the end of Sec. 28 which relates allowed multipole moments to the total angular momentum quantum number.

32□THE VARIATION METHOD

The variation method can be used for the approximate determination of the lowest or ground-state energy level of a system when there is no closely related problem that is capable of exact solution, so that the perturbation method is inapplicable. It can also be applied to systems that are described by a nonseparable Schrödinger equation, in which case numerical solutions are extremely arduous and the WKB method (Sec. 34) cannot be used.

EXPECTATION VALUE OF THE ENERGY

It was shown in Sec. 10 that, if an arbitrary normalized function ψ is expanded in energy eigenfunctions

$$\psi = \sum_E A_E u_E \qquad \text{where} \qquad Hu_E = Eu_E \tag{32.1}$$

and the u_E form a complete orthonormal set, the expectation value of H for the function ψ is given by

$$\langle H \rangle = \int \psi^* H \psi \, d\tau = \sum_E E|A_E|^2 \tag{32.2}$$

where the integration is extended over the entire range of all the coordinates of the system. It is assumed for convenience in Eqs. (32.1) and (32.2) that the energy eigenvalues are all discrete; this can be accomplished by enclosing the system in a box (Sec. 10), or the summation can be replaced by the symbol S (Sec. 23).

A useful inequality can be derived from Eq. (32.2) by replacing each eigenvalue E in the summation on the right side by the lowest eigenvalue E_0:

$$\langle H \rangle \geq \sum_E E_0|A_E|^2 = E_0 \sum_E |A_E|^2 \tag{32.3}$$

Since $\sum_E |A_E|^2 = 1$ for a normalized function ψ, as was shown in Sec. 10, (32.3) yields the inequality

$$E_0 \leq \int \psi^* H \psi \, d\tau \tag{32.4}$$

In the event that ψ is not normalized, (32.4) evidently can be rewritten as

$$E_0 \leq \frac{\int \psi^* H \psi \, d\tau}{\int |\psi|^2 \, d\tau} \tag{32.5}$$

CHAPTER VII

THE VARIATION METHOD AND OTHER APPROXIMATE METHODS

There are many problems of wave mechanics which cannot be conveniently treated either by direct solution of the wave equation or by the use of perturbation theory. The helium atom, discussed in the next chapter, is such a system. No direct method of solving the wave equation has been found for this atom, and the application of perturbation theory is unsatisfactory because the first approximation is not accurate enough while the labor of calculating the higher approximations is extremely great.

In many applications, however, there are methods available which enable approximate values for the energy of certain of the states of the system to be computed. In this chapter we shall discuss some of these, paying particular attention to the *variation method*, inasmuch as this method is especially applicable to the lowest energy state of the system, which is the state of most interest in chemical problems.

26. THE VARIATION METHOD

26a. The Variational Integral and Its Properties.—We shall show[1] in this section that the integral

$$E = \int \phi^* H \phi d\tau \qquad (26\text{–}1)$$

is an upper limit to the energy W_0 of the lowest state of a system. In this equation, H is the complete Hamiltonian operator $H\left(\frac{h}{2\pi i}\frac{\partial}{\partial q}, q\right)$ for the system under discussion (Sec. 12*a*) and $\phi(q)$ is any normalized function of the coordinates of the system satisfying the auxiliary conditions of Section 9*c* for a satisfactory wave function. The function ϕ is otherwise completely unrestricted; its choice may be quite arbitrary, but the more wisely it is chosen the more closely will E approach the energy W_0.

[1] C. ECKART, *Phys. Rev.* **36**, 878 (1930).

If we used for our function ϕ, called the *variation function*, the true wave function ψ_0 of the lowest state, E would equal W_0; that is,

$$E = \int \psi_0^* H \psi_0 d\tau = W_0, \qquad (26\text{–}2)$$

since

$$H\psi_0 = W_0\psi_0.$$

If ϕ is not equal to ψ_0 we may expand ϕ in terms of the complete set of normalized, orthogonal functions $\psi_0, \psi_1, \cdots, \psi_n, \cdots$, obtaining

$$\phi = \sum_n a_n \psi_n, \qquad \text{with} \qquad \sum_n a_n^* a_n = 1. \qquad (26\text{–}3)$$

