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
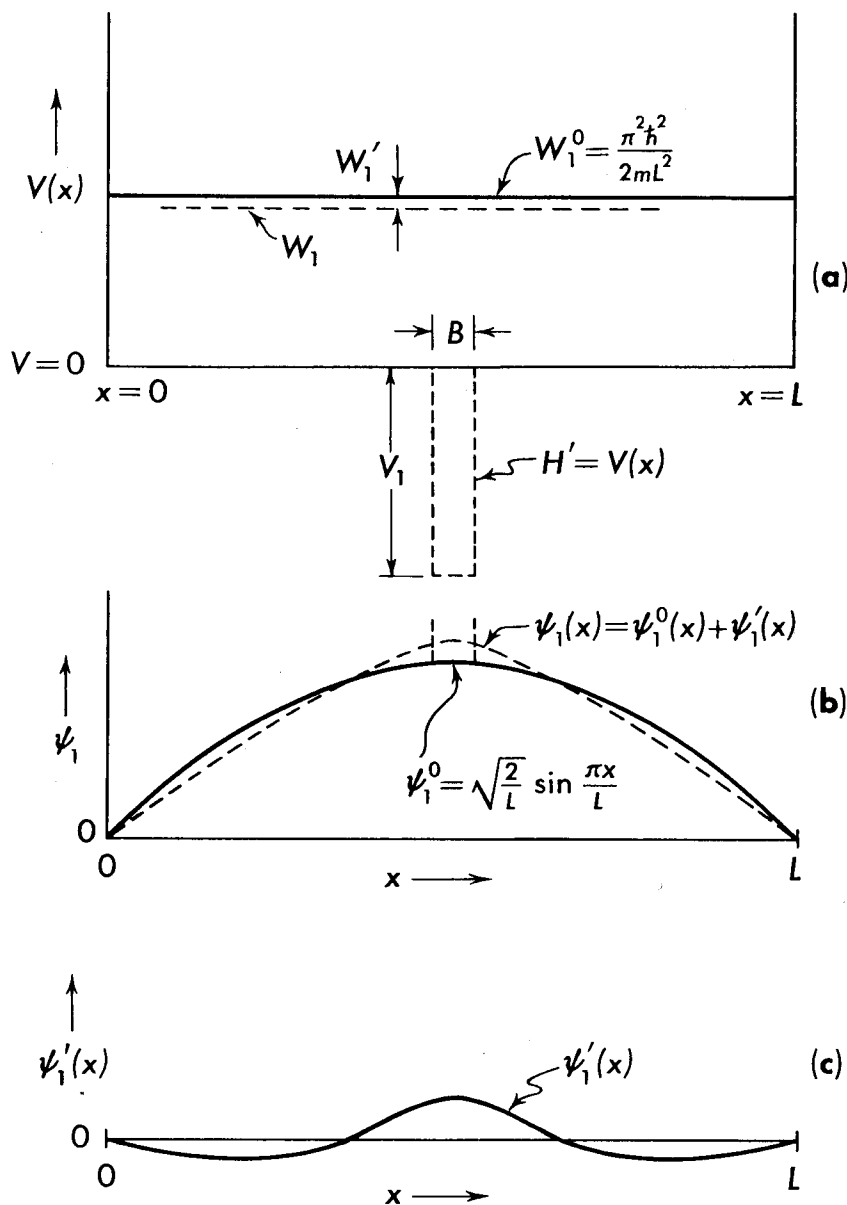

Fig. 7.3. A one-dimensional system containing a small, central potential well.

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
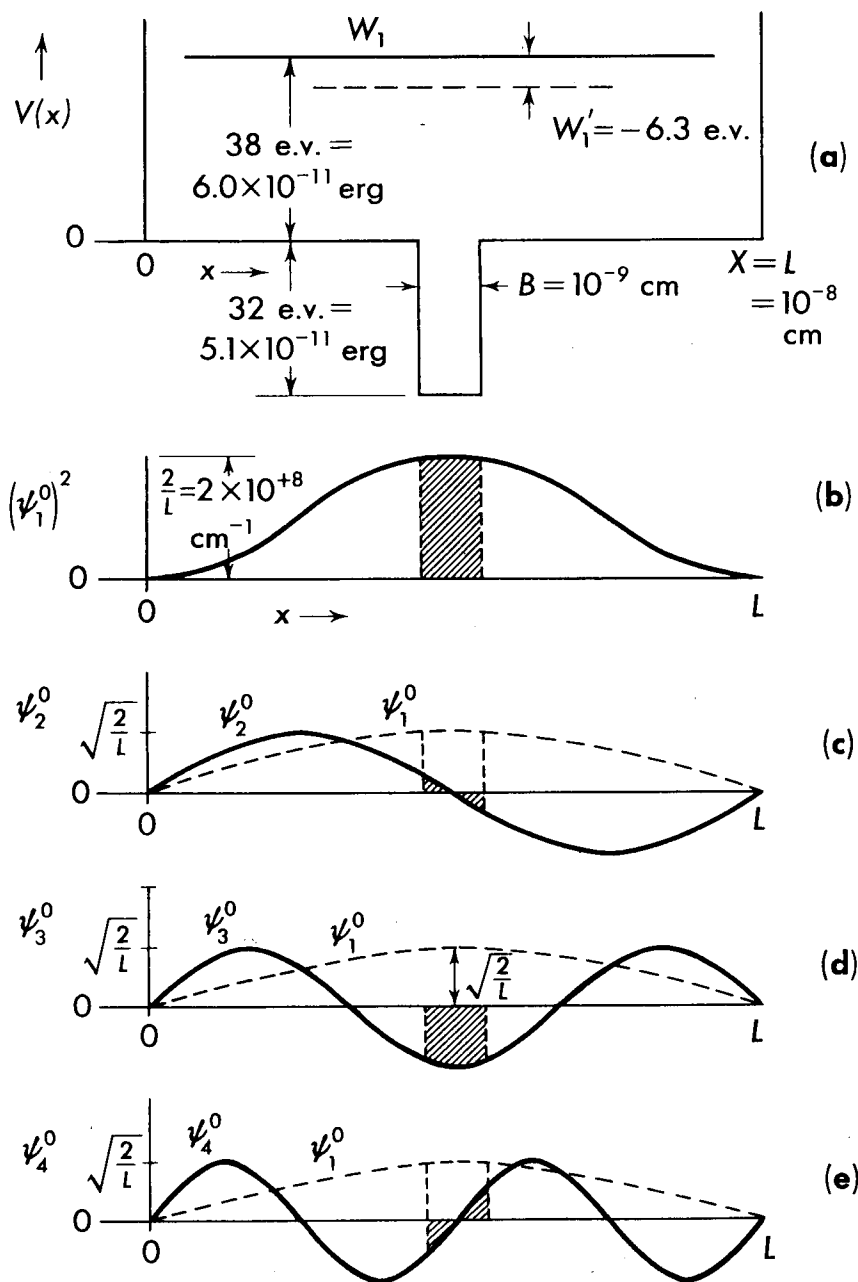
Fig. 7.4. A sample calculation using perturbation theory.

