March 7, 2012

Hydrogen 2

http://www.walter-fendt.de/ph14e/bohrh.htm

http://webphysics.davidson.edu/faculty/dmb/hydrogen/intro_hyd.html

http://demonstrations.wolfram.com/HydrogenOrbitals/

http://demonstrations.wolfram.com/SphericalHarmonics/

http://www.falstad.com/qmatom/

http://www.evilmadscientist.com/article.php/atomiccookies

http://www.tp1.physik.uni-siegen.de/~brandt/books/index.php?ID=IQM

http://www.tp1.physik.uni-siegen.de/~brandt/talks/TalkOnIQ_Web.pdf

http://www.tp1.physik.uni-siegen.de/~brandt/talks/OT-Schroedinger.wav

http://www.youtube.com/watch?v=CC7Sg41Bp-U

http://www.youtube.com/watch?v=HZ_W3EAfp6I

http://www.falstad.com/qm1d/

http://www.falstad.com/qmatom/

http://www.falstad.com/qm2dcirc/

Conclude Angular M mentum

$$\frac{1}{p^{2}} machanical approximation maring main
primatic moment moving change
$$\frac{1}{p^{2}} magnetic moment moving change
$$\frac{1}{p^{2}} = macha is maring ?
A: The productivity condent (FLOX)
$$\left[\left(\psi(\vec{x}) \right)^{2} = \psi^{*}(\vec{x}) \psi(\vec{x}) = \rho_{KO} \otimes O_{ENC}(TY) \\
1 d L^{-1} \rho(x) dx \\
2 d L^{-2} \rho(x,y) dA \\
3 d L^{-3} \rho(\vec{x}) dV \\
p(\vec{x},t) = \psi^{*}(\vec{x},t) \psi(\vec{x},t) \\
want A continuoity eduation
$$\frac{3}{p} + \frac{1}{p^{2}} = \frac{1}{p^{2}} = 0 \\
\frac{1}{p^{3}} = \left(\frac{-i\frac{\pi}{2}}{2m} \right) \left[\psi^{*} \nabla \psi - \nabla \psi^{*} \psi \right] \\
= \frac{\pi}{m} Tm \left[\psi^{*} \nabla \psi \right] = A \approx \left[\psi^{*} \frac{\pi}{2m} \nabla \psi \right]$$$$$$$$$$

No. 2011 A set of the contract of the contract

APPLY TO HYDROLEN

$$\vec{f}_{nkm} (\vec{n}) = \frac{\pi}{2mi} \quad \vec{\Phi}_{nkm}^{*} (\vec{n}) \quad \nabla \quad \vec{\Phi}_{nkm} (\vec{n}) + cc$$
FOR ANY WAVEFON $\Psi(\vec{n})$
 $\Psi(\vec{n}) = A(\vec{n}) e^{i \Phi(\vec{n})}$
 $\Psi(\vec{n}) = A(\vec{n}) e^{i \Phi(\vec{n})}$
 $A(\vec{n}) \ge 0$
 $0 \le \varphi(\vec{n}) \le 2\pi$
 $P(\vec{n}) dV = A^{L}(\vec{n}) dV$
PLOB DENSITY DEDENDS ONLY ON AMPLITUDE
 $\vec{f} = \frac{\pi}{m} A^{L}(\vec{n}) \quad \nabla \quad \varphi(\vec{n})$
PLOE CURRENT DEDENDS ON AMP AND PHASE

FOR HYDROGEN

$$A_{mRm}(\vec{x}) = |R_{mL}(x)| |Y_{Lm}(\theta, \varphi)|$$

$$M(RPR \quad \varphi_{mLm}(\vec{x})) = m \hbar$$

$$\vec{t}(\vec{x}) = \frac{\hbar}{m} \quad \frac{m}{r \sin \theta} \quad P_{mRm}(\vec{x}) \quad \hat{e}_{\varphi}$$

$$(\vec{x}) = \frac{\pi}{m} \quad \frac{m}{r \sin \theta} \quad P_{mRm}(\vec{x}) \quad \hat{e}_{\varphi}$$

$$m \ge 0 \quad ccw$$

$$m \le 0 \quad cw$$

$$m = 0 \quad NO \ PROB \ CUARENT$$

In the second state of the second state.

HOW MUCH ANGULAR MOMENTUM? $dL_2 = (\mu \vec{n} \times \vec{j}) d^3 n$ 1 = reduced mass also to avoid confusion with m $L_{2} = \mu \int (\vec{n} \times \vec{j}) \cdot \vec{e}_{2} d^{3}n$ = $\mu \int |\vec{j}| r \sin \theta d^3 r$ = $m \hbar \int P_{mem}(\vec{z}) d^3r$ $L_{2} = m \hbar$

Additional Brand True Theory (2014) Associate Additional Brand True Theory (2014) Addition Additional Brand True Theory (2014) Addition TIME - DEPENDENCE

$$\begin{split}
\bar{\Phi}_{mkm}(\vec{\lambda}) \\
\bar{\Phi}_{mkm}(\vec{\lambda};t) &= \bar{\Phi}_{mkm}(\vec{\lambda}) e \\
&= R_{mk}(\lambda) P_{km}(\theta) e^{im\varphi} e^{-iE_{m}t/\xi} \\
&= R_{mk}(\lambda) P_{km}(\theta) e^{im\varphi} e^{-iE_{m}t/\xi} \\
&= i(m\varphi - \omega_{m}t) \\
&= e
\end{split}$$

 $\omega_m = E_m/\hbar$

Is constructed to the second se

=> BEAUTIFUL SPINNING BALLS.

SO WHAT IS SPINNING? OHANIAN AJP 54 500 (1996) AJP 68 259 (2000) KITA THE PROB CURRENT IS FLOWING S THE FIELD IS SPINNING 5 CIRCULATING FLOW OF ENERAL BELINFANTE 1929 ñ's CIRCULATING FLOW OF CHARGE GORDON 1928 THIS IS A CLASSICAL PICTURE! OM: no E na B only real and virtual photons !

1.21, 2019 1.12, 2019 1.13, 2.14

And the second stand of the second se

WHAT IS SPIN? Real particles have intrinsic angular momentum. The associated degree of freedom is called spin. Fixed property of the particle; you cannot change it. You can change L. CLASSICAL PICTURE -7 L SUN GAATH O kay, maybe the electron is like a little sittle spinning ball. How bost does it spin?

Mational Brand

HOW BIE IS AN ELECTRON?
TWO CLASSICAL ANSWERS
(1) The elemined radius
$$R_0$$

 $\begin{pmatrix} coulon B \\ RNBERY \end{pmatrix} = \begin{pmatrix} ABCT MASS \\ BNERKY \end{pmatrix}$
 $\frac{e^2}{RO} = mc^2$
 $R_0 = \frac{e^2}{mc^2} = 2 \cdot PIJ9 \times 10^{-16} \text{m}$
 $R_0 \sim 3 \times 10^{-5} \text{ Å} = \frac{a_0}{(IJJ)^2}$
ANCH SMALLER THAN AN ATOM
PHYSICAL MEANINE : E&M some metric
 $Second plete endtung core action
 $R_c = \frac{t_0}{mc} \sim 4 \times 10^{-3} \text{ Å}$
 $R_c = \frac{a_0}{IJJ} = IJJR_0$
PHYSICAL MEANINE : indectio electro acotticity cross section$

a ha increase the PARA in the second second second is the second second second is a second se

THOMPSON SCATTERING $\Lambda \Lambda \Lambda \Lambda \longrightarrow$. FLGE PHOTON ELECTRON E= Eon con (Kt-wt) -7 F= ma $-eE_0 = m \frac{d^2 \chi}{d t^2}$ a= -e Eo $\frac{d\sigma}{d\sigma} = \kappa_0^2 \left[\hat{\epsilon}_1 \cdot \hat{\epsilon}_s \right]^2$ SERGULL DIAGRAM = ro sin 20 COMPTON SCATTERING Įφ р HO TO N $\delta \lambda = \frac{h}{mc} \left(1 - \cos \varphi \right) = 0.02426 \text{ Å} \left(1 - \cos \varphi \right)$ $\frac{d\sigma}{d\rho} = R_{c}^{2} = (137)^{2} R_{0}^{2}$

El sol - a solutional And - El sub and Poset - as esta entre Robert - a solutional Poset - as - as esta esta - a sub and - a sub and - a sub-

HOW EAST WOULD THE ELECTEON SPIN?

$$L = \frac{1}{2} \frac{1}{5}$$

$$L = \frac{1}{2} \frac{1}{5}$$

$$L = I W = \left(\frac{1}{5}mR^{2}\right)\left(\frac{m}{R}\right) = \frac{1}{5}mWR$$

$$\Rightarrow N = \frac{5}{4} \frac{5}{mR}$$

$$R = R_{0} \Rightarrow V_{0} = 1/2 c \qquad SOPERLUMINAL!$$

$$R = R_{0} \Rightarrow V_{0} = 1/2 5 c \qquad STILL SOPERLUMINAL ...$$
PRESENT UNDERSTANDING:
The sleeting is a point particle.
Nothing inside do spin!
The sleeting is a point particle.
Nothing inside do spin!
The sleeting is a point particle.
Nothing inside do spin!
The protect has internet structure 3 guarda
intrivic angular momentum of the guarda
relite angular momentum of the guarda

2. al. Construct PRASE Country Construction Provided Transfer Country Count LECTURE 1

MARCH 31 2003

THIS WEEK: SPIN
THIS WEEK: SPIN
UP UNTIL NOW, SCHRODINGER EAN

$$H | \Psi \rangle = i \frac{\pi}{4t} \frac{d}{4t} | \Psi \rangle$$

 $H | \Psi \rangle = i \frac{\pi}{4t} \frac{d}{4t} | \Psi \rangle$
DOES NOT INCLUPE SPIN!
TWO WAYS TO INCLUPE SPIN:
(1) PAULI - SCH ROPINGER EQN
 $H | \Psi | (\chi) = i \frac{\pi}{4t} \frac{d}{4t} | \Psi | \chi \rangle$
NON-ALLATIVISTIC, RANY SPIN
FOR SPIN 1
 $\Psi | (\chi) = \left(\frac{\Psi_{+} (\chi)}{\Psi_{-} (\chi)} \right)$
FOR SPIN 1
 $\Psi | (\chi) = \left(\frac{\Psi_{+} (\chi)}{\Psi_{0} (\chi)} \right)$
FOR SPIN 0
 $\Psi | (\chi) = (\Psi | (\chi))$
 $\Psi | (\chi) = (\Psi | (\chi))$
 $\Psi | (\chi) = (\Psi | (\chi))$

50 WHAT IS SPINNING? OHANIAN AJP 54 500 (1986) AJP <u>68</u> 259 (2000) KITA L THE PROB CURRENT IS FLOWING م مر S THE FIELD IS SPINNING 5 CIRCULATING FLOW OF ENERGY BELINFANTE 1939 CIRCULATING FLOW OF CHARGE GOLDON 1928 Ĩ, THIS IS A CLASSICAL PICTURE! QM: no E no B only real and virtual photons !

s subaile - service - service

Hattonal Brand Town Connection And

large number of such repetitions into our teaching. It may bore a few poor students, but almost all benefit.

IX. THE IMPORTANCE OF CALCULATING WITH NUMBERS

The world has changed quite a bit in the past 30 or 40 years. When I was an undergraduate we learned that there are only four angles in this world, namely, 30°, 45°, 60°, and 90°. Furthermore, all measurements are divisible by 2, often by 3 and 4, and, curiously, not infrequently by 49. It came as something of a surprise, when I embarked on experimental research, to find that most measurements are embarrassingly inelegant numbers, and that angles, as often as not, wander somewhere between those canonical values we learned in class.

I understand why my student problems had such remarkably simple numbers. It was just that nobody liked long division, and the alternatives were few.

Of course, we did have pocket calculators, or, more accurately, hip calculators. But they were hard to use, required a fair amount of manual dexterity to get results accurate to three figures. They were slow, and very expensive. My present shirt pocket calculator, whose batteries have already lasted two years, not only gives me nine figures and hyperbolic functions, but even does arithmetic in hexadecimal. It cost \$14.29. When students grumble about the expense, I delight to tell them that my 1945 log log duplex trig calculator, required on every test, cost me \$176 (in 1985 dollars, using an average inflation rate of 5% per annum). My point is this. Calculating power today is dirt cheap. It costs far less than textbooks and it lasts from one course to another. It gives us the opportunity to teach the physics of the real world rather than the physics of the textbook. Our students, furthermore, at least our technically inclined students, will spend their lives making use of these calculators.

This needs to be recognized in what we do in our calculus-based physics. Thirty, 60, and 90 ought to be reduced to their proper place. In my classes, tests, if not textbook problems, have angles like 27.6°. Automobiles have speeds of 37 km/h. Electrons move in orbits of radius 0.26 centimeters. The only difficulties students have with this is that too frequently their calculations seem to be accurate to one part in ten to the ninth.

All this is fine for the science and engineering students. What about the liberal arts students? Years ago, I would not have dreamed of asking them to buy slide rules. I hesitate now to ask them to have calculators, yet I note that almost all do. I continue to give them problems with nice numbers, yet I find them using a calculator to divide 8 by 4. I'm beginning to think that they too should always deal with real-world numbers. If they have to use a calculator to divide 8 by 4, they might as well be dividing 8.63 by 4.79.

By now I have run the device of numbers into the ground. It has given me a handy framework to air my grievances about and my hopes for physics teaching. I hope I will hear more about these dirty problems of physics teaching in less than ideal circumstance from the rest of you. Let me thank the AAPT once again for giving me this award. Thank you all for hearing me out.

What is spin?

Hans C. Ohanian Rensselaer Polytechnic Institute, Troy, New York 12180

(Received 5 February 1984; accepted for publication 1 May 1985)

According to the prevailing belief, the spin of the electron or of some other particle is a mysterious internal angular momentum for which no concrete physical picture is available, and for which there is no classical analog. However, on the basis of an old calculation by Belinfante [Physica 6, 887 (1939)], it can be shown that the spin may be regarded as an angular momentum generated by a circulating flow of energy in the wave field of the electron. Likewise, the magnetic moment may be regarded as generated by a circulating flow of charge in the wave field. This provides an intuitively appealing picture and establishes that neither the spin nor the magnetic moment are "internal"—they are not associated with the internal structure of the electron, but rather with the structure of its wave field. Furthermore, a comparison between calculations of angular momentum in the Dirac and electromagnetic fields shows that the spin of the electron is entirely analogous to the angular momentum carried by a classical circularly polarized wave.

