

including the new term or terms, guided only by the basic postulates. This amounts, as we have seen, to finding certain characteristic functions of space, $\psi_n(x, y, z)$ or $\psi_n(r, \theta, \phi)$, which together with the time factor, $e^{-iWt/\hbar}$, satisfy the requirements of all of the postulates. This process is not particularly simple, even in highly symmetrical systems, and for systems that depart from perfect rectangular or circular symmetry it becomes difficult or impossible. Mathematically, this is often owing to the impossibility of separating the variables. In any case, for only a handful of systems can the eigenfunctions be found in mathematically closed form.¹ This makes the few sets of eigenfunctions that *are* known—such as the hydrogen-like eigenfunctions—of great value. For many systems the exact wave equation contains, in dominant form, the terms that belong to the symmetrical, solvable system, *plus* some terms of relatively small influence. The assumption is then made that the exact eigenfunctions of the true wave equation do not differ greatly from the known eigenfunctions of the symmetrical, solvable system which is similar to the true system. The known eigenfunctions are used as a starting point, and corrections are then calculated by approximate methods. This technique is often surprisingly successful, even when the corrections are quite large. The terms of relatively small influence in the wave equation which cause it to differ from the equation of a symmetrical, solvable system are called “perturbation terms.”

Today, in the applications of quantum mechanics, practically all calculations being made are of the type described above—i.e., perturbation calculations.

In this chapter we shall be concerned with finding the eigenfunctions which belong to systems that have a small, time-independent difference from known, symmetrical systems. In Chapter 10, we will consider perturbations that are not constant in time.

Perturbation theory for the steady state, first applied by Schrödinger in 1926, is based on the reasonable assumption that a small change in the Hamiltonian operator will result in a correspondingly small change in the eigenfunctions of the system. In terms of the acoustical model in Figure 7.1, if the deformation in the corner is very small, the enclosure will resonate at *almost* the same set of frequencies and have *almost* the same standing-wave patterns as when the deformation is entirely missing. As the deformation is made larger and larger, however, the characteristic frequencies and the associated standing-wave patterns will become more and more different from those of the perfectly symmetrical box.

7.1. Perturbation theory, nondegenerate level

Let the exact Hamiltonian H be given by

$$H = H^0 + \lambda H' \quad [7-1]$$

¹ There are a few other types of symmetry, such as cylindrical and ellipsoidal, which permit separation of variables and exact solutions.

where H^0 is the operator, derived for the unperturbed system with known eigenfunctions ψ_n^0 and eigenvalues W_n^0 . That is,

$$H^0\psi_n^0 = W_n^0\psi_n^0 \quad [7-2]$$

The term H' is the perturbation term, derived by the usual operator-substitution method of Postulate II. The factor λ is a constant² whose value will be set anywhere between 0 and 1. Its purpose is to control the size or magnitude of the perturbation for a reason that will be apparent shortly. We can regard λ as a "control knob" which varies the effect of the perturbation all the way from 0 up to its full value. We look then at any particular eigenvalue W_n and at any particular point in space, x_1, y_1, z_1 , where we observe the amplitude ψ of the wave function. How will the eigenvalue, and the eigenfunction (at x_1, y_1, z_1) change as the perturbation is increased from 0 to its full value? We can only suppose that they will vary in some smooth manner from their "starting points" W_n^0 , and $\psi_n^0(x_1, y_1, z_1)$. Whether ψ_n becomes larger or smaller than ψ_n^0 as the magnitude of the perturbation increases depends upon the point (x, y, z) in space where ψ_n is being examined. ψ_n may be unchanged at some points, increase in some regions, and decrease in other regions. Thus, after the perturbation is completely "turned on" (i.e., $\lambda = 1$), we find that the new eigenfunction ψ_n will, in general, be everywhere different from ψ_n^0 . There is no reason, furthermore, to expect W_n or $\psi_n(x, y, z)$ to deviate in an exactly linear manner from their "starting points" W_n^0 and $\psi_n^0(x, y, z)$, so we must allow for some curvature. In Figure 7.2, for each case, we approximate the true curve with a linear term in λ , with a coefficient W_n' , or $\psi_n'(x_1, y_1, z_1)$, plus a second-degree term, in λ^2 , which has different—and here, smaller—coefficients W_n'' and $\psi_n''(x_1, y_1, z_1)$. If the curvature is sharper, it may be necessary to synthesize the true curve with terms dependent upon λ^3, λ^4 , etc. We shall be concerned here only with "first-order" approximations. *This means that we shall restrict ourselves to perturbations in which, even when the perturbation is "on" at full intensity ($\lambda = 1$), the square-law terms are in all cases small compared to the linear terms.*

