\delta\langle D|\widehat{H}|D\rangle = {} & \sum_{i=1}^{N}\langle\delta\psi_i|\hat{h}|\psi_i\rangle \\ & + \sum_{i=1}^{N}\sum_{j=1}^{N}\left\{\langle\delta\psi_i\psi_j|\tfrac{1}{r_{12}}|\psi_i\psi_j\rangle - \langle\delta\psi_i\psi_j|\tfrac{1}{r_{12}}|\psi_j\psi_i\rangle\right\} \\ & + \sum_{i=1}^{N}\langle\psi_i|\hat{h}|\delta\psi_i\rangle \\ & + \sum_{i=1}^{N}\sum_{j=1}^{N}\left\{\langle\psi_i\psi_j|\tfrac{1}{r_{12}}|\delta\psi_i\psi_j\rangle - \langle\psi_i\psi_j|\tfrac{1}{r_{12}}|\psi_j\delta\psi_i\rangle\right\}.\end{aligned} \tag{18.5}$$

We have used rewritings like

$$\begin{aligned}\sum_{i=1}^{N}\sum_{j=1}^{N}\langle\psi_i\delta\psi_j|\tfrac{1}{r_{12}}|\psi_i\psi_j\rangle & = \sum_{i=1}^{N}\sum_{j=1}^{N}\langle\psi_j\delta\psi_i|\tfrac{1}{r_{12}}|\psi_j\psi_i\rangle \\ & = \sum_{i=1}^{N}\sum_{j=1}^{N}\langle\delta\psi_i\psi_j|\tfrac{1}{r_{12}}|\psi_i\psi_j\rangle\end{aligned} \tag{18.6}$$

which involves renamings of summation indices, and draws on the first relation contained in Eq. (16.55).

The expectation value of the Hamiltonian is only given by the simple expression $\langle D|\hat{H}|D\rangle$ when the spin-orbitals $\psi_1, \psi_2, \dots, \psi_N$ form an orthonormal set. It follows that these orbitals must be kept orthonormal during the variation, if (18.5) all along is to represent the change in the expectation value of $\hat{H}$. This corresponds to the requirement

$$\delta\langle\psi_i|\psi_j\rangle = 0, \quad i,j = 1,2,\dots,N, \tag{18.7}$$

or,

$$\langle\delta\psi_i|\psi_j\rangle + \langle\psi_i|\delta\psi_j\rangle = 0, \quad i,j = 1,2,\dots,N. \tag{18.8}$$

A necessary condition for $\langle D|\hat{H}|D\rangle$ to represent a minimum when evaluated with the spin-orbitals $\psi_1, \psi_2, \dots, \psi_N$ is then, that the expression (18.5) should vanish for any variation which is in accordance with (18.8). This condition leads, in a straightforward manner, to the Hartree–Fock equations.

It is, howwever, expedient to simplify the notation still further by introducing the so-called *Hartree–Fock operator*

$$\hat{F} = \hat{h} + \sum_{j=1}^{N}(\hat{J}'_j - \hat{K}'_j) \tag{18.9}$$

where $\hat{h}$ is the one-electron operator defined in (18.3), and $\hat{J}'_j$ and $\hat{K}'_j$ are integral operators defined through the relations

$$\boxed{\begin{aligned} \hat{J}'_j\psi(x_1) &= \int \psi_j^*(x_2)\psi_j(x_2)\tfrac{1}{r_{12}}dx_2\,\psi(x_1), \\ \hat{K}'_j\psi(x_1) &= \int \psi_j^*(x_2)\psi(x_2)\tfrac{1}{r_{12}}dx_2\,\psi_j(x_1). \end{aligned}} \tag{18.10}$$

$\hat{J}'_j$ is called a *Coulomb operator*. It may be interpreted as giving the electrostatic porential from an electron in the orbital ψ_j. $\hat{K}'_j$ is called an *exchange operator*. It represents what is known as a *non-local potential*, a notation which refers to the fact that one must know $\psi(x)$ at all values of x, in order to evaluate $\hat{K}'_j\psi(x)$ at a particular point. The Coulomb operator represents, on the other hand, a *local potential*. To evaluate $\hat{J}'_j\psi(x)$ it is sufficient to know $\psi(x)$ at the point x.

It is easy to verify that each of the operators $\hat{h}$, $\hat{J}'_j$ and $\hat{K}'_j$ are Hermitian. $\hat{F}$ is therefore also a Hermitian operator.

The expression (18.5) may now be written in the more compact form

$$\delta\langle D|\hat{H}|D\rangle = \sum_{i=1}^{N}\left\{\langle\delta\psi_i|\hat{F}|\psi_i\rangle + \langle\psi_i|\hat{F}|\delta\psi_i\rangle\right\}, \tag{18.11}$$

and the condition that $\delta\langle D|\hat{H}|D\rangle$ vanish becomes

$$\sum_{i=1}^{N}\left\{\langle\delta\psi_i|\hat{F}|\psi_i\rangle + \langle\psi_i|\hat{F}|\delta\psi_i\rangle\right\} = 0. \tag{18.12}$$

The spin-orbitals for which $\delta\langle D|\hat{H}|D\rangle$ is a minimum are the Hartree–Fock orbitals. Eq. (18.12) represents a necessary condition on these orbitals, which implies that it is these particular orbitals that occur in (18.12) and (18.8). We introduce the notation $\mathcal{V}_I$ for the function space spanned by these orbitals, i. e., for the set of all functions of the form

$$\psi_I = \sum_{k=1}^{N} c_k\psi_k. \tag{18.13}$$

The notion $\mathcal{V}_{II}$ is used for the complementary function space, i. e., for the set of all functions of the form

$$\psi_{II} = \sum_{\mu=N+1}^{\infty} c_\mu\psi_\mu. \tag{18.14}$$

Here, the 'unoccupied' orbitals $\psi_{N+1}, \psi_{N+2}, \ldots$ have been so chosen that they form a complete orthonormal set of functions, when taken together with the 'occupied' orbitals $\psi_1, \psi_2, \ldots, \psi_N$. In other words, any function $\psi(x)$ may be written as

$$\psi = \sum_{k=1}^{N} c_k\psi_k + \sum_{\mu=N+1}^{\infty} c_\mu\psi_\mu. \tag{18.15}$$

We express this symbolically as

$$\mathcal{V} = \mathcal{V}_I \oplus \mathcal{V}_{II}. \tag{18.16}$$

For the coefficients in (18.15) we have the usual expressions

$$c_k = \langle\psi_k|\psi\rangle, \qquad c_\mu = \langle\psi_\mu|\psi\rangle, \tag{18.17}$$

in analogy with Eq. (5.140). We use Roman subscripts for functions in $\mathcal{V}_I$, Greek subscripts for functions in $\mathcal{V}_{II}$.

The condition (18.12) must be satisfied for the set of all possible variations $(\delta\psi_1, \delta\psi_2, \ldots, \delta\psi_N)$ which are consistent with (18.8). It must therefore hold for any particular instances. For our purpose, it is sufficient to consider a variation of the form

$$\delta\psi_i = c\psi_\lambda, \quad \delta\psi_k = 0, \quad k \neq i. \tag{18.18}$$

This variation will certainly satisfy (18.8), since ψ_λ belongs to $\mathcal{V}_{II}$ (cf. our convention concerning subscripts).

Inserting (18.18) in (18.12) gives

$$c^*\langle\psi_\lambda|\hat{F}|\psi_i\rangle + c\langle\psi_i|\hat{F}|\psi_\lambda\rangle = 0. \tag{18.19}$$

Replacing c by ic gives instead

$$-ic^*\langle\psi_\lambda|\hat{F}|\psi_i\rangle + ic\langle\psi_i|\hat{F}|\psi_\lambda\rangle = 0, \tag{18.20}$$

or, after multiplication by i,

$$c^*\langle\psi_\lambda|\hat{F}|\psi_i\rangle - c\langle\psi_i|\hat{F}|\psi_\lambda\rangle = 0. \tag{18.21}$$

Adding and subtracting Eqs. (18.19) and (18.21) shows then that

$$\begin{aligned}\langle\psi_\lambda|\hat{F}|\psi_i\rangle &= 0,\\ \langle\psi_i|\hat{F}|\psi_\lambda\rangle &= 0.\end{aligned} \tag{18.22}$$

These relations must hold for any ψ_i in $\mathcal{V}_I$ and any ψ_λ in $\mathcal{V}_{II}$.

The implication of this result is that the expansion

$$\hat{F}\psi_i = \sum_{k=1}^{N} \epsilon_{ki}\psi_k + \sum_{\mu=N+1}^{\infty} \epsilon_{\mu i}\psi_\mu \tag{18.23}$$

must terminate after the N^{th} term. For in the same way as in Sec. 5.10, Eq. (5.151), we get

$$\begin{aligned}\epsilon_{ki} &= \langle\psi_k|\hat{F}|\psi_i\rangle,\\ \epsilon_{\mu i} &= \langle\psi_\mu|\hat{F}|\psi_i\rangle,\end{aligned} \tag{18.24}$$

while Eq. (18.22) shows that $\langle\psi_\mu|\hat{F}|\psi_i\rangle$, and hence $\epsilon_{\mu i}$, is zero. Eq. (18.23) becomes accordingly

$$\boxed{\hat{F}\psi_i = \sum_{k=1}^{N} \epsilon_{ki}\psi_k, \qquad i = 1, 2, \ldots, N} \tag{18.25}$$

The N equations (18.25) are the *Hartree–Fock equations* which the spin-orbitals $\psi_1, \psi_2, \ldots, \psi_N$ have to satisfy. We note that the orbitals—through the operators $\hat{J}'_j$ and $\hat{K}'_j$ defined by Eq. (18.10)—also occur in the definition of the Hartree–Fock operator $\hat{F}$. The Hartree–Fock equations are, therefore, a set of coupled integro-differential equations.

The coefficients ϵ_{ki}, for which Eq. (18.24) gives explicit expressions, are the elements of a Hermitian matrix (because $\hat{F}$ is Hermitian). They are usually referred to as *Lagrangian multipliers*. This designation refers to the fact that Eq. (18.25) may be derived by requiring that the quantity

$$I = \langle D|\hat{H}|D\rangle - \sum_{i=1}^{N}\sum_{j=1}^{N} \epsilon_{ij}\langle\psi_j|\psi_i\rangle \tag{18.26}$$

be a minimum for *arbitrary* variations $(\delta\psi_1, \delta\psi_2, \ldots, \delta\psi_N)$. This method draws on a general way of handling constraints (in the present case (18.8)), due to the eighteenth century, French mathematician Joseph Louis Lagrange. A comparison of the method applied here and the method of Lagrange is given elsewhere.[4]

At this stage we recall the theorem, proved in Sec. 13.6, Eq. (13.76), that a Slater determinant—apart from a factor—is invariant under a linear transformation of the spin-orbitals that define it. This implies, apparently, that any set of N orthonormal spin-orbitals in V_I must satisfy a set of equations of the form (18.25), for any such set defines the same determinant.

It is now easy to show (*vide infra*) that $\hat{F}$ is independent of the way in which the orthonormal set $\psi_1, \psi_2, \ldots, \psi_N$ is chosen within V_I. In other words, $\hat{F}$ is an invariant. This implies, in particular, that the matrix $\{\epsilon_{ki}\}$ may be diagonalized by a unitary transformation. Hence, suitable linear combinations

$$\psi_i^c = \sum_{j=1}^{N} U_{ji}\psi_j \tag{18.27}$$

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[4] J. P. Dahl, H. Johansen, D. R. Truax, and T. Ziegler, Chem. Phys. Letters **6**, 64 (1970).

can be found, for which the Hartree–Fock equations take on the following *canonical form* (we leave out the superscript c):

$$\boxed{\hat{F}\psi_i = \epsilon_i\psi_i, \qquad i = 1, 2, \ldots, N.} \tag{18.28}$$

The preservation of orthonormality is secured by the requirement that U_{ji} be a unitary matrix, as discussed in detail in Sec. 15.1.

The canonical form is apparently the simplest of the equivalent forms in which the Hartree–Fock equations may appear. As a consequence, this form plays a preferred role in many applications of the theory. In addition, Eq. (18.28) looks much like a one-electron Schrödinger equation. It is thus through the canonical form that one comes closest to the ideas of the so-called *independent particle model* according to which each electron finds itself in a stationary state, determined by an effective potential from the nuclei and the remaining electrons.