I. INTRODUCTION

When Goudsmit and Uhlenbeck proposed the hypothesis of the spin of the electron, they had in mind a mechanical picture of the electron as a small rigid body rotating about its axis. Such a picture had earlier been considered by Kronig and discarded on the advice of Pauli, Kramers, and Heisenberg, who deemed it a fatal flaw of this picture that

500 Am. J. Phys. 54 (6), June 1986

the speed of rotation—calculated from the magnitude of the spin and a plausible estimate of the radius of the electron—was in excess of the speed of light. However, the great success of the spin hypothesis in explaining the Zeeman effect and the doublet structure of spectral lines quickly led to its acceptance.¹ Since the naive mechanical picture of spin proved untenable, physicists were left with the concept of spin minus its physical basis, like the grin of the Cheshire cat. Pauli pontificated that spin is "an essentially quantum-mechanical property,...a classically not describable two-valuedness"² and he insisted that the lack of a concrete picture was a satisfactory state of affairs:

After a brief period of spiritual and human confusion, caused by a provisional restriction to 'Anschaulichkeit', a general agreement was reached following the substitution of abstract mathematical symbols, as for instance psi, for concrete pictures. Especially the concrete picture of rotation has been replaced by mathematical characteristics of the representations of rotations in three-dimensional space.³

Thus physicists gradually came to regard the spin as an abstruse quantum property of the electron, a property not amenable to physical explanation.

Judging from statements found in modern textbooks on atomic physics and quantum theory, one would think our understanding of spin (or the lack thereof) has not made any progress since the early years of quantum mechanics. The spin is usually said to be a nonorbital, "internal," "intrinsic," or "inherent" angular momentum (the words are often used interchangeably, although they should not be), and it is often treated as an irreducible entity that cannot be explained further. Sometimes the (unsubstantiated) suggestion is made that the spin is due to an (unspecified) internal structure of the electron.⁴ And sometimes the consolation is offered that the spin arises in a natural way from Dirac's equation⁵ or from the analysis of the representations of the Lorentz group. It is true that the Dirac equation contains a wealth of information about spin: The equation tells us that the spinor wavefunctions are indeed endowed with a spin angular momentum of $\hbar/2$, it supplies the mathematical description of the kinematics of a freeelectron or other particle of spin one-half, and-in conjunction with the principle of minimal coupling-it supplies the equations governing the dynamics of a charged particle immersed in a electromagnetic field, equations which directly yield the correct value of the gyromagnetic ratio for the electron. It is also true that the analysis of the representations of the Lorentz group is very informative: The analysis tells us that the quantum-mechanical wavefunctions must be certain types of tensors or spinors characterized by a value of the mass and (if the mass is not negative) an integer or half-integer value of the spin. But in all of this the spin merely plays the role of an extra, nonorbital angular momentum of unknown etiology. Thus the mathematical formalism of the Dirac equation and of group theory demands the existence of the spin to achieve the conservation of angular momentum and to construct the generators of the rotation group, but fails to give us any understanding of the physical mechanism that produces the spin.

The lack of a concrete picture of the spin leaves a grievous gap in our understanding of quantum mechanics. The prevailing acquiescence to this unsatisfactory situation becomes all the more puzzling when one realizes that the means for filling this gap have been at hand since 1939, when Belinfante⁶ established that the spin could be regarded as due to a circulating flow of energy, or a momentum density, in the electron wave field. He established that this picture of the spin is valid not only for electrons, but also for photons, vector mesons, and gravitons-in all cases the spin angular momentum is due to a circulating energy flow in the fields. Thus contrary to the common prejudice, the spin of the electron has a close classical analog: It is an angular momentum of exactly the same kind as carried by the fields of a circularly polarized electromagnetic wave. Furthermore, according to a result established by Gordon in 1928, the magnetic moment of the electron is due to the circulating flow of charge in the electron wave field. This means that neither the spin nor the magnetic moment are internal properties of the electron-they have nothing to do with the internal structure of the electron, but only with the structure of its wave field.

Unfortunately, this clear picture of the physical origin of the spin and of the magnetic moment has not received the wide recognition it deserves, perhaps because neither Belinfante nor Gordon loudly proclaimed that their calculations provided a new physical explanation of the spin and of the magnetic moment. These calculations are sometimes reproduced in texts on quantum field theory,⁸ but usually without any commentary on their physical interpretation. In the present paper, it is my objective to revive these forgotten explanations of the spin and the magnetic moment in the hope that the intuitive picture of circulating energy and charge will become part of the lore learned by all students of physics. I want to emphasize that, in contrast to some other attempts at explaining the spin,⁹ the present explanation is completely consistent with the standard interpretation of quantum mechanics.

A crucial ingredient in Belinfante's calculation of the spin angular momentum is the use of the symmetrized energy-momentum tensor. It is well known that in a field theory we can construct several energy-momentum tensors, all of which satisfy the conservation law $\partial_{\nu} T^{\mu\nu} = 0$, and all of which yield the same net energy $(\int T^{00} d^3x)$ and momentum $(\int T^{k0} d^3x)$ as the canonical energy-momentum tensor.¹⁰ These diverse energy-momentum tensors differ by terms of the form $\partial_{\alpha} U^{\mu\nu\alpha}$, which are antisymmetric in the last two indices $(U^{\mu\nu\alpha} = -U^{\mu\alpha\nu})$, and therefore identically satisfy the conservation law $\partial_{\nu}\partial_{\alpha}U^{\mu\nu\alpha} = 0$. Belinfante showed that by a suitable choice of the term $\partial_{\alpha} U^{\mu\nu\alpha}$, it is always possible to construct a symmetrized energy-momentum tensor $(T^{\mu\nu} = T^{\nu\mu})$. The symmetrized energy-momentum tensor has the distinctive advantage that the angular momentum calculated directly from the momentum density T^{k0} is a conserved quantity (in the absence of external torques). This means that the momentum density gives rise to both orbital angular momentum and spin angular momentum. If instead of the symmetrized energy-momentum tensor, we were to use the unsymmetrized canonical energy-momentum tensor, then the momentum density would not give rise to the spin angular momentum. This does not mean that the spin would vanish from the theory-an examination of the conservation law for angular momentum shows that the spin emerges as a mysterious extra quantity that must be added to the orbital angular momentum to achieve conservation-but the simple and clear physical mechanism underlying spin would vanish. I will take it for granted that the symmetrized energy-momentum tensor is the correct energy-momentum

501 Am. J. Phys., Vol. 54, No. 6, June 1986

electron:7,13

$$-ec\bar{\psi}\gamma^{k}\psi = -(e\hbar/2mi)\left[\bar{\psi}\partial_{k}\psi - (\partial_{k}\bar{\psi})\psi\right]$$
$$-(e\hbar/2m)\partial_{\nu}(\bar{\psi}\sigma^{k\nu}\psi). \qquad (20)$$

Here the first term is a convection current density associated with the translational motion of the electron. For an electron in a state with orbital angular momentum, this convection current density gives rise to an orbital magnetic moment. The second term is a spin current density, which is nonzero even in the rest frame of the electron.¹⁴ For example, if the electron is in the state specified by Eq. (14), the flow lines for the spin current are closed circles, as they are for the momentum density, but of the opposite direction.¹⁵ Obviously, such a current will generate a magnetic moment of the opposite direction as the spin.

To establish the general relationship between this magnetic moment and the spin, we decompose the spin current density into two terms:

$$j_{S}^{k} = -\frac{e\hbar}{2m}\partial_{\nu}\left(\bar{\psi}\sigma^{k\nu}\psi\right)$$
$$= -\frac{e\hbar}{2m}\partial_{n}\,\bar{\psi}\sigma^{kn}\psi - \frac{e\hbar}{2mc}\frac{\partial}{\partial t}\left(\bar{\psi}\sigma^{k0}\psi\right). \tag{21}$$

This can be rewritten as

$$\mathbf{j}_{s} = \nabla \mathbf{X} \mathbf{M} + \frac{\partial \mathbf{P}}{\partial t}, \qquad (22)$$

where

$$\mathbf{M} = -\left(e\hbar/2m\right)\psi^{\dagger}\gamma^{0}\sigma\psi \tag{23}$$

and

$$\mathbf{P} = (ie\hbar/2mc)\psi^{\dagger}\gamma^{0}\alpha\psi. \tag{24}$$

Thus j_s is the sum of a magnetization current density and a polarization current density. The former is associated with a magnetic moment per unit volume $M = -(e\hbar/2m)\psi^{\dagger}\gamma^{0}\sigma\psi$ and the latter with an electric dipole moment per unit volume $\mathbf{P} = (ie\hbar/2mc)\psi^{\dagger}\gamma^{0}\alpha \psi$. Equation (23) implies that the magnetic moment of the electron is

$$\mathbf{m} = \int \mathbf{M} \, d^3 x = -\frac{e\hbar}{2m} \int \psi^{\dagger} \gamma^0 \mathbf{\sigma} \psi \, d^3 x. \tag{25}$$

[Alternatively, the magnetic moment can be calculated as the moment of the magnetization current,

$$\mathbf{m} = \frac{1}{2} \int \mathbf{x} \times (\nabla \times \mathbf{M}) d^3 \mathbf{x}.$$
 (26)

An integration by parts shows that this expression is equivalent to Eq. (25).]

Comparing Eq. (25) with (18) we see that, apart from the factor of γ^0 , the magnetic moment coincides with -e/m times the spin. More precisely, the magnetic-moment operator coincides with $-e\gamma^0/m$ times the spin operator,

$$\mathbf{m}_{\rm op} = -(e/m)\gamma^0 \mathbf{S}_{\rm op}.$$
 (27)

This is, of course, the usual result for the magnetic moment of the electron. The standard derivation¹⁶ of this result does not proceed via the definitions (25) or (26) of the magnetic moment; instead, it proceeds via the Dirac equation by investigating the response of the electron to an external magnetic field, a response that is found to have form expected for a magnetic moment. Thus the standard deri-

Am. J. Phys., Vol. 54, No. 6, June 1986 504

vation fails to provide a physical picture of the mechanism underlying the magnetic moment. Incidentally, the standard derivation explicitly invokes the principle of minimal coupling. This principle enters the above calculation implicitly, through the assumption that the relevant current density is simply $-e\psi\gamma^{k}\psi$, rather than some more complicated expression with, say, an extra term proportional to $\partial_{\nu} \bar{\psi} \sigma^{\mu\nu} \psi$ (such extra terms are required to account for the "anomalous" magnetic moments of the proton and the neutron).

Finally, what about the electric dipole moment. Eq. (24)? In the nonrelativistic limit, $\gamma^0 \alpha$ is an "odd" operator whose matrix elements are of order 1/m. Hence P is of order $1/m^2$, which must be neglected in the nonrelativistic limit. This means that the electron has no electric dipole moment in its own rest frame. However, a moving electron has an electric dipole moment in the laboratory frame. This electric dipole moment can be regarded as arising from the relativistic transformation law for electromagnetic fields: A moving magnetic moment gives rise to an electric moment (and vice versa).

V. CONCLUSIONS

The calculations in the preceding sections should lay to rest the common misconception that spin is an essentially quantum-mechanical property. What these calculations show is that spin is essentially a wave property, but whether the wave is classical or quantum mechanical is of secondary importance. The only fundamental difference between the spins of a classical wave and a quantum-mechanical wave is that the spin of the former is a continuous macroscopic parameter, whereas the spin of the latter is quantized and is represented by a quantum-mechanical operator. The argument is often made that since the spin of a quantum-mechanical particle-such as photon-has a fixed magnitude, it is not possible to proceed to the classical limit of large quantum numbers, and consequently the spin must be regarded as a quantum property without classical analog. But this argument is flawed: Although we cannot proceed to the limit of large quantum numbers for a single particle, we can proceed to the limit of large occupation numbers for a system of many particles. A circularly polarized light wave is an example of a system in which the classical macroscopic spin angular momentum arises from the addition of a large number of quantum spins. Such a classical limit is also possible for electrons, but we must take the precaution of placing the electrons in different orbital states whenever we place them in the same spin state. The Einstein-de Haas effect and the magnetization found in permanent magnets involve classical limits brought about by a large number of electron spins and magnetic moments.

The physical picture of spin presented in the preceding sections has great intuitive appeal because it confirms our deep prejudice that angular momentum ought to be due to some kind of rotational motion. But the rotational motion consists of a circulation of energy in the wave fields, rather than a rotation of some kind of rigid body. The spin is intrinsic, or inherent, i.e., it is a fixed feature of the wave field that does not depend on environmental circumstances. But it is not internal, i.e., it is not within the internal structure of the electron or photon (of course, the structure of the wave field is crucial to the spin, but this is not what is usually meant by internal structure).

> Hans C. Ohanian 504

A conspicuous feature of the above physical picture is the close kinship of spin and orbital angular momentum: Both are due to the energy flow in the wave fields, and the distinction between them hinges on the mathematical separation of the angular momentum associated with the flow into two independent portions. Since this physical picture treats the spin and the orbital angular momentum in the same way, it gives us as good an understanding of spin as of orbital angular momentum. We no longer need to regard the spin as a mysterious entity.

¹For the early history of spin, see the article by B. L. van der Waerden in Theoretical Physics in the Twentieth Century, edited by M. Fierz and V. F. Weisskopf (Interscience, New York, 1960); Wolfgang Pauli: Wissenschaftlicher Briefwechsel mit Bohr, Einstein, Heisenberg u.a., edited by A. Hermann, K. V. Meyenn, and V. F. Weisskopf (Springer, New York, 1979); M. Jammer, The Conceptual Development of Quantum Mechanics (McGraw-Hill, New York, 1966); and the articles by S. A. Goudsmit and G. E. Uhlenbeck in Phys. Today 29 (6), 40 (June, 1976). ²M. Jammer, Ref. 1, pp. 152 and 153.