and the energy eigenvalues are,

$$W_n^0 = n^2\pi^2\hbar^2/2mL^2$$

Let the mass $= 9.11 \times 10^{-28}$ gm, $L = 10^{-8}$ cm. Since $\hbar = 1.054 \times 10^{-27}$ erg sec, we have

$$\psi_n^0 = \sqrt{2 \times 10^8} \sin n\pi x/10^{-8} \text{ (cm)}^{-(1/2)}$$

The lowest energy level is[5]

$$W_1^0 = 6\cdot 0 \times 10^{-11} \text{ erg, or } 38 \text{ e.v.}$$

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[5] If $\hbar = 1.054 \times 10^{-34}$ joule sec, $m = 9.11 \times 10^{-31}$ kg, and $L = 10^{-10}$ m, then $W_1^0 = 6.0 \times 10^{-18}$ joule (1 e.v. $= 1.6 \times 10^{-19}$ joule).

With the aid of Figure 7.4d, one can see at once that $H'_{41} = 0$, and therefore $a_4 = 0$.

As higher a_j's are calculated, one should use exact integration in the calculation of the intensity of the odd-numbered components, because the eigenfunctions vary more rapidly inside the perturbing well, although by symmetery
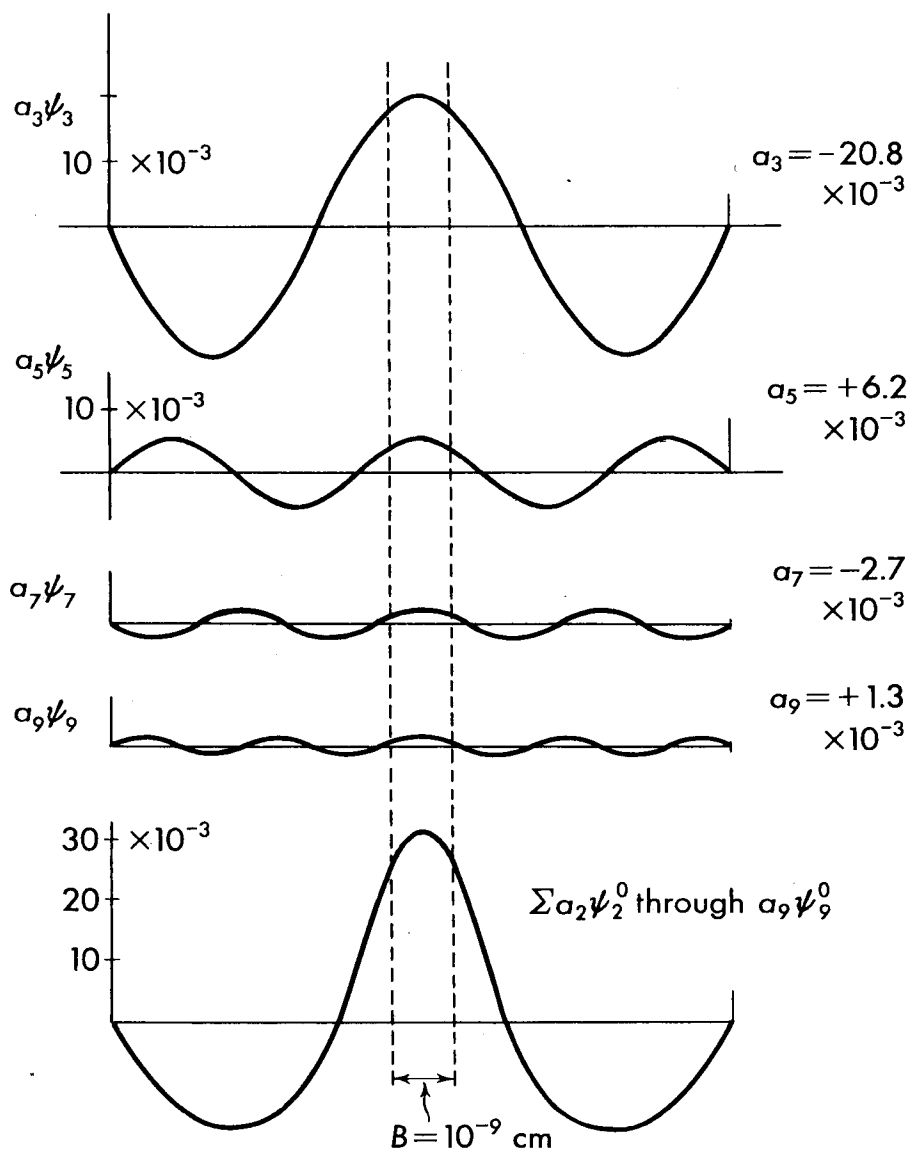

Fig. 7.5. The calculated corrections to the zero-order state ψ_1^0 of the system of Figure 7·4.

all of the even-numbered components are always exactly zero. Because the denominator $W_j^0 - W_1^0$ appears in the calculation of a_j, the magnitude of a_j becomes smaller with increasing $W_j^0 - W_1^0$.

Continuing the calculation of the a_j's, we find the amplitude of the terms up through $n = 9$. These are shown in Figure 7.5. The component wave functions are drawn to scale, with the correct sign. At the bottom of Figure

STEADY-STATE PERTURBATION THEORY. NONDEGENERATE CASE

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In Chapters 3 and 4 we found the eigenfunctions of certain simple, highly symmetrical systems. These eigenfunctions correspond to standing-wave patterns of matter waves which resonate within the bounding potential walls much as sound waves resonate in a room with highly reflecting walls, or electromagnetic waves resonate in a conducting cavity. Indeed, the basic techniques of Chapters 3 and 4 will locate the resonant frequencies of any bounded system containing waves. Once the wave equation and the boundary conditions are specified, a set of natural resonant frequencies, each with its characteristic stationary wave pattern, is determined. For example, in a rectangular room with highly reflecting walls, a resonance will occur whenever an integral number of half wavelengths equals one of the sides of the rectangle. In Figure 7.1a, plane waves of sound, whose crests are λ meters apart, are seen moving to the right in a rectangular box. These waves will soon be reflected from the wall on the right and then travel toward the left. If there is an integral number of half wavelengths along the edge (5 half wavelengths are illustrated in the figure), a standing-wave pattern will occur. A closed pipe containing sound waves develops its characteristic frequencies in just this way.

