

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

$$a_m = \frac{-H'_{mn}}{(W_m^0 - W_n^0)}, \quad (n \neq m) \quad [7-17]$$

where

$$H'_{mn} = \int \psi_m^{0*} H' \psi_n^0 d\tau \quad [7-18]$$

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  $\psi_n$  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  $\psi_n$  sets upon  $a_n$ , we write the perturbed eigenfunction

$$\psi_n = \lambda a_1 \psi_1^0 + \lambda a_2 \psi_2^0 + \cdots + (1 + \lambda a_n) \psi_n^0 + \cdots \quad [7-19]$$

where only  $a_n$  is undetermined. We then form the complex conjugate  $\psi_n^*$ , multiply it into  $\psi_n$ , 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,

$$1 = 1 + \lambda(a_n^* + a_n) + \lambda^2(a_1^* a_1 + a_2^* a_2 + \cdots + a_n^* a_n + \cdots) \quad [7-20]$$

We neglect the second-order ( $\lambda^2$ ) terms, and note that [7-20] is true for arbitrary  $\lambda$  if  $2 \times (\text{real part of } a_n) = 0$ . 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

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

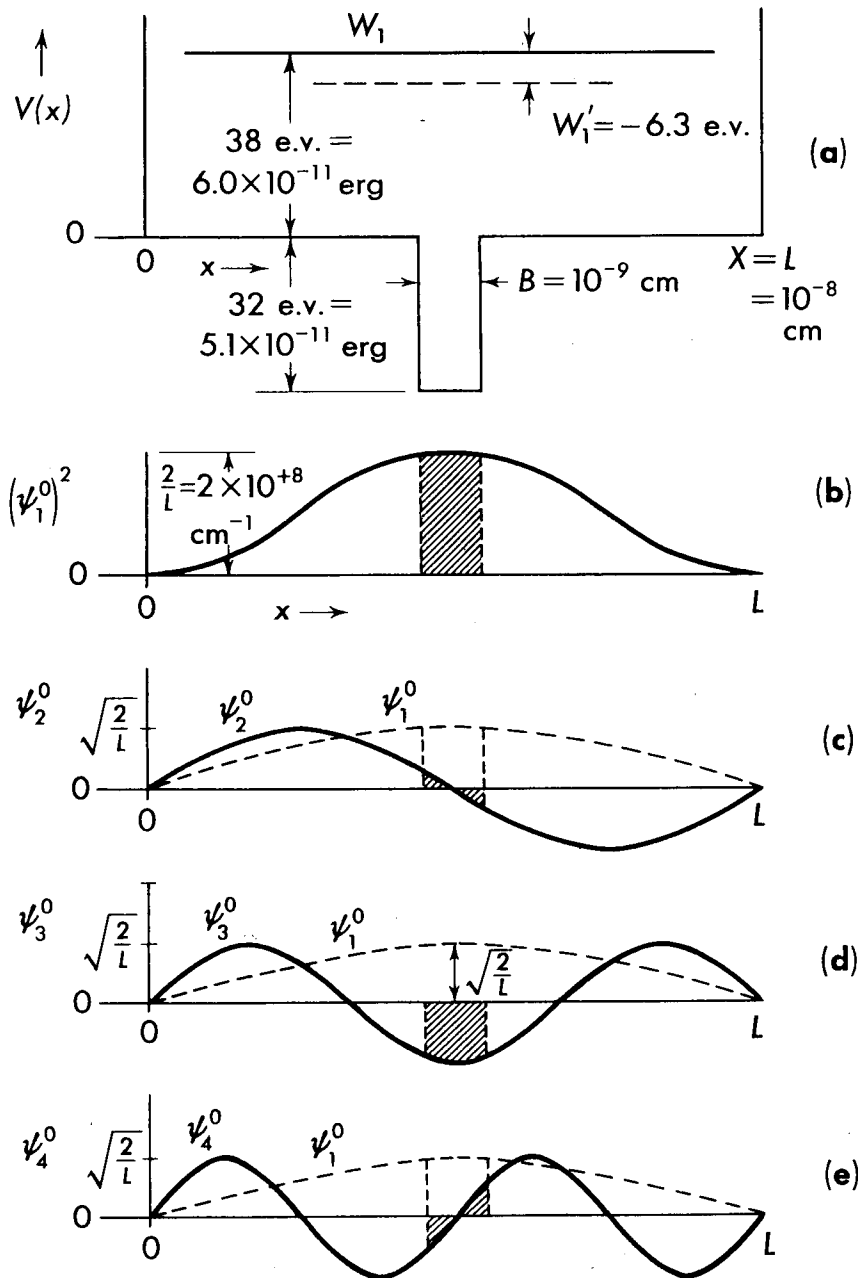


Fig. 7.4. A sample calculation using perturbation theory.