³B. L. van der Waerden, Ref. 1, p. 216.

⁴For instance, P. A. M. Dirac, *The Principles of Quantum Mechanics* (Oxford U. P., Oxford, 1958), p. 142; D. S. Saxon, *Elementary Quantum Mechanics* (Holden-Day, San Francisco, 1968), p. 191.

⁵A. Beiser, Perspectives of Modern Physics (McGraw-Hill, New York, 1969), p. 225, goes so far as to claim that "...Dirac was able to show on the basis of a relativistic quantum-mechanical treatment that particles

having the charge and mass of the electron must have just the intrinsic angular momentum and magnetic moment attributed to them by Goudsmit and Uhlenbeck". This is somewhat of an exaggeration since, without prior knowledge of the spin of the electron, we cannot know that Dirac's equation is applicable.

F. J. Belinfante, Physica 6, 887 (1939).

7W. Gordon, Z. Phys. 50, 630 (1928).

⁸For example, G. Wentzel, *Quantum Theory of Fields* (Interscience, New York, 1949).

⁹For instance, D. Hestenes, Am. J. Phys. 47, 5 (1979).

¹⁰A clear discussion of the canonical versus the symmetrized energy-momentum tensor is given by D. E. Soper, *Classical Field Theory* (Wiley, New York, 1976).

¹¹L. Rosenfeld, Mem. Acad. R. Belg. 18, no. 6 (1940).

¹²The notation for spinors employed here is that of J. D. Bjorken and S. D. Drell, *Relativistic Quantum Mechanics* (McGraw-Hill, New York, 1964). The notation of Wentzel is slightly different.

¹³The Gordon decomposition is often used in spinor calculations (see, e.g., Ref. 12), but its importance in establishing a physical picture for the origin of spin seems to have been forgotten.

¹⁴Note that the convection current and the spin current are separately conserved:

 $\partial_{\mu} [\bar{\psi} \partial^{\mu} \psi - (\partial^{\mu} \bar{\psi}) \psi] = 0 \text{ and } \partial_{\mu} \partial_{\nu} (\bar{\psi} \sigma^{\mu\nu} \psi) = 0.$

This is an immediate consequence of the antisymmetry of $\sigma^{\mu\nu}$.

¹⁵Within the nonrelativistic approximation, the "small" components can be ignored when evaluating the right-hand side of Eq. (20), but they cannot be ignored when evaluating the left-hand side. ¹⁶Reference 12.

The quest for ultrahigh energies

Andrew M. Sessler

Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

(Received 11 February 1985; accepted for publication 22 May 1985)

A categorization is given of all the methods for accelerating particles. It is shown that in principle one can employ the large fields of a laser for this purpose as well as the wake fields of intense lowenergy particle beams. Discussion is given of four acceleration schemes which offer the possibility of attaining very high-energy particles; namely, the inverse free-electron laser accelerator, the beat-wave accelerator, the wake-field accelerator, and the two-beam accelerator.

I. INTRODUCTION

Ever since Cockcroft and Walton first produced nuclear reactions by means of a particle accelerator, in that case an electrostatic accelerator, physicists have bent their ingenuity to the development of ever-more powerful machines. The devices which have been developed include some remarkable machines, such as the cyclotron and the betatron, and some truly innovative concepts such as strong focusing and stochastic cooling.¹⁻⁴

Of course, the driving force behind this effort has been the ever-opening science which ever-higher energy has made possible. The machines on the forefront of elementary particle physics are truly marvels of engineering. One thinks of the Tevatron at Fermilab or the CERN Super Proton Synchrotron (SPS), with which the intermediate bosons were discovered in 1983. Today, the physics of elementary particles demands very *large* machines such as these two, and under construction are even larger machines such as the Large Electron Positron Collider (LEP) which will have a circumference of 27 km. Under serious consideration is the Superconducting Super Collider (SSC), the arguments for which have been presented recently.⁵

Although the arguments for the SSC are most compelling, and we believe that it should be built, it is clear that the progression of ever-larger machines cannot go on forever. Yet, one can be sure that the scientific desire for ever-higher energies will continue unabated. In fact, if one looks back over the last five decades, then one sees an almost exponential rise in the available particle energy, as is de-

505 Am. J. Phys. 54 (6), June 1986

Virtual probability current associated with the spin

Katsunori Mita

Department of Physics, St. Mary's College of Maryland, St. Mary's City, Maryland 20686

(Received 25 January 1999; accepted 9 July 1999)

A simple derivation of the spin probability current density from the expectation value of the spin operator is given. The properties of the spin probability current density are then examined in detail. We show that the spin probability current is solenoidal, virtual, and gives null contribution to the momentum of the particle. Expressions of the spin probability current density are derived for the Gaussian wave packet and the *s* states of the hydrogen atom. © 2000 American Association of Physics Teachers.

I. INTRODUCTION

The spin current is a concept not often treated in textbooks of quantum mechanics, appearing in a very small number of texts. In the text by Landau and Lifshitz, the spin current density is derived, without mentioning its name, in an analysis of the current density for a charged particle moving in an external magnetic field.¹ In a more recent text, Greiner introduces the spin current density ad hoc, and without an example, drawing an analogy with the magnetization current density of classical electromagnetic theory.²

The lack of coverage is also reflected in this journal. We again find only a couple of papers on the spin current. Parker derived the hyperfine structure Hamiltonian for hydrogen by evaluating the magnetic field at the nucleus due to the electron's spin current density.³ In an attempt to obtain a concrete physical picture of the spin, Ohanian used the spin current to argue that "the spin may be regarded as an angular momentum generated by a circulating flow of energy in the wave field of the electron."⁴ His discussion is based on the momentum density of the Dirac field obtained from the symmetrized energy-momentum tensor. Though Ohanian's picture of the spin is intuitively appealing, it unfortunately goes beyond the level of undergraduate quantum mechanics, and is difficult to introduce in a classroom setting.

Except for Ohanian's paper, in all of the references previously cited, the spin current is introduced in conjunction with a magnetic field, whether the field is external or the electron's own. From this situation, one may acquire the impression that the spin current exists only in the context of the magnetic properties of the electron. Such is not the case.

In this article, we offer a straightforward derivation of the spin probability current, within the scope of nonrelativistic quantum mechanics, without relying on the magnetic properties of the electron (Sec. II). We then investigate the properties of the spin probability current (Sec. III). We will show that the spin probability current is solenoidal, virtual, and gives null contribution to the particle's momentum. Finally, expressions of spin probability current densities are derived for the Gaussian wave packet and the *s* states of the hydrogen atom, and their physical properties are examined (Sec. IV).

II. DERIVATION OF THE SPIN PROBABILITY CURRENT DENSITY

For a quantum particle of mass m, the expectation value of the orbital angular momentum operator L can be written in the form

$$\langle \mathbf{L} \rangle = m \int_{V_0} \mathbf{r} \times \mathbf{j} d^3 r, \qquad (1)$$

where **j** is the probability current density defined by

$$\mathbf{j} = \frac{\hbar}{i2m} (\psi^* \nabla \psi - \psi \nabla \psi^*), \qquad (2)$$

and V_0 denotes the entire space. The probability current density **j** satisfies the equation of continuity

$$\frac{\partial}{\partial t}(\psi^*\psi) + \nabla \cdot \mathbf{j} = 0, \qquad (3)$$

expressing the local conservation of probability. Equation (1) expresses the orbital angular momentum of a quantum particle in terms of the circulating probability current. Equation (1) is derived in Appendix A.

For a particle with spin $\hbar/2$, we will rewrite the expectation value of the spin operator

$$\langle \mathbf{S} \rangle = \frac{\hbar}{2} \int_{V_0} \psi^{\dagger} \boldsymbol{\sigma} \psi d^3 r \tag{4}$$

in the same form as the orbital probability current, as expressed in Eq. (1). Following Ohanian, the idea is that the spin is another form of angular momentum due to another kind of circulating "current." The nature of this current is investigated in Sec. III. In Eq. (4), ψ denotes a two-component spinor.

To carry this out, first observe the vector identity

$$\nabla(\mathbf{A} \cdot \mathbf{B}) = (\mathbf{B} \cdot \nabla)\mathbf{A} + (\mathbf{A} \cdot \nabla)\mathbf{B} + \mathbf{B} \times (\nabla \times \mathbf{A}) + \mathbf{A} \times (\nabla \times \mathbf{B}),$$
(5)

and let $\mathbf{A} = \mathbf{r}$ and $\mathbf{B} = \psi^{\dagger} \boldsymbol{\sigma} \psi$ in Eq. (5). Then we obtain

$$\psi^{+}\boldsymbol{\sigma}\psi = \frac{1}{2}\mathbf{r} \times [\boldsymbol{\nabla} \times (\psi^{\dagger}\boldsymbol{\sigma}\psi)] - \frac{1}{2}\boldsymbol{\nabla}[\mathbf{r} \cdot (\psi^{\dagger}\boldsymbol{\sigma}\psi)] + \frac{1}{2}\sum_{i=1}^{3}\frac{\partial}{\partial x_{i}}[x_{i}(\psi^{+}\boldsymbol{\sigma}\psi)].$$
(6)

Integrating Eq. (6) over the entire space, we have

Gyroscopes

http://www.eng.umd.edu/HAMLET/Gyro http://www.um.es/fem/Ejs/EjsExamples3.3/Simulations/Gryscope.html http://www.stuleja.org/vscience/osp/contents/osp3d/gyroscope.html http://faculty.ifmo.ru/butikov/Applets/Gyroscope.html

NMR

http://mutuslab.cs.uwindsor.ca/schurko/nmrcourse/animations.html
http://mutuslab.cs.uwindsor.ca/schurko/nmrcourse/alimations/precess/precess.htm
http://mutuslab.cs.uwindsor.ca/schurko/nmrcourse/animations/eth_anim/hahnecho.gif
http://mutuslab.cs.uwindsor.ca/schurko/nmrcourse/animations/eth_anim/puls_evol.gif
http://mutuslab.cs.uwindsor.ca/schurko/nmrcourse/animations/animated_gifs/Fid_one_line.gif
http://mutuslab.cs.uwindsor.ca/schurko/nmrcourse/animations/animated_gifs/Fid_one_line.gif
http://mutuslab.cs.uwindsor.ca/schurko/nmrcourse/animations/animated_gifs/Fid_two_lines.gif
http://mutuslab.cs.uwindsor.ca/schurko/nmrcourse/animations/animated_gifs/Fid_two_lines.gif

Rabi Oscillations

http://jdhosts.net/michaud/RabiOscillations.html

Real chemistry

http://www.files.chem.vt.edu/chem-dept/hbell/simulation/hb2/ftsimstuff/simulateinfo.htm http://vam.anest.ufl.edu/forensic/nmr.html http://www.bruker-nmr.de/guide/eNMR/chem/NMRnuclei.html

NMR and MRI Videos

http://www.magritek.com/videos.html http://www.youtube.com/watch?v=ctwX05xK4PU

Just for fun

http://web.mit.edu/8.13/www/JLExperiments/Hooray.mp3
http://web.mit.edu/8.13/www/JLExperiments/Twinkle.mp3
http://www.youtube.com/watch?v=GFIvXVMbII0&feature=related
http://www.youtube.com/watch?v=SwulzwGMMwc&feature=related
http://www.youtube.com/watch?v=SXx2VVSNDMo&feature=related
http://www.youtube.com/watch?v=SMLDNBLDks&&feature=related
http://www.youtube.com/watch?v=STX2VSNDMo&feature=related
http://www.youtube.com/watch?v=STX2VSNDMO&feature=fox

PLOCEED AS BEFORE

$$L^{\perp} | \alpha_{1}\beta \rangle = \alpha | \alpha_{1}\beta \rangle$$

$$L_{2} | \alpha_{1}\beta \rangle = \beta | \alpha_{1}\beta \rangle$$

$$L_{2} | \alpha_{1}\beta \rangle = \beta | \alpha_{1}\beta \rangle$$

$$L_{2} | \alpha_{1}\beta \rangle = \beta | \alpha_{1}\beta \rangle$$

$$L_{2} | \alpha_{1}\beta \rangle = \beta | \alpha_{1}\beta \rangle$$

$$L_{2} | L_{2} | \alpha_{1}\beta \rangle = \beta | \alpha_{1}\beta \rangle$$

$$L_{2} | L_{2} | \alpha_{1}\beta \rangle = (\beta + \beta) [L_{2} | \alpha_{1}\beta \rangle]$$

$$= (\beta + \beta) [L_{2} | \alpha_{1}\beta \rangle]$$

$$CONCLUDE$$

$$L_{2} | \alpha_{1}\beta \rangle = \alpha e^{\frac{1}{\alpha_{1}}} o\beta L_{2} with e^{\alpha \beta} \beta + \beta$$

$$L_{2} | \alpha_{1}\beta \rangle = \alpha e^{\frac{1}{\alpha_{1}}} o\beta L_{2} with e^{\alpha \beta} \beta + \beta$$

$$L_{2} | \alpha_{1}\beta \rangle = \alpha e^{-\beta} \beta + \beta$$

$$L_{3} | \alpha_{1}\beta \rangle = \alpha e^{-\beta} \beta + \beta$$

$$L_{4} | \alpha_{1}\beta \rangle = \alpha e^{-\beta} \beta + \beta$$

Magnetic Resonance Imaging (MRI) http://www.cis.rit.edu/htbooks/mri/ http://www.mritutor.org/mritutor/index.html http://www.e-mri.org/nmr/learning-objectives.html

Nuclear Magnetic Resonance (NMR) http://en.wikipedia.org/wiki/Nuclear_magnetic_resonance http://en.wikipedia.org/wiki/NMR_spectroscopy http://en.wikipedia.org/wiki/Magnetic_resonance_imaging http://en.wikipedia.org/wiki/Functional_magnetic_resonance_imaging