Substitution of this expansion in the integral for E leads to the equation

$$E = \sum_n \sum_{n'} a_n^* a_{n'} \int \psi_n^* H \psi_{n'} d\tau = \sum_n a_n^* a_n W_n, \qquad (26\text{–}4)$$

inasmuch as the functions ψ_n satisfy the equations

$$H\psi_n = W_n \psi_n. \qquad (26\text{–}5)$$

Subtracting W_0, the lowest energy value, from both sides gives

$$E - W_0 = \sum_n a_n^* a_n (W_n - W_0). \qquad (26\text{–}6)$$

Since W_n is greater than or equal to W_0 for all values of n and the coefficients $a_n^* a_n$ are of course all positive or zero, the right side of Equation 26–6 is positive or zero. We have therefore proved that E is always an upper limit to W_0; that is,

$$E \geqslant W_0. \qquad (26\text{–}7)$$

This theorem is the basis of the variation method for the calculation of the approximate value of the lowest energy level of a system. If we choose a number of variation functions $\phi_1, \phi_2, \phi_3, \cdots$ and calculate the values $E_1, E_2, E_3, \cdots$ corresponding to them, then each of these values of E is greater than the energy W_0, so that the lowest one is the nearest to W_0. Often the functions $\phi_1, \phi_2, \phi_3, \cdots$ are only distinguished by having different values of some parameter. The process of

since $m\omega^2 = K$, the spring constant. The energies are thus shifted by an amount which is independent of the oscillator's state.

Problem 8.21 Fill in the mathematical steps leading to (8.61).

Problem 8.22 The problem we have just treated approximately is one for which a simple exact solution is available. Insert into the original equation (4.95*b*) the new perturbing energy, and note that by changing x to a new variable $\xi + \lambda$, with a suitable value for λ, one can cancel the perturbing $\hat{H}^{(1)}$, leaving the whole problem substantially in its unperturbed form. Show that the new energy is exactly equal to (8.61), so that all higher-order perturbations must vanish exactly.

Problem 8.23 Find the perturbed energy and wave function for the oscillator in its ground state, using the method developed in the first part of this section.

Problem 8.24 Calculate the third term of the series (8.19) and compare the result with (8.20).

8.6 The Variation Principle

An entirely different approach to the problem of finding approximate wave functions and energies is suggested by the question: "If I can guess a wave function of reasonable form which contains one or two adjustable parameters, how can I choose the parameters so as to get the best fit?" First, we need to decide exactly what is meant by "the best fit," and this is most easily seen if for a moment we restrict attention to finding the ground state of the system (this is what one usually wants anyhow). Let us pose the following problem: If instead of the correct normalized wave function ψ_0 (the subscript referring to the lowest energy state) we use an erroneous, but still normalized function ψ, how does the energy of the state ψ compare with the true energy E_0? This question can be answered at once. Let ψ_n be the nth exact normalized eigenfunction of $\hat{H}$ (of course, we do not know what it is), and expand ψ in terms of the ψ_n,

$$\psi = \Sigma c_n \psi_n \tag{8.62}$$

where, because of the normalization of ψ, we have

$$\Sigma |c_n|^2 = 1 \tag{8.63}$$

by (5.5). The expectation value of $\hat{H}$ in the state ψ is, by (5.6),

$$W \equiv \langle \hat{H} \rangle_\psi = \Sigma |c_n|^2 E_n \tag{8.64}$$

If E_0 is the ground-state energy, we have the inequality

$$W \geq \Sigma |c_n|^2 E_0$$

$$E = \sum_i \sum_j a_i^* a_j \int \psi_i^* H \psi_j \, d\tau \tag{9.36}$$

Since $H\psi_j = E_j\psi_j$, and the ψ's are orthogonal, Eq. (9.36) becomes

$$E = \sum_j a_j^* a_j E_j \tag{9.37}$$

The sum over all j of $a_j^* a_j$ is 1, and therefore $E \geqslant E_0$; E is equal to E_0 only if the a_j are zero for all $j \neq 0$, in which case $\Phi = \psi_0$ which means that we have chosen the true wave function for Φ. The worse the choice made for Φ, the greater will be the admixture of states above the ground state, leading to higher estimates of E.

In general, Φ should be chosen to resemble as closely as possible the form to be expected on physical grounds. For example, for nuclear problems a rapidly attenuating wave function should be used, such as an exponentially decaying wave function. A good approximate wave function is a known wave function appropriate to a very similar potential, that is, an unperturbed ground state wave function whose potential energy is assumed only slightly different from the actual potential energy. The only alteration required in the known wave function is to make Φ a function of some unspecified parameter, say α. The integral in Eq. (9.34) is then calculated as a function of α and the result minimized with respect to α, the resultant E being the closest estimate obtainable with the chosen wave function. If we use unnormalized wave functions, Eq. (9.34) may be rewritten

$$E = \frac{\int \Phi^*(\alpha, \mathbf{r})\left(\frac{-\hbar^2}{2m}\nabla^2 + V\right)\Phi(\alpha, \mathbf{r})\, d\tau}{\int \Phi^*(\alpha, \mathbf{r})\Phi(\alpha, \mathbf{r})\, d\tau} \tag{9.38}$$

