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$$\frac{d}{dt} a_m(t) = -\frac{i}{\hbar} \sum_{n=1}^{\infty} a_n(t) \int \Psi_m^{0*} H' \Psi_n^0 d\tau \quad [10-11]$$

where  $m = 1, 2, 3, 4, \dots$ .

*This is the basic law of time-dependent perturbation theory.* It gives the rate of change of the  $m$ th component of the expansion [10-9], which describes the true, time-varying wave function of the system. The rate of change of the amplitude  $a_m$  depends upon the magnitude of the other amplitudes and also upon a set of matrix elements,  $\int \Psi_m^{0*} H' \Psi_n^0 d\tau$ , which "connect," by means of  $H'$ , the pure state  $\Psi_m^0$  with each of the other pure states  $\Psi_n^0$ .<sup>3</sup>

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The fundamental equation [10-11] looks deceptively simple. It stands for a whole set of equations (in general, an infinite set) *each* of which has a large number of terms (in general, an infinite number). We write out these equations (in part) to provide a better appreciation of their nature.

$$\begin{aligned} -\frac{\hbar}{i} \frac{da_1}{dt} &= a_1 \int \Psi_1^{0*} H' \Psi_1^0 d\tau + a_2 \int \Psi_1^{0*} H' \Psi_2^0 d\tau + \dots + a_k \int \Psi_1^{0*} H' \Psi_k^0 d\tau + \dots \\ -\frac{\hbar}{i} \frac{da_2}{dt} &= a_1 \int \Psi_2^{0*} H' \Psi_1^0 d\tau + a_2 \int \Psi_2^{0*} H' \Psi_2^0 d\tau + \dots + a_k \int \Psi_2^{0*} H' \Psi_k^0 d\tau + \dots \\ &\vdots \\ &\vdots \\ &\vdots \\ -\frac{\hbar}{i} \frac{da_k}{dt} &= a_1 \int \Psi_k^{0*} H' \Psi_1^0 d\tau + a_2 \int \Psi_k^{0*} H' \Psi_2^0 d\tau + \dots + a_k \int \Psi_k^{0*} H' \Psi_k^0 d\tau + \dots \\ &\vdots \\ &\vdots \\ &\vdots \end{aligned} \quad [10-12]$$

<sup>3</sup> If, in addition to  $H^0$ ,  $H$  contains a time-independent term  $H'$ (space) as well as a time-dependent term  $H'$ (space, time), one first applies time-independent perturbation theory to get the corrected wave functions, and then uses these wave functions in the time-dependent theory. This process is illustrated below in Sec. 10.5.

We equate separately each power of  $\lambda$ . For zero order,

$$(d/dt) a_1^0 = 0; (d/dt) a_2^0 = 0; \cdots; (d/dt) a_k^0 = 0; \cdots \quad [10-15]$$

That is, if the time-dependent part of the Hamiltonian is zero, then each  $a_m$  (which determines the amplitude of the component  $\Psi_m^0$  of the complete wave function  $\Psi$ ), if determined at one time, is unchanged for any other time. This same result, for the time-independent Hamiltonian, was obtained in Chapter 7.

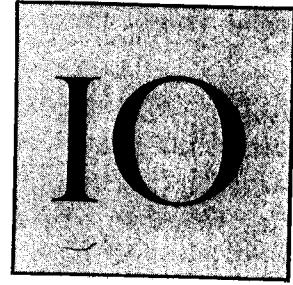
Equating all terms of  $\lambda^1$ , we have the set of equations

$$\begin{aligned} -\frac{\hbar}{i} \frac{da_1'}{dt} &= a_1^0 \int \Psi_1^{0*} H' \Psi_1^0 d\tau + a_2^0 \int \Psi_1^{0*} H' \Psi_2^0 d\tau + \cdots + a_k^0 \int \Psi_1^{0*} H' \Psi_k^0 d\tau + \cdots \\ -\frac{\hbar}{i} \frac{da_2'}{dt} &= a_1^0 \int \Psi_2^{0*} H' \Psi_1^0 d\tau + a_2^0 \int \Psi_2^{0*} H' \Psi_2^0 d\tau + \cdots + a_k^0 \int \Psi_2^{0*} H' \Psi_k^0 d\tau + \cdots \\ &\vdots \\ -\frac{\hbar}{i} \frac{da_k'}{dt} &= a_1^0 \int \Psi_k^{0*} H' \Psi_1^0 d\tau + a_2^0 \int \Psi_k^{0*} H' \Psi_2^0 d\tau + \cdots + a_k^0 \int \Psi_k^{0*} H' \Psi_k^0 d\tau + \cdots \\ &\vdots \\ &\vdots \end{aligned} \quad [10-16]$$

This set of *approximate* equations differs from the exact set [10-12] by the presence, on the right, of the constant zero-order coefficients  $a_m^0$  and by the presence, on the left, of the *corrections*,  $a_m'$ , to the zero-order coefficients  $a_m^0$ .

The  $a_m^0$ 's are merely the initial conditions. They measure the intensity of vibration of all of the modes of the unperturbed system that are needed to form the actual wave function at  $t = t_0$ . The equations [10-16] give the growth or decline of the amplitude of vibration of each of the natural modes of the system. Since  $H'$  is assumed to be small, the corrections to the amplitudes,  $a_m'$ , are also small. Thus, although all the vibrations can either grow or decrease as time proceeds, the changes from their initial values will not be very large.

One speaks of a typical mode of vibration, or "proper" vibration (such as that represented by  $\Psi_1^0$ , as being "connected," via  $H'$ , to each of the other modes. The exact equation [10-12] shows that, as time proceeds, the state  $\Psi_k^0$  "feeds amplitude" into the state  $\Psi_1^0$  at a rate given by  $a_k \int \Psi_1^{0*} H' \Psi_k^0 d\tau$ , and that the reverse process goes on at a rate given by  $a_1 \int \Psi_k^{0*} H' \Psi_1^0 d\tau$ . This is a completely continuous process. *The perturbation  $H'$  acts constantly to reshuffle the degree of excitation of the modes.* If it is suddenly terminated the system remains, thereafter, with exactly constant amplitudes for each proper



# TIME-DEPENDENT PERTURBATION THEORY

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Up to now, all the quantitative calculations have been concerned with the Hamiltonian functions which are independent of time—and therefore with Hamiltonian operators,  $H$ , which are independent of time. In a real sense, however, all that we have done so far is a mathematical exercise, because when the Hamiltonian is time-independent, *nothing observable ever happens*.