From nobelprize.org

http://nobelprize.org/nobel_prizes/medicine/laureates/2003/lauterbur-interview.html http://nobelprize.org/nobel_prizes/medicine/laureates/2003/mansfield-interview.html http://nobelprize.org/nobel_prizes/medicine/laureates/2003/illpres/ http://www.chemheritage.org/exhibits/online_exhibits/lauterbur/index.html



http://nobelprize.org/educational_games/medicine/mri/index.html



 $< jm | J^2 | jm > = j(j+1)$



CAN GENERALIZE TO N PARTICLES

$$\rightarrow 3N$$
 deque of fundine + time
SCHRODINGER EQUATION TOSE
 $H = \frac{\vec{p}_{\perp}^{1L}}{Lm} + \frac{\vec{p}_{\perp}^{2L}}{Lm} + V(\vec{n}_{\perp},\vec{n}_{\perp})$
 $\left[-\frac{\hbar^{L}}{Lm} - \frac{\vec{p}_{\perp}^{2L}}{Lm} + V(\vec{n}_{\perp},\vec{n}_{\perp})\right] + (\vec{n}_{\perp},\vec{n}_{\perp},t)$
 $\left[-\frac{\hbar^{L}}{Lm} - \frac{\vec{p}_{\perp}}{Lm} - \frac{4L}{Lm} - \frac{\vec{p}_{\perp}}{V_{\perp}} + V(\vec{n}_{\perp},\vec{n}_{\perp})\right] + (\vec{n}_{\perp},\vec{n}_{\perp},t)$
 $= i \frac{\hbar}{4t} \frac{d}{4t} + (\vec{n}_{\perp},\vec{n}_{\perp},t)$
 $= i \frac{\hbar}{4t} \frac{d}{4t} + (\vec{n}_{\perp},\vec{n}_{\perp},t)$
 $(3N+1)$ Dim
 $I DON'T WANT TO FERMINE FOR $H O IFF ER!$
 $BREAL PROBLEM INTO PIECES...$$



$$\begin{bmatrix} -\frac{\hbar^{2}}{2\mu} \quad \vec{\nabla}_{n}^{\perp} - \frac{\hbar^{2}}{2m} \quad \vec{\nabla}_{n}^{\perp} + v(\vec{z}) \end{bmatrix} \quad \mathbf{F} \cdot \mathbf{g} \qquad \text{ansatz}$$

$$= i \frac{\hbar}{4t} \quad (\mathbf{F} \cdot \mathbf{g})$$

$$\frac{1}{\mathbf{F}_{i}(\vec{z}, \epsilon)} \begin{bmatrix} -\frac{\hbar^{2}}{2\mu} \quad \vec{\nabla}_{n}^{\perp} + v(\vec{z}) - i \frac{\hbar}{4t} \quad \mathbf{g} \\ -\frac{\hbar}{2\mu} \quad \vec{\nabla}_{n}^{\perp} + v(\vec{z}) - i \frac{\hbar}{4t} \quad \mathbf{g} \\ -\frac{\hbar}{2\mu} \quad \vec{\nabla}_{n}^{\perp} + v(\vec{z}) - i \frac{\hbar}{4t} \quad \mathbf{g} \\ -\frac{\hbar}{2\mu} \quad \vec{\nabla}_{n}^{\perp} + i \frac{\hbar}{4t} \quad \mathbf{g} \\ = \frac{1}{\mathbf{F}_{i}(\mathbf{g})} \quad \mathbf{g} \quad (\vec{z}, t) \\ = \frac{1}{\mathbf{F}_{i}(\mathbf{g})} \quad \mathbf{g} \quad (\vec{z}, t) \\ \vec{\nabla}_{n}^{\perp} + i \frac{\hbar}{4t} \quad \mathbf{g} \\ = \frac{1}{\mathbf{F}_{i}(\mathbf{g})} \quad \mathbf{g} \quad \vec{z}_{i}(t) \\ \vec{\nabla}_{n}^{\perp} + i \frac{\hbar}{4t} \quad \mathbf{g} \\ \vec{z} \\ \vec{z}$$

$$rester as the advector of the term of term of the term of term of the term of term of the term of te$$

SEPARATION CONSTANT En
energy enjagedence = expension endered

$$\frac{1}{\Psi_{m}} \left[-\frac{h^{2}}{2 e_{pn}} \vec{\nabla}_{n}^{2} + \sqrt{(\vec{n})} \right] \Psi_{m}(\vec{n}) = E_{m}$$

$$E_{m} = \frac{1}{h(6)} \left[i \frac{h}{h} \frac{dh}{dt} \right]$$

$$KPGPT \qquad \frac{dh}{dt} = -i \frac{E_{m}}{h} \frac{h}{dt}$$

$$\left[-\frac{h^{2}}{2 \mu} \vec{\nabla}_{n}^{2} + \sqrt{(\vec{n})} \right] \Psi_{m}(\vec{n}) = E_{m} \Psi_{m}(\vec{n})$$
TISE
3d TISE for relative metric dependence
So, THE AMERAY E(FANSTATES ARIE

$$\frac{\Psi_{m}(\vec{n},\vec{k},t) = f(\vec{k},t) g(\vec{n},t) = E_{m}(\vec{n}) e^{-i\vec{k}_{m}t/h}$$

$$= e^{-i\vec{k}_{m}t/h} \frac{f(\vec{k},t)}{h} e^{-i\vec{k}_{m}t/h}$$

$$TISE \left[-\frac{\hbar^{2}}{2\mu} \overrightarrow{\nabla}^{L} + v(\overrightarrow{n}) \right] \Psi_{m}(\overrightarrow{n}) = E_{m} \Psi_{m}(\overrightarrow{n})$$

$$SPECIAL CASE control potential $V(\overrightarrow{n}) = V(n) = -\frac{e^{L}}{n} I+vpedGRN$

$$-\frac{2e^{L}}{n} I+vpedGRN$$

$$-\frac{2e^{L}}{n} I+vpedGRN$$

$$V(n) \overrightarrow{n} = periody = pometric = 7 \overrightarrow{L} \overrightarrow{n} = conserved$$

$$SEPARATE ALAIN = product = ansatz$$

$$\Psi_{m}(\overrightarrow{n}) = R(n) A_{L}(\overrightarrow{0}, \Psi)$$

$$\left[-\frac{\hbar^{L}}{2\mu} \overrightarrow{\nabla}^{L} + v(n) \right] R(n) A_{L}(\overrightarrow{0}, \Psi)$$

$$= E_{m} R(n) - 4 (\overrightarrow{0}, \Psi)$$

$$= -\frac{\hbar^{L}}{2\mu} \left[-\frac{1}{n} \frac{2^{L}}{2\mu n} n + -\frac{1}{n^{L}} \left\{ -\frac{2L}{2\mu n} + \cot{\theta} -\frac{2}{2\theta} + \frac{1}{2\theta n^{L}} - \frac{2L}{2\mu n} \right\} \right]$$$$

NEW TISE

$$\begin{bmatrix} -\frac{\hbar^{2}}{2\mu n} & \frac{\lambda^{L}}{2\mu n^{L}} & n - \frac{c^{2}}{n} + \frac{2(2+i)\hbar^{2}}{2\mu n^{L}} \end{bmatrix} R_{m} = E_{m} R_{m}$$
Id PLOBLEM
WITH EFFRCTIVE PITENTIAL
U APP (n) = $-\frac{c^{L}}{n} + \frac{2(2+i)\hbar^{2}}{2\mu n^{L}}$
COULONB
ATTRACTION
Etal
E

Make the radial equation dimensionless
START TO SOLVE
made equation dimensionless
$$n \rightarrow p$$

length $a_0 = \frac{4L}{me^L}$ Bowle RADIUS = 0.5LR
 $p = \pi/a_0$ dimensionless length
 $mangp = \epsilon_0 = \frac{k^L}{2ma_0^2} = -13.6 \text{ ev}$ RYDEREC
 $E = \lambda^L$
 $\lambda^L = \epsilon_n/\epsilon_0$ dimensionless energy
 $\frac{2ma_0^L}{\pi L} \left[-\frac{\pi L}{2m\pi} - \frac{\lambda^L}{2m^L} + \frac{4^L R(k+1)}{2m\pi^L} - \frac{a^L}{\pi} \right] R_m L = \epsilon_m R_m R$
 $\pi + \left[-\frac{a_0^L}{\pi} - \frac{2L}{2\pi L^L} + \frac{4L(k+1)}{2m\pi^L} - \frac{LmeL}{\pi L} - \frac{a_0^L}{\pi} \right] LmL = \lambda^L R_m R$
 $= -\frac{2^L}{2\left(\frac{\pi}{m}\right)^L} + \frac{L(k+1)}{p^L} - \left(\frac{2}{4\pi}\right)\left(\frac{4\pi}{\pi}\right)$
 $\int S = \pi R_m R$
 $\left[-\frac{a_0^L}{a_0^L} - \frac{L(k+1)}{p^L} + \frac{L}{p} - \lambda^L \right] S(p) = 0$



$$\frac{d}{d\rho} \left[-\lambda e^{-\lambda\rho} Y + e^{-\lambda\rho} \frac{dY}{d\rho} \right]$$

$$+\lambda^{L} e^{-\lambda\rho} Y - \lambda e^{-\lambda\rho} \frac{dY}{d\rho} + \lambda e^{-\lambda\rho} \frac{dY}{d\rho} + e^{-\lambda\rho} \frac{d^{L}Y}{d\rho^{L}}$$

$$-2\lambda \dots$$

$$e^{-\lambda\rho} \left[\frac{dL}{d\rho^{L}} - 2\lambda \frac{d}{d\rho} + \lambda^{L} - \frac{2(L+i)}{\rho^{L}} + \frac{2}{\rho} - \lambda^{L} \right] Y(\rho) = 0$$
what is able the equation and that $\psi(n) \to 0$ is $n \to 0$
Solve using power series
$$\frac{1}{\psi(\rho)} = \rho^{m} \sum_{m=0}^{\infty} c_{m} \rho^{m} = \sum_{m=0}^{\infty} c_{m} \rho^{m+m}$$

$$\frac{1}{m} \sum_{m=0}^{m} c_{m} \rho^{m} = \sum_{m=0}^{\infty} c_{m} \rho^{m+m}$$

$$\frac{1}{d\rho} \left[\sum_{m=0}^{\infty} c_{m} \rho^{m+m} \right] = \sum_{m=0}^{\infty} (m+m) c_{m} \rho^{(m+m-1)}$$

$$\frac{d^{L}Y}{d\rho^{L}} = \frac{d}{d\rho} \left[\sum_{m=0}^{\infty} (m+m) c_{m} \rho^{(m+m-1)} \right] = \sum_{m=0}^{\infty} (m+m) (m+m-1) c_{m} \rho^{(m+m-1)}$$

lowest power of p is (m-2) TH. (pl+m)(pl+m-1) Cop^{m-2} - $\frac{2(2+1)}{p^2}$ Cop^m $\left[m(m-1) - \ell(\ell+1)\right] c_0 = 0 \qquad = > m = \ell+1$ coefficient of the (m+m-2) TH TERM $\sum_{m=0}^{\infty} (m+m)(m+m-1) Cm \rho = 2\lambda(m+m) Cm \rho$ $+ \frac{2}{p!} c_m p^{(m+m)-1} - \frac{L(L+1)}{p!} c_m p^{(m+m)-2}$ = 0 $[m+m](m+m-1) - l(l+1)] Cm + [-2\lambda (m-1+m) + 2] Cm-1 = 0$ $\int [(m+\ell+1) (m+\ell) - \ell(\ell+1)] Cm = 2 [(m+\ell)\lambda - 1] Cm-1$ L= m-1 $m [m+2e+1] Cm = 2 [(m+2)\lambda -1] Cm-1$ relation $C_m = \frac{2[(m+\ell)\lambda - i]}{n[m+\ell\ell + i]} C_{m-1}$ recursion special values of A terminale for hydrogen energy eigenvalues TWO CONPITIONS 1) POLYNOMIAL STARTS WITH P 2+1 finite 410) POLYNOMIAL STOPS WITH PM+2 finite energy Z)

regneracy is

$$c_{m} = \frac{2\left[\left(m+2\right)\lambda - i\right]}{m\left(m+2k+1\right)} \quad c_{m-1}$$

$$(m+2)\lambda - 1 = 0$$

$$\lambda = \left(\frac{i}{m+2}\right) = \frac{1}{(j+k)}$$

$$mapp \qquad \lambda^{k} = \frac{E_{m}}{E_{0}}$$

$$E_{m} = -\frac{1}{(j+k)^{k}} \quad E_{0}$$

$$E_{m} = -\frac{1}{m^{k}} \quad E_{0}$$

$$\frac{E_{m} = -\frac{1}{m^{k}} \quad E_{0}}{\left[\frac{E_{m} - \frac{1}{m^{k}}}{E_{0}}\right]}$$

$$\frac{P_{m}e_{m}(\vec{x}') = -2me(n) \quad Yem(\theta, \varphi) = -\frac{e^{-\lambda \rho}}{e_{0}\rho} \quad Y_{m}e(\rho) \quad Yem(\theta, \varphi)$$

$$= N \quad e^{-\rho/m} \left[-\frac{Yme(\rho)}{\rho}\right] \quad Yem(\theta, \varphi)$$

$$Y \quad gree from \ e^{-imm}$$

$$[] \quad gree from \ e^{-imm}$$

Associated Laguerre Polynomials

Some wag once said the nice thing about standards is that there are so many to choose from. I have been trying to come to grips with the difference between what I presented in class and the formulae in Sakurai. It is easy to explain the differences on the basis of different conventions about the associated Laguerre polynomials.

If you want to skip details, a main result is that Sakurai and *Mathematica* use different conventions. If we call $\mathcal{L}_n^q(\rho)$ the convention of Sakurai and $L_p^{(q)}(\rho)$ the convention of *Mathematica*, we have

$$\mathcal{L}_{p+q}^{q}(\rho) = (p+q)!(-1)^{q}L_{p}^{(q)}(\rho)$$

Below are the details. They are presented somewhat in the order of my investigation and not according to the shorted derivation of the above result.

Differential equation

I have consulted two well known books on mathematical functions that adhere to the same index convention, but have different normalization conventions. The first book that I consulted by Abramowitz & Stegun states on pg 778, Eqs. (22.5.16) and (22.5.17):

$$L_n^{(0)}(x) = L_n(x)$$
$$L_n^{(m)}(x) = (-1)^m \frac{d^m}{dx^m} [L_{n+m}(x)]$$

Also, on pg 781, in Eq. (22.6.15), the differential equation is given.

$$x\frac{d^2}{dx^2}L_n^{(\alpha)}(x) + (\alpha + 1 - x)\frac{d}{dx}L_n^{(\alpha)}(x) + nL_n^{(\alpha)}(x) = 0.$$

The differential equation is very valuable, but being linear, does not tell us anything about the normalization.