The use of λ in this manner is really a mathematical artifice. It is possible to identify, without its use, the different "orders" of the approximation. However, if we regard λ as a "control knob" on the magnitude of the perturbation H' , and if we use λ and λ^2 to identify the linear and "square-law" dependence of the correction terms as in Figure 7.2, we will be able to simply and clearly identify the "first-order" and the "second-order" corrections. Eventually we will neglect all terms involving λ^2 (second-order terms), *but first we must identify them.* Thus, during the subsequent calculations we shall retain λ only long enough to determine which part of the corrections to the W_n^0 's and the ψ_n^0 's are linear in λ (first-order corrections), and then we will set $\lambda = 1$ —i.e., establish the perturbation at its normal magnitude. For certain man-made perturbations,

² No relationship to wavelength λ .

such as the application of electric or magnetic fields to an atom, one can actually control the size of the perturbation. Perturbations inherent in the system itself—such as the electron-electron interaction of the helium atom—cannot, of

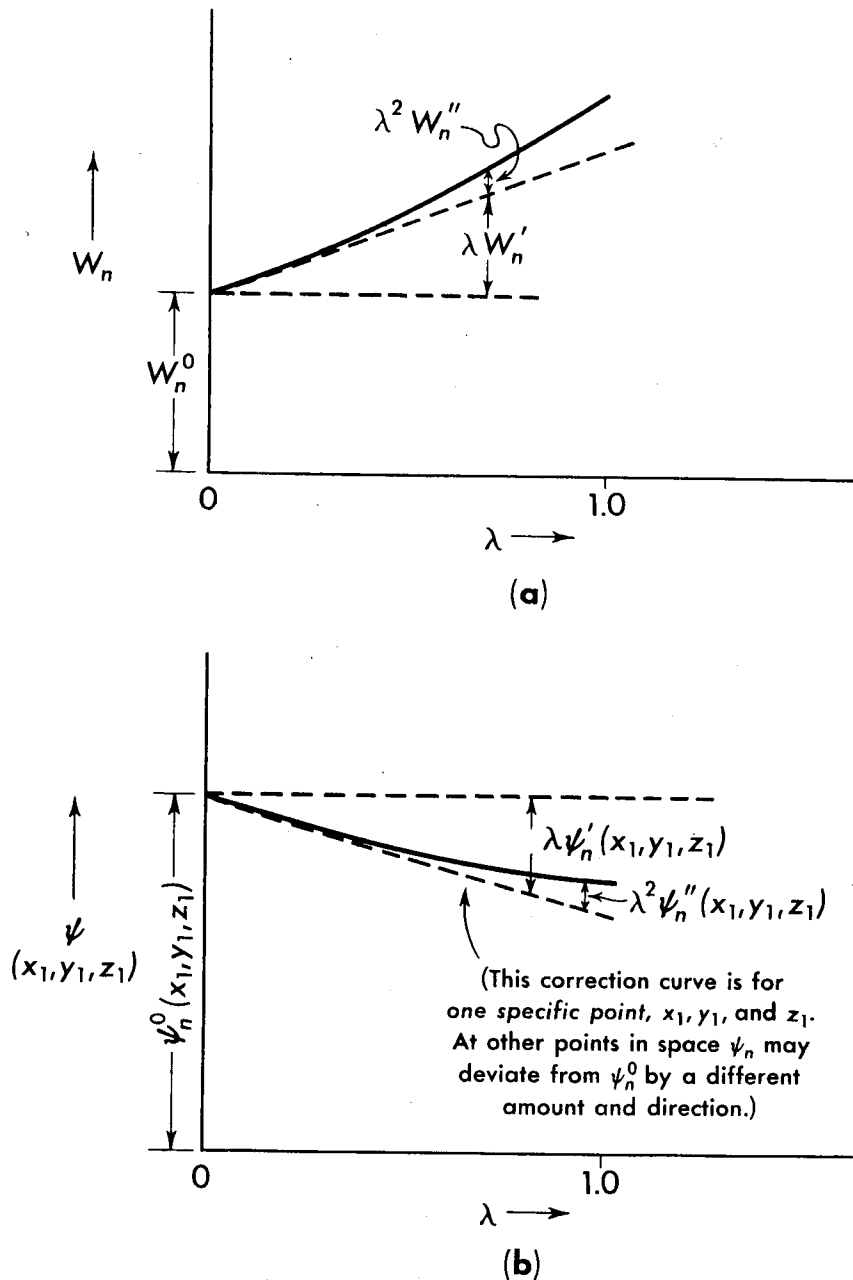


Fig. 7.2. The variation in an eigenvalue W_n and an eigenfunction ψ_n (at a particular point in space) as a function of the magnitude of the perturbation (controlled by λ).

course, be controlled, and if the second-order (λ^2) terms *happen* to be large when $\lambda = 1$ (the only possible value of λ , in reality), there is no alternative but to continue the theory and the calculations to the higher orders. Here, we

shall only consider the case where, even when $\lambda = 1$, (i.e., the perturbation is set at the actual magnitude required in the problem), the λ^2 terms in Figure 7.2 are of small magnitude compared to the λ -dependent terms.

The way in which the “true” values of W_n and $\psi_n(x_1y_1z_1)$ vary as the perturbation is “turned on” is not initially known. Thus, in Figure 7.2, the “true” curves are arbitrarily drawn. They illustrate that in principle the λ and the λ^2 terms can have coefficients of different magnitude and sign. In fact, it is in general true that at *each point* in space $\psi_n(x, y, z)$ will have a *different* dependence (in both magnitude and direction) upon the intensity of the perturbation (the value of λ). We expect, therefore, that a complete description of the corrections to $\psi_n^0(x, y, z)$ will be much more elaborate than the description of the correction to W_n^0 .