The actual solution of the Hartree–Fock equations is usually carried out by the *Self-Consistent Field* method (SCF method). This is an iterative procedure by which one begins by guessing a 'reasonable' set of occupied orbitals $\psi_1, \psi_2, \ldots, \psi_N$. With these functions, one constructs the Hartree–Fock operator (18.9) and solves the equations (18.28) with $\hat{F}$ as a fixed operator. In this way, a new set of orbitals is arrived at. These allow the construction of a better $\hat{F}$ with which Eq. (18.28) may again be solved, etc. The iteration is stopped when the difference between the orbital sets from successive steps become insignificant. The Hartree–Fock field is then said to be self-consistent. In practise, it is often necessary to apply special techniques to achieve self-consistency.

We close the present section by verifying the above made assertion that $\hat{F}$ is invariant under a unitary transformation of the form

$$\psi_j = \sum_{l=1}^{N} U_{lj}\tilde{\psi}_l, \qquad j = 1, 2, \ldots, N. \tag{18.29}$$

We do this by showing that the quantity

$$\gamma(x, x') = \sum_{j=1}^{N} \psi_j(x)\psi_j^*(x') \tag{18.30}$$

is an invariant. This is an equivalent problem, for a comparison with the expression (18.9) shows that $\hat{F}$ depends upon the orbitals $\psi_1, \psi_2, \ldots, \psi_N$ through this quantity.

Inserting (18.29) in (18.30) gives

$$\begin{aligned}\gamma(x,x') &= \sum_{j=1}^{N}\sum_{k=1}^{N}\sum_{l=1}^{N} U_{kj}U_{lj}^{*}\tilde{\psi}_k(x)\tilde{\psi}_l^{*}(x') \\ &= \sum_{k=1}^{N}\sum_{l=1}^{N} \delta_{kl}\tilde{\psi}_k(x)\tilde{\psi}_l^{*}(x') \qquad (18.31) \\ &= \sum_{k=1}^{N} \tilde{\psi}_k(x)\tilde{\psi}_k^{*}(x')\end{aligned}$$

where Eq. (15.12) has been used in going from the first to the second line. The form invariance of $\gamma(x,x')$, and hence of $\hat{F}$, is now evident.

The quantity $\gamma(x,x')$ is called the *one-electron density matrix*. It is a central entity to which we shall return in the next chapter.

18.2 Spin Restrictions

To determine the most general solutions of the Hartree–Fock equations (18.28), as spin-orbitals of the form (10.17), is a very complicated task. Usually, one imposes the restriction that the spin-orbitals be eigenfunctions of $\hat{s}_z$, that is, they must be of the form (10.21). Let us assume that n spin-orbitals have α spin while the remaining $N-n$ spin-orbitals have β spin. The determinant (18.1) becomes then

$$D = |\overset{+}{\varphi}_1\overset{+}{\varphi}_2\cdots\overset{+}{\varphi}_n\bar{\varphi}_{n+1}\cdots\bar{\varphi}_N|. \qquad (18.32)$$

Such a determinant is an eigenfunction of $\hat{S}_z$ with the eigenvalue

$$M_S = n - \tfrac{1}{2}N, \qquad (18.33)$$

in the usual atomic units. Conversely, it may be shown[5] that any N-electron determinant which is an eigenfunction of $\hat{S}_z$ with this eigenvalue, is of the from (18.32), or else it can be brought on that form through a transformation of the type (13.76). To find the energetically most favorable determinant of the form (18.32) is therefore equivalent to solving the variational problem $\delta\langle D|\hat{H}|D\rangle = 0$; with the subsidiary condition that D be an eigenfunction of $\hat{S}_z$ with the eigenvalue $n-\frac{1}{2}N$.

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[5] P.-O. Löwdin, J. Appl. Phys. Suppl. **33**, 251 (1962).

It is quite easy to see how the Hartree–Fock equations are modified when, besides the orthonormality conditions (18.2), we impose the restriction that D is to be varied only within the class of determinants which have n *spin-up orbitals* and $N - n$ *spin-down orbitals.* The expression (18.11) for the variation of $\langle D|\hat{H}|D\rangle$ will still hold. But the expression (18.9) for the Hartree–Fock operator may be simplified by introducing purely spatial Coulomb and exchange operators, $\hat{J}_j$ and $\hat{K}_j$. In accord with the notion of Sec. 16.4, we define

$$\boxed{\begin{aligned} \hat{J}_j\varphi(\boldsymbol{r}_1) &= \int \varphi_j^*(\boldsymbol{r}_2)\varphi_j(\boldsymbol{r}_2)\tfrac{1}{r_{12}}dv_2\,\varphi(\boldsymbol{r}_1), \\ \hat{K}_j\varphi(\boldsymbol{r}_1) &= \int \varphi_j^*(\boldsymbol{r}_2)\varphi(\boldsymbol{r}_2)\tfrac{1}{r_{12}}dv_2\,\varphi_j(\boldsymbol{r}_1). \end{aligned}} \tag{18.34}$$

With all spin-orbitals being of the form (10.21), we may perform the integration over the spin variable in (18.10) to get

$$\begin{aligned} \hat{J}_j'\psi_i(x_1) &= \hat{J}_j\psi_i(x_1), \\ \hat{K}_j'\psi_i(x_1) &= \delta(m_{si}, m_{sj})\hat{K}_j\psi_i(x_1). \end{aligned} \tag{18.35}$$

Thus, the exchange operator $\hat{K}_j'$ annihilates all spin-orbitals with spin functions different from that of ψ_j itself.

As one easily verifies, these results allow us to write the Hartree–Fock operator (18.9) as

$$\hat{F} = \hat{h} + \sum_{j=1}^{N}\hat{J}_j - \sum_{j=1}^{n}\hat{K}_j(\tfrac{1}{2} + \hat{s}_z) - \sum_{j=n+1}^{N}\hat{K}_j(\tfrac{1}{2} - \hat{s}_z). \tag{18.36}$$

This operator commutes with $\hat{s}_z$. That the Hartree–Fock orbitals are supposed to be eigenfunctions of $\hat{s}_z$ is therefore a consistent assumption (cf. the theorem (5.120)). The expression (18.24) for ϵ_{ki} also shows that the Lagrangian multipliers connecting a spin-up orbital with a spin-down orbital must be zero (Apply the theorem (5.74) with $\hat{F}$ replaced by $\hat{s}_z$ and $\hat{G}$ by $\hat{F}$). This implies, in turn, that it becomes possible to eliminate the spin functions in the Hartree–Fock equations and write, instead of (18.25),

$$\begin{aligned} \hat{F}^{\uparrow}\varphi_i &= \sum_{k=1}^{n}\epsilon_{ki}\varphi_k, \qquad i = 1, 2, \dots, n, \\ \hat{F}^{\downarrow}\varphi_j &= \sum_{l=n+1}^{N}\epsilon_{lj}\varphi_l, \qquad j = n+1, \dots, N, \end{aligned} \tag{18.37}$$

where we have introduced spin-up and spin-down Hartree–Fock operators by the definition

$$\begin{aligned}\hat{F}^{\uparrow} &= \hat{h} + \sum_{j=1}^{N} \hat{J}_j - \sum_{j=1}^{n} \hat{K}_j, \\ \hat{F}^{\downarrow} &= \hat{h} + \sum_{j=1}^{N} \hat{J}_j - \sum_{j=n+1}^{N} \hat{K}_j.\end{aligned} \tag{18.38}$$

We may now perform unitary transformations like (18.29) within the orbital sets $(\varphi_1, \varphi_2, \ldots, \varphi_n)$ and $(\varphi_{n+1}, \varphi_{n+2}, \ldots, \varphi_N)$ separately, to obtain the equations (18.37) in the canonical form

$$\boxed{\begin{aligned}\hat{F}^{\uparrow}\varphi_i &= \epsilon_i \varphi_i, \qquad i = 1, 2, \ldots, n, \\ \hat{F}^{\downarrow}\varphi_j &= \epsilon_j \varphi_j, \qquad j = n+1, \ldots, N.\end{aligned}} \tag{18.39}$$

These equations are, then, the Hartree–Fock equations associated with a determinant of the form (18.32).

We observe that $\hat{F}^{\uparrow}$ and $\hat{F}^{\downarrow}$ become identical if the exchange terms are neglected, or if these terms happen to be the same in the two operators. The two sets of equations in (18.39) have the same solutions in such cases. In other words, the spin-up and spin-down orbitals are taken from the same set of spatial orbitals. But the general case makes $\hat{F}^{\uparrow}$ and $\hat{F}^{\downarrow}$ different, and the spin-up orbitals do not go with the same set of spatial functions as the spin-down orbitals. One talks about *different orbitals for different spins* (DODS). It should be noticed that the spin-up orbitals are mutually orthogonal, as are the spin-down orbitals, but there are no orthogonality conditions between the two types of orbitals.

The SCF theory based on (18.39) is referred to as *Unrestricted Hartree–Fock* (UHF) theory. In the case of atoms, one even uses this designation with one more restriction imposed, namely, that the spin-orbitals in the determinant D of Eq. (18.32) should be also eigenfunctions of $\hat{\ell}_z$. An equivalent way of putting this is to require that D be an eigenfunction of $\hat{L}_z$, with a definite eigenvalue M_L. The new restriction may be treated in exactly the same manner as the spin restriction, by observing that the Hartree–Fock operator now also commutes with $\hat{\ell}_z$.

18.3 Conventional Hartree–Fock Theory

The most widely used version of Hartree–Fock theory operates with spin-orbitals of the form (10.21), but requires in addition that the spatial orbitals reflect the full symmetry of the operator $\hat{h}$, defined in Eq. (18.3). This means that the spatial orbitals are eigenfunctions of $\hat{\ell}^2$ in the atom, and eigenfunctions of $\hat{\ell}_z^2$ in the diatomic molecule. In a general molecule, they must span irreducible representations of the point group defined by the nuclear framework. Such spatial orbitals are called symmetry orbitals, and the restrictions involved are referred to as *symmetry restrictions.*

The symmetry restrictions are augmented by *equivalence restrictions*, according to which all spatial orbitals are to be taken from an orthonormal set with the property that if φ_i is a member of the set, so is any partner of φ_i. Partners are here defined as functions that transform into linear combinations of each other under the action of angular-momentum operators and/or symmetry operations. Furthermore, it is required that the spin-up and the spin-down orbitals should be taken from the same set of spatial orbitals. This leads to the well-known concept of doubly occupied orbitals: each spatial orbital may occur twice in the same determinant, once associated with an α spin function, once with a β spin function.

The use of symmetry orbitals makes it possible to construct total wavefunctions which themselves honor the symmetry of the problem, as linear combinations of a minimum number of determinants. These wavefunctions correspond closely to the atomic and molecular many-electron wavefunctions that we constructed in Chapters 16 and 17.

The Hartree–Fock theory associated with such a description of electronic states is known as *Conventional Hartree–Fock* theory or *Restricted Hartree–Fock* (RHF) theory. In order to see how the basic equations are modified by the additional constraints, let us consider an N-electron state described by a single determinant of the form

$$D = |\overset{+}{\varphi}_1\overset{+}{\varphi}_2\cdots\overset{+}{\varphi}_n\overset{-}{\varphi}_1\overset{-}{\varphi}_2\cdots\overset{-}{\varphi}_m|, \qquad m \le n, \tag{18.40}$$

in which m orbitals are doubly occupied. The variation of $\langle D|\widehat{H}|D\rangle$ is still given by (18.11), and the form (18.36) still applies. We obtain therefore, by observing the definitions (18.38),

$$\begin{aligned}\delta\langle D|\widehat{H}|D\rangle &= \sum_{i=1}^{N}\left\{\langle\delta\psi_i|\hat{F}|\psi_i\rangle + \langle\psi_i|\hat{F}|\delta\psi_i\rangle\right\}\\ &= \sum_{i=1}^{n}\left\{\langle\delta\varphi_i|\hat{F}^{\uparrow}|\varphi_i\rangle + \langle\varphi_i|\hat{F}^{\uparrow}|\delta\varphi_i\rangle\right\}\\ &\quad+\sum_{i=1}^{m}\left\{\langle\delta\varphi_i|\hat{F}^{\downarrow}|\varphi_i\rangle + \langle\varphi_i|\hat{F}^{\downarrow}|\delta\varphi_i\rangle\right\},\end{aligned} \tag{18.41}$$

or,

$$\begin{aligned}\delta\langle D|\widehat{H}|D\rangle &= \sum_{i=1}^{m}\left\{\langle\delta\varphi_i|\hat{F}^{\uparrow}+\hat{F}^{\downarrow}|\varphi_i\rangle + \langle\varphi_i|\hat{F}^{\uparrow}+\hat{F}^{\downarrow}|\delta\varphi_i\rangle\right\}\\ &\quad+\sum_{i=m+1}^{n}\left\{\langle\delta\varphi_i|\hat{F}^{\uparrow}|\varphi_i\rangle + \langle\varphi_i|\hat{F}^{\uparrow}|\delta\varphi_i\rangle\right\}.\end{aligned} \tag{18.42}$$

This is a special case of the more general expression

$$\delta E = \sum_{i=1}^{n}\left\{\langle\delta\varphi_i|\hat{F}^{i}|\varphi_i\rangle + \langle\varphi_i|\hat{F}^{i}|\delta\varphi_i\rangle\right\}, \tag{18.43}$$

for which the condition $\delta E = 0$ leads to the Hartree–Fock equations

$$\hat{F}^{i}\varphi_i = \sum_{j=1}^{n}\lambda_{ji}\varphi_j, \qquad i = 1,2,\ldots,n, \tag{18.44}$$

with $\{\lambda_{ji}\}$ being a Hermitian matrix. This result may be derived by the use of methods similar to those applied in Sec. 18.1, as shown elsewhere.[6] The characteristic feature of (18.44) is that each orbital has its own Hartree–Fock operator.