Another well known book by Morse & Feshbach on pg 784, in an unnumbered equation three lines from the bottom of the page gives their convention for the associated Laguerre polynomials.

$$L_n^m(z) = (-1)^m \frac{d^m}{dx^m} [L_{n+m}^0(z)] \; .$$

The differential equation is also given a few lines above:

$$z\frac{d^2}{dz^2}L_n^a(z) + (a+1-z)\frac{d}{dz}L_n^a(z) + nL_n^a(z) = 0.$$

Morse & Feshbach do not put the upper index in parentheses, otherwise, it looks like these conventions might agree. We can be pretty certain that in these two books the $L_n^{(a)}$ is a polynomial of degree n. However, we will soon see that the normalizations don't agree in the two books.

Sakurai convention

Now, let's turn to Sakurai. On pg 454 in Eq. (A.6.4), we find

$$L_p^q(\rho) = \frac{d^q}{d\rho^q} L_p(\rho)$$

This leads us to conclude that L_p^q is of degree p - q, and makes the result above plausible. In fact, if the normalizations were the same, we would expect:

 $\mathcal{L}^q_{p+q}(
ho) = rac{d^q}{d
ho^q} L_{p+q}(
ho) = (-1)^q L_p^{(q)}(
ho) \qquad ext{Not quite correct!} \; .$

Class Derivation

In class, I presented the differential equation for the associated Laguerre polynomials as stated by *Mathematica*,

$$xy'' + (a+1-x)y' + ny = 0.$$

This is the same convention as Abramowitz & Stegun and Morse & Feshbach.

In class, we found we needed to solve this differential equation:

$$\rho L'' + (2(l+1) - \rho)L' + (\lambda - l - 1)L = 0 ,$$

but $\lambda = n$, the total quantum number, and n - l - 1 = n' the radial quantum number. So, we have

$$\rho L'' + (2l + 1 + 1 - \rho)L' = n'L = 0 .$$

In the notation of Abramowitz & Stegun, *Mathematica* or the Morse & Feshbach index convention, the solution to the differential equation is

$$L_{n'}^{(2l+1)}(\rho) = L_{n-l-1}^{(2l+1)}(\rho)$$

In Sakurai notation, $L_{n-l-1}^{(2l+1)}(\rho) = (-1)^{2l+1} \mathcal{L}_{n+l}^{2l+1} = -\mathcal{L}_{n+l}^{2l+1}$. This explains the indices for R_{nl} in Sakurai in the equation above (A.6.3).

Pinning Down the Normalizations

We still need to consider normalization conventions, and that can be done from the generating function or from what is know as Rodrigues' formula. In fact, in retrospect, it seems that just looking at the Rodrigues' formulae in the three books might have been the easiest way to proceed.

In Abramowitz & Stegun, we find on pg 785, Eq. (22.11.6)

$$L_n^{(\alpha)}(x) = \frac{1}{n!} e^x x^{-\alpha} \frac{d^n}{dx^n} [x^{n+\alpha} e^{-x}] .$$

On pg 784 of Morse & Feshbach, we find

$$L_n^a(z) = \frac{\Gamma(a+n+1)}{\Gamma(n+1)} \frac{e^z}{z^{\alpha}} \frac{d^n}{dz^n} [z^{a+n} e^{-z}] .$$

If we set α and a to zero, we can compare with Sakurai, which states in Eq. (A.6.5)

$$L_p(\rho) = e^{\rho} \frac{d^p}{d\rho^p} (\rho^p e^{-\rho}) \,.$$

We immediately see that Sakurai agrees in normalization with Morse & Feshbach, at least for the Laguerre polynomials, if not for the associated Laguerre polynomials. However, the two books on mathematical methods differ by a factor of (n + a)! in their normalizations with Abramowitz & Stegun convention being smaller by division by that factor. Morse & Feshbach include a small table of associated Laguerre polynomials at the bottom of page 784. They have $L_0^n = n!$, whereas Abramowitz & Stegun according to Eq. (22.4.7) have $L_0^{(\alpha)} = 1$. The only remaining mystery is which normalization convention *Mathematica* obeys. With this command

$$Table[\{n, LaguerreL[0, n, x]\}, \{n, 0, 6\}]$$

you will easily find that all results are 1 and *Mathematica* follows the Abramowitz & Stegun normalization.

Further, I coded up the Rodrigues' formula with the Sakurai convention and compared with $(p+q)!(-1)^q L_p^{(q)}$ where the I used the *Mathematica* function LaguerreL[p,q,x]. They were in agreement.

Mystery solved! Quantum mechanics and children can now sleep soundly at night.

The Separation of Variables

Chapter 10 The Hydrogen Atom

There are many good reasons to address the hydrogen atom beyond its historical significance. Though hydrogen spectra motivated much of the early quantum theory, research involving the hydrogen remains at the cutting edge of science and technology. For instance, transitions in hydrogen are being used in 1997 and 1998 to examine the constancy of the fine structure constant over a cosmological time scale². From the view point of pedagogy, the hydrogen atom merges many of the concepts and techniques previously developed into one package. It is a particle in a box with spherical, soft walls. Finally, the hydrogen atom is one of the precious few realistic systems which can actually be solved analytically.

The Schrodinger Equation in Spherical Coordinates

In chapter 5, we separated time and position to arrive at the time independent Schrodinger equation which is

$$\mathcal{H} \left| E_i \right\rangle = E_i \left| E_i \right\rangle, \tag{10-1}$$

where E_i are eigenvalues and $|E_i\rangle$ are energy eigenstates. Also in chapter 5, we developed a one dimensional position space representation of the time independent Schrodinger equation, changing the notation such that $E_i \to E$, and $|E_i\rangle \to \psi$. In three dimensions the Schrodinger equation generalizes to

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi = E\psi,$$
 TISE

where ∇^2 is the Laplacian operator. Using the Laplacian in spherical coordinates, the Schrödinger equation becomes

$$-\frac{\hbar^2}{2m} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \psi + V(r)\psi = E\psi.$$
(10 - 2)

In spherical coordinates, $\psi = \psi(r, \theta, \phi)$, and the plan is to look for a variables separable solution such that $\psi(r, \theta, \phi) = R(r) Y(\theta, \phi)$. We will in fact find such solutions where $Y(\theta, \phi)$ are the spherical harmonic functions and R(r) is expressible in terms of associated Laguerre functions. Before we do that, interfacing with the previous chapter and arguments of linear algebra may partially explain why we are proceeding in this direction.

Complete Set of Commuting Observables for Hydrogen

Though we will return to equation (10-2), the Laplacian can be expressed

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\left(\frac{\partial^2}{\partial \theta^2} + \frac{1}{\tan\theta}\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right).$$
 (10-3)

Compare the terms in parenthesis to equation 11–33. The terms in parenthesis are equal to $-\mathcal{L}^2/\hbar^2$, so assuming spherical symmetry, the Laplacian can be written

radial plus angular

 $abla^2 = rac{\partial^2}{\partial r^2} + rac{2}{r}rac{\partial}{\partial r} - rac{\mathcal{L}^2}{r^2\hbar^2},$

angular => spherical harmonics

 2 Schwarzschild. "Optical Frequency Measurement is Getting a Lot More Precise," Physics Today 50(10) 19–21 (1997).

and the Schrodinger equation becomes

$$\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{\mathcal{L}^2}{r^2\hbar^2}\right) + V(r)\right]\psi = E\psi.$$
(10-4)

Assuming spherical symmetry, which we will have because a Coulomb potential will be used for V(r), we have complicated the system of chapter 11 by adding a radial variable. Without the radial variable, we have a complete set of commuting observables for the angular momentum operators in \mathcal{L}^2 and \mathcal{L}_z . Including the radial variable, we need a minimum of one more operator, if that operator commutes with both \mathcal{L}^2 and \mathcal{L}_z . The total energy operator, the Hamiltonian, may be a reasonable candidate. What is the Hamiltonian here? It is the group of terms within the square brackets. Compare equations (10–1) and (10–4) if you have difficulty visualizing that. In fact,

H commutes with

angular momentum

$$\left[\mathcal{H}, \mathcal{L}^2\right] = 0, \quad \text{and} \quad \left[\mathcal{H}, \mathcal{L}_z\right] = 0,$$

so the Hamiltonian is a suitable choice. The complete set of commuting observables for the hydrogen atom is \mathcal{H} , \mathcal{L}^2 , and \mathcal{L}_z . We have all the eigenvalue/eigenvector equations, because the time independent Schrodinger equation is the eigenvalue/eigenvector equation for the Hamiltonian operator, *i.e.*, the the eigenvalue/eigenvector equations are

simultaneous eigenvalue and eigenvector problem

$$\mathcal{H} |\psi\rangle = E_n |\psi\rangle, \\ \mathcal{L}^2 |\psi\rangle = l(l+1)\hbar^2 |\psi\rangle, \\ \mathcal{L}_z |\psi\rangle = m\hbar |\psi\rangle,$$

where we subscripted the energy eigenvalue with an n because that is the symbol conventionally used for the energy quantum number (per the particle in a box and SHO). Then the solution to the problem is the eigenstate which satisfies all three, denoted $|n, l, m\rangle$ in abstract Hilbert space. The representation in position space in spherical coordinates is

$$r, \theta, \phi | n, l, m > = \psi_{nlm}(r, \theta, \phi).$$

Example 10–1: Starting with the Laplacian included in equation (10–2), show the Laplacian can be express as equation (10–3).

< 1

$$\begin{aligned} \nabla^2 &= \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \\ &= \frac{1}{r^2} \left(2r \frac{\partial}{\partial r} + r^2 \frac{\partial^2}{\partial r^2} \right) + \frac{1}{r^2 \sin \theta} \left(\cos \theta \frac{\partial}{\partial \theta} + \sin \theta \frac{\partial^2}{\partial \theta^2} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \\ &= \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} + \frac{1}{r^2 \tan \theta} \frac{\partial}{\partial \theta} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \\ &= \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \left(\frac{\partial^2}{\partial \theta^2} + \frac{1}{\tan \theta} \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right), \end{aligned}$$

which is the form of equation (10-3).

Example 10–2: Show $\left[\mathcal{H}, \mathcal{L}^2\right] = 0.$

$$\left[\mathcal{H}, \mathcal{L}^2 \right] = \mathcal{H}\mathcal{L}^2 - \mathcal{L}^2 \mathcal{H}$$

$$= \left[-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{\mathcal{L}^2}{r^2 \hbar^2} \right) + V(r) \right] \mathcal{L}^2 - \mathcal{L}^2 \left[-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} - \frac{\mathcal{L}^2}{r^2 \hbar^2} \right) + V(r) \right]$$
$$= -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} \mathcal{L}^2 - \frac{\hbar^2}{2m} \frac{2}{r} \frac{\partial}{\partial r} \mathcal{L}^2 + \frac{\hbar^2}{2m} \frac{\mathcal{L}^4}{r^2 \hbar^2} + \frac{\hbar^2}{2m} V(r) \mathcal{L}^2$$
$$+ \frac{\hbar^2}{2m} \mathcal{L}^2 \frac{\partial^2}{\partial r^2} + \frac{\hbar^2}{2m} \mathcal{L}^2 \frac{2}{r} \frac{\partial}{\partial r} - \frac{\hbar^2}{2m} \frac{\mathcal{L}^4}{r^2 \hbar^2} - \frac{\hbar^2}{2m} \mathcal{L}^2 V(r)$$
$$= -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} \mathcal{L}^2 - \frac{\hbar^2}{2m} \frac{2}{r} \frac{\partial}{\partial r} \mathcal{L}^2 + \frac{\hbar^2}{2m} V(r) \mathcal{L}^2 + \frac{\hbar^2}{2m} \mathcal{L}^2 \frac{\partial^2}{\partial r^2} + \frac{\hbar^2}{2m} \mathcal{L}^2 \frac{2}{r} \frac{\partial}{\partial r} - \frac{\hbar^2}{2m} \mathcal{L}^2 V(r)$$

where the third and seventh terms in \mathcal{L}^4 sum to zero. The spherical coordinate representation of \mathcal{L}^2 is

$$\mathcal{L}^2 = -\hbar^2 \left(\frac{\partial^2}{\partial \theta^2} + \frac{1}{\tan \theta} \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right)$$

and has angular dependence only. The partial derivatives with respect to the radial variable act only on terms without radial dependence. Partial derivatives with respect to angular variables do not affect the potential which is a function only of the radial variable. Therefore, the order of the operator products is interchangeable, and

$$\left[\mathcal{H}, \mathcal{L}^{2}\right] = -\frac{\hbar^{2}}{2m}\mathcal{L}^{2}\frac{\partial^{2}}{\partial r^{2}} - \frac{\hbar^{2}}{2m}\mathcal{L}^{2}\frac{2}{r}\frac{\partial}{\partial r} + \frac{\hbar^{2}}{2m}\mathcal{L}^{2}V(r) + \frac{\hbar^{2}}{2m}\mathcal{L}^{2}\frac{\partial^{2}}{\partial r^{2}} + \frac{\hbar^{2}}{2m}\mathcal{L}^{2}\frac{2}{r}\frac{\partial}{\partial r} - \frac{\hbar^{2}}{2m}\mathcal{L}^{2}V(r) = 0.$$

Instead of the verbal argument, we could substitute the angular representation of \mathcal{L}^2 , form the 18 resultant terms, explicitly interchange nine of them, and get the same result.