Suppose now, as in Figure 7.1b, the symmetry is destroyed by covering one corner with a small flat, reflecting surface. The plane waves of Figure 7.1a will now no longer be reflected cleanly from the right-hand wall. The

simple standing-wave pattern that will occur in the upper diagram depends upon the fact that the plane waves propagating to the right are superimposed upon the reflected plane waves propagating to the left.

What will happen in Figure 7.1b? Clearly, the simple resonance due to plane waves propagating to the right and to the left is upset, for even waves
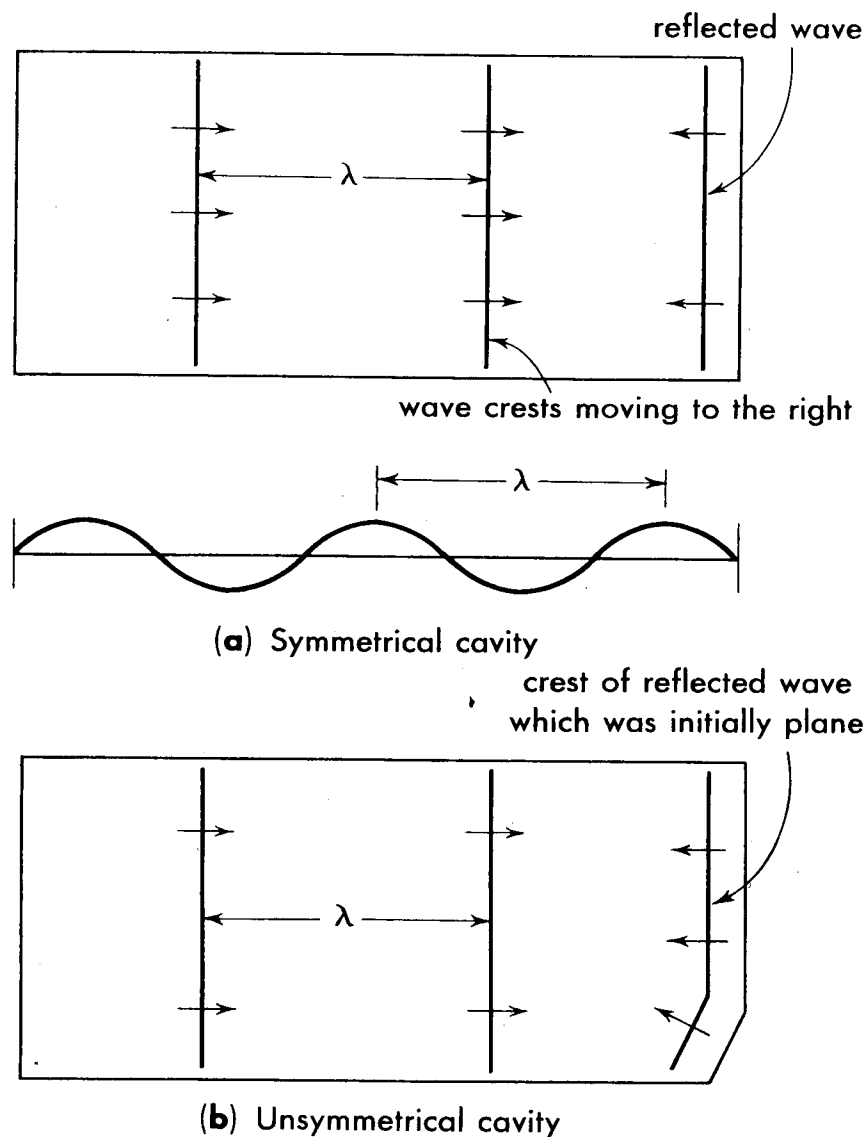
reflected wave

wave crests moving to the right

(a) Symmetrical cavity

crest of reflected wave
which was initially plane

(b) Unsymmetrical cavity

Fig. 7.1. Waves in cavities with reflecting walls.

that are initially plane will soon be going in many directions owing to the reflections from the odd corner. Rather than solve the problem just posed for sound waves, we will turn to a similar situation involving matter waves and see what changes in the pattern of resonance occur when a small, not necessarily symmetrical, change is made in what was originally a highly symmetrical potential well.

In principle, we can set up, and solve, the exact Schrödinger wave equation

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, $e^{-iWt/h}$, 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 assumpton 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

$$H = H^0 + \lambda H'$$

[7–1

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[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,

$$H^0\psi_n^0 = W_n^0\psi_n^0 \qquad\qquad [7\text{--}2$$

The term H' is the perturbation term, derived by the usual operator-substitution method of Postulate II. The factor λ is a constant[2] 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 ψ_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 ψ_n (x, y, z) to deviate in an exactly linear manner from their "starting points" W_n^0 and ψ_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 ψ_n' (x_1, y_1, z_1), plus a second-degree term, in λ^2, which has different—and here, smaller—coefficients W'' and $\psi''(x_1, y_1, z_1)$. 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,