Thus we obtain, from (18.42), the following equations

$$\begin{aligned}(\hat{F}^{\uparrow}+\hat{F}^{\downarrow})\varphi_i &= \sum_{k=1}^{n}\lambda_{ki}\varphi_k, &\qquad i &= 1,2,\ldots,m,\\ \hat{F}^{\uparrow}\varphi_j &= \sum_{l=1}^{n}\lambda_{lj}\varphi_l, &\qquad j &= m+1,\ldots,n.\end{aligned} \tag{18.45}$$

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[6] See the reference of footnote 18.4.

As usual, we may reduce these equations further by performing unitary transformations on the set of orbitals defining D. However, only such transformations are allowed that leave m orbitals doubly occupied. This implies that we may perform unitary transformations within the sets $\varphi_1, \varphi_2, \ldots, \varphi_m$ and $\varphi_{m+1}, \ldots, \varphi_n$ separately, but no mixing between the sets is allowed.The canonical form of (18.45) is therefore

$$\boxed{\begin{aligned} (\hat{F}^{\uparrow} + \hat{F}^{\downarrow})\varphi_i &= \lambda_{ii}\varphi_i + \sum_{k=m+1}^{n} \lambda_{ki}\varphi_k, \qquad i = 1, 2, \ldots, m, \\ \hat{F}^{\uparrow}\varphi_k &= \lambda_{kk}\varphi_k + \sum_{i=1}^{m} \lambda_{ik}\varphi_i, \qquad k = m + 1, \ldots, n. \end{aligned}} \tag{18.46}$$

Thus, not all off-diagonal multipliers may be eliminated.

An important exception is obtained when $n = m$, in which case $\hat{F}^{\uparrow}$ and $\hat{F}^{\downarrow}$ become identical. The determinant (18.40) now has n doubly occupied orbitals, and we may write

$$\boxed{\begin{aligned} &\hat{F}_c\varphi_i = \epsilon_i\varphi_i, \qquad i = 1, 2, \ldots, n, \\ &\hat{F}_c = \hat{h} + \sum_{j=1}^{n}(2\hat{J}_j - \hat{K}_j). \end{aligned}} \tag{18.47}$$

The presence of off-diagonal multipliers is characteristic of open-shell systems where not all orbitals are doubly occupied. Their mission is to ensure orthogonality between orbitals with different occupancy. If the multipliers were neglected, the orbitals would, as a rule, no longer be orthogonal, for they would then be eigenfunctions of different Hermitian operators. However, if some symmetry is present in the system, off-diagonal multipliers only occur between orbitals with the same symmetry. Multipliers between orbitals of different symmetries vanish due to the theorem (5.74) (cf. the discussion between Eqs. (18.36) and (18.37)).

In closing this section, let us emphasize that most Hartree–Fock calculations work with orbitals that are expanded in basis sets of non-orthogonal functions, usually Slater- or Gaussian-type orbitals (cf. Secs. 11.7 and 12.4). Thus, the Hartree-Fock equations become a set of matrix equations, usually referred to as Roothaan's equations, in honor of the Dutch-American physicist Clemens

C. J. Roothaan whose pioneering work has been very influential.[7]

18.4 The Correlation Problem

The importance of the Hartree–Fock method and the concepts it introduces is very great. Nevertheless, we do not obtain an exact solution to the electronic Schrödinger equation by this method. For the ground state, it is easy to set up a simple measure for the accuracy of the method by drawing on the variational theorem (12.12). This theorem ensures us that the Hartree–Fock energy, E_{HF}, lies above the exact ground-state energy, E_0. The quantity

$$E_{corr} = E_0 - E_{HF} \tag{18.48}$$

is therefore a reasonable measure for the accuracy. It is called the *correlation energy*. For the helium atom and the hydrogen molecule it amounts to -1.1 eV.

The problem of improving the description beyond the Hartree-Fock description, with the ultimate goal to reach the exact solution of the Schrödinger equation, is known as the *correlation problem*. The first step may be taken by constructing linear combinations of a moderate number of determinants by including determinants corresponding to different electron configurations, as discussed in Sec. 11.6. This is the method of limited configuration interaction. The coefficients in the linear combination are determined by the variational method. In a refined version of the method, one writes down the explicit energy expression for the linear combination of determinants and determines the orbitals and the coefficients by varying this expression directly. This method is known as the *Multi-Configuration Self-Consistent Field* (MCSCF) method. A powerful variant is the so-called *Complete Active Space Self-Consistent Field* (CASSCF) method.

With modern computers, one may go far beyond the Hartree-Fock description and the description based upon configuration interaction with a moderate number of determinants. One may add more and more orbitals, add flexibiliy to the orbitals by means of built-in parameters, and then construct linear combinations of the many, many determinants defined by the orbitals. In this way it becomes possible to treat difficult systems with success and to account for many fine details of electronic structure.

It should be emphasized that these extensive methods often draw on the theory of the symmetric groups (permutation groups) and the unitary groups.

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[7] C. C. J. Roothaan, Rev. Mod. Phys. **23**, 69 (1951).

They involve advanced numerical methods and, finally, they are far from always formulated directly in terms of Slater determinants.

The correlation problem may also be attacked by other powerful methods. Especially noteworthy are the procedures based on *Many- Body Perturbation Theory* (MBPT) and the so-called *Coupled-Cluster* (CC) methods.

The methods we have discussed or referred to above are all so-called *ab initio* methods. By this we mean that the methods attempt to solve the many-electron Schrödinger equation as strictly as possible, using only the fundamental constants as well as the mass and charge of the nuclear particles from experiment. The many-electron wavefunction is at the forefront of the description. In the next chapter we shall discuss a method which instead focuses on the electron density. This method is also referred to as an *ab initio* method.

Supplementary Reading

The bibliography, entries [25], [28], [34], [39], [40].

Chapter 19

Density-Functional Theory

Contents

Following the discussion of Hartree–Fock theory in the previous chapter, we shall now turn to density-functional theory (DFT). As emphasized at the end of the previous chapter, this description of electronic structure focuses on the electron density rather than the wavefunction. It is essentially a ground-state theory, in the sense that it rests on the variational theorem (12.12) which only applies to the ground state of an atom or a molecule.[1]

To suspend the wavefunction is, of course, a radical undertaking. It is, however, well known that the energy of an N-electron system may be expressed in terms of the so-called two-electron density matrix. In the Hartree–Fock approximation, it may even be expressed in terms of the one-electron density matrix. The diagonal terms of this matrix give the electron density. Hence,

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[1] In systems with symmetry, the variational theorem may be applied to the lowest state of each symmetry. The same holds for density-functional theory.

the gap between Hartree–Fock theory and density-functional theory is smaller than it might at first be thought.

The common ground of Hartree–Fock theory and density-functional theory is the field of density matrices. The present chapter aims at putting this assertion in perspective. We begin therefore with a section on reduced density matrices and the role they play in determining the energy of an N-electron system.[2] Next, we consider the density matrices when the wavefunction is a single determinant, which is the Hartree–Fock case. We then proceed to density-functional theory and its justification, which rests on the so-called Hohenberg–Kohn theorem. In the final section we derive and discuss the Kohn–Sham equations which form the DFT basis for a self-consistent determination of the electron density.

19.1 Reduced Density Matrices

Having introduced the wavefunction $\Psi(\boldsymbol{r},t)$ in Sec. 3.1, we commented on its physical interpretation in Sec. 3.4. Assuming that the wavefunction was normalized to unity, we interpreted $\Psi^*(\boldsymbol{r},t)\Psi(\boldsymbol{r},t)$ as a probability density in position space. But we also underlined the fact, that far from all information about the quantum-mechanical state of the particle is contained in this quantity. We referred, in particular, to the linear momentum of the particle and contended that we need the full information contained in $\Psi(\boldsymbol{r},t)$ to make statistical predictions about the linear momentum. This point was explicitly illustrated in Secs. 6.2 and 6.3, with the wavefunction (6.29) as an example. It may also be well ilustrated by evaluating the expectation value of the Hamiltonian (3.16).

To conform to the notation of the previous sections, let us write $\varphi(\boldsymbol{r})$ for a single-particle spin-free wavefunction. (We suppress its possible dependence on time.) Let us also write the Hamiltonian as

$$\hat{h} = -\frac{1}{2}\nabla^2 + v(\boldsymbol{r}), \tag{19.1}$$

in atomic units. For an electron moving in the electrostatic field from K nuclei,

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[2] For a general discussion of reduced density matrices see, in particular:
K. Husimi, Proc. Phys. Math. Soc. Japan **22**, 264 (1940).
P.-O. Löwdin, Phys. Rev. **97**, 1474, 1490, 1509 (1955).
R. McWeeny, Rev. Mod. Phys. **32**, 335 (1960).

the form of $v(\boldsymbol{r})$ is determined by the last term in Eq. (18.3), i. e.,

$$v(\boldsymbol{r}) = -\sum_{g=1}^{K} \frac{Z_g}{r_g}. \tag{19.2}$$

But it may also contain contributions from, for instance, external electric fields. In what follows it is expedient to refer to $v(\boldsymbol{r})$ as the *external potential.*

For the expectation value of the Hamiltonian we get

$$\begin{aligned}\langle \hat{h} \rangle &= \int \varphi^*(\boldsymbol{r})(-\tfrac{1}{2}\nabla^2)\varphi(\boldsymbol{r})dv + \textstyle\int \varphi^*(\boldsymbol{r})v(\boldsymbol{r})\varphi(\boldsymbol{r})dv \\ &= \int \varphi^*(\boldsymbol{r})(-\tfrac{1}{2}\nabla^2)\varphi(\boldsymbol{r})dv + \textstyle\int v(\boldsymbol{r})\rho(\boldsymbol{r})dv,\end{aligned} \tag{19.3}$$

where

$$\rho(\boldsymbol{r}) = \varphi(\boldsymbol{r})\varphi^*(\boldsymbol{r}) \tag{19.4}$$

is the probability density in position space. We shall refer to it as the electron density.

To evaluate the expectation value of the external potential, it suffices to know the electron density $\rho(\boldsymbol{r})$. But this is not sufficient for evaluating the expectation value of the kinetic energy—which depends on the momentum operator. We need the wavefunction itself or, equivalently, the so-called *density matrix*

$$\rho(\boldsymbol{r}, \boldsymbol{r}') = \varphi(\boldsymbol{r})\varphi^*(\boldsymbol{r}'). \tag{19.5}$$

Like the electron density, it is bilinear in the wavefunction. Its diagonal elements, obtained by putting $(\boldsymbol{r} = \boldsymbol{r}')$, define the electron density.

$$\rho(\boldsymbol{r}, \boldsymbol{r}) = \rho(\boldsymbol{r}). \tag{19.6}$$

In terms of the density matrix, Eq. (19.3) may be written

$$\langle \hat{h} \rangle = \int [(-\tfrac{1}{2}\nabla^2)\rho(\boldsymbol{r}, \boldsymbol{r}')]_{\boldsymbol{r}'=\boldsymbol{r}} dv + \textstyle\int v(\boldsymbol{r})\rho(\boldsymbol{r})dv, \tag{19.7}$$

where we put $\boldsymbol{r}' = \boldsymbol{r}$ after operating with the kinetic-energy operator, but before completing the integration.