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<sup>5</sup>

$$W_1^0 = 6.0 \times 10^{-11} \text{ erg, or } 38 \text{ e.v.}$$

<sup>5</sup> 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  $0.5 \times 10^{-8}$  cm, and zero elsewhere.

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

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

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,

$$\begin{aligned} H'_{11} &= -10.2 \times 10^{-12} \text{ erg} \\ &= -6.3 \text{ e.v.} \end{aligned}$$

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  $\psi_2^0$  "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 symmetry

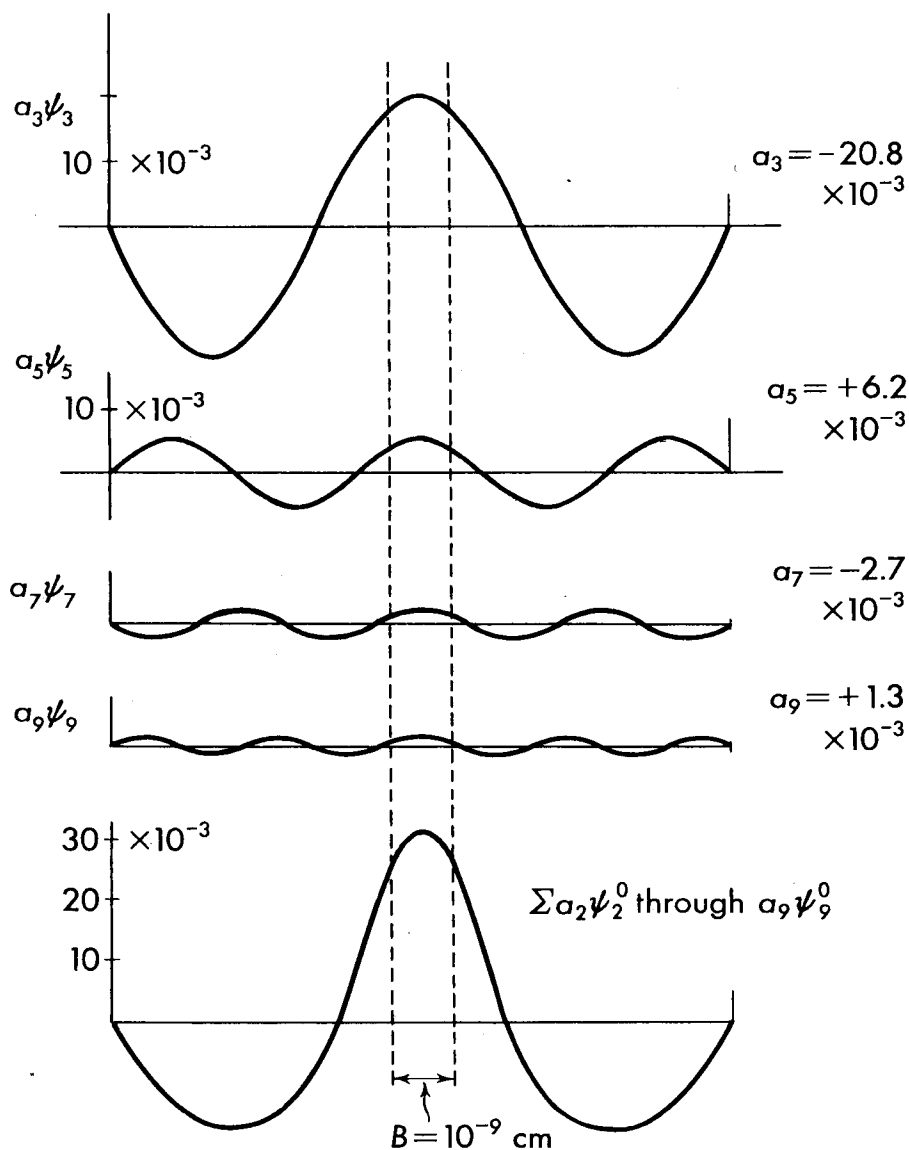


Fig. 7.5. The calculated corrections to the zero-order state  $\psi_1^0$  of the system of Figure 7.4.

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  $\psi_1'$  needed to convert the zero-order wave function for this stage,  $\psi_1^0$ , into the true (to first-order) wave function,  $\psi_1$ . 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  $n = 1i$  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

$$\begin{aligned}\psi_1 = \psi_1^0 + (-20.8 \times 10^{-3})\psi_3^0 + (6.2 \times 10^{-3})\psi_5^0 \\ + (-2.7 \times 10^{-3})\psi_7^0 + (1.3 \times 10^{-3})\psi_9^0 + \dots\end{aligned}$$

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<sup>6</sup> 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

<sup>6</sup> 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  $x_2, y_2, z_2$ .  $\psi^0$  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  $\psi_{100}$  are exactly known.