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[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
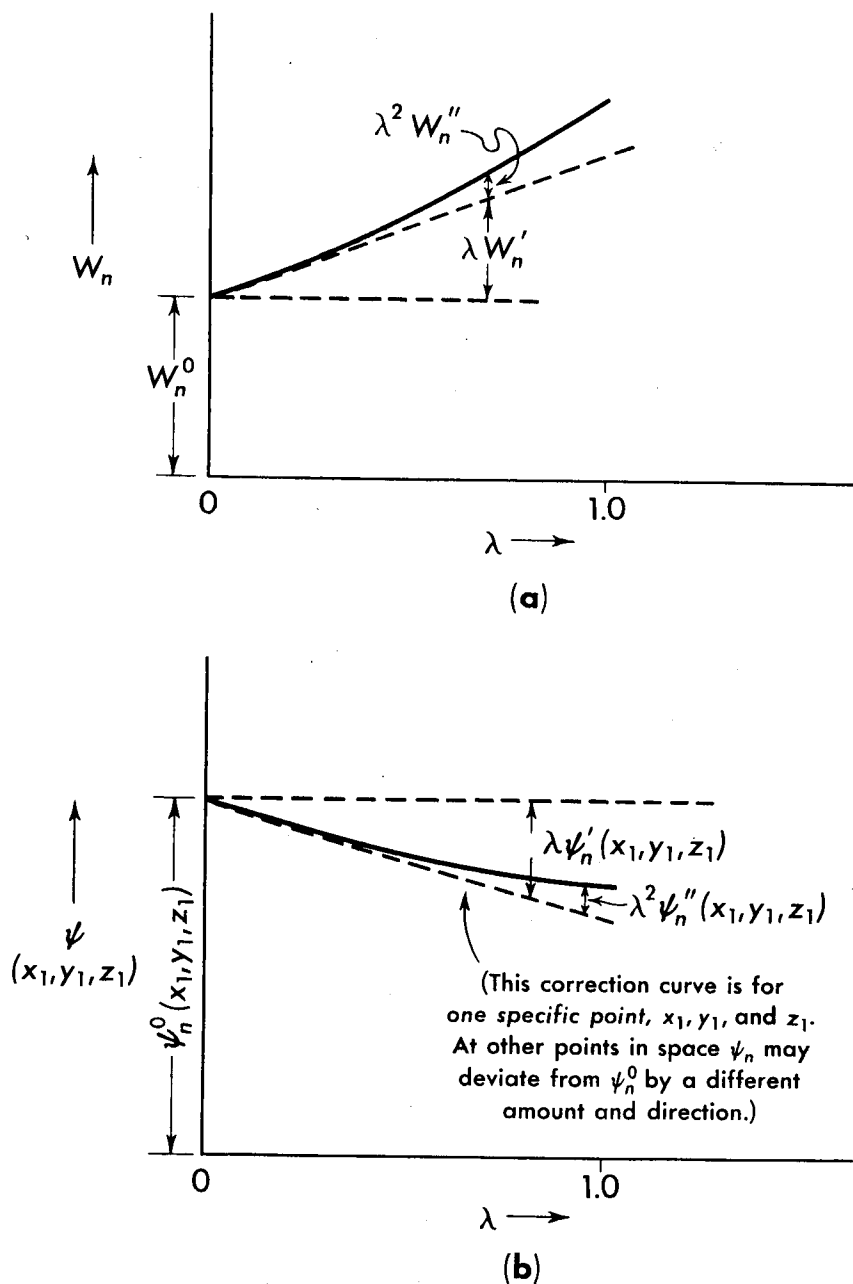

Fig. 7.2. The variation in an eigenvalue W_n and an eigenfunction ψ_n (at a particular point in space) as a function of the magnitude of the perturbation (controlled by λ).

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 $\psi_n(x_1 y_1 z_1)$ 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

$$\psi_n = \psi_n^0 + \lambda \psi_n' + \lambda^2 \psi_n'' + \cdots \qquad [7\text{–}3\,]^3$$

$$W_n = W_n^0 + \lambda W_n' + \lambda^2 W_n'' + \cdots \qquad [7\text{–}4\,]^3$$

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

$$H\Psi = -(\hbar/i)(\partial/\partial t)\Psi \qquad [7\text{–}5$$

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

$$H\psi = W\psi \qquad [7\text{–}6$$

where, as far as the separation of [7–5) is concerned, $W =$ 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

$$H\psi_n = W_n\psi_n \qquad [7\text{–}7$$

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

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[3] Note: Here the primes do *not* mean differentiation. ψ' (*x, y, z*) gives that part of the correction to ψ_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 in-adequate.

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

$$(H^0\psi_n^0 - W_n^0\psi_n^0) + \lambda(H^0\psi_n' + H'\psi_n^0 - W_n^0\psi_n' - W_n'\psi_n^0)$$
$$+ \lambda^2(H^0\psi_n'' + H'\psi_n' - W_n^0\psi_n'' - W_n'\psi_n' - W_n''\psi_n^0)$$
$$+ \lambda^3(\ \cdots\ ) + \cdots$$
$$= 0 \qquad [7\text{-}8$$

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

$$H^0\psi_n' - W_n^0\psi_n' = (W_n' - H')\,\psi_n^0 \qquad [7\text{-}9$$

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
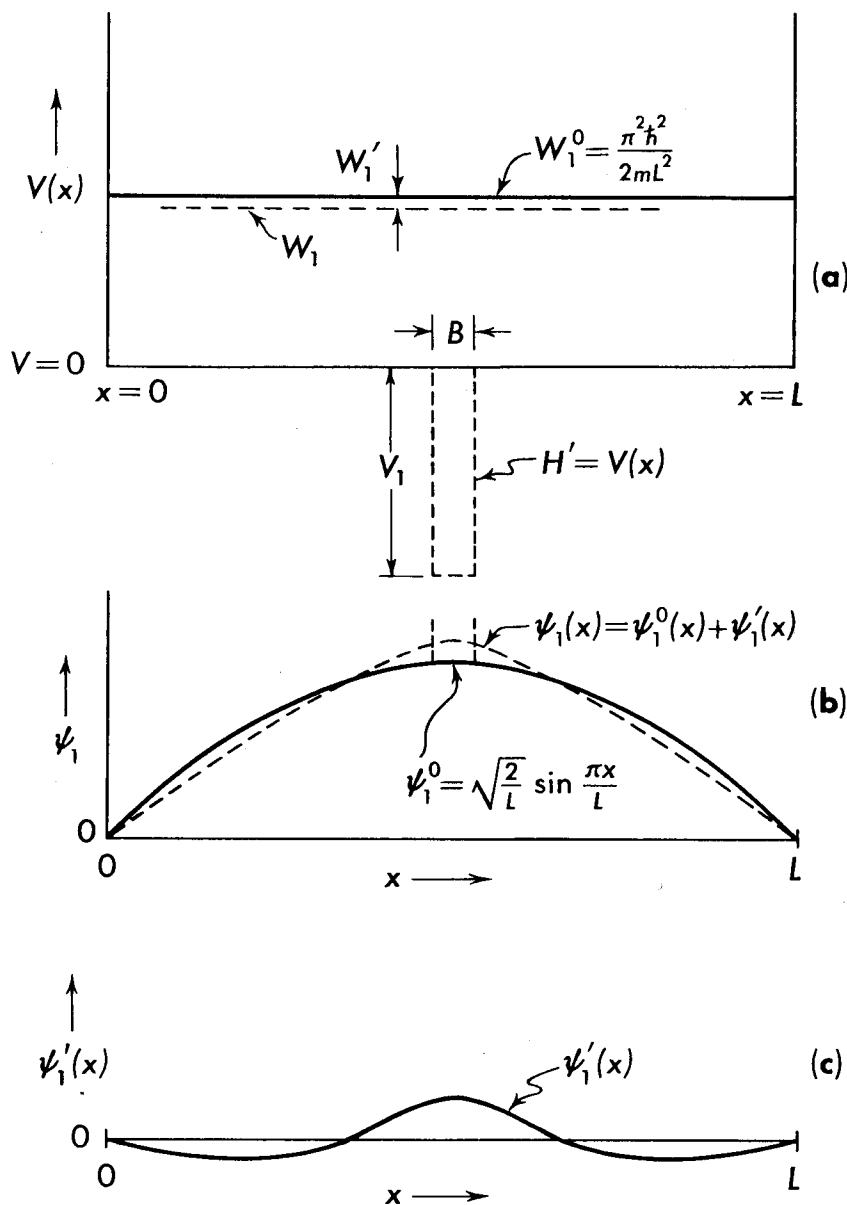

Fig. 7.3. A one-dimensional system containing a small, central potential well.