Consider first a system in the pure vibration of a stationary state. Its probability density,  $\Psi^*\Psi$ , is constant in time. The expectation value of the system energy is constant. If it is a three-dimensional system, such as the hydrogen atom in the  $l = 1$  state, the expectation value of the magnitude of its angular momentum is constant and, along any specified axis, the component of its angular momentum is a constant—depending upon which of the  $m$ -quantum numbers appears in its eigenfunction. Such a state of affairs will go on forever unless the system is interfered with in some way. In the earlier chapters we performed imaginary experiments which consisted of *interfering with the system*, usually in some rather violent manner. For example, we imagined that, to locate the particle, we inserted a series of slits into the space occupied by the system and turned on some accelerating potential that pulled the particle through the nearest slit (thus locating it). Then, after much magnification, we observed a macroscopic pulse of current which implied that the amplifier in question received the particle at its input. This process can scarcely be described by a time-independent system energy (Hamiltonian) with its cor-

responding time-independent operator. Clearly, the results of laboratory experiments cannot be predicted unless the system energy is, in some manner, time-dependent.

Consider next a system in an arbitrary superposition of its pure vibrations, that is, eigenstates. We can *calculate*, as in Section 5.1, that the probability density is now changing with time, but to observe where the particle *is* requires, once again, interference with the system, so that this changing probability does not lead to any observable consequences. We saw in Chapter 5 that for “mixed” states, including wave packets, the amplitude of each pure vibration remained constant with time. The systematic changes in  $\Psi^*\Psi$  are due merely to the “beating together” of the “proper” or pure resonant frequencies, each of constant amplitude, which characterize the system. The expectation value of the energy is still constant with time, although it is now the weighted sum of the characteristic energies of the pure vibrations. The weighting factor is merely  $a_j^*a_j$ —which measures the intensity of the  $j$ th proper vibration. Until we interfere with the system, we will never be able to find out what the intensities of the different possible vibrations actually are.

The expectation-value formula of Postulate V provides the link between theory and observation, but when it is used with stationary-state wave functions and time-independent operators its predictions cannot be verified. There is no way to observe a completely isolated atomic system.

Thus, when the Hamiltonian is time-independent, nothing observable ever happens.

Clearly, then, the practical uses of quantum mechanics must be intimately associated with time-dependent Hamiltonian operators, and also with much larger systems—such as one consisting of  $N$  atoms, an optical grating, and a photographic plate—in some definite geometrical arrangement. At  $t = 0$  the atoms are excited by a pulse of electrons, and the photographic plate is blank. At some later time, the atoms are in their ground states, and the photographic plate has dark lines on it in certain measurable places and with certain measurable intensities. This realistic, complete system is certainly not in any stationary state, or in a superposition of stationary states.

It may come as something of a shock to discover, after nine chapters, that we have yet to get down to the business of predicting experiments in a realistic, logically consistent way. Nonetheless, only with a thorough grasp of the formal mathematics of the stationary states can we deal with time-varying Hamiltonians. As we shall see, only with the aid of the familiar ortho-normal eigenfunctions can the time-dependent wave equation be made tractable.

This textbook seeks primarily to teach what quantum mechanics *is*, and not to explore the intriguing (and very important) byways of philosophical interpretation. We have diverged from this principle here only to highlight the great importance of time-dependent calculations. Even though it comes late in the textbook it is, in a sense, the very heart of the theory. We shall be content to limit time-dependent calculations to only one or two of the theory's

most simple applications, since these will suffice to illuminate the important concepts.

### 10.1. Time-dependent perturbation theory

Basically, we are looking for solutions,  $\Psi(x, y, z, t)$ , of the wave equation of Postulate II,

$$H\Psi = -(\hbar/i)(\partial/\partial t)\Psi \quad [10-1]$$

which, at all times, are well behaved and possess an integrable square, as required by Postulates III and IV. Unfortunately, for even a single particle, when  $H$  is a function of  $t$  the dependence of  $\Psi$  upon the four variables  $x, y, z$ , and  $t$  usually makes the direct solution of the equation very difficult.<sup>1</sup> We fall back, therefore, upon some set of known stationary-state eigenfunctions which, because of their ortho-normality, provide a tractable means of describing the true  $\Psi$ 's of [10-1]. In an artificial manner, therefore, we split the true Hamiltonian into two parts.

$$H = H^0(x, y, z, p_x, p_y, p_z) + H'(x, y, z, p_x, p_y, p_z, t) \quad [10-2]$$

where  $H^0$  is time independent and has eigenfunctions  $\Psi_n^0$ , which are either known or can be found. These eigenfunction are found by the same method that we have used on many occasions. The equation to be solved is:

$$H^0\Psi = -(\hbar/i)(\partial/\partial t)\Psi \quad [10-3]$$

We set  $\Psi = \psi(x, y, z) e^{-i(W/\hbar)t}$ , and separate [10-3] into two equations. The space-dependent equation is

$$H^0\psi = W\psi$$

which has, of course, a solution for every value of  $W$ , the separation constant. It possesses *well-behaved* solutions of *integrable square*,  $\psi_n^0$ , only when  $W$  has certain values,  $W_n^0$ . Thus, each of the set of eigenfunctions obeys an equation.