Let us now consider an N-electron system in a state described by the wavefunction $\Psi(x_1, x_2, \ldots, x_N)$. We shall derive reduced expressions for the expectation values of operators like

$$\hat{F} = \sum_{i=1}^{N} \hat{f}(x_i) \tag{19.8}$$

and

$$\hat{G} = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}{}' \hat{g}(x_i, x_j). \tag{19.9}$$

These are the kind of operators for which we evaluated matrix elements between Slater determinants in Sec. 16.3. Here, we consider the expectation values for a general N-electron wavefunction. Let us first treat the operator $\hat{F}$.

We begin by noting that each $\hat{f}(x_i)$ conributes equally to $\langle\Psi|\hat{F}|\Psi\rangle$. We have, for instance,

$$\begin{aligned}\int \Psi^*(x_1, x_2, \ldots, x_N)\hat{f}(x_2)\Psi(x_1, x_2, \ldots, x_N)dx_1 dx_2 \cdots dx_N \\ = \int \Psi^*(x_2, x_1, \ldots, x_N)\hat{f}(x_1)\Psi(x_2, x_1, \ldots, x_N)dx_1 dx_2 \cdots dx_N \\ = \int \Psi^*(x_1, x_2, \ldots, x_N)\hat{f}(x_1)\Psi(x_1, x_2, \ldots, x_N)dx_1 dx_2 \cdots dx_N.\end{aligned} \tag{19.10}$$

We have renumbered the coordinates over which we integrate, and next used that both Ψ and Ψ^* change sign under the interchange of particles 1 and 2. In all, we get

$$\begin{aligned}&\langle\Psi|\hat{F}|\Psi\rangle = \\ &\quad N\int \Psi^*(x_1, x_2, \ldots, x_N)\hat{f}(x_1)\Psi(x_1, x_2, \ldots, x_N)dx_1 dx_2 \cdots dx_N.\end{aligned} \tag{19.11}$$

Defining the so-called *reduced one-electron density matrix*

$$\gamma(x, x') = N\int \Psi(x, x_2, \ldots, x_N)\Psi^*(x', x_2, \ldots, x_N)dx_2 \cdots dx_N \tag{19.12}$$

allows us to write

$$\langle\Psi|\hat{F}|\Psi\rangle = \int [\hat{f}(x)\gamma(x, x')]_{x'=x}dx. \tag{19.13}$$

If $\hat{f}$ is independent of spin we may integrate over the spin variable to get

$$\langle\Psi|\hat{F}|\Psi\rangle = \int [\hat{f}(\boldsymbol{r})\rho(\boldsymbol{r}, \boldsymbol{r}')]_{\boldsymbol{r}'=\boldsymbol{r}}dv, \tag{19.14}$$

where

$$\rho(\boldsymbol{r}, \boldsymbol{r}') = \int [\gamma(x, x')]_{\varsigma'=\varsigma}d\varsigma \tag{19.15}$$

is the spinless one-electron density matrix. Its diagonal elements give the electron density $\rho(\boldsymbol{r})$, as in Eq. (19.6). We note that

$$\int \rho(\boldsymbol{r})dv = \int \gamma(x,x)dx = N. \tag{19.16}$$

The expectation value of the operator $\hat{G}$, Eq. (19.9), may similarly be written

$$\langle\Psi|\hat{G}|\Psi\rangle = \int\int [\hat{g}(x_1,x_2)\Gamma(x_1,x_2,x_1',x_2')]_{x_1'=x_1,x_2'=x_2}dx_1dx_2, \tag{19.17}$$

where

$$\Gamma(x_1,x_2,x_1',x_2') = \frac{N(N-1)}{2}\int\int \Psi(x_1,x_2,x_3\ldots,x_N)\Psi^*(x_1',x_2',x_3\ldots,x_N)dx_3\cdots dx_N \tag{19.18}$$

is the *reduced two-electron density matrix.* We shall only need the expression (19.17) when $\hat{g}(x_1,x_2) = 1/r_{12}$. $\hat{G}$ is then the operator representing the electron-electron repulsion energy,

$$\hat{G} = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}{}' \frac{1}{r_{12}}, \tag{19.19}$$

and the expression (19.17) simplifies to

$$\langle\Psi|\hat{G}|\Psi\rangle = \int\int \frac{1}{r_{12}}\rho_2(\boldsymbol{r}_1,\boldsymbol{r}_2)dv_1dv_2, \tag{19.20}$$

where

$$\rho_2(\boldsymbol{r}_1,\boldsymbol{r}_2) = \int\int \Gamma(x_1,x_2,x_1,x_2)d\varsigma_1d\varsigma_2. \tag{19.21}$$

The quantity $\rho_2(\boldsymbol{r}_1,\boldsymbol{r}_2)$ is the *two-electron density*. It is normalized to the number of electron pairs,

$$\int\int \rho_2(\boldsymbol{r}_1,\boldsymbol{r}_2)dv_1dv_2 = \int\int \Gamma(x_1,x_2,x_1,x_2)dx_1dx_2 = \frac{N(N-1)}{2}. \tag{19.22}$$

We note that

$$\int \Gamma(x_1,x_2,x_1',x_2)dx_2 = \frac{(N-1)}{2}\gamma(x_1,x_1') \tag{19.23}$$

and

$$\int \rho_2(\boldsymbol{r}_1, \boldsymbol{r}_2) dv_2 = \frac{(N-1)}{2} \rho(\boldsymbol{r}_1). \tag{19.24}$$

Collecting the above results, allows us to write the expectation value of the Hamiltonian (18.3) in terms of reduced density matrices. We rewrite the Hamiltonian as

$$\boxed{\begin{aligned} \widehat{H} &= \sum_{i=1}^{N} (-\frac{1}{2}\nabla_i^2) + \sum_{i=1}^{N} v(\boldsymbol{r}_i) + \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}{}' \frac{1}{r_{ij}}, \\ v(\boldsymbol{r}_i) &= -\sum_{g=1}^{K} \frac{Z_g}{r_{ig}}, \end{aligned}} \tag{19.25}$$

and get

$$\boxed{\begin{aligned} E = \langle \Psi | \widehat{H} | \Psi \rangle &= \int [(-\tfrac{1}{2}\nabla^2)\rho(\boldsymbol{r}, \boldsymbol{r}')]_{\boldsymbol{r}'=\boldsymbol{r}} dv + \int v(\boldsymbol{r})\rho(\boldsymbol{r}) dv \\ &+ \int\int \frac{1}{r_{12}} \rho_2(\boldsymbol{r}_1, \boldsymbol{r}_2) dv_1 dv_2. \end{aligned}} \tag{19.26}$$

This is a fundamental result. In deriving it, we have used relations like those of Eq. (19.10). We argued that these relations hold because Ψ is an antisymmetric wavefunction. It is, however, obvious that they also hold if Ψ is a symmetric wavefunction. Hence, the expression (19.26) does not distinguish between fermions and bosons.

19.2 Single Slater Determinant

It is instructive and of great interest to specify the one- and two-electron density matrices for the single Slater determinant (16.1). This may be done by drawing on the expressions (16.41), case c, and (16.46), case d. For the expectation values of the operators (19.8) and (19.9), those expressions give

$$\langle D | \hat{F} | D \rangle = \sum_{i=1}^{N} \langle \psi_i | \hat{f} | \psi_i \rangle \tag{19.27}$$

and

$$\langle D|\hat{G}|D\rangle = \frac{1}{2}\sum_{k=1}^{N}\sum_{l=1}^{N}\{\langle\psi_k\psi_l|\hat{g}|\psi_k\psi_l\rangle - \langle\psi_k\psi_l|\hat{g}|\psi_l\psi_k\rangle\} \tag{19.28}$$

We have included the mutually cancelling $k = l$ terms in the double sum.

Comparing the expressions (19.13) and (19.27) yields immediately

$$\gamma(x, x') = \sum_{i=1}^{N}\psi_i(x)\psi_i^*(x'). \tag{19.29}$$

If D is of the form (18.32), such that each spin-orbital may be written as $\varphi(\boldsymbol{r})$ times an α or a β spin function, the definition (19.15) gives

$$\rho(\boldsymbol{r}, \boldsymbol{r}') = \sum_{i=1}^{N}\varphi_i(\boldsymbol{r})\varphi_i^*(\boldsymbol{r}'), \tag{19.30}$$

and hence the following expression for the electron density

$$\rho(\boldsymbol{r}) = \sum_{i=1}^{N}\varphi_i(\boldsymbol{r})\varphi_i^*(\boldsymbol{r}). \tag{19.31}$$

Previously, we have used this expression on intuitive grounds as, for instance, in Eq. (4.77).

Next, a comparison between the expressions (19.17) and (19.28) yields

$$\begin{aligned}\Gamma(x_1, x_2, x_1', x_2') &= \frac{1}{2}\sum_{k=1}^{N}\sum_{l=1}^{N}[\psi_k(x_1)\psi_l(x_2)\psi_k^*(x_1')\psi_l^*(x_2') \\ &\qquad - \psi_k(x_1)\psi_l(x_2)\psi_l^*(x_1')\psi_k^*(x_2')] \\ &= \frac{1}{2}[\gamma(x_1, x_1')\gamma(x_2, x_2') - \gamma(x_1, x_2')\gamma(x_2, x_1')].\end{aligned} \tag{19.32}$$

The diagonal becomes

$$\Gamma(x_1, x_2, x_1, x_2) = \frac{1}{2}[\gamma(x_1, x_1)\gamma(x_2, x_2) - \gamma(x_1, x_2)\gamma(x_2, x_1)]. \tag{19.33}$$

Integration over the spin variables, as in Eq. (19.21), gives then

$$\rho_2(\boldsymbol{r}_1, \boldsymbol{r}_2) = \frac{1}{2}\rho(\boldsymbol{r}_1)\rho(\boldsymbol{r}_2) - \frac{1}{2}\int\int\gamma(x_1, x_2)\gamma(x_2, x_1)d\varsigma_1 d\varsigma_2. \tag{19.34}$$

Inserting the above results in (19.26) leads to the following expression for the energy of a single determinant

$$\boxed{\begin{aligned} E = \langle D|\widehat{H}|D\rangle = &\int [(-\tfrac{1}{2}\nabla^2)\rho(\boldsymbol{r},\boldsymbol{r}')]_{\boldsymbol{r}'=\boldsymbol{r}} dv + \int v(\boldsymbol{r})\rho(\boldsymbol{r})dv \\ &+\frac{1}{2}\int\int \frac{\rho(\boldsymbol{r}_1)\rho(\boldsymbol{r}_2)}{r_{12}}dv_1dv_2 - \frac{1}{2}\int\int \frac{\gamma(x_1,x_2)\gamma(x_2,x_1)}{r_{12}}dx_1dx_2. \end{aligned}} \tag{19.35}$$

Thus, the energy, E, of a single determinant can be evaluated, once we know the one-electron density matrix $\gamma(x_1, x_1')$. We say that E is a functional of $\gamma(x_1, x_1')$. It is consistent with this result that also the Hartree–Fock operator is determined by $\gamma(x_1, x_1')$, as we found at the end of Sec. 18.1.

When D is of the form (18.32), so that $\rho(\boldsymbol{r}, \boldsymbol{r}')$ may be written as in Eq. (19.30), the above expression becomes

$$\boxed{\begin{aligned} E = \langle D|\widehat{H}|D\rangle = &-\frac{1}{2}\sum_{i=1}^{N}\int \varphi_i^*(\boldsymbol{r})\nabla^2\varphi_i(\boldsymbol{r})dv + \int v(\boldsymbol{r})\rho(\boldsymbol{r})dv \\ &+\frac{1}{2}\int\int \frac{\rho(\boldsymbol{r}_1)\rho(\boldsymbol{r}_2)}{r_{12}}dv_1dv_2 - \frac{1}{2}\int\int \frac{\gamma(x_1,x_2)\gamma(x_2,x_1)}{r_{12}}dx_1dx_2. \end{aligned}} \tag{19.36}$$

Let us write Eqs. (19.35) and (19.36) as

$$E = T + E_{ne} + J + E_x. \tag{19.37}$$

In accordance with an earlier discussion, following Eq. (16.58), the various terms in this expression may be interpreted as follows: T is the kinetic energy of the N electrons. E_{ne} is the potential energy of the electrons in the external field (the field of the nuclei). J is the self-energy of the electron distribution $\rho(\boldsymbol{r})$. E_x is the exchange term. With reference to Eq. (16.58), we have that

$$\begin{aligned} J &= \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N} J'_{ij}, \\ E_x &= -\frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N} K'_{ij}. \end{aligned} \tag{19.38}$$

The form of E_{ne} in (19.35) and (19.36) is exactly the classical expression for the interaction of a continuous charge distribution with an external field. Similarly, J is the classical expression for a continuous charge distribution's interaction with itself. It amounts to the interaction of $N^2/2$ pairs. But since a point charge does not interact with itself, the correct number of interacting pairs is only $N(N-1)/2$. Thus, J contains a non-physical interaction of $N/2$ pairs. This self-interaction corresponds to the diagonal terms in the sums of Eq. (19.38). The diagonal terms in the first sum is cancelled by the diagonal terms in the second sum, because $J'_{ii} = K'_{ii}$. (This is the last relation in Eq. (16.56).) An important part of the exchange term, E_x, has therefore the mission of removing the self-interaction. The remainder of the exchange term reduces the repulsion energy between electrons with parallel spins, relative to the interaction between those with opposite spin (an effect of the antisymmetry built into a determinantal wavefunction).