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* ψ_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

$$\psi_n' = \sum_j a_j \psi_j^0 \qquad [7\text{-}10]^4$$

That is, the correction terms added to the nth 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 $\sqrt{2/L} \sin j\pi x/L$ ($j = 1, 2, 3, \cdots$) 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

$$\sum_j a_j (W_j^0 - W_n^0) \psi_j^0 = (W_n' - H') \psi_n^0 \qquad [7\text{-}11]$$

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 nth, and neglect writing the superscript (n).

cannot be interchanged, in order, with the eigenfunction $\psi_n^0{}^*$ (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

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

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,

$$W_n' = \int \psi_n^0{}^* H' \psi_n^0 \, d\tau \qquad\qquad [7\text{-}12$$
$$\text{all configuration space}$$

Since H' is given and the zero-order eigenfunction ψ_n^0 is known, the energy correction W_n' to the nth 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 $\psi_m^0{}^*$. 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 nth zero-order eigenfunction, so here n is fixed. Also, we have used the complex conjugate of a *particular* zero-order eigenfunction $\psi_m^0{}^*$ 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,

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

Solving for a_m, the amplitude of the mth 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,

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

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 catastrophy 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 kth level, the complete calculation we have just outlined for the nth 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

$$W_n = W_n^0 + H_{nn}' \qquad \text{[7-14}$$

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

$$H_{nn}' = \int \psi_n^{0*} H' \psi_n^0 \, d\tau \qquad \text{[7-15}$$

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

$$\psi_n = \psi_n^0 + a_1\psi_1^0 + a_2\psi_2^0 + a_3\psi_3^0 + \cdots + a_{n-1}\psi_{n-1}^0 + a_n\psi_n^0$$
$$+ a_{n+1}\psi_{n+1}^0 + \cdots \qquad \text{[7-16}$$

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

from [7-13] *except* a_n, for which $m = n$, and therefore [7-13] is inapplicable. With this one exception, therefore, [7-13] gives each of the a's

$$a_m = \frac{-H'_{mn}}{(W^0_m - W^0_n)}, \qquad (n \neq m) \qquad [7\text{--}17$$

where

$$H'_{mn} = \int \psi^{0}_{m}{}^* \, H' \, \psi^0_n \, d\tau \qquad [7\text{--}18$$

The symbols H'_{nn} and H'_{mn} are called the matrix elements of the operator H' with respect to the specified eigenfunctions. These expressions, because of their appearance, are easy to confuse with the perturbation operator H', but they are of course very different, since they imply an important operation involving H' and two eigenfunctions.

How can the only undetermined constant, a_n, in [7-16] be found? We have one requirement left—the new wave function ψ_n must be normalized. It is basic to perturbation theory that the amplitude of the perturbed zero-order eigenfunction does not change appreciably, but in first-order theory we regard this amplitude as being constant. To see what limits the normalization of ψ_n sets upon a_n, we write the perturbed eigenfunction

$$\psi_n = \lambda a_1 \psi^0_1 + \lambda a_2 \psi^0_2 + \cdots + (1 + \lambda a_n) \, \psi^0_n + \cdots \qquad [7\text{--}19$$

where only a_n is undetermined. We then form the complex conjugate ψ^*_n, multiply it into ψ_n, insert the volume element $d\tau$, integrate term-by-term over all configuration space, and set $\int \psi^*_n \psi_n \, d\tau = 1$, with the result,

$$1 = 1 + \lambda(a^*_n + a_n) + \lambda^2(a^*_1 a_1 + a^*_2 a_2 + \cdots + a^*_n a_n + \cdots) \qquad [7\text{--}20$$

We neglect the second-order (λ^2) terms, and note that [7-20] is true for arbitrary λ if 2 × (real part of a_n) = 0. The undetermined imaginary part is of no physical significance. In actual first-order calculations, one sets $a_n = 0$.

7.2.   A sample calculation for a nondegenerate level

To see how the theory in the previous section is applied, we return to the problem of Figure 7.3. In this simple one-dimensional case we were able from general considerations to predict the approximate consequences of the addition of the perturbing potential well in the center of the one-dimensional box. We will now use the theory to calculate the same results.

For a single particle of mass m, in a one-dimensional box, with infinite walls at $x = 0$ and $x = L$, without the perturbing potential, the amplitude eigenfunctions are