We make the assumptions

$$\psi_n = \psi_n^0 + \lambda\psi_n' + \lambda^2\psi_n'' + \dots \quad [7-3^3]$$

$$W_n = W_n^0 + \lambda W_n' + \lambda^2 W_n'' + \dots \quad [7-4^3]$$

where ψ_n and W_n are the eigenfunctions and eigenvalues, respectively, of the true wave equation,

$$H\Psi = -(\hbar/i)(\partial/\partial t)\Psi \quad [7-5]$$

which, since H is time independent, separates into two equations in the manner described in Chapter 3. The amplitude equation is

$$H\psi = W\psi \quad [7-6]$$

where, as far as the separation of [7-5] is concerned, $W = \text{any constant}$.

For certain discrete values of W , W_n (yet to be found), the true wave equation [7-6] has well-behaved solutions of integrable square, ψ_n (yet to be found), so that, of the infinity of ψ 's and W 's possible in [7-6], only those which obey

$$H\psi_n = W_n\psi_n \quad [7-7]$$

are possible eigenfunctions of real systems. Equation [7-7] is the true wave equation for the system. We know that it must have eigenvalues and eigenfunctions, but there is one practical difficulty—the operator H has such a form that we have no means of solving the problem exactly by standard analytical mathematical methods. It usually happens that the spatial variables in [7-7] cannot be separated, with the result that numerical methods, even with the aid of a large automatic computer, are often not practical. We are forced, therefore, to turn to some method of approximation. We do this, however, *not* because the postulates are deficient—[7-7] *is* the true wave equation and it *does* have exact solutions corresponding precisely to the states of the system

³ Note: Here the primes do *not* mean differentiation. $\psi'(x, y, z)$ gives that part of the correction to $\psi_n^0(x, y, z)$ at each point in space, which is linear in λ .

it represents—but *only* because, in this case, the mathematical tools are inadequate.

To find an approximate solution to [7-7], therefore, we insert H in the form given by [7-1]. For ψ_n and W_n we substitute the series given by [7-3] and [7-4] respectively. After arranging the terms according to powers of λ , we have

$$\begin{aligned} (H^0\psi_n^0 - W_n^0\psi_n^0) + \lambda(H^0\psi_n' + H'\psi_n^0 - W_n^0\psi_n' - W_n'\psi_n^0) \\ + \lambda^2(H^0\psi_n'' + H'\psi_n' - W_n^0\psi_n'' - W_n'\psi_n' - W_n''\psi_n^0) \\ + \lambda^3(\dots) + \dots \\ = 0 \end{aligned} \quad [7-8]$$