Example 10–3: Show $[\mathcal{H}, \mathcal{L}_z] = 0.$

$$\begin{split} \left[\mathcal{H},\mathcal{L}_{z}\right] &= \mathcal{H}\mathcal{L}_{z} - \mathcal{L}_{z} \mathcal{H} \\ &= \left[-\frac{\hbar^{2}}{2m}\left(\frac{\partial^{2}}{\partial r^{2}} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{\mathcal{L}^{2}}{r^{2}\hbar^{2}}\right) + V(r)\right]\mathcal{L}_{z} - \mathcal{L}_{z}\left[-\frac{\hbar^{2}}{2m}\left(\frac{\partial^{2}}{\partial r^{2}} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{\mathcal{L}^{2}}{r^{2}\hbar^{2}}\right) + V(r)\right] \\ &= -\frac{\hbar^{2}}{2m}\frac{\partial^{2}}{\partial r^{2}}\mathcal{L}_{z} - \frac{\hbar^{2}}{2m}\frac{2}{r}\frac{\partial}{\partial r}\mathcal{L}_{z} + \frac{\hbar^{2}}{2m}\frac{\mathcal{L}^{2}\mathcal{L}_{z}}{r^{2}\hbar^{2}} + \frac{\hbar^{2}}{2m}V(r)\mathcal{L}_{z} \\ &\qquad + \frac{\hbar^{2}}{2m}\mathcal{L}_{z}\frac{\partial^{2}}{\partial r^{2}} + \frac{\hbar^{2}}{2m}\mathcal{L}_{z}\frac{2}{r}\frac{\partial}{\partial r} - \frac{\hbar^{2}}{2m}\frac{\mathcal{L}_{z}\mathcal{L}^{2}}{r^{2}\hbar^{2}} - \frac{\hbar^{2}}{2m}\mathcal{L}_{z}V(r) \\ &= -\frac{\hbar^{2}}{2m}\frac{\partial^{2}}{\partial r^{2}}\mathcal{L}_{z} - \frac{\hbar^{2}}{2m}\frac{2}{r}\frac{\partial}{\partial r}\mathcal{L}_{z} + \frac{\hbar^{2}}{2m}V(r)\mathcal{L}_{z} + \frac{\hbar^{2}}{2m}\mathcal{L}_{z}\frac{\partial^{2}}{\partial r^{2}} + \frac{\hbar^{2}}{2m}\mathcal{L}_{z}\frac{2}{r}\frac{\partial}{\partial r} - \frac{\hbar^{2}}{2m}\mathcal{L}_{z}V(r) \end{split}$$

where the third and seventh terms in $\mathcal{L}^2 \mathcal{L}_z$ sum to zero because we already know those two operators commute. The spherical coordinate representation of \mathcal{L}_z is

$${\cal L}_z = -i\hbar {\partial\over\partial\phi}$$

and has angular dependence only. Again there are no partial derivatives which affect any term of the other operator, or the potential V(r), in any of the operator products. Therefore, the order of the operator products is interchangeable, and

$$\left[\mathcal{H},\mathcal{L}_{z}\right] = -\frac{\hbar^{2}}{2m}\mathcal{L}_{z}\frac{\partial^{2}}{\partial r^{2}} - \frac{\hbar^{2}}{2m}\mathcal{L}_{z}\frac{2}{r}\frac{\partial}{\partial r} + \frac{\hbar^{2}}{2m}\mathcal{L}_{z}V(r) + \frac{\hbar^{2}}{2m}\mathcal{L}_{z}\frac{\partial^{2}}{\partial r^{2}} + \frac{\hbar^{2}}{2m}\mathcal{L}_{z}\frac{2}{r}\frac{\partial}{\partial r} - \frac{\hbar^{2}}{2m}\mathcal{L}_{z}V(r) = 0.$$

Separating Radial and Angular Dependence

In this and the following three sections, we illustrate how the angular momentum and magnetic moment quantum numbers enter the symbology from a calculus based argument. In writing equation (10-2), we have used a representation, so are no longer in abstract Hilbert space. One of the consequences of the process of representation is the topological arguments of linear algebra are obscured. They are still there, simply obscured because the special functions we use are orthogonal, so can be made orthonormal, and complete, just as bras and kets in a dual space are orthonormal and complete. The primary reason to proceed in terms of a position space representation is to attain a position space description. One of the by-products of this chapter may be to convince you that working in the generality of Hilbert space in Dirac notation can be considerably more efficient. Since we used topological arguments to develop angular momentum in the last chapter, and arrive at identical results to those of chapter 11, we rely on connections between the two to establish the meanings of of l and m. They have the same meanings within these calculus based discussions.

As noted, we assume a variables separable solution to equation (10-2) of the form

product ansatz $\psi(r,\theta,\phi) = R(r)Y(\theta,\phi).$ (10-5)

An often asked question is "How do you know you can assume that?" You do not know. You assume it, and if it works, you have found a solution. If it does not work, you need to attempt other methods or techniques. Here, it will work. Using equation (10-5), equation (10-2) can be written

put it in
$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) R(r) Y(\theta, \phi) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) R(r) Y(\theta, \phi) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} R(r) Y(\theta, \phi) - \frac{2m}{\hbar^2} \left[V(r) - E \right] R(r) Y(\theta, \phi) = 0$$

futz around $\Rightarrow Y(\theta, \phi) \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) R(r) + R(r) \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) Y(\theta, \phi) + R(r) \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} Y(\theta, \phi) - \frac{2m}{\hbar^2} \left[V(r) - E \right] R(r) Y(\theta, \phi) = 0.$

Dividing the equation by $R(r) Y(\theta, \phi)$, multiplying by r^2 , and rearranging terms, this becomes

Find it works!
$$\left\{\frac{1}{R(r)}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)R(r) - \frac{2mr^2}{\hbar^2}\left[V(r) - E\right]\right\}$$
 depends only on r

depends only on angles $+ \left[\frac{1}{Y(\theta,\phi)\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) Y(\theta,\phi) + \frac{1}{Y(\theta,\phi)\sin^2\theta} \frac{\partial^2}{\partial\phi^2} Y(\theta,\phi) \right] = 0.$

The two terms in the curly braces depend only on r, and the two terms in the square brackets depend only upon angles. With the exception of a trivial solution, the only way the sum of the groups can be zero is if each group is equal to the same constant. The constant chosen is known as the **separation constant**. Normally, an arbitrary separation constant, like K, is selected and then you solve for K later. In this example, we are instead going to stand on the shoulders of

=> they must be constant

some of the physicists and mathematicians of the previous 300 years, and make the enlightened choice of l(l+1) as the separation constant. It should become clear l is the angular momentum quantum number introduced in chapter 11. Then

$$\frac{1}{R(r)}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)R(r) - \frac{2mr^2}{\hbar^2}\left[V(r) - E\right] = l(l+1)$$
(10-6)

ansatz

which we call the radial equation, and

$$\frac{1}{Y(\theta,\phi)\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)Y(\theta,\phi) + \frac{1}{Y(\theta,\phi)\sin^2\theta}\frac{\partial^2}{\partial\phi^2}Y(\theta,\phi) = -l(l+1), \quad (10-7)$$

which we call the **angular equation**. Notice the signs on the right side are opposite so they do, in fact, sum to zero

The Angular Equation

The solutions to equation (10–7) are the spherical harmonic functions, and the l used in the separation constant is, in fact, the same used as the index l in the spherical harmonics $Y_{l,m}(\theta, \phi)$. In fact, it is the angular momentum quantum number. But where is the index m? How is the magnetic moment quantum number introduced? To answer these questions, remember the spherical harmonics are also separable, *i.e.*, $Y_{l,m}(\theta, \phi) = f_{l,m}(\theta) g_{n}(\phi)$. We will use such a solution in the angular equation, without the indices until we see where they originate. Using the solution $Y(\theta, \phi) = f(\theta) g(\phi)$ in equation (10–7),

$$\frac{1}{f(\theta) g(\phi) \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) f(\theta) g(\phi) + \frac{1}{f(\theta) g(\phi) \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} f(\theta) g(\phi) = -l(l+1)$$

$$\Rightarrow \frac{1}{f(\theta) \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) f(\theta) + \frac{1}{g(\phi) \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} g(\phi) = -l(l+1).$$

Multiplying the equation by $\sin^2 \theta$ and rearranging,

only on theta
$$\longrightarrow \frac{\sin\theta}{f(\theta)} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta}\right) f(\theta) + l(l+1) \sin^2\theta + \frac{1}{g(\phi)} \frac{\partial^2}{\partial\phi^2} g(\phi) = 0.$$

The first two terms depend only on θ , and the last term depends only on ϕ . Again, the only non-trivial solution such that the sum is zero is if the groups of terms each dependent on a single variable is equal to the same constant. Again using an enlightened choice, we pick m^2 as the separation constant, so

$$\frac{\sin\theta}{f(\theta)}\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\right)f(\theta) + l(l+1)\sin^2\theta = m^2,\tag{10-8}$$

simple phi equation
$$\frac{1}{g(\phi)} \frac{d^2}{d\phi^2} g(\phi) = -m^2,$$
 (10-9)

and that is how the magnetic moment quantum number is introduced. Again, (10-8) and (10-9) need to sum to zero so the separation constant has opposite signs on the right side in the two equations.

m is "enlightened"

only on phi

choice for phi

The Azimuthal Angle Equation

aka, the phi equation, the magnetic quantum number equation, ...

The solution to the azimuthal angle equation, equation (10-9), is

$$g(\phi) = e^{im\phi} \Rightarrow g_m(\phi) = e^{im\phi},$$
 (10 - 10)

where the subscript m is added to $g(\phi)$ because it is now clear there are as many solutions as there are allowed values of m.

Example 10–4: Show $g_m(\phi) = e^{im\phi}$ is a solution to equation (10–9).

$$\frac{d^2}{d\phi^2}g_m(\phi) = \frac{d^2}{d\phi^2}e^{im\phi} = \frac{d}{d\phi}(im)e^{im\phi} = (im)^2e^{im\phi} = -m^2g_m(\phi).$$

Using this in equation (10-9),

$$\frac{1}{g(\phi)}\frac{d^2}{d\phi^2}g(\phi) = -m^2 \quad \Rightarrow \quad \frac{1}{g(\phi)}\Big(-m^2g_m(\phi)\Big) = -m^2 \quad \Rightarrow \quad -m^2 = -m^2,$$

therefore $g_m(\phi) = e^{im\phi}$ is a solution to equation (10–9).

The Polar Angle Equation

aka, the theta equation

This section is a little more substantial than the last. Equation (10–8) can be written

$$\sin\theta \frac{d}{d\theta} \left(\sin\theta \frac{d}{d\theta}\right) f(\theta) + l(l+1) \sin^2\theta f(\theta) - m^2 f(\theta) = 0.$$

Evaluating the first term,

$$\sin\theta \frac{d}{d\theta} \left(\sin\theta \frac{d}{d\theta}\right) f(\theta) = \sin\theta \frac{d}{d\theta} \left(\sin\theta \frac{df(\theta)}{d\theta}\right)$$
$$= \sin\theta \left(\cos\theta \frac{df(\theta)}{d\theta} + \sin\theta \frac{d^2f(\theta)}{d\theta^2}\right)$$
$$= \sin^2\theta \frac{d^2f(\theta)}{d\theta^2} + \sin\theta \cos\theta \frac{df(\theta)}{d\theta}.$$

Using this, equation (10-8) becomes

$$\sin^2\theta \,\frac{d^2f(\theta)}{d\theta^2} + \sin\theta\,\cos\theta\,\frac{df(\theta)}{d\theta} + l(l+1)\,\sin^2\theta\,f(\theta) - m^2\,f(\theta) = 0. \tag{10-11}$$

We are going to change variables using $x = \cos \theta$, and will comment on this substitution later. We then need the derivatives with respect to x vice θ , so

$$\frac{d f(\theta)}{d\theta} = \frac{d f(x)}{dx} \frac{dx}{d\theta} = \frac{d f(x)}{dx} \left(-\sin \theta \right) = -\sin \theta \frac{d f(x)}{dx},$$

and

$$\frac{d^2 f(\theta)}{d\theta^2} = \frac{d}{d\theta} \left(-\sin\theta \, \frac{d f(x)}{dx} \right) = -\cos\theta \, \frac{d f(x)}{dx} - \sin\theta \, \frac{d}{d\theta} \, \frac{d f(x)}{dx}$$
$$= -\cos\theta \, \frac{d f(x)}{dx} - \sin\theta \, \frac{d}{dx} \, \frac{dx}{d\theta} \, \frac{d f(x)}{dx} = -\cos\theta \, \frac{d f(x)}{dx} - \sin\theta \, \frac{d}{dx} \left(-\sin\theta \right) \frac{d f(x)}{dx}$$
$$= -\cos\theta \, \frac{d f(x)}{dx} + \sin^2\theta \, \frac{d^2 f(x)}{dx^2}.$$

Substituting just the derivatives in the equation (10–11),

$$\sin^2\theta \left(\sin^2\theta \frac{d^2f(x)}{dx^2} - \cos\theta \frac{df(x)}{dx}\right) + \sin\theta\cos\theta \left(-\sin\theta \frac{df(x)}{dx}\right) + l(l+1)\sin^2\theta f(x) - m^2f(x) = 0,$$

which gives us an equation in both θ and x, which is not formally appropriate. This is, however, an informal text, and it becomes difficult to keep track of the terms if all the substitutions and reductions are done at once. Dividing by $\sin^2 \theta$, we get

$$\sin^2 \theta \, \frac{d^2 f(x)}{dx^2} - \cos \theta \, \frac{d f(x)}{dx} - \cos \theta \, \frac{d f(x)}{dx} + l(l+1) \, f(x) - \frac{m^2}{\sin^2 \theta} f(x) = 0$$

The change of variables is complete upon summing the two first derivatives, using $\cos \theta = x$, and **associated** $\sin^2 \theta = 1 - \cos^2 \theta = 1 - x^2$, which is

Legendre
$$(1-x^2)\frac{d^2 f(x)}{dx^2} - 2x\frac{d f(x)}{dx} + l(l+1)f(x) - \frac{m^2}{1-x^2}f(x) = 0.$$

This is the **associated Legendre equation**, which reduces to **Legendre equation** when m = 0. The function has a single argument so there is no confusion if the derivatives are indicated with primes, and the associated Legendre equation is often written

$$\left(1 - x^2\right)f''(x) - 2x\,f'(x) + l(l+1)\,f(x) - \frac{m^2}{1 - x^2}f(x) = 0,$$

and becomes the Legendre equation, Legendre equation when m=0

$$\left(1 - x^2\right) f''(x) - 2x f'(x) + l(l+1) f(x) = 0,$$

when m = 0. The solutions to the associated Legendre equation are the associated Legendre polynomials discussed briefly in the last section of chapter 11. To review that in the current context, associated Legendre polynomials can be generated from Legendre polynomials using

$$P_{l,m}(x) = (-1)^m \sqrt{(1-x^2)^m} \frac{d^m}{dx^m} P_l(x),$$

where the $P_l(x)$ are Legendre polynomials. Legendre polynomials can be generated using

The solutions are

the associated

$$P_l(x) = \frac{(-1)^l}{2^l l!} \frac{d^l}{dx^l} (1 - x^2)^l.$$

Solutions are the Legendre polynomials

Legendre polynomials

The use of these generating functions was illustrated in example 11-26 as intermediate results in calculating spherical harmonics.