We now add the perturbation,<sup>7</sup>

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

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  $\psi_{100}$  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.<sup>8</sup>

<sup>7</sup> 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,  $H' = (1/4 \pi \epsilon_0) e^2/r$  joules, where  $(1/4 \pi \epsilon_0) = 9 \times 10^9$  nt m<sup>2</sup>/coulomb.

<sup>8</sup> 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  $\psi_n''$ , 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

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

In the true wave equation, we substitute:

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

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

obtaining [7-8] (see text).

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

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

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

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

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

correction to the  $n$ th level,

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

We repeat the above operation, except using  $\psi_m^{0*}$ , ( $m \neq n$ ), 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  $m = 1, 2, 3, \dots$  except,  $m \neq n$ . [7-13]

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

$$W_n = W_n^0 + W'_n \quad [7-21]$$

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

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

$$\psi_n = \psi_n^0 + a_1 \psi_1^0 + a_2 \psi_2^0 + a_3 \psi_3^0 + \dots + (0) \psi_n^0 + \dots \quad [7-22]$$

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  $\psi_k$ .

## 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,  $\psi'_3$ , to the zero-order wave function  $\psi_3^0$ .

*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,  $\psi'_2$ , to the zero-order wave function  $\psi_2^0$ . 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.



## STEADY-STATE PERTURBATION THEORY. NONDEGENERATE CASE

---

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  $\lambda$  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

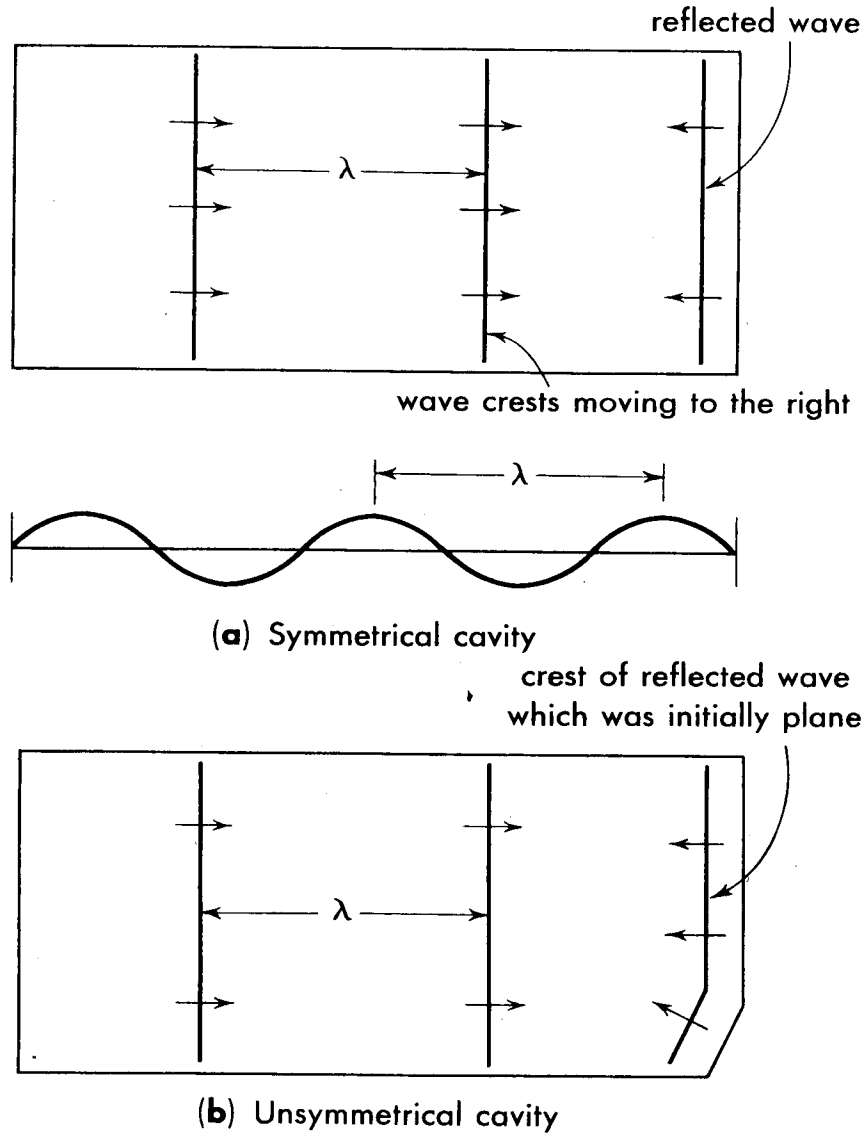


Fig. 7.1. Waves in cavities with reflecting walls.

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