These considerations will be suggestive for a rewriting of the general expression (19.26) in the following sections.

19.3 The Hohenberg-Kohn Theorem

The expression (19.26) shows that the expectation value of $\widehat{H}$ for an N-electron system may be evaluated without knowing the full N-electron wavefunction. What we need is an explicit expression for the two-electron density matrix. For a single determinant, Eq. (19.35) shows that an explicit expression for the one-electron density matrix will do.

In 1964, the American physicists Pierre Hohenberg and Walter Kohn showed the remarkable theorem that the ground-state energy of an N-electron system is a functional of the one-electron density $\rho(\boldsymbol{r})$.[3] They turned this observation into a variational theorem for the ground-state energy in terms of the density instead of the many-electron wavefunction.

To prove the Hohenberg-Kohn theorem, construct the N-electron Hamiltonian (19.25) for two different external potentials, $v(\boldsymbol{r})$ and $v'(\boldsymbol{r})$, differing in more than just an additive constant. We call the two Hamiltonians $\widehat{H}$ and $\widehat{H}'$, and note that

$$\widehat{H} - \widehat{H}' = \sum_{i=1}^{N} [v(\boldsymbol{r}_i) - v'(\boldsymbol{r}_i)]. \tag{19.39}$$

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[3] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B 864 (1964).

We assume that the electronic ground states corresponding to $\widehat{H}$ and $\widehat{H}'$ are non-degenerate. We denote the respective normalized ground-state wavefunctions by Ψ and Ψ', and the corresponding ground-state energies by E and E'. Thus, we have

$$\widehat{H}\Psi = E\psi, \qquad \widehat{H}'\Psi' = E'\psi'. \tag{19.40}$$

Expressions for the one-electron densities, $\rho(\boldsymbol{r})$ and $\rho'(\boldsymbol{r})$, can be easily written down by exploiting Eqs. (19.12), (19.15) and (19.6). We shall now show that these two densities cannot be identical.

To this purpose, we invoke the variational theorem (12.12) and write

$$\langle\Psi|\widehat{H}'|\Psi\rangle > E', \qquad \langle\Psi'|\widehat{H}|\Psi'\rangle > E. \tag{19.41}$$

We have used that Ψ' is an approximate wavefunction with respect to $\widehat{H}$ and, conversely, that Ψ is an approximate wavefunction with respect to $\widehat{H}'$. From Eq. (19.40) we also get

$$\langle\Psi|\widehat{H}|\Psi\rangle = E, \qquad \langle\Psi'|\widehat{H}'|\Psi'\rangle = E'. \tag{19.42}$$

By combining the four relations in (19.41) and (19.42) we get

$$\langle\Psi|\widehat{H}' - \widehat{H}|\Psi\rangle + \langle\Psi'|\widehat{H} - \widehat{H}'|\Psi'\rangle > 0, \tag{19.43}$$

and hence, by exploiting Eq. (19.39),

$$\int [v'(\boldsymbol{r}) - v(\boldsymbol{r})]\rho(\boldsymbol{r})dv + \int [v(\boldsymbol{r}) - v'(\boldsymbol{r})]\rho'(\boldsymbol{r})dv > 0. \tag{19.44}$$

Putting $\rho'(\boldsymbol{r}) = \rho(\boldsymbol{r})$ makes the left-hand side of this relation zero. The relation is then self-contradictory, and we conclude that $\rho(\boldsymbol{r})$ and $\rho'(\boldsymbol{r})$ cannot be identical when $v(\boldsymbol{r})$ and $v'(\boldsymbol{r})$ are different, in accordance with what we claimed above.

For each $v(\boldsymbol{r})$, there is a $\rho(\boldsymbol{r})$ satisfying the condition

$$\int \rho(\boldsymbol{r})dv = N. \tag{19.45}$$

Allowing for all types of external potentials, not just potential fields from nuclei, it is reasonable to assume that the relation $v(\boldsymbol{r}) \rightarrow \rho(\boldsymbol{r})$ covers all smooth densities satisfying Eq. (19.45). This assumption has been shown to be correct under quite general conditions. Hence, $\rho(\boldsymbol{r})$ determines $v(\boldsymbol{r})$. But when $v(\boldsymbol{r})$ is known, as in (19.25), then so is the N-electron Hamiltonian $\widehat{H}$. Solving the Schrödinger equation gives us the ground-state wavefunction Ψ. Degeneracies may occur, and may be dealt with, but we shall assume that the ground state is non-degenerate. Knowing Ψ allows us finally to evaluate the ground-state energy E and cast it in the form (19.26). Thus, we may write

$$E = E[\rho], \tag{19.46}$$

and express this relation by saying that E is a functional of ρ. This is the *Hohenberg-Kohn theorem.*

Let us now settle on some fixed external potential. We know then, from the variational theorem (12.12), that $\langle\Psi|\widehat{H}|\Psi\rangle$ is a minimum for the exact ground-state wavefunction. Hence, we conclude that $\delta E[\rho]$ vanishes when we vary ρ about the exact ρ, while keeping the external potential fixed. $E[\rho]$ is a minimum with respect to such variations. This is the variational theorem associated with the Hohenberg-Kohn theorem.

The Hohenberg-Kohn theorem does not give us a prescription for evaluating the functional $E[\rho]$. An appropriate transformation of the expression (19.26) allows us, however, to give explicit expressions for important parts of $E[\rho]$, as we shall see in the next section.

19.4 The Kohn–Sham Equations

Let us, in analogy with Eq. (19.34), write the two-particle density in Eq. (19.26) as

$$\rho_2(\boldsymbol{r}_1,\boldsymbol{r}_2) = \frac{1}{2}\Big(\rho(\boldsymbol{r}_1)\rho(\boldsymbol{r}_2) + C_2(\boldsymbol{r}_1,\boldsymbol{r}_2)\Big), \tag{19.47}$$

where $C_2(\boldsymbol{r}_1,\boldsymbol{r}_2)$ is a two-electron *correlation function*. Eq. (19.26) becomes then

$$\begin{aligned} E[\rho] = &\int [(-\tfrac{1}{2}\nabla^2)\rho(\boldsymbol{r},\boldsymbol{r}')]_{\boldsymbol{r}'=\boldsymbol{r}}dv + \int v(\boldsymbol{r})\rho(\boldsymbol{r})dv \\ &+ \frac{1}{2}\int\int \frac{\rho(\boldsymbol{r}_1)\rho(\boldsymbol{r}_2)}{r_{12}}dv_1dv_2 + \frac{1}{2}\int\int \frac{C_2(\boldsymbol{r}_1,\boldsymbol{r}_2)}{r_{12}}dv_1dv_2. \end{aligned} \tag{19.48}$$

As we pointed out in connection with Eq. (19.26), the look of this expression is the same for fermions and bosons. The fact that electrons are fermions is therefore buried in the form of $\rho(\boldsymbol{r},\boldsymbol{r}')$ and $C_2(\boldsymbol{r}_1,\boldsymbol{r}_2)$.

As to the first term in (19.48), it was suggested by Kohn and Sham[4] that it be expressed in a form similar to the first term in Eq. (19.36), plus a remainder. Furthermore, they suggested that the remainder be combined with the last term in (19.48) to give a new term, E_{xc}, denoted the *exchange-correlation energy*. The expression (19.48) is thus transformed into

$$\boxed{\begin{aligned} E[\rho] = &-\frac{1}{2}\sum_{i=1}^{N}\int \varphi_i^*(\boldsymbol{r})\nabla^2\varphi_i(\boldsymbol{r})dv + \int v(\boldsymbol{r})\rho(\boldsymbol{r})dv \\ &+\frac{1}{2}\int\int \frac{\rho(\boldsymbol{r}_1)\rho(\boldsymbol{r}_2)}{r_{12}}dv_1dv_2 + E_{xc}[\rho]. \end{aligned}} \tag{19.49}$$

Obviously, there is no simple expression for $E_{xc}[\rho]$.

The orbitals $\varphi_1(\boldsymbol{r}), \varphi_2(\boldsymbol{r}), \ldots, \varphi_N(\boldsymbol{r})$ are the *Kohn–Sham orbitals*. With the spin dependence added through α and β spin functions in the usual way, they are supposed to form an orthonormal set. By the expression (19.30), they define a fermion density matrix for a Slater determinant of the form (18.32). This density matrix is, however, not supposed to be the correct density matrix for our N-electron system. Nevertheless, it is required that its diagonal elements be correct, so that

$$\rho(\boldsymbol{r}) = \sum_{i=1}^{N}\varphi_i(\boldsymbol{r})\varphi_i^*(\boldsymbol{r}). \tag{19.50}$$

is the exact one-electron density.

There are many ways of representing $\rho(\boldsymbol{r})$ in the form (19.50). But we now require that the orbitals $\varphi_1(\boldsymbol{r}), \varphi_2(\boldsymbol{r}), \ldots, \varphi_N(\boldsymbol{r})$ be self-consistent field orbitals, satisfying a one-electron equation obtained by varying the expression (19.49).

By varying $\rho(\boldsymbol{r})$ about the exact $\rho(\boldsymbol{r})$, we get

$$\delta E[\rho] = \int \frac{\delta E[\rho]}{\delta\rho(\boldsymbol{r})}\delta\rho(\boldsymbol{r})dv, \tag{19.51}$$

where $\delta E[\rho]/\delta\rho(\boldsymbol{r})$ is called the functional derivative of $E[\rho]$. We require that $\delta E[\rho]$ be zero for all variations that preserve the number of particles, that is, for all variations that satisfy

$$\int \delta\rho(\boldsymbol{r})dv = 0, \tag{19.52}$$

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[4] W. Kohn and L. J. Sham, Phys. Rev. **140**, A 1133 (1965).

which is obtained from Eq. (19.45). It is obvious that $\delta E[\rho]$ will be zero for any $\delta\rho(\boldsymbol{r})$ that satisfies Eq. (19.52) if $\delta E[\rho]/\delta\rho(\boldsymbol{r})$ is a constant. If $\delta E[\rho]/\delta\rho(\boldsymbol{r})$ is some non-constant function, then $\delta E[\rho]$ might well be zero for some variation $\delta\rho(\boldsymbol{r})$. It would, however, be easy to find a neighboring $\delta\rho(\boldsymbol{r})$ that would make $\delta E[\rho]$ different from zero. Hence, we conclude that

$$\frac{\delta E[\rho]}{\delta\rho(\boldsymbol{r})} = \mu, \tag{19.53}$$

where μ is a constant. Adapting a thermodynamic terminology, we call μ the *chemical potential*.

To proceed, we invoke Eq. (19.50) and write

$$\delta\rho(\boldsymbol{r}) = \sum_{i=1}^{N} \varphi_i(\boldsymbol{r})\delta\varphi_i^*(\boldsymbol{r}) + \sum_{i=1}^{N} \varphi_i^*(\boldsymbol{r})\delta\varphi_i(\boldsymbol{r}). \tag{19.54}$$

We then go through a number of steps similar to those of Sec. 18.1, and end up with a set of equations that parallel the Hartree–Fock equations (18.28). To write them down, we note that Eq. (18.28) formally derives from the expression (18.12) by keeping only the term $\langle\delta\psi_i|\hat{F}|\psi_i\rangle$. This amounts to putting

$$\delta\rho(\boldsymbol{r}) = \varphi_i(\boldsymbol{r})\delta\varphi_i^*(\boldsymbol{r}). \tag{19.55}$$

With this $\delta\rho(\boldsymbol{r})$, Eq. (19.49) leads to the following expression for $\delta E[\rho]$,

$$\delta E[\rho] = \int \Big\{ -\tfrac{1}{2}\nabla^2 + v(\boldsymbol{r}) + v_C(\boldsymbol{r}) + v_{xc}(\boldsymbol{r}) \Big\} \varphi_i(\boldsymbol{r})\delta\varphi_i^*(\boldsymbol{r}), \tag{19.56}$$

where

$$v_C(\boldsymbol{r}_1) = \int \frac{\rho(\boldsymbol{r}_2)}{r_{12}} dv_2, \tag{19.57}$$

and

$$v_{xc}(\boldsymbol{r}) = \frac{\delta E_{xc}[\rho]}{\delta\rho(\boldsymbol{r})}. \tag{19.58}$$

$v_C(\boldsymbol{r})$ is the *Coulomb potential*. It is given by the classical expression for the electrostatic potential at $\boldsymbol{r}$ due to the electron distribution $\rho(\boldsymbol{r})$. Strictly speaking, the expression should be preceded by a minus sign, because the electron is negatively charged. It is, however, convenient to stick to the present sign convention. Since $v_{xc}(\boldsymbol{r})$ derives from the exchange-correlation energy, it is called the *exchange-correlation potential*.