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

or

$$H^0\Psi_n^0 = -(\hbar/i)\partial\Psi_n^0/\partial t = W_n^0\Psi_n^0 \quad [10-3a]$$

Each  $\psi_n^0$  is an eigenfunction of the operator  $H^0$ , corresponding to the eigenvalue  $W_n^0$ . The most general well-behaved solution to [10-3] is a linear combination of the complete set of  $\Psi_n^0$ 's,

$$\Psi^0 = \sum_n a_n \Psi_n^0$$

<sup>1</sup> Since now [10-1] cannot, in general, be "separated" into two equations, one space-dependent, and the other time-dependent.

where

$$\Psi_n^0 = \psi_n^0 e^{-i\frac{W_n t}{\hbar}} \text{ and } \sum_n a_n^* a_n = 1 \quad [10-4]$$

From the foregoing, which is a brief review of time-independent theory, we turn to the problem of time dependence. The part of the true Hamiltonian  $H$  (which makes the wave equation intractable) has all been lumped into  $H'$ .  $H'$  can depend upon position, momentum, and time. For example, an electromagnetic wave, passing through an atom, will not have the same influence at all points at a given instant since it is varying in both time and space. Also, electrons with velocity (momentum) will be affected by the magnetic field as well as by the electric field, but the electric field is the only one experienced by electrons momentarily at rest. Thus,  $H'$  can depend upon the momentum operators  $p_x$ ,  $p_y$ , and  $p_z$ , as well as position and time.

Writing  $H$  in two parts, as in [10-2], the true wave equation [10-1], becomes

$$(H^0 + H')\Psi = -(\hbar/i)(\partial/\partial t)\Psi \quad [10-5]$$

At all times,  $\Psi$  must meet the requirements of the basic postulates. Let us suppose, as in Section 5.1, that at  $t = t_0$ ,  $\Psi$  has some given form,  $\Psi(x, t_0)$ . Our objective is to find  $\Psi$  at some later time, where  $\Psi$  is at all times governed by [10-5].  $\Psi(x, t_0)$  provides the initial conditions without which specific solutions to a partial differential equation are impossible. For example, each specific solution of a second-order *ordinary* differential equation is determined by two numbers at  $t = t_0$ , the value of the variable and the value of slope. We shall see shortly, that if a partial differential equation of the type [10-5] is given a *whole function*,  $\Psi(x, t_0)$ , for its initial conditions, then at all later (or earlier) times, the equation determines a unique function,  $\Psi(x, t)$ . We have already seen, in Section 5.1, a simple example of this type of calculation. There we had a Hamiltonian operator  $H$  which was independent of  $t$ . This form of  $H$  simplified the computations, but the basic process we have just been discussing occurred. The argument in Section 5.1 can be summarized as follows: We were given an initial function  $\Psi(x, t_0)$  [5-8], which we then synthesized by the series of orthogonal functions,  $\sum_n a_n(t_0) \Psi_n^0(x, t_0)$  [5-9]. We then found, by substitution into the wave equation

$$H\Psi = -(\hbar/i)(\partial/\partial t)\Psi \quad [5-1]$$

that

$$\Psi(x, t) = \sum_n a_n(t_0) \Psi_n^0(x, t) \quad [5-15]$$

is a solution to the wave equation at *any* time  $t$  and reduces, of course, when  $t = t_0$ , to the initial function. The problem at hand differs from the one of Section 5.1 only in the fact that  $H$  is now time-dependent. The time dependence of  $H$  will cause differences in the method of analysis of the problem, but the basic principles employed will be the same. In particular, we will use, once

again, a series of orthogonal functions to synthesize both the initial wave function  $\Psi(x, t_0)$  and also  $\Psi(x, t)$ . For simplicity we continue to use a one-dimensional system, and in Figure 10.1a we draw, schematically, the wave function  $\Psi(x, t_0)$ , plotted against  $x$ . (We assume here that  $\Psi(x, t_0)$  is real, so

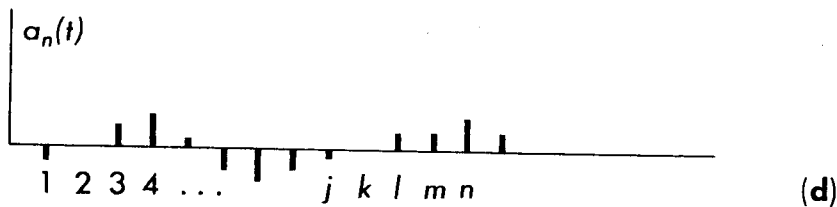
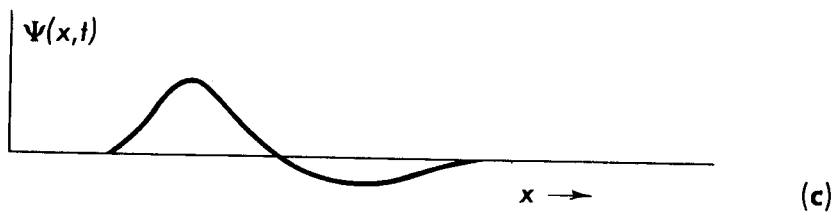
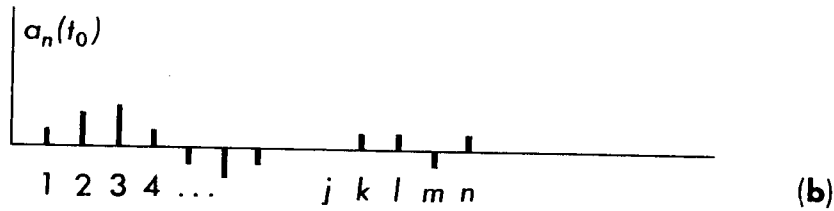
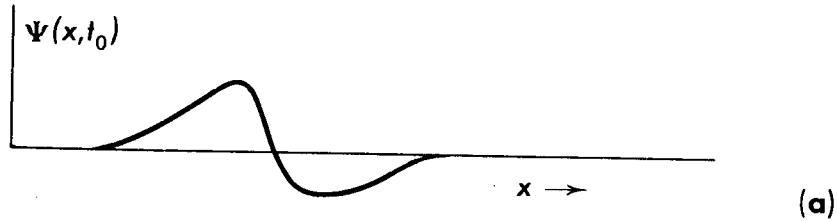


Fig. 10.1. The wave function of a system at two different times,  $t = t_0$  and  $t = t$ , and the amplitude spectra of the eigenfunctions needed to synthesize each of the two different functions of  $x$ .

that it can be plotted in two dimensions.) As we have seen in Section 5.1, as long as  $\Psi(x, t_0)$  is a bounded function, we have almost complete freedom in assuming any shape for it, such as that in Figure 10.1. We can synthesize any reasonable shape from the right combination of the complete set of orthogonal

eigenfunctions, whose domain in space covers the entire region where the function to be synthesized is non-zero. Thus, we set

$$\Psi(x, t_0) = \sum_n a_n(t_0) \Psi_n^0(x, t_0) \quad [10-6]$$

where the  $a_n(t_0)$ 's are given by

$$a_n(t_0) = \int \Psi_n^{0*}(x, t_0) \Psi(x, t_0) dx \quad [10-7]$$

and where, since  $\Psi(x, t_0)$  is normalized,

$$\sum_n a_n(t_0)^* a_n(t_0) = 1 \quad [10-8]$$

In schematic form, Figure 10.1b gives the "spectrum" of  $\Psi(x, t_0)$  in terms of the amplitudes of its components. Each amplitude is calculated by [10-7].