This equation must be true for all values of λ . Providing the series is properly convergent, [7-8] can only be true when each of the coefficients of powers of λ vanish separately. The zero-order equation, obtained by setting the coefficient of λ^0 equal to 0, is

$$H^0\psi_n^0 = W_n^0\psi_n^0$$

which is merely the solvable equation [7-2]. The first-order equation is

$$H^0\psi_n' - W_n^0\psi_n' = (W_n' - H')\psi_n^0 \quad [7-9]$$

In this equation $\psi_n'(x, y, z)$ and W_n' are both unknown. W_n' is an unknown constant and $\psi_n'(x, y, z)$ is an unknown *function*.

We neglect the equation derived from setting the λ^2 coefficient equal to zero, since we assume that, even when $\lambda = 1$, the corrections to W_n^0 and ψ_n^0 , which are dependent upon λ^2 , are small compared to those dependent upon λ .

The equation obtained from [7-8] by setting the coefficient of λ^2 equal to zero is the second-order equation. It can be solved by basically the same method shortly to be described for the first-order equation.

Before turning to the mathematical problem of calculating the first-order corrections to the energy and to the wave function that are made necessary by the introduction of a small perturbation, we shall first discuss a simple case graphically, with the aid of Figure 7.3. (Problems 7.1 and 7.2 are concerned with the mathematical analysis of a specific numerical example of a system with the form of Figure 7.3.)

In Figure 7.3a the unperturbed potential energy function forms a one-dimensional box with infinite walls at $x = 0$ and at $x = L$. In between, the potential energy is zero. The lowest eigenstate of the unperturbed system has the normalized wave function $\psi_1^0 = \sqrt{2/L} \sin \pi x/L$, as was found in Chapter 3, and an energy $W_1^0 = \pi^2 \hbar^2 / 2mL^2$.

We now add a potential well, V_1 ergs in depth and B cm in width, centered at $x = L/2$. Thus $H' = -V_1$ in the range $x = (L/2) - B/2$ to $(L/2) + B/2$, and is zero elsewhere inside the box. If B , or V_1 , or both, are small enough, we will expect that the true wave function, for the system including the perturba-

tion will differ only slightly from the zero-order wave function, and the true eigenvalue will differ only slightly from the zero-order eigenvalue.

Figure 7.3b shows the correct shape for the true eigenfunction. The shape can be derived qualitatively by simple arguments. Near $x = L/2$, and without