We now put the expression (19.56) equal to zero. Adding the orthonormality conditions for the orbitals, and performing a unitary transformation similar to that of Eq. (18.27), we obtain the Kohn–Sham equations

$$\boxed{\Big\{-\tfrac{1}{2}\nabla^2 + v(\boldsymbol{r}) + v_C(\boldsymbol{r}) + v_{xc}(\boldsymbol{r})\Big\}\varphi_i(\boldsymbol{r}) = \epsilon_i\varphi_i(\boldsymbol{r})} \tag{19.59}$$

As discussed in connection with Eq. 18.10, the Hartree–Fock equations are complicated by the fact that the Hartree–Fock operator contains exchange operators that represent non-local potentials. The Kohn–Sham equations are much simpler in this respect, since all potentials that occur in (19.59) are local. The problem is, of course, that since no simple expression exists for $E_{xc}[\rho]$, no simple expression exists for $v_{xc}(\boldsymbol{r})$ either. Apart from this, the Kohn–Sham equations are solved in a self-consistent way by methods similar to those used for the Hartree–Fock equations. In particular, extensive use is made of basis-set expansions of the orbitals.

To get exact results from Hartree–Fock theory, it is necessary to add a significant amount of configuration interaction. In contrast to this situation, the results obtained by solving the Kohn–Sham equations are supposed to be exact, that is, one obtains the correct ground-state energy and the correct ground-state density by solving these equations. But the form of $E_{xc}[\rho]$, and hence of $v_{xc}(\boldsymbol{r})$ is needed. Today, quite elaborate expressions for $E_{xc}[\rho]$ have been determined, by combining general insight in electronic-structure theory with careful parametrization based on experimental results for selected atoms and molecules.

Current expressions for $E_{xc}[\rho]$ are frequently presented in the form

$$E_{xc}[\rho] = \int \epsilon_{xc}[\rho]\rho(\boldsymbol{r})dv, \tag{19.60}$$

where $\epsilon_{xc}[\rho]$ is referred to as the exchange-correlation energy per electron. It is usually represented as a function containing various powers of $\rho(\boldsymbol{r})$ and $\nabla\rho(\boldsymbol{r})$. Often, it contains separate contributions for densities associated with α and β spin, so that non-degenerate states may also be dealt with.

Supplementary Reading

The bibliography, entries [34], [39], [41].

Appendix A

Complex Numbers and Quantum Mechanics

The time-dependent Schrödinger equation (3.1) contains the imaginary unit i, and so does the time-dependent wavefunction of a stationary state, Eq. (3.5). The imaginary unit also appears in the Schrödinger operators of Sec. 3.3. In addition, coefficients in superpositions like that of Eqs. (4.88) and (4.89) will generally be complex. Thus, complex numbers are omnipresent in quantum mechanics.

Complex numbers have also an important role to play in the classical sciences, for instance in the description of wave motion and devises based on alternating electric currents. But in all such cases one ends up by taking the real or imaginary part of a complex number, and complex numbers may be avoided altogether, at the expense of elegance of description.

Not so in quantum mechanics. It is true, of course, that probabilities must always be real, and so must the magnitude of a quantity that can be measured. But the probability amplitudes that determine these quantities cannot be restricted to the domain of the real numbers. Accordingly, one often meets complex wavefunctions in the applications of quantum mechanics.

We must, of course, refer the reader to the mathematical text books if he or she feels uncomfortable with complex numbers. Most complex wavefunctions that we encounter in this text are, however, quite simple and donot go beyond the complex exponential function

$$e^{w} = e^{u+iv} = e^{u}e^{iv}. \tag{A.1}$$

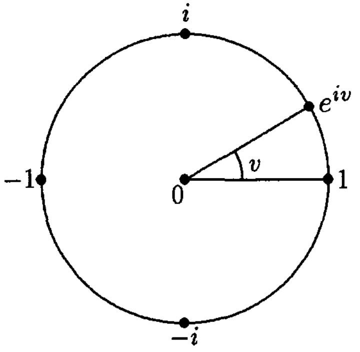

Figure A.1: The unit circle in the complex plane.

Here, $w = u + iv$ is a general complex variable. Its real part is u and its imaginary part v. Both u and v are real and $i^2 = -1$. The complex conjugate of w is $w^* = u - iv$, and the magnitude of w is

$$|w| = \sqrt{w^* w} = \sqrt{u^2 + v^2}. \tag{A.2}$$

The magnitude of the complex number e^w defined by Eq. (A.1) is seen to be

$$|e^w| = \sqrt{e^{u-iv} e^{u+iv}} = \sqrt{e^{2u}} = e^u. \tag{A.3}$$

We also refer to e^u as the modulus of the complex number e^w. v is called its argument.

By comparing the Taylor expansions of e^{iv} and e^{-iv} with the Taylor expansions of $\cos v$ and $\sin v$, one finds that

$$\begin{aligned} e^{iv} &= \cos v + i \sin v, \\ e^{-iv} &= \cos v - i \sin v. \end{aligned} \tag{A.4}$$

Combining these equations gives us *Euler's relations*,

$$\begin{aligned} \cos v &= \frac{1}{2}\left(e^{iv} + e^{-iv}\right), \\ \sin v &= \frac{1}{2i}\left(e^{iv} - e^{-iv}\right). \end{aligned} \tag{A.5}$$

The first of the expressions (A.4) shows that the complex number $e^u e^{iv}$ lies on the circle of radius e^u, centered on the origin of the complex plane, the argument v being the angle measured on this circle from the positive real axis. Clearly, the argument is only determined modulo 2π. Hence,

$$e^{i(v+2n\pi)} = e^{iv}, \qquad n = 0, \pm 1, \pm 2, \ldots \tag{A.6}$$

The complex exponential function (A.1) is consequently periodic with the period $2\pi i$.

The values of the function e^{iv} all lie on the unit circle in the complex plane. Note, in particular, the following special values

$$\begin{aligned} e^{\pm 2\pi i} &= e^0 = 1, \\ e^{\pm \pi i} &= -1, \\ e^{\pi i/2} &= i, \\ e^{-\pi i/2} &= -i. \end{aligned} \tag{A.7}$$

Appendix B

Atomic Units

B.1 The International System of Units (SI)

The following are excerpts from a manual prepared by the International Union of Pure and Applied Chemistry (IUPAC).[1]

> By convention physical quantities are organized in a dimensional system built upon seven *base quantities*, each of which is regarded as having its own dimension. These base quantities and the symbols used to denote them are as follows.
>
> | Physical quantity | Symbol for quantity |
> |---|---|
> | length | l |
> | mass | m |
> | time | t |
> | electric current | I |
> | thermodynamic temperature | T |
> | amount of substance | n |
> | luminous intensity | I_v |
>
> All other physical quantities are called *derived quantities* and are regarded as having dimensions algebraically derived from the seven base quantities by multiplication and division.
>
> *Example*:
> dimension of (energy) = dimension of (mass × length^2 × time^{-2}).

---

[1] I. Mills, T. Cvitas, K. Homann, N. Kallay, and K. Kuchitsu, *Quantities, Units and Symbols in Physical Chemistry*, Blackwell, London, 1988, Secs. 1.2 and 3.1.

> The International System of units (SI) was adopted by the 11th General Conference on Weights and Measures (CGPM) in 1960. It is a coherent system of units built from seven *SI base units*, one for each of the seven dimensionally independent base quantities: they are the metre, kilogram, second, ampere, kelvin, mole, and candela, for the dimensions length, mass, time, electric current, thermodynamic temperature, amount of substance, and luminous intensity, respectively ... The *SI derived units* are expressed as products of powers of the base units ...
>
> It is recommended that only SI units be used in science and technology (with SI prefixes where appropriate). Where there are special reasons for making an exception to this rule, it is recommended always to define the units in terms of SI units.

On the background of these excerpts, we shall now introduce an alternative set of units which is more practical in most quantum-chemical work.

B.2 Atomic Units

The Schrödinger equation for the electron in a hydrogen atom (with infinitely heavy nuclear mass) is

$$\left(-\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}\right)\psi = E\psi, \tag{B.1}$$

cf. Chapter 8. m_e is the mass of the electron,

$$m_e = 9.10938 \times 10^{-31}\text{kg}, \tag{B.2}$$

e is the elementary electric charge,

$$e = 1.60218 \times 10^{-19}\text{C}, \tag{B.3}$$

$\hbar$ is Planck's constant (the quantum of action) divided by 2π,

$$\hbar = 1.05457 \times 10^{-34}\text{J s}, \tag{B.4}$$

and $4\pi\varepsilon_0$ is 4π times ε_0, the so-called permittivity of vacuum,

$$4\pi\varepsilon_0 = 1.11265 \times 10^{-10}\text{F m}^{-1}. \tag{B.5}$$

We also list the Bohr radius,

$$a_0 = \frac{\hbar^2}{m_e}\frac{4\pi\varepsilon_0}{e^2} = 0.52918 \times 10^{-10}\text{m}. \tag{B.6}$$

The SI values of these physical quantities are obviously awkward to work with because of the large negative powers of 10, and hence it is natural to choose new base units instead of the meter, the kilogram, the second, and the ampere.

We choose these base units such that the values of the four dimensionally independent quantities m_e, e, $\hbar$, and $4\pi\varepsilon_0$ all become equal to 1. Eq. (B.6) then shows that the value of a_0 also becomes 1. The resulting system of units is called *atomic units*.

It is not necessary to choose an explicit set of four quantities as base quantities. Some possible choices are: (mass, charge, action, permittivity), (mass, charge, action, length), and (mass, charge, length, energy). In accordance with this, we don't attach specific names to the various units. We simply talk about the au of mass, the au of charge, the au of action, etc. Exceptions are the au of length, which is also called the bohr, and the au of energy, which is also called the hartree.

Thus we write:

$m_e = 1$ au of mass,
$e = 1$ au of charge,
$\hbar = 1$ au of action,
$4\pi\varepsilon_0 = 1$ au of permittivity,
$a_0 = 1$ au of length $= 1$ bohr,
$E_0 = -1/2$ au of energy $= -1/2$ hartree,

where E_0 defines the ground state solution of Eq. (B.1),

$$E_0 = -\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \frac{m_e}{2\hbar^2}. \tag{B.7}$$

It is even quite common practice simply to write au, without an accompanying qualifier. In the spirit of the IUPAC recommendations this is certainly bad practice.