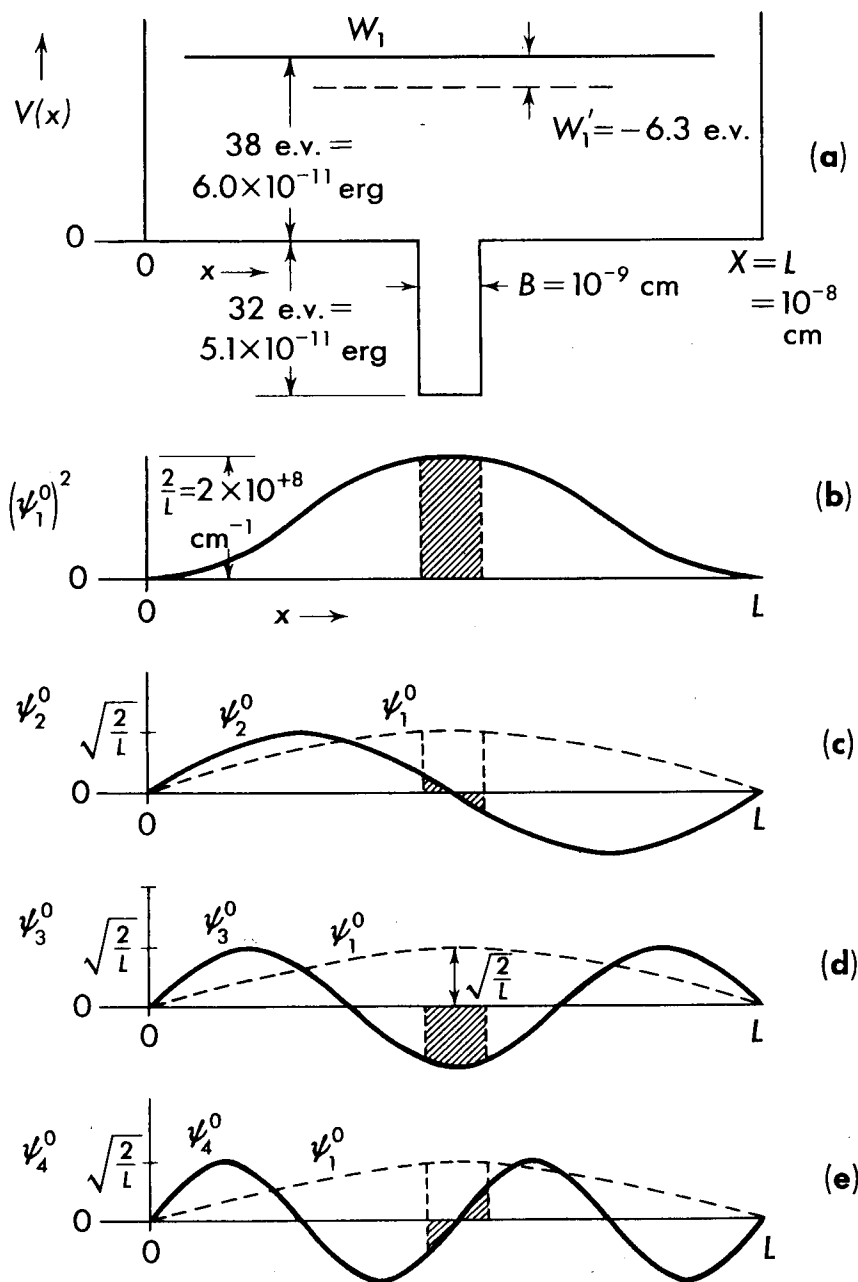$$\psi^0_n = \sqrt{\frac{2}{L}} \sin n\pi x/L$$

Fig. 7.4. A sample calculation using perturbation theory.

and the energy eigenvalues are,

$$W_n^0 = n^2\pi^2\hbar^2/2mL^2$$

Let the mass $= 9.11 \times 10^{-28}$ gm, $L = 10^{-8}$ cm. Since $\hbar = 1.054 \times 10^{-27}$ erg sec, we have

$$\psi_n^0 = \sqrt{2 \times 10^8} \sin n\pi x/10^{-8} \text{ (cm)}^{-(1/2)}$$

The lowest energy level is[5]

$$W_1^0 = 6 \cdot 0 \times 10^{-11} \text{ erg, or } 38 \text{ e.v.}$$

[5] If $\hbar = 1.054 \times 10^{-34}$ joule sec, $m = 9.11 \times 10^{-31}$ kg, and $L = 10^{-10}$ m, then $W_1^0 = 6.0 \times 10^{-18}$ joule (1 e.v. $= 1.6 \times 10^{-19}$ joule).

This is plotted on the potential energy diagram at the top of Figure 7.4.

Let $H' = -5.1 \times 10^{-11}$ erg (or -32 e.v.) in an interval B, of 10^{-9} cm, centered at 0.5×10^{-8} cm, and zero elsewhere.

We first calculate H'_{11}, the first-order correction to the energy level W_1^0.

$$H'_{11} = \frac{2}{10^{-8}} \int_{x=4.5\times10^{-9}}^{x=5.5\times10^{-9}} (-5.1 \times 10^{-11}) \sin^2(\pi x/10^{-8}) \, dx$$

which, from Figure 7.4b, can be seen to be very nearly equal to

$$(2 \times 10^{+8} \text{ cm}^{-1})(-5.1 \times 10^{-11} \text{ erg})(10^{-9} \text{ cm}).$$

Thus,

$$H'_{11} = -10.2 \times 10^{-12} \text{ erg}$$

$$= -6.3 \text{ e.v.}$$

The addition of the potential well lowers the original 38 e.v. level to 31.7 e.v. This lowering of the characteristic energy of the first resonance, or eigenstate, by the addition of the potential well is in agreement with the qualitative arguments used in connection with Figure 7.3.

We next calculate the amplitude of the ψ_2^0 "component" present in the correction to the zero-order wave function. By [7-13],

$$a_2 = \frac{H'_{21}}{W_2^0 - W_1^0} = \frac{-\int \sqrt{\frac{2}{L}} \sin(2\pi x/10^{-8})(-5.1 \times 10^{-11}) \sqrt{\frac{2}{L}} \sin(\pi x/10^{-8}) \, dx}{(2^2 - 1)(6.0 \times 10^{-11})}$$

where the integration runs from

$$x = (5.0 - 0.5) \times 10^{-9}$$

to

$$x = (5.0 + 0.5) \times 10^{-9} \text{ cm},$$

since H' is zero everywhere else. Examination of Figure 7.4c shows at once, however, that the integral H'_{21} will be zero, since the two shaded areas have opposite sign and are equal in magnitude. Thus $a_2 = 0$.

The calculation of a_3 can be performed approximately with the aid of Figure 7.4d, since both functions are essentially constant over the range of integration.

$$H'_{31} \cong \underbrace{(\sqrt{2/L})}_{\psi_3^0} \underbrace{(-5.1 \times 10^{-11})}_{H'} \underbrace{(-\sqrt{2/L})}_{\cong \psi_1^0} \underbrace{(10^{-9})}_{\Delta x}; \quad L = 10^{-8} \text{ cm}$$

$$H'_{31} \cong +1.02 \times 10^{-11} \text{ erg}$$

$$a_3 \cong \frac{-H'_{31}}{W_3^0 - W_1^0} = -\frac{1.02 \times 10^{-11} \text{ erg}}{(3^2 - 1) \, 6.0 \times 10^{-11} \text{ erg}} = -.0208$$

With the aid of Figure 7.4d, one can see at once that $H'_{41} = 0$, and therefore $a_4 = 0$.