At a different time,  $t$ , the solution to [10-5] will, in general, have a different form, such as in Figure 10.1c. This too can be synthesized from the basic  $\Psi_n^0$ 's. Since it has a different shape it will, in general, have different amplitudes,  $a_n(t)$ , of the basic  $\Psi_n^0$ 's, as sketched in Figure 10.1d. We see that, by merely specifying the  $a_n$ 's at any time, we can describe the general solution  $\Psi(x, t)$ . The theory is concerned, therefore, with the calculation of the  $a_n(t)$ 's in the general expansion,

$$\Psi(x, t) = \sum_n a_n(t) \Psi_n^0(x, t) \quad [10-9]$$

The step we have just taken is very important. What we have done is this: we have given up any effort to handle  $\Psi(x, t)$  directly in terms of its spatial variable  $x$ . *From here on, we shall describe the wave function  $\Psi(x, t)$  in terms of the amplitudes of the components of the orthogonal series expansion which are needed to synthesize it.* Since  $H$  is time dependent the spatial form of  $\Psi$  is changing from moment to moment, and the amplitudes of the components that are needed to synthesize  $\Psi$  must *also* be changing from moment to moment. For this reason, we must regard the  $a_n$ 's functions of time, as is indicated in [10-9] and illustrated in Figure 10.1. The method of describing a function by means of the *time* variation of its components may seem indirect and perhaps unnecessarily complicated, but it is really simple compared to trying to work *directly* with the unknown function of space and time. A partial differential equation, even more than an ordinary differential equation, can look deceptively simple and yet be extremely difficult to solve. The method of the "variation of constants" which we use here is very powerful and general.

Substituting the series [10-9] for  $\Psi$  in the complete wave equation [10-5], we have,<sup>2</sup>

$$\sum_n a_n(t) H^0 \Psi_n^0 + \sum_n a_n(t) H' \Psi_n^0 = -\frac{\hbar}{i} \sum_n \left[ \frac{d}{dt} a_n(t) \right] \Psi_n^0 - \frac{\hbar}{i} \sum_n a_n(t) \frac{\partial \Psi_n^0}{\partial t} \quad [10-10]$$

<sup>2</sup> Note:  $H'(t)$  cannot involve the operator  $\partial/\partial t$ , as this operator is used in representing the *total* energy.



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$$\frac{d}{dt} a_m(t) = -\frac{i}{\hbar} \sum_{n=1}^{\infty} a_n(t) \int \Psi_m^{0*} H' \Psi_n^0 d\tau \quad [10-11]$$

where  $m = 1, 2, 3, 4, \dots$ .

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<sup>3</sup> If, in addition to  $H^0$ ,  $H$  contains a time-independent term  $H'$ (space) as well as a time-dependent term  $H'$ (space, time), one first applies time-independent perturbation theory to get the corrected wave functions, and then uses these wave functions in the time-dependent theory. This process is illustrated below in Sec. 10.5.

Since the number of basic eigenfunctions is, in general, infinite, the set of equations [10-12] is infinite in size and has an infinite number of unknowns,  $a_1, a_2, a_3, \dots$ . The equations are all first-order, ordinary differential equations, and we assume, or are given, the value of each of the  $a_j$ 's at  $t = t_0$ . Since all of the  $\Psi_j^0$ 's are known and  $H'$  is given, there is enough information to determine all of the  $a_j$ 's at any time  $t$ . Note that if  $H'(t) = 0$ , all of the  $a_j$ 's are constants.<sup>4</sup>

Up to this point there has been no approximation, and [10-12] is *fully equivalent to the original wave equation* [10-1] or [10-5].  $H^0$  does not appear explicitly in [10-12], but it is there nonetheless, due to the selection of the basic  $\Psi_j^0$ 's as the set of functions used to synthesize the true wave function. The choice of the particular set of  $\Psi_j^0$ 's as the basic functions used in the expansion [10-9] is often referred to as "the choice of representation."

So formidable a set of equations as [10-12] cannot, in general, be easily solved without some simplifying conditions and approximations. We shall assume that the effect of  $H'$  on the system is small compared to that of  $H^0$ , that is, we shall now regard  $H'$  as a perturbation. We then develop a new form of perturbation theory appropriate to the time-dependent nature of the perturbing term.

As in Chapter 7, we imagine that the intensity of the perturbation  $H'$  can be controlled by multiplying it by a parameter  $\lambda$ . We therefore set

$$H = H^0 + \lambda H' \quad [10-13]$$

and allow  $\lambda$  to vary from 0 to 1.<sup>5</sup> As this occurs, we expect each of the  $a$ 's to vary, but not necessarily in a purely linear manner, with  $\lambda$ . Thus, we assume that

$$a_m = a_m^0 + \lambda a_m' + \lambda^2 a_m'' + \dots \quad [10-14]$$

This is the same type of variation as that of  $\psi$  in Figure 7.2. We are interested in the *linear* part of this variation and, for a good first-order approximation, we require, as in Figure 7.2, that even when  $\lambda = 1$  the square term  $\lambda^2 a_m''$  is small compared to the linear term  $\lambda a_m'$ .