In defense of such practice, we may take the point of view that all physical quantities involved may be considered to have the same dimension, and hence that only one unit, au, is needed. To do so is, of course, quite heretical, but it is the kind of sin that many scientists commit. After all, one may always refer to the words *by convention* in the opening remarks of Sec. (B.1). In atomic units, the numerical values of atomic and molecular quantities are freed of the annoying large negative powers of ten. In writing equations, a further simplification is achieved if it is assumed that all quantities are actually measured in atomic units. For then we need no longer write the quantities of value 1 explicitly. Thus, the Schrödinger equation (B.1) may be written

$$\left(-\frac{1}{2}\nabla^2 - \frac{1}{r}\right)\psi = E\psi. \tag{B.8}$$

By solving this equation, we automatically get the energies in hartrees and the distances in bohrs. If we so desire, we may then convert the results to SI units via Eq. (B.6) which shows that

$$1 \text{ bohr} = 0.529177 \times 10^{-10}\text{m}, \tag{B.9}$$

and via the following definition of the so-called *hartree energy* E_h,

$$E_h = -2E_0 = \left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \frac{m_e}{\hbar^2} = 4.35975 \times 10^{-18}\text{J}, \tag{B.10}$$

which shows that

$$1 \text{ hartree} = 4.35975 \times 10^{-18}\text{J}. \tag{B.11}$$

The conversion of other au values to SI values is easily accomplished by referring to a typical combination of fundamental constants. Thus it follows from Eq. (2.59) in the form

$$p_n = \frac{Z\hbar}{na_0}, \tag{B.12}$$

that the electron in a hydrogen atom (with infinitely heavy nuclear mass), moving in the first classical Bohr orbit, has a momentum of 1 au of momentum and a velocity of 1 au of velocity. The expression for the velocity is obtained from Eq. (B.12) by dividing by m_e, and thus we get ($Z = 1$ and $n = 1$)

$$\begin{aligned} 1 \text{ au of velocity} &= \frac{1.05457 \times 10^{-34}\text{J s}}{(9.10939 \times 10^{-31}\text{kg}) \times (0.529177 \times 10^{-10}\text{m})} \\ &= 2.18768 \times 10^{6}\text{m s}^{-1}. \end{aligned} \tag{B.13}$$

It is also easy to derive, from the content of Sec. 2.5, that the time of revolution in the first Bohr orbit is given by

$$t_1 = 2\pi\left(\frac{4\pi\varepsilon_0}{e^2}\right)^2 \frac{\hbar^3}{m_e} = 2\pi \times 2.41888 \times 10^{-17}\text{s}. \tag{B.14}$$

Hence,

$$1 \text{ au of time} = 2.41888 \times 10^{-17}\text{s}. \tag{B.15}$$

By referring to the so-called fine-structure constant,

$$\alpha = \frac{e^2}{4\pi\varepsilon_0}\frac{1}{c\hbar} = 7.29735 \times 10^{-3} = \frac{1}{137.036}, \tag{B.16}$$

we also find that c, the speed of light, equals 137.036 au.

Appendix C

Curvilinear Coordinate Systems

The transition from a set of Cartesian coordinates (x, y, z) to a set of *curvilinear coordinates* (q_1, q_2, q_3) is defined by three continuously differentiable transformation equations,

$$x = x(q_1, q_2, q_3), \quad y = y(q_1, q_2, q_3), \quad z = z(q_1, q_2, q_3) \tag{C.1}$$

with inverses,

$$q_1 = q_1(x, y, z), \quad q_2 = q_2(x, y, z), \quad q_3 = q_3(x, y, z). \tag{C.2}$$

By this transformation, a point P in space may be equivalently labeled by its Cartesian coordinates (x, y, z) and its curvilinear coordinates (q_1, q_2, q_3).

If we move away from the point P to an adjacent point P', both sets of coordinates undergo infinitesimal changes. These changes are connected by the equations

$$\begin{pmatrix} dx \\ dy \\ dz \end{pmatrix} = \begin{pmatrix} \frac{\partial x}{\partial q_1} & \frac{\partial x}{\partial q_2} & \frac{\partial x}{\partial q_3} \\ \frac{\partial y}{\partial q_1} & \frac{\partial y}{\partial q_2} & \frac{\partial y}{\partial q_3} \\ \frac{\partial z}{\partial q_1} & \frac{\partial z}{\partial q_2} & \frac{\partial z}{\partial q_3} \end{pmatrix} \begin{pmatrix} dq_1 \\ dq_2 \\ dq_3 \end{pmatrix} \tag{C.3}$$

where all derivatives must be evaluated at the point P.

The distance, ds, between P and P' is called the line element. It is given by the quadratic differential form

$$ds^2 = dx^2 + dy^2 + dz^2 = \sum_{i=1}^{3} \sum_{j=1}^{3} g_{ij} dq_i dq_j \tag{C.4}$$

where

$$g_{ij} = \frac{\partial x}{\partial q_i}\frac{\partial x}{\partial q_j} + \frac{\partial y}{\partial q_i}\frac{\partial y}{\partial q_j} + \frac{\partial z}{\partial q_i}\frac{\partial z}{\partial q_j} \tag{C.5}$$

The functions $g_{ij}(q_1, q_2, q_3)$ define the components of the so-called *metric tensor*.

We note that g_{ij} is the scalar product between the two vectors, $\mathbf{t}_i$ and $\mathbf{t}_j$, defined by the ith and jth columns of the above matrix. Thus,

$$\mathbf{t}_i = \left(\frac{\partial x}{\partial q_i}, \frac{\partial y}{\partial q_i}, \frac{\partial z}{\partial q_i}\right), \qquad i = 1, 2, 3. \tag{C.6}$$

We may consider these vectors to be centered at the point P. They give the directions to the neighboring point obtained when only one of the q-coordinates is varied. From Eq. (C.3) we get for instance, that $(dq_1, dq_2, dq_3) = (dq, 0, 0)$ implies that $d\mathbf{r} = (dx, dy, dz) = \mathbf{t}_1 dq$. Thus, we may consider $\mathbf{t}_1$, $\mathbf{t}_2$ and $\mathbf{t}_3$ as a set of local basis vectors centered at P. Obviously, it will simplify matters if these vectors are mutually orthogonal. For this to be the case we must have that

$$\boxed{g_{ij} = \mathbf{t}_i \cdot \mathbf{t}_j = 0 \qquad \text{if } i \neq j} \tag{C.7}$$

The curvilinear coordinate system is then said to be *orthogonal.* We shall restrict ourselves to this case in the following. The determinant, g, of the metric tensor is then

$$g = g_{11}g_{22}g_{33}. \tag{C.8}$$

The length of the vector $\mathbf{t}_i$ is $\sqrt{g_{ii}}$, and the volume spanned by the three orthogonal $\mathbf{t}$-vectors is accordingly equal to $\sqrt{g}$. The volume element, dv, at the point P is therefore

$$dv = dxdydz = \sqrt{g}dq_1dq_2dq_3. \tag{C.9}$$

It is also easy to see that $\sqrt{g}$, apart from a possible minus sign, is the value of the determinant associated with the transformation matrix of Eq. (C.3), the so-called *Jacobian.* To see this, multiply the said matrix with its transpose and use the orthogonality relation (C.7) to show that the product matrix has the determinant g. Use finally that a matrix and its transpose have the same determinant.

We have now found the expression for the volume element in orthogonal curvilinear coordinates. Further analysis leads to expressions for other geometrical quantities as well. One finds, in particular, that the Laplacian of a function u is expressed as follows

$$\begin{aligned}\nabla^2 u &\equiv \frac{\partial^2 u}{\partial x^2}+\frac{\partial^2 u}{\partial y^2}+\frac{\partial^2 u}{\partial z^2}\\ &= \sqrt{\frac{1}{g}}\left[\frac{\partial}{\partial q_1}\left(\frac{\sqrt{g}}{g_{11}}\frac{\partial u}{\partial q_1}\right)+\frac{\partial}{\partial q_2}\left(\frac{\sqrt{g}}{g_{22}}\frac{\partial u}{\partial q_2}\right)+\frac{\partial}{\partial q_3}\left(\frac{\sqrt{g}}{g_{33}}\frac{\partial u}{\partial q_3}\right)\right].\end{aligned} \tag{C.10}$$

With this result at our disposal, we may express the Schrödinger equation and other partial differential equations containing the Laplacian in a variety of useful coordinate systems.

For spherical polar coordinates (Sec. 8.2) we have that

$$\left\{\begin{array}{lll} x &=& r\sin\theta\cos\phi,\\ y &=& r\sin\theta\sin\phi,\\ z &=& r\cos\theta.\end{array}\right. \tag{C.11}$$

Hence, we find,

$$\begin{pmatrix} dx\\ dy\\ dz\end{pmatrix} = \begin{pmatrix} \sin\theta\cos\phi & r\cos\theta\cos\phi & -r\sin\theta\sin\phi\\ \sin\theta\sin\phi & r\cos\theta\sin\phi & r\sin\theta\cos\phi\\ \cos\theta & -r\sin\theta & 0\end{pmatrix}\begin{pmatrix} dr\\ d\theta\\ d\phi\end{pmatrix}. \tag{C.12}$$

By evaluating the elements of the metric tensor from the expression (C.5) we check that the orthogonality conditions (C.7) are satisfied and obtain

$$g_{rr}=1, \qquad g_{\theta\theta}=r^2, \qquad g_{\phi\phi}=r^2\sin^2\theta. \tag{C.13}$$

Hence, we get

$$\boxed{ds^2 = dr^2 + r^2 d\theta^2 + r^2\sin^2\theta\, d\phi^2}\,, \tag{C.14}$$

$$\boxed{dv = r^2\sin\theta\, dr d\theta d\phi}\,, \tag{C.15}$$

and

$$\boxed{\nabla^2 u = \frac{\partial^2 u}{\partial r^2}+\frac{2}{r}\frac{\partial u}{\partial r}+\frac{1}{r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial u}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 u}{\partial\phi^2}\right]}\,. \tag{C.16}$$

It is also of importance to know how the gradient of a function may be expressed in curvilinear coordinates. The gradient of u is defined as

$$\nabla u = \left(\frac{\partial u}{\partial x}, \frac{\partial u}{\partial y}, \frac{\partial u}{\partial z}\right). \tag{C.17}$$

To express it in the new coordinates, we simply use the well-known chain rule for partial differentiation and get

$$\left(\frac{\partial u}{\partial x}, \frac{\partial u}{\partial y}, \frac{\partial u}{\partial z}\right) = \left(\frac{\partial u}{\partial q_1}, \frac{\partial u}{\partial q_2}, \frac{\partial u}{\partial q_3}\right) \begin{pmatrix} \frac{\partial q_1}{\partial x} & \frac{\partial q_1}{\partial y} & \frac{\partial q_1}{\partial z} \\ \frac{\partial q_2}{\partial x} & \frac{\partial q_2}{\partial y} & \frac{\partial q_2}{\partial z} \\ \frac{\partial q_3}{\partial x} & \frac{\partial q_3}{\partial y} & \frac{\partial q_3}{\partial z} \end{pmatrix}. \tag{C.18}$$

To evaluate the matrix in Eq. (C.18) let us, as a very special case, put u equal to x and subsequently use that $\partial x/\partial x = 1$, $\partial x/\partial y = 0$, $\partial x/\partial z = 0$. Eq. (C.18) becomes then

$$(1, 0, 0) = \left(\frac{\partial x}{\partial q_1}, \frac{\partial x}{\partial q_2}, \frac{\partial x}{\partial q_3}\right) \begin{pmatrix} \frac{\partial q_1}{\partial x} & \frac{\partial q_1}{\partial y} & \frac{\partial q_1}{\partial z} \\ \frac{\partial q_2}{\partial x} & \frac{\partial q_2}{\partial y} & \frac{\partial q_2}{\partial z} \\ \frac{\partial q_3}{\partial x} & \frac{\partial q_3}{\partial y} & \frac{\partial q_3}{\partial z} \end{pmatrix}. \tag{C.19}$$

Two similar equations are obtained by putting u equal to y and z, respectively. Together, the three equations show that the product of the matrix in Eq. (C.18) and the matrix in Eq. (C.3) equals the unit matrix. We may therefore evaluate the matrix in Eq. (C.18) as the inverse of the matrix in Eq. (C.3). As remarked in the discussion following Eq. (C.9), the determinant of that matrix is either $+\sqrt{g}$ or $-\sqrt{g}$, so the inversion is easy to carry out. In the case of spherical polar coordinates we find

$$\left(\frac{\partial u}{\partial x}, \frac{\partial u}{\partial y}, \frac{\partial u}{\partial z}\right) = \left(\frac{\partial u}{\partial r}, \frac{\partial u}{\partial \theta}, \frac{\partial u}{\partial \phi}\right) \begin{pmatrix} \sin\theta\cos\phi & \sin\theta\sin\phi & \cos\theta \\ \frac{1}{r}\cos\theta\cos\phi & \frac{1}{r}\cos\theta\sin\phi & -\frac{1}{r}\sin\theta \\ -\frac{1}{r}\frac{\sin\phi}{\sin\theta} & \frac{1}{r}\frac{\cos\phi}{\sin\theta} & 0 \end{pmatrix} \tag{C.20}$$

The difference between the transformation properties of the two vectors (dx, dy, dz) and $(\partial u/\partial x, \partial u/\partial y, \partial u/\partial z)$ is worth noticing. According to Eq. (C.3) the former transforms as a column vector, whereas the latter according to Eq. (C.18) transforms as a row vector. The difference is a fundamental one. In the language of tensor calculus, (dx, dy, dz) is a *contravariant* vector and $(\partial u/\partial x, \partial u/\partial y, \partial u/\partial z)$ is a *covariant* vector.