As higher a_j's are calculated, one should use exact integration in the calculation of the intensity of the odd-numbered components, because the eigenfunctions vary more rapidly inside the perturbing well, although by symmetery
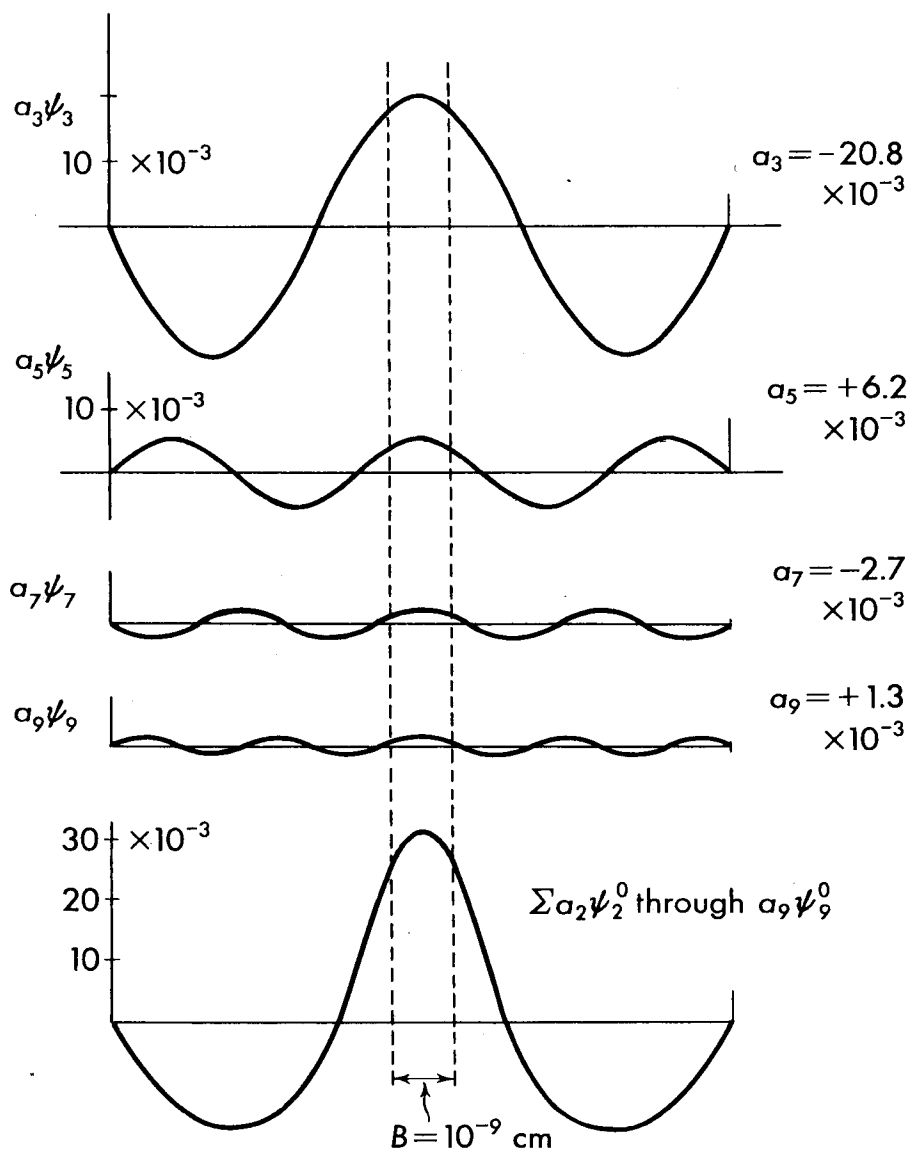

Fig. 7.5. The calculated corrections to the zero-order state ψ_1^0 of the system of Figure 7·4.

all of the even-numbered components are always exactly zero. Because the denominator $W_j^0 - W_1^0$ appears in the calculation of a_j, the magnitude of a_j becomes smaller with increasing $W_j^0 - W_1^0$.

Continuing the calculation of the a_j's, we find the amplitude of the terms up through $n = 9$. These are shown in Figure 7.5. The component wave functions are drawn to scale, with the correct sign. At the bottom of Figure

7.5 the terms $a_2\psi_2^0$ through $a_9\psi_9^0$ have been added together to give the correction ψ_1' needed to convert the zero-order wave function for this stage, ψ_1^0, into the true (to first-order) wave function, ψ_1. This correction term is seen to have the same shape as the one sketched in Figure 7.3c, which was deduced from general considerations.

Except for the terms for $n = 11$ and higher, which rapidly decrease in amplitude and can be neglected, we now have the true wave function expressed as a superposition of zero-order wave functions.

The normalized, true (to first-order) wave function for the lowest level of the system, including perturbation, is

$$\psi_1 = \psi_1^0 + (-20.8 \times 10^{-3})\,\psi_3^0 + (6.2 \times 10^{-3})\,\psi_5^0$$
$$+ (-2.7 \times 10^{-3})\,\psi_7^0 + (1.3 \times 10^{-3})\,\psi_9^0 + \cdots$$

The characteristic energy belonging to this wave function is

$$W_1 = W_1^0 - 1.02 \times 10^{-11}\ \text{erg}$$

A mathematically exact solution of the problem will produce a function $\psi_1(x)$ and a characteristic energy W_1 which are nearly indistinguishable from the above approximate results. Estimating the accuracy of a perturbation calculation is an advanced subject which will not be considered here.

This sample calculation has in it all the essential features of any perturbation calculation for a nondegenerate level in any one-, two-, or three-dimensional system. The only difference in the other systems is that the basic zero-order eigenfunctions in which the true wave function is expressed are different functions of space. One general feature is always present, however. The larger the perturbation, the greater the inaccuracy of the first-order calculations.

In some cases calculations using this theory can be compared with the results of actual experiments. Such a case is the calculation of the lowest energy level of the helium atom, for which $Z = 2$ and for which there are two electrons surrounding the nucleus. The details of this problem can be found in other textbooks[6] and only the main points will be outlined here.

Assume first that for the zero-order system the two electrons do not sense each other's presence in any way but have a potential energy due solely to the presence of the nucleus. The potential energy for the system is then

$$V = -(Ze^2/r_1) - (Ze^2/r_2)$$

where r_1 locates the first electron at x_1, y_1, z_1, and r_2 locates the second electron at x_2, y_2, z_2. Each of the kinetic energy terms is dependent on only three of the six coordinates. We neglect the motion of the nucleus. If the operators are substituted for the dynamical variables according to Postulate II, the resulting zero-order wave equation can be separated into two, one dependent upon

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[6] See, for example, L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (1935, McGraw-Hill Book Co., Inc., New York): p. 162.

x_1, y_1, z_1, and the other on x_2, y_2, z_2. ψ^0 is the product of two hydrogen-like wave functions, each dependent upon one set of coordinates. The zero-order energy W^0 is the sum of the individual energies of the two electrons, each in the coulomb field of a nucleus with $Z = 2$.

Thus the zero-order wave function and the zero-order energy for each electron in the state ψ_{100} are exactly known.