We substitute [10-14] for the  $a_m$ , and  $\lambda H'$  for  $H'$  into [10-12]. The  $k$ th equation of the set becomes

$$\begin{aligned} -\frac{\hbar}{i} \frac{d}{dt} (a_k^0 + \lambda a_k' + \lambda^2 a_k'') &= (a_k^0 + \lambda a_k' + \lambda^2 a_k'') \\ &+ \int \Psi_k^{0*} \lambda H' \Psi_1^0 d\tau + \dots \\ &+ (a_k^0 + \lambda a_k' + \lambda^2 a_k'') \\ &+ \int \Psi_k^{0*} \lambda H' \Psi_k^0 d\tau + \dots \quad [10-12a] \end{aligned}$$

<sup>4</sup> It is a common practice to denote the set of quantities,  $a_1, a_2, a_3, \dots$  etc., by the expression "the  $a_j$ 's." Equivalent expressions are "the  $a_k$ 's" or "the  $a_m$ 's". The letter subscript is merely a "running index" and is of no significance in itself. Similarly the expression, "the  $\Psi_j^0$ 's" is equivalent to "the  $\Psi_k^0$ 's", etc.

<sup>5</sup> As in Chapter 7,  $\lambda$  is a mathematical device whose purpose is to make easier the "sorting out" of the different orders of approximation.

We equate separately each power of  $\lambda$ . For zero order,

$$(d/dt) a_1^0 = 0; (d/dt) a_2^0 = 0; \cdots; (d/dt) a_k^0 = 0; \cdots \quad [10-15]$$

That is, if the time-dependent part of the Hamiltonian is zero, then each  $a_m$  (which determines the amplitude of the component  $\Psi_m^0$  of the complete wave function  $\Psi$ ), if determined at one time, is unchanged for any other time. This same result, for the time-independent Hamiltonian, was obtained in Chapter 7.

Equating all terms of  $\lambda^1$ , we have the set of equations

$$\begin{aligned} -\frac{\hbar}{i} \frac{da_1'}{dt} &= a_1^0 \int \Psi_1^{0*} H' \Psi_1^0 d\tau + a_2^0 \int \Psi_1^{0*} H' \Psi_2^0 d\tau + \cdots + a_k^0 \int \Psi_1^{0*} H' \Psi_k^0 d\tau + \cdots \\ -\frac{\hbar}{i} \frac{da_2'}{dt} &= a_1^0 \int \Psi_2^{0*} H' \Psi_1^0 d\tau + a_2^0 \int \Psi_2^{0*} H' \Psi_2^0 d\tau + \cdots + a_k^0 \int \Psi_2^{0*} H' \Psi_k^0 d\tau + \cdots \\ &\vdots \\ &\vdots \\ -\frac{\hbar}{i} \frac{da_k'}{dt} &= a_1^0 \int \Psi_k^{0*} H' \Psi_1^0 d\tau + a_2^0 \int \Psi_k^{0*} H' \Psi_2^0 d\tau + \cdots + a_k^0 \int \Psi_k^{0*} H' \Psi_k^0 d\tau + \cdots \\ &\vdots \\ &\vdots \\ &\vdots \end{aligned} \quad [10-16]$$

This set of *approximate* equations differs from the exact set [10-12] by the presence, on the right, of the constant zero-order coefficients  $a_m^0$  and by the presence, on the left, of the *corrections*,  $a_m'$ , to the zero-order coefficients  $a_m^0$ . The  $a_m^0$ 's are merely the initial conditions. They measure the intensity of vibration of all of the modes of the unperturbed system that are needed to form the actual wave function at  $t = t_0$ . The equations [10-16] give the growth or decline of the amplitude of vibration of each of the natural modes of the system. Since  $H'$  is assumed to be small, the corrections to the amplitudes,  $a_m'$ , are also small. Thus, although all the vibrations can either grow or decrease as time proceeds, the changes from their initial values will not be very large.

One speaks of a typical mode of vibration, or "proper" vibration (such as that represented by  $\Psi_1^0$ , as being "connected," via  $H'$ , to each of the other modes. The exact equation [10-12] shows that, as time proceeds, the state  $\Psi_k^0$  "feeds amplitude" into the state  $\Psi_1^0$  at a rate given by  $a_k \int \Psi_1^{0*} H' \Psi_k^0 d\tau$ , and that the reverse process goes on at a rate given by  $a_1 \int \Psi_k^{0*} H' \Psi_1^0 d\tau$ . This is a completely continuous process. *The perturbation  $H'$  acts constantly to reshuffle the degree of excitation of the modes.* If it is suddenly terminated the system remains, thereafter, with exactly constant amplitudes for each proper

vibration. In the first-order equations [10-16], however, we permit the re-shuffling process to proceed only a relatively small amount from the initial set of amplitudes. (See the discussion following [10-17], below.)

## 10.2. Constant perturbation

The set of first-order differential equations [10-16] takes on a particularly simple form for the case where  $a_k^0 = 1$  and all the other  $a_m^0$ 's are zero—that is, where the initial state of the system is the pure state  $\Psi_k^0$ . Only *one* column of terms, the  $k$ th column, survives. Furthermore, we will assume for the first example that  $H'$  is independent of time.<sup>6</sup> However,  $H'$  must depend upon space, since otherwise all of the off-diagonal matrix elements would be zero. Thus, we let  $H' = f(x)$ . We ask what the amplitudes will be at some later time,  $t_1$ . As before, we symbolize  $\int \psi_m^{0*} H' \psi_k^0 d\tau$  by  $H'_{mk}$ , the “matrix element” of the operator  $H'$  with respect to the two eigenfunctions  $\psi_m^0$  and  $\psi_k^0$ . The integrand involves space, and perhaps the momentum operators, but not time.

For these conditions, since only the  $k$ th column in [10-16] survives, and since  $\Psi_m^0 = \psi_m^0 e^{-i\frac{W_m^0}{\hbar}t}$ , the set of equations becomes

$$\begin{aligned} -(\hbar/i)(d/dt) a'_1 &= H'_{1k} e^{i\omega_{1k}t} \\ -(\hbar/i)(d/dt) a'_2 &= H'_{2k} e^{i\omega_{2k}t} \\ a'_k &= 0 \\ -(\hbar/i)(d/dt) a'_m &= H'_{mk} e^{i\omega_{mk}t} \end{aligned} \quad [10-17]$$

where  $\omega_{mk} = (W_m^0 - W_k^0)/\hbar$ ;  $H'_{mk} = \int \psi_m^{0*} H' \psi_k^0 d\tau = \int \psi_m^{0*} f(x) \psi_k^0 d\tau$ .  $a'_k$  must be zero since, in first-order, our basic assumption is that  $a_k$  not only equals unity at  $t = 0$ , but also does not deviate appreciably from unity at later times.