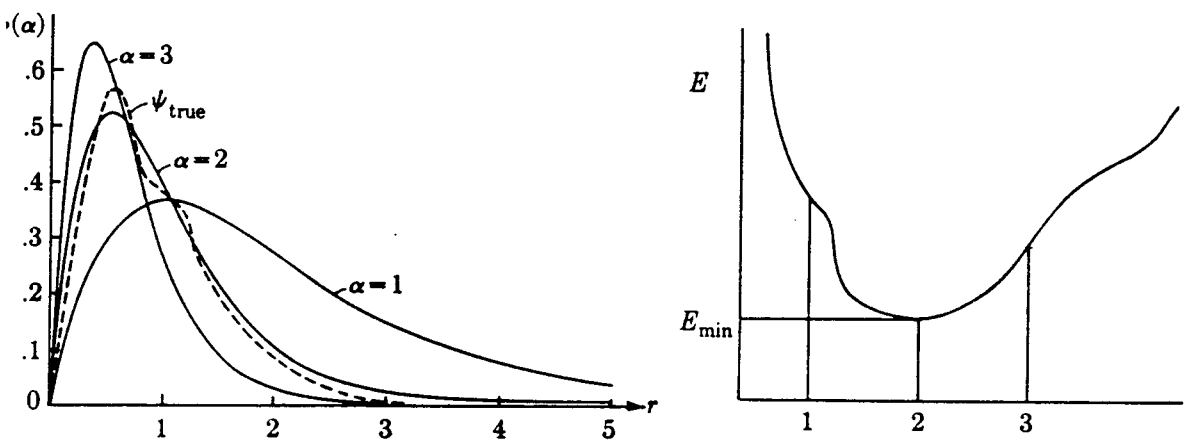

FIGURE 9.1 Illustration of how an approximate wave function $\Phi = re^{-\alpha r}$ may be adjusted to represent most closely an illustrative true wave function ψ_{true} (dashed line) by choice of the value of the parameter α that minimizes E given by Eq. (9.38) $\int \Phi H \Phi \, d\tau / \int \Phi^2 \, d\tau$.

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Ch 16

The Variational and WKB Methods

16.1. The Variational Method

More often than not, it is impossible to find exact solutions to the eigenvalue problem of the Hamiltonian. One then turns to approximation methods, some of which will be described in this and the following chapters. In this section we consider a few examples that illustrate the *variational method.*

Our starting point is the inequality

$$E[\psi] \equiv \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \geq E_0 \tag{16.1.1}$$

where E_0 is the lowest eigenvalue of H, i.e., the ground-state energy. Although this result was proved earlier, let us recall the idea behind it. $E[\psi]$ is just the mean value of the energy in the state $|\psi\rangle$. The inequality states that the mean value cannot be less than the lowest value that enters the average. More formally, if $|\psi\rangle$ is expanded in terms of the eigenfunctions $|E_n\rangle$ of H,

$$E[\psi] = \frac{\sum E_n |\langle E_n | \psi \rangle|^2}{\sum |\langle E_n | \psi \rangle|^2} \geq \frac{E_0 \sum |\langle E_n | \psi \rangle|^2}{\sum |\langle E_n | \psi \rangle|^2} = E_0 \tag{16.1.2}$$

This inequality suggests a way (at least in principle) of determining the ground-state energy and eigenket. We take all the kets in the Hilbert space one by one and make a table of the corresponding $E[\psi]$. At the end we read off the lowest entry and the ket that goes with it. Clearly this is not a practical algorithm. What one does in practice is to consider just a subset (not necessarily a subspace) of vectors which are parametrized by some variables $(\alpha, \beta, \gamma, \ldots)$ and which have the general features one expects of the true ground-state ket. In this limited search $E[\psi]$ reduces a function of the parameters, $E(\alpha, \beta, \ldots)$. We then find the values $(\alpha_0, \beta_0, \ldots)$ which minimize E. This minimun $E(\alpha_0, \beta_0, \ldots)$ provides an upper bound on E_0.

CHAPTER 7

THE VARIATIONAL PRINCIPLE

7.1 THEORY

Suppose you want to calculate the ground state energy, E_{gs}, for a system described by the Hamiltonian H, but you are unable to solve the (time-independent) Schrödinger equation. The **variational principle** will get you an *upper bound* for E_{gs}, which is sometimes all you need, and often, if you're clever about it, very close to the exact value. Here's how it works: Pick *any normalized function* ψ *whatsoever*; I claim that

$$\boxed{E_{gs} \leq \langle \psi | H | \psi \rangle \equiv \langle H \rangle.} \qquad [7.1]$$

That is, the expectation value of H, in the (presumably incorrect) state ψ is certain to *overestimate* the ground state energy. Of course, if ψ just happens to be one of the *excited* states, then *obviously* $\langle H \rangle$ exceeds E_{gs}; the point is that the same holds for any ψ whatsoever.

Proof: Since the (unknown) eigenfunctions of H form a complete set, we can express ψ as a linear combination of them:[1]

$$\psi = \sum_n c_n \psi_n, \quad \text{with} \quad H\psi_n = E_n \psi_n.$$

[1] If the Hamiltonian admits scattering states, as well as bound states, then we'll need an integral as well as a sum, but the argument is unchanged.