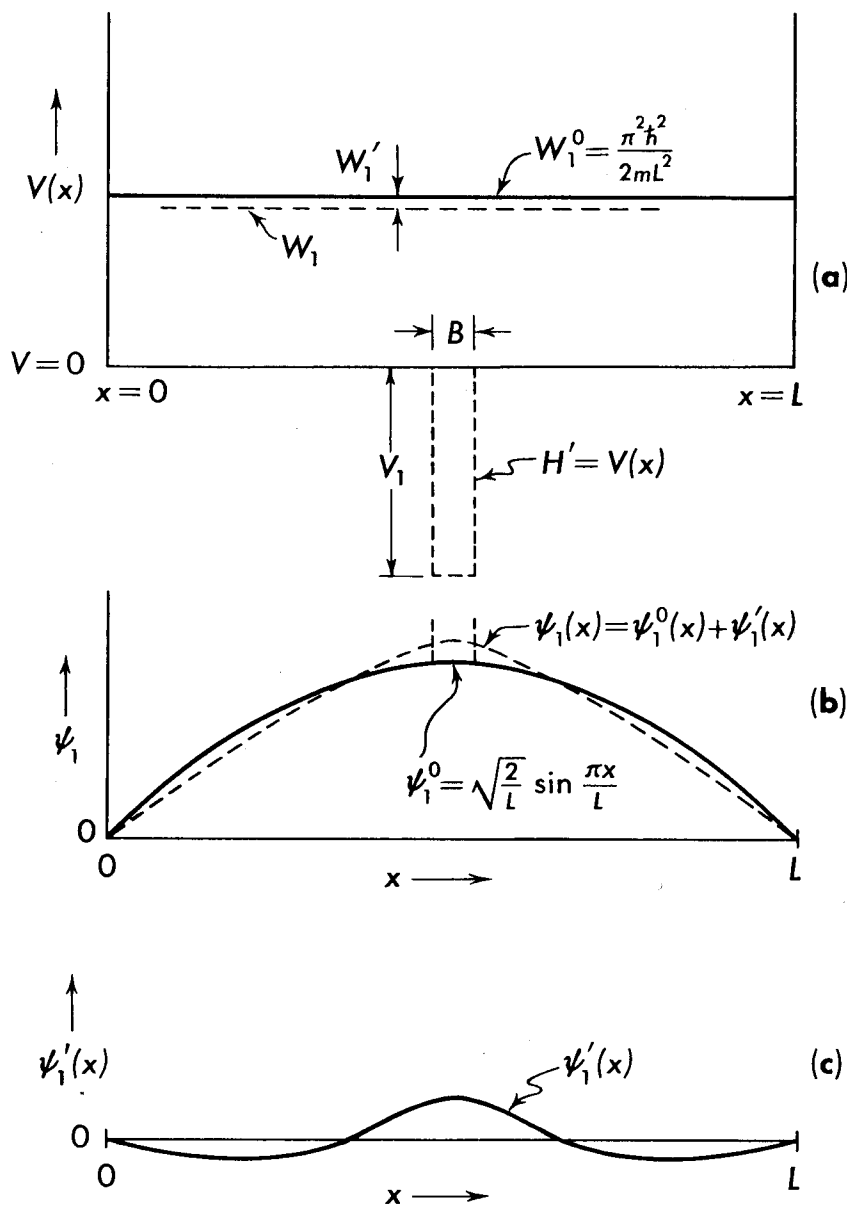


Fig. 7.3. A one-dimensional system containing a small, central potential well.

the perturbing well, the curvature of ψ , ($d^2\psi/dx^2$) is nearly constant. When the new well is added, the curvature of ψ in the region B must be considerably greater than it was before, and therefore greater than the curvature just outside the well. This occurs since, in the region B , the difference between the potential energy and the total energy is much greater. Inside the region B the true wave

function ψ_1 must have the form of a sinusoidal wave, but of short wavelength, with a maximum centered at $x = L/2$. The short wavelength sinusoidal function must, by the postulates, join smoothly (in amplitude and in slope) at *both* boundaries [at $x = (L/2) - (B/2)$ and at $x = (L/2) + (B/2)$] to the rest of the wave function (also of sinusoidal form but of longer wavelength) which exists outside the small potential well. Since the new wave function experiences such sharp curvature in the region of the narrow well, it is clear that *outside* the narrow well the wave function does not need to curve quite as sharply as it did before the narrow well was added. Thus, in spite of its longer wavelength outside the narrow well, the new ψ can still satisfy the boundary conditions (zero amplitude at the infinitely high potential barriers). Since long wavelength is associated with small momentum and thus with small kinetic energy, one should expect the new value of the characteristic energy W_1 (Figure 7.3a) to be lower than the original value W_1^0 , and indeed this expectation is quantitatively confirmed by the more detailed calculations which follow.

Figure 7.3c gives the *correction* $\psi'_1(x)$ which must be added to the zero-order wave function ψ_1^0 to produce the true wave function ψ_1 . We can see that the *correction* to the zero-order wave function has a different magnitude and sign in different spatial regions.

The over-all magnitude of ψ_1 may be adjusted to make it normalized, i.e. $\int_{-\infty}^{+\infty} \psi_1^* \psi_1 dx = 1$. This has been done, in an approximate manner, for Figure 7.3b. We shall see below, however, that the first-order theory always assumes that the correction terms to ψ are small and that renormalization is not necessary.

The addition of the particular perturbation of Figure 7.3 happens to produce a new system which is exactly solvable, so that it is possible to compare the exact and the approximate solutions. In general, however, this situation does not occur. Suppose, for example, that the added perturbation were not a simple square well, but had some other shape for which there happened to be no closed-form solution. Perturbation theory would still work as well as ever, but the exact solution could not be found, at least by simple mathematical means.

The system in Figure 7.3 gives an example of how, for small perturbations, the true wave function is really much like the zero-order wave function, and the shift in the characteristic energy, from the zero-order energy, is small. It also gives, in graphic form, the nature of the two unknown expressions in the first-order equation [7-9]. W'_1 is merely a simple number, but $\psi'(x)$ is an unknown *function* of x . How can we determine this function? The key step is to express $\psi'_1(x)$ as a series of a complete set of orthogonal functions.