The first few Legendre polynomials are listed in table 10–1. Our interest in those is to generate associated Legendre functions. The first few associated Legendre polynomials are listed in table 10-2.

symmetry around z-axis (m = 0)

 $P_0(x) = 1 \qquad P_3(x) = \frac{1}{2} (5x^3 - 3x)$ $P_1(x) = x \qquad P_4(x) = \frac{1}{8} (35x^4 - 30x^2 + 3)$ $P_2(x) = \frac{1}{2} (3x^2 - 1) \qquad P_5(x) = \frac{1}{8} (63x^5 - 70x^3 + 15x)$

Table 10 - 1. The First Six Legendre Polynomials.

no symmetry around z-axis $\begin{aligned} P_{0,0}(x) &= 1 & P_{2,0}(x) = \frac{1}{2} \left(3x^2 - 1 \right) \\ P_{1,1}(x) &= -\sqrt{1 - x^2} & P_{3,3}(x) = -15 \left(\sqrt{1 - x^2} \right)^3 \\ P_{1,0}(x) &= x & P_{3,2}(x) = 15x \left(1 - x^2 \right) \\ P_{2,2}(x) &= 3 \left(1 - x^2 \right) & P_{3,1}(x) = -\frac{3}{2} \left(5x^2 - 1 \right) \sqrt{1 - x^2} \\ P_{2,1}(x) &= -3x \sqrt{1 - x^2} & P_{3,0}(x) = \frac{1}{2} \left(5x^3 - 3x \right) \end{aligned}$

associated Legendre polynomials

Legendre

Polynomials

Table 10 - 2. The First Few Associated Legendre Polynomials.

Two comment concerning the tables are appropriate. First, notice $P_l = P_{l,0}$. That makes sense. If the Legendre equation is the same as the associated Legendre equation with m = 0, the solutions to the two equations must be the same when m = 0. Also, many authors will use a positive sign for all associated Legendre polynomials. This is a different choice of phase. We addressed that following table 11-1 in comments on spherical harmonics. We choose to include a factor of $(-1)^m$ with the associated Legendre polynomials, and the sign of all spherical harmonics will be positive as a result.

Finally, remember the change of variables $x = \cos \theta$. That was done to put the differential equation in a more elementary form. In fact, a dominant use of associated Legendre polynomials is in applications where the argument is $\cos \theta$. One example is the generating function for spherical harmonic functions.

Spherical Harmonics

and

$$f_{l,m}(\theta,\phi) = (-1)^m \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} P_{l,m}(\cos\theta) e^{im\phi} \qquad m \ge 0,$$
 (10 - 10)

$$Y_{l,-m}(\theta,\phi) = Y_{l,m}^*(\theta,\phi), \qquad m < 0,$$

where the $P_{l,m}(\cos\theta)$ are associated Legendre polynomials. If we need a spherical harmonic with m < 0, we will calculate the spherical harmonic with m = |m|, and then calculate the adjoint.

To summarize the last three sections, we separated the angular equation into an azimuthal and a polar portion. The solutions to the azimuthal angle equation are exponentials including the magnetic moment quantum number in the argument. The solutions to the polar angle equation are the associated Legendre polynomials, which are different for each choice of orbital angular momentum and magnetic moment quantum number. Both quantum numbers are introduced into the respective differential equations as separation constants. Since we assumed a product of the two functions to get solutions to the azimuthal and polar parts, the solutions to the original angular equation (10–7) are the products of the two solutions $P_{l,m}(\cos\theta) e^{im\phi}$. These factors are included in equation (10–10). All other factors in equation (10–12) are simply normalization constants. The products $P_{l,m}(\cos\theta) e^{im\phi}$ are the spherical harmonic functions, the alternating sign and radical just make the orthogonal set orthonormal.

Associated Laguerre Polynomials and Functions

The azimuthal equation was easy, the polar angle equation a little more substantial, but you will likely percieve the solution to the radial equation as plain, old heavy! There is no easy way to do this. Our approach will be to relate the radial equation to the associated Laguerre equation, for which the associated Laguerre functions are solutions. A popular option to solve the radial equation is a power series solution, for which we will refer you to Griffiths³, or Cohen–Tannoudji⁴.

Laguerre polynomials are solutions to the Laguerre equation

$$x L_{i}^{''}(x) + (1-x) L_{i}(x) + j L_{i}(x) = 0.$$

The first few Laguerre polynomials are listed in table 10–3.

Laguerre Polynomials

 $L_0(x) = 1$ $L_1(x) = -x + 1$ $L_2(x) = x^2 - 4x + 2$ $L_3(x) = -x^3 + 9x^2 - 18x + 6$ $L_4(x) = x^4 - 16x^3 + 72x^2 - 96x + 24$ $L_5(x) = -x^5 + 25x^4 - 200x^3 + 600x^2 - 600x + 120$ $L_6(x) = x^6 - 36x^5 + 450x^4 - 2400x^3 + 5400x^2 - 4320x + 720$ Table 10 - 3. The First Seven Laguerre Polynomials.

Laguerre polynomials of any order can be calculated using the generating function

$$L_j(x) = e^x \frac{d^j}{dx^j} e^{-x} x^j.$$

The Laguerre polynomials do not form an orthogonal set. The related set of Laguerre functions,

$$\phi_j(x) = e^{-x/2} L_j(x) \tag{10-13}$$

is orthonormal on the interval $0 \le x < \infty$. The Laguerre functions are not solutions to the Laguerre equation, but are solutions to an equation which is related.

Just as the Legendre equation becomes the associated Legendre equation by adding an appropriate term containing a second index, the associated Laguerre equation is

$$x L_j^{k''}(x) + (1 - x + k) L_j^{k'}(x) + j L_j^k(x) = 0, \qquad (10 - 14)$$

³ Griffiths, Introduction to Quantum Mechanics (Prentice Hall, Englewood Cliffs, New Jersey, 1995), pp. 134–141.

⁴ Cohen-Tannoudji, Diu, and Laloe, *Quantum Mechanics* (John Wiley & Sons, New York, 1977), pp. 794–797.

which reduces to the Laguerre equation when k = 0. The first few associated Laguerre polynomials are

associated Laguerre polynomials $\begin{array}{ll} L_0^0(x) = L_0(x) & L_0^2(x) = 2 \\ L_1^0(x) = L_1(x) & L_3^0(x) = L_3(x) \\ L_1^1(x) = -2x + 4 & L_3^1(x) = -4x^3 + 48x^2 - 144x + 96 \\ L_0^1(x) = 1 & L_2^3(x) = 60x^2 - 600x + 1200 \\ L_2^0(x) = L_2(x) & L_3^3(x) = -120x^3 + 2160x^2 - 10800x + 14400 \\ L_2^1(x) = 3x^2 - 18x + 18 & L_3^2(x) = -20x^3 + 300x^2 - 1200x + 1200 \\ L_2^2(x) = 12x^2 - 96x + 144 & L_1^3(x) = -24x + 96 \\ L_1^2(x) = -6x + 18 & L_0^3(x) = 6 \\ \end{array}$ Table 10 - 4. Some Associated Laguerre Polynomials.

Notice $L_j^0 = L_j$. Also notice the indices are all non-negative, and either index may assume any integral value. We will be interested only in those associated Laguerre polynomials where k < j for hydrogen atom wave functions.

Associated Laguerre polynomials can be calculated from Laguerre polynomials using the generating function

$$L_j^k(x) = \left(-1\right)^k \frac{d^k}{dx^k} L_{j+k}(x).$$

Example 10–5: Calculate $L_3^1(x)$ starting with the generating function.

We first need to calculate $L_4(x)$, because

$$L_j^k(x) = \left(-1\right)^k \frac{d^k}{dx^k} L_{j+k}(x) \quad \Rightarrow \quad L_3^1(x) = \left(-1\right)^1 \frac{d^1}{dx^1} L_{3+1}(x) = -\frac{d}{dx} L_4(x).$$

Similarly, if you want to calculate L_3^2 , you need to start with L_5 , and to calculate L_4^3 , you need to start with L_7 . So using the generating function,

$$\begin{split} L_4(x) &= e^x \frac{d^4}{dx^4} e^{-x} x^4 \\ &= e^x \frac{d^3}{dx^3} \left(-e^{-x} x^4 + e^{-x} 4x^3 \right) \\ &= e^x \frac{d^2}{dx^2} \left(e^{-x} x^4 - e^{-x} 4x^3 - e^{-x} 4x^3 + e^{-x} 12x^2 \right) = e^x \frac{d^2}{dx^2} \left(e^{-x} x^4 - e^{-x} 8x^3 + e^{-x} 12x^2 \right) \\ &= e^x \frac{d}{dx} \left(-e^{-x} x^4 + e^{-x} 4x^3 + e^{-x} 8x^3 - e^{-x} 24x^2 - e^{-x} 12x^2 + e^{-x} 24x \right) \\ &= e^x \frac{d}{dx} \left(-e^{-x} x^4 + e^{-x} 12x^3 - e^{-x} 36x^2 + e^{-x} 24x \right) \\ &= e^x \left(e^{-x} x^4 - e^{-x} 4x^3 - e^{-x} 12x^3 + e^{-x} 36x^2 + e^{-x} 36x^2 - e^{-x} 72x - e^{-x} 24x + e^{-x} 24 \right) \\ &= e^x e^{-x} \left(x^4 - 16x^3 + 72x^2 - 96x + 24 \right) \\ &= x^4 - 16x^3 + 72x^2 - 96x + 24, \end{split}$$

per table 10–4. Then to get $L_3^1(x)$,

$$L_3^1 = -\frac{d}{dx} L_4(x)$$

= $-\frac{d}{dx} (x^4 - 16x^3 + 72x^2 - 96x + 24)$
= $-(4x^3 - 48x^2 + 144x - 96)$
= $-4x^3 + 48x^2 - 144x + 96,$

per table 10–3

Associated Laguerre polynomials are not orthogonal but **associated Laguerre functions** of the type

$$\Phi_j^k(x) = e^{-x/2} x^{k/2} L_j^k(x)$$

are orthogonal on the interval $0 \le x < \infty$, so can be made an orthonormal set. Again, the $\Phi_j^k(x)$ are not solutions to the associated Laguerre equation but are solutions to a related equation.

We are specifically interested in a slightly different associated Laguerre function than the usual first choice indicated above, *i.e.*, we are interested in

$$y_j^k(x) = e^{-x/2} x^{(k+1)/2} L_j^k(x).$$
(10-15)

These are also not solutions to the associated Laguerre equation, but they are solutions to

$$y_j^{k''}(x) + \left(-\frac{1}{4} + \frac{2j+k+1}{2x} - \frac{k^2 - 1}{4x^2}\right)y_j^k(x) = 0.$$
 (10 - 16)

The reason for our interest in (10–16) and its solutions (10–15), is that equation (10–16) is a form of the radial equation, so the radial functions R(r) we seek are $R_{n,l}(r) = A y_n^l(r)$, where A is simply a normalization constant.

Example 10–6: Show equation (10–15) satisfies equation (10–16).

Unlike some of the toy problems given as examples, this example is a critical connection...unless you take our word for it, and then you should skip this. We are going to use the result of this example as a direct link to the solution of the radial equation. We are going to simplify the notation to minimize clutter, and will explain as we go.

To attain the second derivative, we need the first derivative, and use the notation

$$y = e^{-x/2} x^{(k+1)/2} v,$$

for equation (10–15) where $v = L_j^k(x)$, because the indices do not change and only serve to add clutter, and we can remember the independent variable is x. The first derivative is

$$\begin{split} y' &= -\frac{1}{2} e^{-x/2} x^{(k+1)/2} v + e^{-x/2} \left(\frac{k+1}{2}\right) x^{(k-1)/2} v + e^{-x/2} x^{(k+1)/2} v' \\ &= \left[-\frac{1}{2} v + \left(\frac{k+1}{2x}\right) v + v' \right] e^{-x/2} x^{(k+1)/2} \\ \Rightarrow \quad \left(e^{x/2} x^{-(k+1)/2} \right) y' &= -\frac{1}{2} v + \frac{k+1}{2x} v + v'. \end{split}$$

Notice we adjusted the second term on the right to do the factoring. Using the same adjustment technique, will factor these terms out of the second derivative as we go. These are also factors common to equation (10-15). Since the right side of equation (10-16) is zero, after we substitute the second derivative and the function into (10-16), we will simplify the equation by dividing the equation by common factors, therefore, none of the common factors will enter into the final solution. The exponentials and powers still need to be considered in differentiation, but their inverses will appear on the left and only the terms which have impact will appear on the right. Proceeding....

$$\left(e^{x/2}x^{-(k+1)/2}\right)y'' = \frac{1}{4}v - \frac{1}{2}\frac{k+1}{2x}v - \frac{1}{2}v' - \frac{1}{2}\frac{k+1}{2x}v + \frac{k+1}{2x}\frac{k-1}{2x}v + \frac{k+1}{2x}v' - \frac{1}{2}v' + \frac{k+1}{2x}v' + v''.$$