Each of the above equations has the solution, when each  $a'_m = 0$  at  $t = 0$ ,

$$a'_m(t_1) = -\frac{H'_{mk} e^{i\omega_{mk}t_1} - 1}{\hbar \omega_{mk}} \quad \begin{array}{l} m = 1, 2, 3, \dots \\ m \neq k \end{array} \quad [10-18]$$

Thus, after time  $t_1$  has elapsed, the amplitudes of all of the states (which were originally zero) are now, in general, not zero. We assume that  $a_k$  still has the value of unity at  $t = t_1$ . The  $a'_m$  (although necessarily small compared to one) are now the actual amplitudes of the states. (Normalization of the new wave function is preserved, to first-order, by the assumption:  $|a_k^0(t_1)| = 1$ .)

<sup>6</sup>  $H'$  is time-dependent in the sense that it may be regarded as being “turned on” at  $t = 0$ , and continuing, at constant value, as long as necessary. It is therefore a step function in time.

In the calculation of the expectation values, the term  $(a'_m)^*(a'_m)$  will appear. It measures the probability of finding the system in the state with energy  $W_m^0$  or, alternatively, it measures the probability of occurrence of the value  $W_m^0$  in computing the average energy of the system (see Section 5.2). From [10-18] we calculate<sup>7</sup>

$$(a'_m)^*(a'_m) = \frac{(H'_{mk})^*(H'_{mk}) \sin^2(\frac{1}{2} \omega_{mk} t_1)}{\hbar^2 (\omega_{mk}/2)^2}, \quad m \neq k \quad [10-19]$$

This equation tells how the intensities of the proper vibrations change with time—for the special case where only one level, the  $k$ th, was initially excited and where the spatial perturbation  $H'$  is constant from  $t = 0$  to  $t = t_1$ . In Figure 10.2 a sequence of diagrams shows how the intensity of each of the proper vibrations would appear if the system were examined at  $t = t_1$ ,  $t = 2t_1$  and  $t = 3t_1$ . In Figure 10.2a we show, schematically, a sequence of equally spaced system energy levels. (In most systems, the energy levels are not equally spaced but, over a small range of energy, equal spacing often happens to be a good approximation. In any case, the equal spacing has no basic effect on the principles involved in the discussion.) At  $t = 0$ , by hypothesis, only one level, the  $k$ th, is occupied—so that  $a_k^* a_k = 1$ . During the subsequent intervals, we know that  $a_k^* a_k$  must actually decrease slightly, but in the first-order calculation  $H'$  has so small an influence that the fractional change in  $a_k^* a_k$  is *assumed to be zero*.

In Figure 10.2b we see that, after the perturbation has been effective for  $t_1$  seconds, a broad range of energy levels<sup>8</sup> have developed a finite vibration amplitude, although the levels with energy near  $W_k^0$  are the most strongly affected and there are definite nulls at those energy levels for which

$$(W_m^0 - W_k^0) t_1 / \hbar = 2\pi \quad [10-20]$$

The intensity curve is controlled by the factor

$$\frac{\sin^2(\omega_{mk}/2) t}{(\omega_{mk}/2)^2} \quad [10-21a]$$

which is plotted in Figure 10.2. The peak of this function has the magnitude  $t^2$ , since

$$\lim_{y \rightarrow 0} \left( \frac{\sin^2 yt}{y^2} \right) = t^2 \quad [10-21b]$$

At a later time  $2t_1$ , as in Figure 10.2c, the curve giving the distribution of intensity of excitation of vibration is, because of [10-20], twice as narrow, and

<sup>7</sup> Using the identities  $(1 - e^{ix})^*(1 - e^{ix}) = 2 - e^{ix} - e^{-ix}$ ,  $\sin x = (1/2)(e^{ix} - e^{-ix})$ , and  $\sin^2 x = (1/4)(2 - e^{2ix} - e^{-2ix})$ , we have  $(1 - e^{ix})^*(1 - e^{ix}) = 4 \sin^2 \frac{x}{2}$ .

<sup>8</sup> The continuous curves of Figure 10.2 will give the actual degree of excitation of the levels only if  $H'_{mk}$  is the same for each level,  $W_m^0$ .

because of [10-2|b] four times as high. At a later time  $3t_1$ , the curve is three times narrower and nine times higher than the same curve at  $t = t_1$ . The area under the curve—which measures the total excitation in levels other than the  $k$ th—is thus increasing in proportion to  $t$ . The excitation “piles up” in those