We now add the perturbation,[7]

$$H' = + e^2/r_{12}$$

where r_{12} is the distance between the two electrons. This is the mutual potential energy of repulsion of the two electrons, each with charge e. This is really a quite large perturbation in the sense that the correction energy W' is comparable to the energy of the unperturbed level, and the results based upon it should not be expected to be extremely accurate. The term

$$r_{12} = \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2},$$

depending as it does on all six spatial coordinates, does not permit the separation of the exact wave equation. For this reason perturbation methods, or some numerical methods of solution, must be used.

The first-order correction to the energy is

$$W' = \int \psi_{100,100} \, (Ze^2/r_{12}) \, \psi_{100,100} \, d\tau$$

where $\psi_{100,100}$ is merely the product of two ψ_{100} eigenfunctions as given in Appendix VI, one a function of r_1 and the other of r_2. The volume element $d\tau$ is $(r_1^2 \sin \theta_1 \, d\theta_1 \, d\phi_1 \, dr_1)(r_2^2 \sin \theta_2 \, d\theta_2 \, d\phi_2 \, dr_2)$. The above integral yields the result

$$W' = + 33.82 \text{ e.v.}$$

Since the zero-order energy is $- 108.24$ e.v., the perturbation calculation predicts that the lowest energy level of helium will lie at

$$W_1 = - 74.42 \text{ e.v.}$$

Experimentally, the lowest energy level is found to be

$$W_1 = - 78.62 \text{ e.v.}$$

that is, it requires 78.62 e.v. to completely remove both electrons from a helium nucleus, bringing them to rest at infinity.

Thus, the first-order perturbation calculation gives a 27 per cent correction to the zero-order energy and gives a final result which is 5.5 per cent in error from the experimentally determined value.[8]

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[7] If e is expressed in e.s.u., and r in cm, then H' is in ergs. If e is in coulombs, and r in meters, $H' = (1/4 \pi \varepsilon_0) e^2/r$ joules, where $(1/4 \pi \varepsilon_0) = 9 \times 10^9$ nt m²/coulomb.

[8] A more accurate calculation requires that other effects are included such as "exchange symmetry" (Section 11.9).

As *Z* increases, the relative importance of the electron repulsion becomes less. For example, for quadruply ionized carbon, $Z = 6$, there are two electrons. Here, the correction W' is 10 per cent of the unperturbed energy and the calculated value is only 0.4 per cent in error compared to the experimental value.

The first-order wave functions can also be found by the same principles we have discussed in this section. Due, however, to the geometrical complexity of the hydrogen-like wave functions, and also to the nature of the perturbation H', this calculation is not easy to perform.

We have discussed here only the most simple type of perturbation theory. By extending the method to include the second-order terms in [7–8] (where, for ψ_n'', one substitutes, once again, a series of the basic zero-order eigenfunctions and then proceeds in a manner similar to first-order theory), greatly improved accuracy can often be obtained. In addition to these methods there are many other techniques of approximate calculation that can be found in the more advanced textbooks and in the literature.

7.3. Summary

In this, and in all of the subsequent chapters, the detailed method of presentation loses much of the brevity and essential simplicity of the mathematical argument. Also, for reference purposes, it is convenient to have the key equations brought together. Therefore, we reproduce here, in outline form and with minimum comment, the essential steps in theory developed in this chapter. The equations are identified by the same numbers that are used in the main part of the chapter.

For the *n*th level, the exact or true wave equation is

$$H\psi_n = W\psi_n, \text{ where } H = H^0 + \lambda H' \qquad [7-6], [7-1$$

In the true wave equation, we substitute:

$$\psi_n = \psi_n^0 + \lambda\psi_n', \text{ where } \psi_n' = \sum_j a_j \psi_j^0 \qquad [7-3], [7-10$$

$$W_n = W_n^0 + \lambda W_n' \qquad [7-4$$

obtaining [7–8] (see text).

We set the coefficient of $\lambda^0 = 0$, obtaining

$$H^0 \psi_n^0 = W_n^0 \psi_n^0, \text{ the zero-order equation} \qquad [7-2$$

We set the coefficient of $\lambda^1 = 0$, obtaining

$$\sum_j a_j(W_j^0 - W_n^0) \psi_j^0 = (W_n' - H') \psi_n^0, \text{ the first-order equation} \qquad [7-9], [7-11$$

We multiply the first-order equation from the left by ψ_n^{0*}, insert $d\tau$, and integrate over all configuration space, obtaining *one* equation, which gives the energy

correction to the *n*th level,

$$W'_n = \int \psi_n^{0*} H' \psi_n^0 \, d\tau \equiv H'_{nn} \qquad [7\text{-}12$$

We repeat the above operation, except using ψ_m^{0*}, $(m \neq n)$, obtaining a *set* of equations which gives, by [7-10], the *correction* to the wave function of the *n*th level,

$$a_m = -\frac{\int \psi_m^{0*} H' \psi_n^0 \, d\tau}{W_m^0 - W_n^0} = \frac{-H'_{mn}}{W_m^0 - W_n^0},$$

where $m = 1, 2, 3, \cdots$ except, $m \neq n.$ $\quad [7\text{-}13$

To first-order, set $a_n = 0$. Since all the above results are true for arbitrary λ, we set $\lambda = 1$. Thus, from [7-3] the first-order energy is

$$W_n = W_n^0 + W'_n \qquad [7\text{-}21$$

where W'_n is given by [7-12].

From [7-4] the first-order wave function belonging to W_n is

$$\psi_n = \psi_n^0 + a_1 \psi_1^0 + a_2 \psi_2^0 + a_3 \psi_3^0 + \cdots + (0) \psi_n^0 + \cdots \qquad [7\text{-}22$$

where each a_m is given by [7-13].

For another level—the *k*th—this whole process must be repeated, resulting in a first-order W_k and ψ_k.

PROBLEMS

Problem 7.1. For the system described in Figure 7.4a find, to first-order, the energy value W_3 and the amplitudes, a_j of the two strongest components in the correction, ψ_3', to the zero-order wave function ψ_3^0.

Problem 7.2. For the system of Figure 7.4a find, to first-order, the energy value W_2 and the amplitudes a_j of the two strongest components in the correction, ψ_2', to the zero-order wave function ψ_2^0. Hint; With the aid of diagrams, make a geometrical analysis of the problem, exploiting symmetry, before doing any quantitative calculations.

Problem 7.3. Classically, a particle bound by a potential such as that in Figure 7.4 would, upon losing energy, settle down into the central potential well. Estimate the necessary depth of the central well in Figure 7.4 in order that the quantum-mechanical particle could be bound inside it.