Let us finally consider the *vector operator*

$$\hat{\ell} = -i\mathbf{r} \times \nabla, \tag{C.21}$$

with the Cartesian components

$$\left\{ \begin{array}{rcl} \hat{\ell}_x & = & -i\left(y\dfrac{\partial}{\partial z} - z\dfrac{\partial}{\partial y}\right), \\ \hat{\ell}_y & = & -i\left(z\dfrac{\partial}{\partial x} - x\dfrac{\partial}{\partial z}\right), \\ \hat{\ell}_z & = & -i\left(x\dfrac{\partial}{\partial y} - y\dfrac{\partial}{\partial x}\right), \end{array} \right. \tag{C.22}$$

and the square

$$\hat{\ell}^2 = \hat{\ell}_x^2 + \hat{\ell}_y^2 + \hat{\ell}_z^2. \tag{C.23}$$

We want to express these operators in spherical polar coordinates.

We may refer to the $\hat{\ell}$-operators as the dimensionless angular-momentum operators, for a comparison with Eqs. (5.28) and (5.29) shows that

$$(\hat{l}_x, \hat{l}_y, \hat{l}_z) = \hbar(\hat{\ell}_x, \hat{\ell}_y, \hat{\ell}_z), \tag{C.24}$$

where $\hat{\mathbf{l}} = (\hat{l}_x, \hat{l}_y, \hat{l}_z)$ represents the angular momentum of a particle with position vector $\mathbf{r}$

To evaluate, say $\hat{\ell}_x$, we simply combine the information in Eq. (C.11) with that in Eq. (C.20), and get

$$\begin{aligned} \hat{\ell}_x u &= -i\left(y\frac{\partial u}{\partial z} - z\frac{\partial u}{\partial y}\right) \\ &= ir\sin\theta\sin\phi\left(\cos\theta\frac{\partial u}{\partial r} - \frac{\sin\theta}{r}\frac{\partial u}{\partial \theta}\right) \\ &\quad -ir\cos\theta\left(\sin\theta\sin\phi\frac{\partial u}{\partial r} + \frac{\cos\theta\sin\phi}{r}\frac{\partial u}{\partial \theta} + \frac{\cos\phi}{r\sin\theta}\frac{\partial u}{\partial \phi}\right) \\ &= i\sin\phi\frac{\partial u}{\partial \theta} + i\cot\theta\cos\phi\frac{\partial u}{\partial \phi}. \end{aligned} \tag{C.25}$$

Thus, we are led to the following expressions

$$\boxed{\begin{aligned} \hat{\ell}_x &= i\left(\sin\phi\frac{\partial}{\partial\theta}+\cot\theta\cos\phi\frac{\partial}{\partial\phi}\right), \\ \hat{\ell}_y &= -i\left(\cos\phi\frac{\partial}{\partial\theta}-\cot\theta\sin\phi\frac{\partial}{\partial\phi}\right), \\ \hat{\ell}_z &= -i\frac{\partial}{\partial\phi}. \end{aligned}} \tag{C.26}$$

To evaluate $\hat{\ell}^2$, we note that

$$\hat{\ell}_x^2 u = i\left(\sin\phi\frac{\partial}{\partial\theta}+\cot\theta\cos\phi\frac{\partial}{\partial\phi}\right) i\left(\sin\phi\frac{\partial u}{\partial\theta}+\cot\theta\cos\phi\frac{\partial u}{\partial\phi}\right), \tag{C.27}$$

we then perform the trivial differentiations, and add the results from the evaluation of $\hat{\ell}_y^2 u$ and $\hat{\ell}_z^2 u$. The final result is

$$\boxed{\hat{\ell}^2 = -\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)-\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}} \tag{C.28}$$

This is seen to be the same operator as that occurring in Eq. (C.16). Thus, we have derived the following important expression for the Laplacian

$$\boxed{\nabla^2 = \frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}-\frac{\hat{\ell}^2}{r^2}} \tag{C.29}$$

We have now reached the goal of expressing the operators we need in spherical polar coordinates. The methods we have used are widely applicable and apply to other curvilinear coordinate systems as well. But at this stage we must refer the reader to the rich literature on curvilinear coordinates for further theorems and results.[1]

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[1] See, for example:
H. Margenau and G. M. Murphy, *The Mathematics of Physics and Chemistry*, 2nd Ed., Van Nostrand, New York, 1956, Chapter 5;
P. Moon and D. E. Spencer, *Field Theory Handbook*, Springer-Verlag, Berlin, 1971.

Appendix D

Surface Spherical Harmonics and Special Functions

As mentioned in Sec. 8.3.6, the θ-dependence of the surface spherical harmonics is that of the *associated Legendre functions* $P_\ell^{|m|}(z)$. Considered as a function of $\cos\theta$, $P_\ell^{|m|}(z)$ is defined as

$$P_\ell^{|m|}(\cos\theta) = \sin^{|m|}\theta \left(\frac{d}{d\cos\theta}\right)^{|m|} P_\ell(\cos\theta), \tag{D.1}$$

where $P_\ell(\cos\theta)$ is a *Legendre polynomial*,

$$P_\ell(\cos\theta) = \frac{1}{2^\ell \ell!}\left(\frac{d}{d\cos\theta}\right)^\ell \left(\cos^2\theta - 1\right)^\ell. \tag{D.2}$$

We have, for instance,

$$\begin{cases} P_0(\cos\theta) = 1, \\ P_1(\cos\theta) = \cos\theta, \\ P_2(\cos\theta) = \frac{1}{2}(3\cos^2\theta - 1), \\ P_3(\cos\theta) = \frac{1}{2}(5\cos^3\theta - 3\cos\theta). \end{cases} \tag{D.3}$$

The associated Legendre function $P_\ell^{|m|}(\cos\theta)$ is a solution of the differential equation

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \left(\ell(\ell+1) - \frac{m^2}{\sin^2\theta}\right)\Theta = 0, \tag{D.4}$$

and it is easy to verify that this is the differential equation that originates from the differential equation (8.38) for the surface spherical harmonics, i. e.,

$$\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}+\ell(\ell+1)\right\}Y(\theta,\phi)=0, \qquad \text{(D.5)}$$

when one inserts a function of the form $\Theta(\theta)\exp(\pm im\phi)$, $\Theta(\theta)\cos(|m|\phi)$, or $\Theta(\theta)\sin(|m|\phi)$. This is the form of the functions in Table 8.1 and Table 8.2.

With the proper normalization factor included, one finds the expression

$$\boxed{Y_{\ell,m}(\theta,\phi)=(-1)^{(m+|m|)/2}\sqrt{\frac{2\ell+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}}P_\ell^{|m|}(\cos\theta)e^{im\phi}}\ . \qquad \text{(D.6)}$$

The sign factor in the expression is in accordance with the Condon–Shortley phase convention (Sec. 8.3.5). It is equal to -1 when m is positive and odd, otherwise it equals $+1$.

For further information about the associated Legendre functions, we refer to the literature.[1]

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[1] See, for instance, Chapter 8 in the reference of footnote 2.11. The reader is warned that the same notation may sometimes cover differences in sign and magnitude of incorporated constants.

Appendix E

The δ-Function

Consider the following family of Gaussian functions,

$$G_a(u) = \frac{a}{\sqrt{\pi}} e^{-a^2u^2}, \quad a > 0, \tag{E.1}$$

$$\int_{-\infty}^{\infty} G_a(u)du = 1, \tag{E.2}$$

represented in Fig. E.1 by graphs for three different values of a. As the value of a increases, $G_a(u)$ becomes more and more localized about $u = 0$, and at the same time the height of the function becomes larger and larger, conserving the value of the integral (E.2). We have, in fact, that

$$G_a(0) \to \infty \text{ as } a \to \infty. \tag{E.3}$$

The limit function $G_a(u)$ is certainly not a proper function. It has, however, turned out to be extremely useful to accept it as a *generalized function.*

This generalized function coincides with the so-called δ-function introduced by Dirac.[1] It is denoted by $\delta(u)$ and may be defined solely by its properties, without reference to a limit function as above. First and foremost, these properties are

$$\boxed{\begin{aligned} &\delta(u) = 0 \text{ for } u \neq 0, \\ &\int_{-\infty}^{\infty} \delta(u) = 1. \end{aligned}} \tag{E.4}$$

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[1] P. A. M. Dirac, *The Principles of Quantum Mechanics*, the bibliography, entry [12].

From these properties we get, for any function $f(u)$,

$$\boxed{\int_{-\infty}^{\infty} f(u)\delta(u-u_0) = f(u_0)} \tag{E.5}$$

For the integrand vanishes for all $u \neq u_0$. Hence, we may replace $f(u)$ by $f(u_0)$ and take $f(u_0)$ outside the the integral, which then has the value 1 according to Eq. (E.4).

In addition to the properties (E.4) we also assign the following property to the delta function

$$\boxed{\delta(\alpha u) = \frac{1}{|\alpha|}\delta(u)} \tag{E.6}$$

This property ensures that $\delta(u)$ may be treated like an ordinary function $f(u)$ in the relations

$$\int_{-\infty}^{\infty} f(\alpha u)du = \frac{1}{|\alpha|}\int_{-\infty}^{\infty} f(\alpha u)d(\alpha u) = \frac{1}{|\alpha|}\int_{-\infty}^{\infty} f(u)d(u), \quad \alpha > 0. \tag{E.7}$$

The property (E.6) also implies that $\delta(u)$ is an even function with respect to inversion in the point $x = 0$,

$$\boxed{\delta(-u) = \delta(u)} \tag{E.8}$$

For further properties of $\delta(u)$ we refer to the reference of footnote 1. We also point out that in contemporary mathematics one often refers to the delta function as a so-called distribution.[2]

Besides the family of Gaussian functions, Fig. E.1 shows two more families of functions which have the δ-function as limit function. They are the family of Lorentzian functions,

$$L_b(u) = \frac{1}{\pi}\frac{b}{u^2+b^2}, \quad b > 0 \tag{E.9}$$

for which the δ-function is obtained by letting the parameter b tend to zero, and the following family of functions for which the δ-function is obtained by

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[2] See, for example, I. Richards and H. Youn, *Theory of Distributions: a non-technical introduction*, Cambridge University Press, 1990.

letting the parameter c tend to infinity

$$S_c(u) = \frac{1}{\pi}\frac{\sin(cu)}{u}, \quad c > 0. \tag{E.10}$$

Thus, we may write

$$\lim_{a\to\infty} G_a(u) = \delta(u), \tag{E.11}$$

$$\lim_{b\to 0} L_b(u) = \delta(u), \tag{E.12}$$

$$\lim_{c\to\infty} S_c(u) = \delta(u), \tag{E.13}$$

Obviously, there are many ways of representing the delta function as a limit function. It is, for instance, also of interest to note that

$$\lim_{c\to\infty} \frac{c}{\pi}\left(\frac{\sin(cu)}{cu}\right)^2 = \delta(u) \tag{E.14}$$

which is related to Eqs. (E.10) and (E.13).

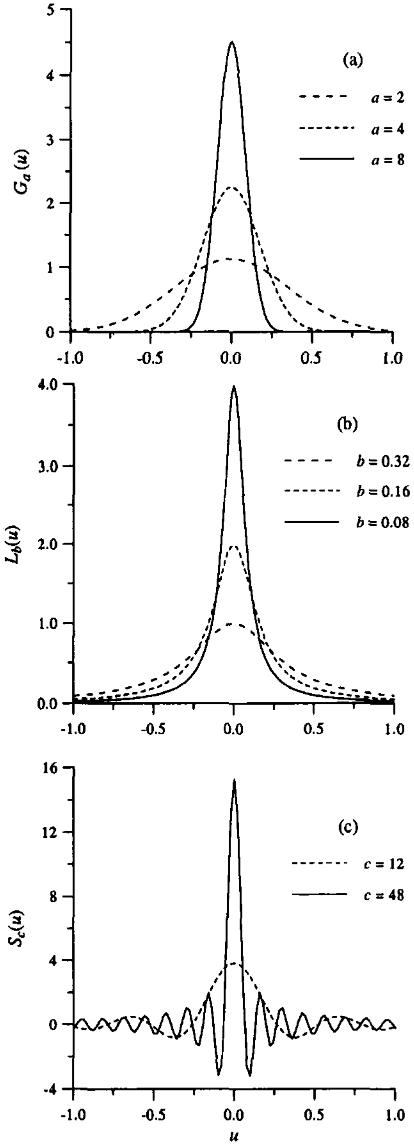

Figure E.1: Three families of functions for which Dirac's δ-function is a limit function. (a): Gaussians, Eq. (E.1), (b): Lorentzians, Eq. (E.9), (c): The family of Eq. (E.10).

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