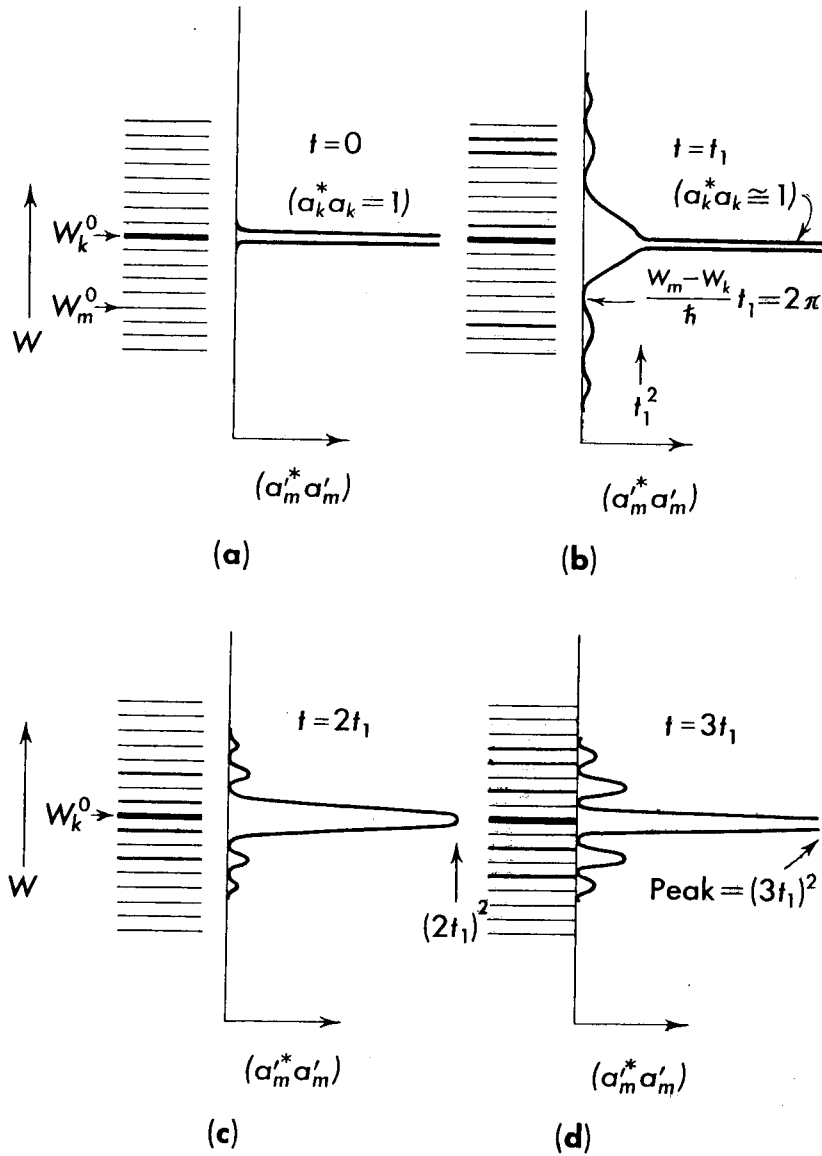


Fig. 10.2. The time variation of the excitation of the proper vibrations (eigenfunctions) caused by the constant perturbation, starting at  $t = 0$ . The density of the horizontal lines indicates the degree of excitation of the level or state.

levels nearest  $W_k^0$ , the effect being more pronounced the longer the perturbation is allowed to continue.

The detailed picture of the excitation process is complicated, except for those levels very near to  $W_k^0$ , which show a steady growth of excitation with  $t^2$ .

At greater distances from  $W_k^0$  the degree of excitation of the levels increases, decreases, increases, etc., with time, in a relatively complicated manner. Those levels far from  $W_k^0$  finally end up with relatively small excitation compared to those very near  $W_k^0$ , which grow steadily.

Unless the perturbation “connects” the  $m$ th state to the  $k$ th—that is, unless  $H'_{mk} \neq 0$ —there will, of course, be no excitation of the  $m$ th level at *any* time. This selectivity of coupling is dependent upon both  $H'$  itself and on the two eigenfunctions that are involved.

$H'_{mk}$  is the source of the “selection rules” of atomic and nuclear spectra. If the perturbation  $H'$  is strong enough, or if it is allowed to proceed long enough, then the amplitude of vibration of the levels away from  $W_k^0$  will become so large that the first-order theory is no longer accurate. Excitation will now begin to “feed” from one newly excited level to another, and also from the newly excited levels back to the original level, at  $W_k^0$ . These secondary effects will always be relatively small as long as  $a_k^* a_k$  is close to unity, since the “flow” of excitation will then be predominantly *from* this one level.

The progressive narrowing of the region of excitation with time as shown in Figure 10.2 provides another example of the uncertainty principle, here relating the accuracy between the measurements of the two “canonically conjugate” variables, energy  $W$ , and time  $t$ . In Figure 10.2b (and equation [10-20]) the location of the null in the band of excited energy levels is located at  $W_m$ , a distance on the energy scale of  $|W_m - W_k| \equiv \Delta W$  from the center of the excitation peak. Thus, the full width at half intensity of the peak is about  $\Delta W$ . Let  $\Delta t \equiv t_1$ , the duration of the excitation, then by [10-20],

$$\Delta W \Delta t = h \quad [10-21c]$$

This equation may be interpreted as follows: Many identical systems are all initially in the state  $k$ . At  $t = 0$  the perturbation  $H'$  is suddenly applied, and then removed  $\Delta t$  seconds later. All the systems are then examined to determine their energy. Most of them will still have the original energy  $W_k$ , but there will be a number with different energies, spread about the center value, with a half-width of about  $\Delta W = 2\pi\hbar/\Delta t$ . Of those that “made the transition sometime within the interval,  $\Delta t$ ,” there is a spread,  $\Delta W$ , in the resulting characteristic energy. This spread is independent of any system parameters, and depends only upon  $\hbar$  and some numerical constant, here unity. If the time of application of the perturbation is doubled, the uncertainty in the energy values of the systems making the transition is halved, etc. Thus, as the uncertainty of the “time of transition” increases (that is, the perturbation is *on* for a longer period of time), the uncertainty in the energy of the affected systems progressively decreases.

### 10.3. Harmonic perturbation

The set of first-order equations [10-17] takes a particularly simple form when the perturbation is a pure sine wave of angular frequency  $\omega_0$ , and which

is constant in amplitude from  $t = 0$  to  $t = t_1$ .

$$H' = A(x) \sin \omega_0 t \text{ for } 0 \leq t \leq t_1 \quad [10-22]$$

$A(x) = \text{constant}$  with respect to time.

The  $m^{\text{th}}$  equation of set [10-16] becomes

$$-\frac{\hbar}{i} \frac{d}{dt} a'_m = H'_{mk} e^{i\omega_{mk}t} \underbrace{\left(-\frac{i}{2}\right) (e^{i\omega_0 t} - e^{-i\omega_0 t})}_{= \sin \omega_0 t} \quad [10-23]$$

$$m = 1, 2, 3, \dots, \quad m \neq k$$

where

$$H'_{mk} = \int \psi_m^{0*} A(x) \psi_k^0 d\tau \quad [10-24]$$

If  $a'_m = 0$  when  $t = 0$ , the integral of [10-23] from 0 to  $t_1$  is

$$-\frac{\hbar}{i} a'_m(t_1) = -\frac{H'_{mk}}{2} \left[ \frac{e^{i(\omega_{mk} + \omega_0)t_1} - 1}{\omega_{mk} + \omega_0} - \frac{e^{i(\omega_{mk} - \omega_0)t_1} - 1}{\omega_{mk} - \omega_0} \right] \quad [10-25]$$

It is clear from this equation that the magnitude of  $a'_m(t_1)$  is going to be unusually large in two regions—at  $\omega_{mk} = \omega_0$  and at  $\omega_{mk} = -\omega_0$ . Thus the states that will be most affected by the perturbation of frequency  $\omega_0$  will have a characteristic energy lying either in the region  $W_m^0 = W_k^0 + \hbar\omega_0$  or in the region  $W_m^0 = W_k^0 - \hbar\omega_0$ . The states between (and beyond) these two regions of excitation will be excited, but not very strongly.