Substituting the second derivative and the function into equation (10–16),

$$y'' + \left(-\frac{1}{4} + \frac{2j+k+1}{2x} - \frac{k^2-1}{4x^2}\right)y = 0,$$

and dividing by the common factor of $e^{-x/2}x^{(k+1)/2}$, the remaining terms are

$$\begin{pmatrix} \frac{1}{4}v - \frac{1}{2}\frac{k+1}{2x}v - \frac{1}{2}v' - \frac{1}{2}\frac{k+1}{2x}v + \frac{k+1}{2x}\frac{k-1}{2x}v + \frac{k+1}{2x}v' - \frac{1}{2}v' + \frac{k+1}{2x}v' + v'' \end{pmatrix} + \begin{pmatrix} -\frac{1}{4} + \frac{2j+k+1}{2x} - \frac{k^2-1}{4x^2} \end{pmatrix} v = 0 \Rightarrow v'' + \frac{1}{4}v - \frac{1}{2}\frac{k+1}{2x}v - \frac{1}{2}v' - \frac{1}{2}\frac{k+1}{2x}v + \frac{k^2}{4x^2}v + \frac{k+1}{2x}v' - \frac{1}{2}v' + \frac{k+1}{2x}v' \\ -\frac{1}{4}v + \frac{2j+k+1}{2x}v - \frac{1}{2}v' + \frac{k+1}{2x}v' \\ -\frac{1}{4}v + \frac{2j+k+1}{2x}v - \frac{k^2}{4x^2}v = 0 \\ \Rightarrow v'' - \frac{k+1}{4x}v - \frac{1}{2}v' - \frac{k+1}{4x}v + \frac{k+1}{x}v' - \frac{1}{2}v' + \frac{j}{x}v + \frac{k+1}{2x}v = 0 \\ \Rightarrow v'' - \frac{k+1}{4x}v - \frac{1}{2}v' - \frac{k+1}{4x}v + \frac{k+1}{x}v' + \frac{j}{x} = 0 \\ \Rightarrow xv'' - xv' + (k+1)v' + jv = 0 \\ \Rightarrow xv'' + (1-x+k)v' + jv = 0 \end{cases}$$
(10-17)

which is the associated Laguerre equation. Since $v = L_j^k(x)$, and the $L_j^k(x)$ are solutions to the associated Laguerre equation, equation (10–17) is equivalent to

$$x L_j^{k''}(x) + (1 - x + k) L_j^{k'}(x) + j L_j^k(x) = 0,$$

which is the associated Laguerre, which we know to be a true statement, so

$$y = e^{-x/2} x^{(k+1)/2} v$$

= $e^{-x/2} x^{(k+1)/2} L_j^k(x)$

are solutions to equation (10-16).

The Reduced Mass

Equation (10-2) describes a single particle in a central potential. The hydrogen atom is a two body problem, and the potential is not central but is dependent upon the distance between the nucleus and the electron. Were we able to anchor the nucleus to a stationary location we could designate an origin, equation (10-2) would be an accurate description. This is not possible, but we can reach a similar end by picturing the center of mass being anchored to a fixed location. If we use the **reduced mass** in place of the electron mass,

$$\mu = \frac{m_p \, m_e}{m_p + m_e},$$

the radial coordinate r accurately describes the distance between the nucleus and the electron. The effect in equation (10–2) is cosmetic; where there was an m representing m_e , it is replaced by μ . Because the proton is about 1836 times more massive than the electron, the reduced mass is nearly identically the electron mass. Many authors simply retain the electron mass. Since the center of mass is not actually anchored, a second set of coordinates is required to track the center of mass using this scheme. This consideration and other details of reducing a two particle problem to a one particle problem are adequately covered in numerous texts, including Chohen–Tannoudji⁵, Levine⁶ and many classical mechanics texts

Solution of the Radial Equation

The radial equation (10–6) using the reduced mass and the Coulomb potential, $V(r) = -e^2/r$, is

$$\frac{1}{R(r)} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) R(r) - \frac{2\mu r^2}{\hbar^2} \left[-\frac{e^2}{r} - E \right] - l(l+1) = 0$$

$$\Rightarrow \quad \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) R(r) - \frac{2\mu r^2}{\hbar^2} \left[-\frac{e^2}{r} - E \right] R(r) - l(l+1) R(r) = 0$$

$$\Rightarrow \quad \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) R(r) + \left[\frac{2\mu r^2}{\hbar^2} \frac{e^2}{r} + \frac{2\mu r^2}{\hbar^2} E - l(l+1) \right] R(r) = 0. \quad (10-18)$$

The plan is to get (10-18) into a form comparable to equation (10-16), and we already know the solutions are equation (10-15). We will be able to glean additional information by comparing the equations term by term. The energy levels of the hydrogen atom and the meaning of the indices of the associated Laguerre polynomials, which will be quantum numbers for the hydrogen atom, will come from the comparison of individual terms.

We will make three substitutions to get the last equation into the form of equation (10–16). The first is

$$y(r) = r R(r) \Rightarrow R(r) = \frac{y(r)}{r}.$$
 (10-19)

⁵ Cohen-Tannoudji, Diu, and Laloe, *Quantum Mechanics* (John Wiley & Sons, New York, 1977), pp. 784–788.

⁶ Levine, *Quantum Chemistry* (Allyn and Bacon, Inc., Boston, Massachusetts, 1983), pp. 101–106.

Making this substitution in the first term and evaluating the derivatives

$$\frac{d}{dr}\left(r^2\frac{d}{dr}\right)R(r) = \frac{d}{dr}\left(r^2\frac{d}{dr}\right)(r^{-1})y(r)$$

$$= \frac{d}{dr}r^2\left[\left(-r^{-2}\right)y(r) + \left(r^{-1}\right)\frac{dy(r)}{dr}\right]$$

$$= \frac{d}{dr}\left[-y(r) + r\frac{dy(r)}{dr}\right]$$

$$= -\frac{dy(r)}{dr} + \frac{dy(r)}{dr} + r\frac{d^2y(r)}{dr^2}$$

$$= r\frac{d^2y(r)}{dr^2}.$$

The substitution serves to eliminate the first derivative. We would have both a first and second derivative if we had evaluated the first term using R(r). With this and the substitution of equation (10–19), equation (10–18) becomes

$$r \frac{d^2 y(r)}{dr^2} + \left[\frac{2\mu re^2}{\hbar^2} + \frac{2\mu r^2}{\hbar^2}E - l(l+1)\right]\frac{y(r)}{r} = 0$$

$$\Rightarrow \quad \frac{d^2 y(r)}{dr^2} + \left[\frac{2\mu e^2}{r\hbar^2} + \frac{2\mu E}{\hbar^2} - \frac{l(l+1)}{r^2}\right]y(r) = 0.$$

The second substitution is essentially to simplify the notation, and is

$$\left(\frac{\epsilon}{2}\right)^2 = -\frac{2\mu E}{\hbar^2} \tag{10-20}$$

where the negative sign on the right indicates we are looking for bound states, states such that E < 0, so including the negative sign here lets us have an ϵ which is real. The last equation becomes

$$\frac{d^2 y(r)}{dr^2} + \left[\frac{2\mu e^2}{r\hbar^2} - \frac{\epsilon^2}{4} - \frac{l(l+1)}{r^2}\right] y(r) = 0$$

The third substitution is a change of variables, and notice it relates radial distance and energy through equation (10-20),

$$x = r\epsilon \quad \Rightarrow \quad r = \frac{x}{\epsilon},$$
 (10 - 21)

$$\Rightarrow dr = \frac{dx}{\epsilon} \Rightarrow \frac{d^2 y(r)}{dr^2} = \frac{d}{dr} \frac{d y(r)}{dr} = \epsilon \frac{d}{dx} \epsilon \frac{d y(x)}{dx} = \epsilon^2 \frac{d^2 y(x)}{dx^2},$$

so our radial equation becomes

$$\epsilon^{2} \frac{d^{2} y(x)}{dx^{2}} + \left[\frac{2\mu e^{2}\epsilon}{x\hbar^{2}} - \frac{\epsilon^{2}}{4} - \epsilon^{2} \frac{l(l+1)}{x^{2}}\right] y(x) = 0$$

$$\Rightarrow \quad \frac{d^{2} y(x)}{dx^{2}} + \left[-\frac{1}{4} + \frac{2\mu e^{2}}{\hbar^{2}\epsilon x} - \frac{l(l+1)}{x^{2}}\right] y(x) = 0, \quad (10-22)$$

and equation (10-22) is equation (10-16) where

$$l(l+1) = \frac{k^2 - 1}{4}, \qquad (10 - 23)$$

and

$$\frac{2\mu e^2}{\hbar^2 \epsilon} = \frac{2j+k+1}{2},$$
(10-24)

Per example 10-6, the solutions are equation (10-15),

$$y_j^k(x) = e^{-x/2} x^{(k+1)/2} L_j^k(x).$$

Eigenenergies from the Solution of the Radial Equation

Equation (10–23) tells us k = 2l + 1.

Example 10–7: Show k = 2l + 1.

Equation (10-23) is

$$\frac{k^2 - 1}{4} = l(l+1)$$

$$\Rightarrow k^2 = 4l(l+1) + 1$$

$$= 4l^2 + 4l + 1$$

$$= (2l+1)^2$$

$$\Rightarrow k = 2l+1.$$

We are going to take what appears to be a slight diversion to evaluate a particular set of factors in equation (10–24), $\hbar^2/\mu e^2$, which recurs repeatedly. Going back to the old quantum theory, this is called the Bohr radius, that is

$$a_0 = \frac{\hbar^2}{\mu e^2} = 0.529 \,\text{\AA}.\tag{10-25}$$

We want to express lengths in terms of the Bohr radius because it is a natural length for the hydrogen atom.

Example 10–8: Show $a_0 = 0.529 \text{ Å}$, using both the electron mass and the reduced mass.

This example is intended to illustrate three simple things. First, $a_0 = 0.529$ Å, second is to work out the CGS units for e^2 , and then to show the electron mass is a very good approximation to the reduced mass in hydrogen. The electrostatic force in MKS and CGS systems is defined

$$\frac{1}{4\pi\epsilon_0} \frac{e_{\rm MKS}^2}{r^2} = F = \frac{e_{\rm CGS}^2}{r^2}$$

$$\Rightarrow e_{\text{CGS}}^2 = \frac{e_{\text{MKS}}^2}{4\pi\epsilon_0} = (1.602 \times 10^{-19} \, C)^2 (8.988 \times 10^9 \, N \cdot m^2 / C^2)$$
$$= 2.307 \times 10^{-28} \, N \cdot m^2 = 2.307 \times 10^{-19} \, dyne \cdot cm^2$$
$$= 2.307 \times 10^{-19} \, erg \cdot cm = 14.42 \, eV \cdot \text{\AA}.$$

 So

$$a_0 = \frac{\hbar^2}{m_e e^2} = \frac{1}{4\pi^2} \frac{(hc)^2}{m_e c^2 e^2} = \frac{1}{4\pi^2} \frac{(1.240 \times 10^4 \, eV \cdot \text{\AA})^2}{(0.5110 \times 10^6 \, eV)(14.42 \, eV \cdot \text{\AA})} = 0.5286 \,\text{\AA}.$$

The reduced mass is

$$\mu = \frac{m_p m_e}{m_p + m_e} = \frac{1.673 \times 10^{-24}}{1.673 \times 10^{-24} + 9.110 \times 10^{-28}} m_e = 0.9995 m_e,$$
$$\Rightarrow \quad \frac{\hbar^2}{\mu e^2} = \frac{\hbar^2}{0.9995 m_e e^2} = \frac{0.5286 \text{ \AA}}{0.9995} = 0.5288 \text{ \AA}.$$

There is 0.03% difference between the electron mass and reduced mass values. Many authors simply use the electron mass and it yields a good approximation. The CGS value of e^2 can be mysterious for those who have worked primarily in MKS units. By the way, the square root $e = 3.797 (eV \cdot \text{Å})^{1/2}$ can be a convenient way to express the charge on the electron in CGS units.

Equation (10–24) gives us the eigenenergies of the hydrogen atom, but requires some development. Since k = 2l + 1,

$$\frac{2j+k+1}{2} = \frac{2j+(2l+1)+1}{2} = j+l+1.$$

From the discussion on associated Laguerre polynomials, the indices j and k are non-negative. The sum j + l + 1 can, therefore, assume any integer values of 1 or greater. We are going to rename it n, or

$$n = j + l + 1. \tag{10-26}$$

The new integer index n is known as the **principal quantum number**. Using the principal quantum number, it follows that the eigenenergies of the hydrogen atom are

$$E_n = -\frac{\hbar^2}{2\mu a_0^2 n^2} = -\frac{13.6 \, eV}{n^2},\tag{10-27}$$

where the quantity 13.6 eV is called the Rydberg, usually denoted R or Ry. The ground state energy is $E_0 = -13.6 eV$ when n = 1. It is often convenient to express excited state energies in terms of the ground state energy.

Example 10–9: Show equation (10–27) follows from equation (10–24).

$$\frac{2\mu e^2}{\hbar^2 \epsilon} = \frac{2j+k+1}{2}$$

$$\Rightarrow \quad j+l+1 = n = \frac{2\mu e^2}{\hbar^2 \epsilon}$$

$$\Rightarrow \quad \epsilon = \frac{2\mu e^2}{\hbar^2 n}$$

$$\Rightarrow \quad \epsilon^2 = \frac{4\mu^2 e^4}{\hbar^4 n^2}.$$

Substituting equation (10–20) to eliminate ϵ and insert energy,

$$-4\frac{2\mu E}{\hbar^2} = \frac{4\mu^2 e^4}{\hbar^4 n^2}$$

$$\Rightarrow \quad E = -\frac{\mu^2 e^4 \hbar^2}{2\mu \hbar^4 n^2} = -\left(\frac{\mu e^2}{\hbar^2}\right)^2 \frac{\hbar^2}{2\mu n^2}$$
$$\Rightarrow \quad E_n = -\frac{\hbar^2}{2\mu a_0^2 n^2}.$$

Inserting numerical values,

$$\begin{split} E_n &= -\frac{\hbar^2}{2\mu a_0^2 n^2} = -\frac{1}{4\pi^2} \frac{(hc)^2}{2(\mu c^2) a_0^2 n^2} \\ &= -\frac{1}{4\pi^2} \frac{(1.24 \times 10^4 \, eV \cdot \mathring{\rm A})^2}{2(0.511 \times 10^6 \, eV)(0.529 \, \mathring{\rm A})^2 n^2} = -\frac{13.6 \, eV}{n^2}, \end{split}$$

so eigenenergies do follow from the solution of the radial equation.