It is at this point that the orthogonality of the basic zero-order wave functions becomes indispensable. As we have seen in Chapter 5, almost any function of space can be synthesized by a superposition of a set of appropriate

eigenfunctions. We assume, therefore, that the correction ψ'_n to the zero-order wave function ψ_n^0 is given by the series

$$\psi'_n = \sum_j a_j \psi_j^0 \quad [7-10]^4$$

That is, the correction terms added to the n th zero-order eigenfunction will be synthesized from a superposition of the complete set of zero-order eigenfunctions. The calculation amounts to finding a particular set of a_j 's which will make the synthesis correct. In the example of Figure 7.3, we ask: What amplitudes of the basic functions $\sqrt{2/L} \sin j\pi x/L$ ($j = 1, 2, 3, \dots$) are needed to synthesize the particular function of x shown in Figure 7.3c?

Each system, of course, will have its own "natural set" of basic, or zero-order, functions which are suitable to the problem.

We substitute [7-10] into the first-order equation [7-9]. The term $H^0 \psi'_n$ becomes

$$H^0 \psi'_n = H^0 \sum_j a_j \psi_j^0 = \sum_j a_j W_j^0 \psi_j^0$$

since $H^0 \psi_j^0 = W_j^0 \psi_j^0$. Thus, [7-9] becomes

$$\sum_j a_j (W_j^0 - W_n^0) \psi_j^0 = (W'_n - H') \psi_n^0 \quad [7-11]$$

This equation is a shorthand statement of the equality of a sum of terms on the left to the expression on the right. The student who is not thoroughly familiar with this type of notation should write out at least the first few terms in the series to obtain a better picture of the real nature of the equation. Expressions involving summation signs are often deceptively simple in appearance.

We are here concerned with the perturbations of a nondegenerate state. This is a state which has the characteristic energy W_n^0 to which there belongs only *one* eigenfunction ψ_n^0 . For example, the ground state of the hydrogen atom (Section 4.8) has the energy W_1 , to which belongs only *one* eigenfunction ψ_{100} , so that this state is nondegenerate. When the characteristic energy is W_2 , however, there are *four* different eigenfunctions, and the state is said to be (fourfold) degenerate.

Our first step is to calculate W'_n , the correction to the zero-order energy, caused by the addition of the perturbation H' to the zero-order Hamiltonian H^0 . We multiply [7-11] from the left by ψ_n^{0*}

$$\sum_j a_j (W_j^0 - W_n^0) \psi_n^{0*} \psi_j^0 = W'_n \psi_n^{0*} \psi_n^0 - \psi_n^{0*} H' \psi_n^0$$

In this operation, we have made use of the fact that the a 's and the W 's are constants and can be interchanged, in order, with ψ_n^{0*} . H' , being an operator,

⁴ The a_j 's in [7-10] all have specific values needed to synthesize the correction to a particular zero-order eigenfunction ψ_n^0 . The a 's are often written, $a_j^{(n)}$. Here, we concentrate on finding the set of a 's which are correct for only one eigenfunction, the n th, and neglect writing the superscript (n).

cannot be interchanged, in order, with the eigenfunction ψ_n^{0*} (except when H' has certain special forms).

We now multiply each term by the volume element $d\tau$ and integrate each term over the full range of all the coordinates,

$$\sum a_j(W_j^0 - W_n^0) \int \psi_n^{0*} \psi_j^0 d\tau = W_n' \int \psi_n^{0*} \psi_n^0 d\tau - \int \psi_n^{0*} H' \psi_n^0 d\tau$$

Since

$$\int \psi_n^{0*} \psi_n^0 d\tau = 1 \text{ and } \int \psi_n^{0*} \psi_j^0 d\tau = 0 \text{ when } j \neq n$$

all of the terms on the left are zero. (The integral is zero when $n \neq j$, and the factor $(W_j^0 - W_n^0)$ is zero when $n = j$.) Thus,

$$W_n' = \int_{\text{all configuration space}} \psi_n^{0*} H' \psi_n^0 d\tau \quad [7-12]$$

Since H' is given and the zero-order eigenfunction ψ_n^0 is known, the energy correction W_n' to the n th nondegenerate level can be calculated directly from [7-12].

The next step is to find *each* of the a_j 's which, in the series [7-10], specify the unknown correction ψ_n' . When ψ_n' is added to ψ_n^0 , we have the true (to first-order) wave function ψ belonging to the true (to first-order) energy $W_n = W_n^0 + W_n'$. This is done in the same manner as in the calculation for W_n' , except that each term in [7-11] is now multiplied from the left by the complex conjugate of a *different* zero-order eigenfunction, say ψ_m^{0*} . Again, we multiply by the volume element $d\tau$ and integrate over all of the coordinates. Equation [7-11] becomes,

$$\sum_j a_j(W_j^0 - W_n^0) \int \psi_m^{0*} \psi_j^0 d\tau = W_n' \int \psi_m^{0*} \psi_n^0 d\tau - \int \psi_m^{0*} H' \psi_n^0 d\tau$$

The left side of this equation is a sum of terms in each of which j has a different value, identifying, in turn, each of the complete set of the zero-order eigenfunctions. We are in the process of finding the correction to the n th zero-order eigenfunction, so here n is fixed. Also, we have used the complex conjugate of a *particular* zero-order eigenfunction ψ_m^{0*} to multiply [7-11], so that here m is fixed. Due to the orthogonality of the zero-order eigenfunctions, the left side of the above equation is zero whenever $j \neq m$, leaving, on the left, only one term—for which $j = m$. Since we have specifically assumed that $m \neq n$, the first term on the right is zero. Thus,

$$a_m(W_m^0 - W_n^0) = - \int_{\text{all configuration space}} \psi_m^{0*} H' \psi_n^0 d\tau$$

Solving for a_m , the amplitude of the m th component in the *correction* ψ' to the unperturbed eigenfunction ψ_n^0 , which is needed to produce the true (to first-

order) eigenfunction ψ_n ,

$$a_m = - \frac{\int \psi_m^{0*} H' \psi_n^0 d\tau}{W_m^0 - W_n^0}, \quad m \neq n \quad [7-13]$$

There may be an infinite number of these equations if the complete set of zero-order eigenfunctions is infinite in number. Thus, to find the true ψ_n for just *one* of the eigenfunctions of the perturbed system requires a great deal of calculation. Usually only a finite number of the a_m 's, calculated by [7-13], have a significant magnitude. Each a_m depends upon the form of the perturbation H' and upon the spatial form of the two *different* functions, ψ_m^0 and ψ_n^0 , in [7-13].

We see, from [7-13], why it is that this theory is valid only when applied to a nondegenerate level. Suppose that the state whose eigenfunction is ψ_m^0 has the same characteristic energy value as that state whose eigenfunction is ψ_n^0 —in other words, two different eigenfunctions belong to the same energy level (we say that this level is twofold degenerate). When this happens a_m will, in general, become infinite, making the correction ψ_m' infinite and therefore unsuitable as part of a wave function. This catastrophe will be avoided only if it also happens that the integral forming the numerator of [7-13] goes to zero whenever the denominator does.

In the next chapter we will discuss the method of avoiding infinite a_m 's even though degeneracy exists.

To find the true eigenfunction and the true characteristic energy of some different, nondegenerate level, k , it is necessary to repeat, for the k th level, the complete calculation we have just outlined for the n th level. Thus, a system that has relatively simple, closed-form expressions for its zero-order eigenfunctions will have, after the addition of a perturbation, eigenfunctions that are describable only with the aid of a long table of the a_j 's—one *complete list* for *each* of the eigenstates. The new eigenfunctions are still describable in terms of the original ones, but each eigenfunction now appears in the relatively clumsy form of a particular series of the zero-order eigenfunctions. The value of the true (to first-order) W_n is

$$W_n = W_n^0 + H'_{nn} \quad [7-14]$$

where by the symbol H'_{nn} we designate the right side of [7-12],

$$H'_{nn} = \int \psi_n^{0*} H' \psi_n^0 d\tau \quad [7-15]$$

By [7-3] and [7-10], the first-order wave function for the n th eigenstate is

$$\begin{aligned} \psi_n = \psi_n^0 + a_1 \psi_1^0 + a_2 \psi_2^0 + a_3 \psi_3^0 + \cdots + a_{n-1} \psi_{n-1}^0 + a_n \psi_n^0 \\ + a_{n+1} \psi_{n+1}^0 + \cdots \end{aligned} \quad [7-16]$$

Each of the a_m 's ($m = 1, 2, 3, 4, \cdots$) in this equation can be calculated