To determine the magnitude of excitation of the  $m$ th state at time  $t_1$ , we must calculate  $a'_m(t_1)^* a'_m(t_1)$ . If we change the sign of  $i$  wherever it appears in [10-25] and multiply the result into [10-25], we obtain four terms. There are two “resonance” terms, one with  $(\omega_{mk} + \omega_0)^2$  in the denominator, and one with  $(\omega_{mk} - \omega_0)^2$  in the denominator. There are two “cross” terms, each with  $(\omega_{mk} + \omega_0)(\omega_{mk} - \omega_0)$  in the denominator. In Problem 10.2, we see that near either of the resonance regions the cross terms are very small, and also the *other* resonance term is small. Thus, near  $W_m^0 = W_k^0 + \hbar\omega_0$ ,

$$[a'_m(t_1)]^* [a'_m(t_1)] \cong \frac{H'_{mk}{}^* H'_{mk}}{(2\hbar)^2} \frac{\sin^2 [(\omega_{mk} - \omega_0) t_1/2]}{[(\omega_{mk} - \omega_0)/2]^2} \quad [10-26]$$

and, near  $W_m^0 = W_k^0 - \hbar\omega_0$ ,

$$[a'_m(t_1)]^* [a'_m(t_1)] \cong \frac{H'_{mk}{}^* H'_{mk}}{(2\hbar)^2} \frac{\sin^2 [(\omega_{mk} + \omega_0) t_1/2]}{[(\omega_{mk} + \omega_0)/2]^2} \quad [10-27]$$

These two resonance curves are plotted in Figure 10.3. In Figure 10.3a we see the initial condition. Only one state, the  $k$ th, is occupied. In Figure 10.3b the states near the two resonance regions are beginning to increase their amplitudes of vibration. At still later times, Figures 10.3c and 10.3d, the



resonance regions are getting narrower (as  $1/t$ ) and more intense at their maxima (as  $t^2$ ). Thus the total excitation of each resonance region grows in proportion to  $t$ , the duration of the perturbation. (In these figures we assume, for con-

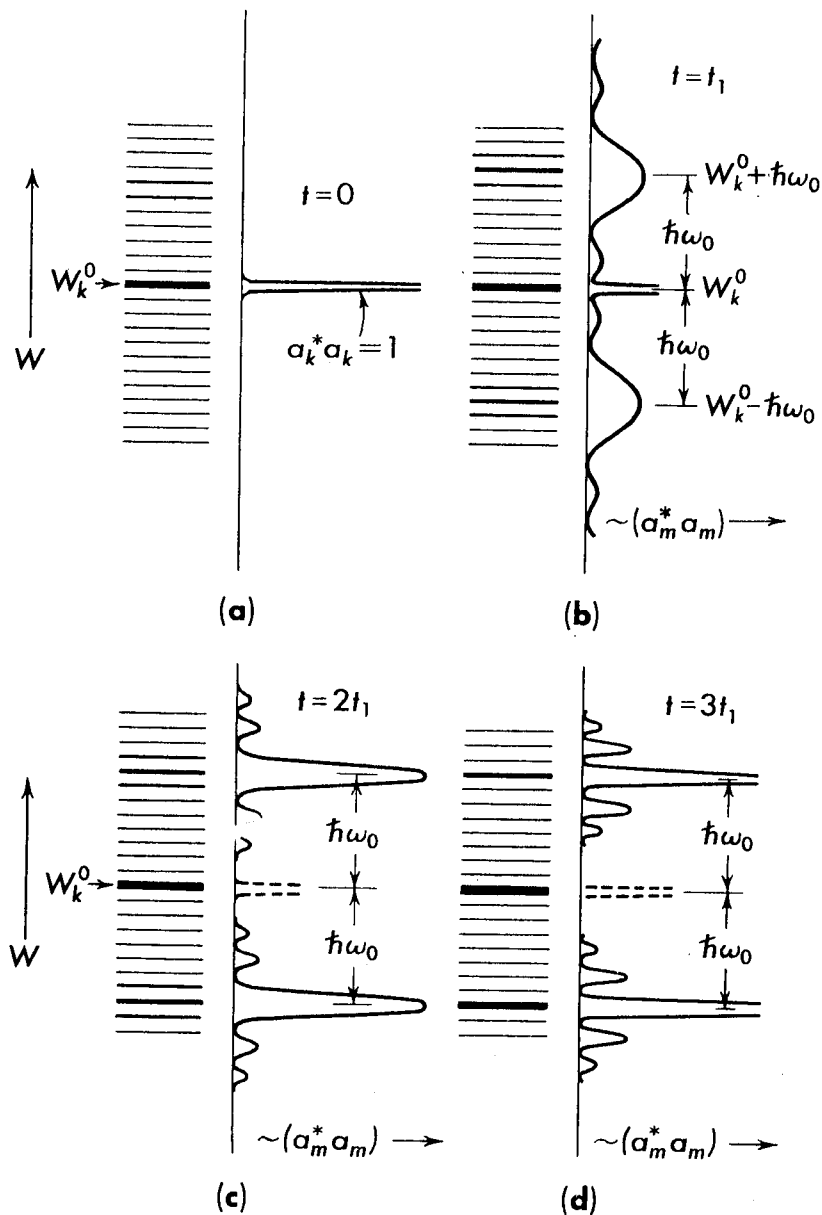


Fig. 10.3. The time variation of the excitation of the proper vibrations caused by a harmonic perturbation, starting at  $t = 0$ . The density of the horizontal lines indicates qualitatively the degree of excitation of the level or state.

venience, that the matrix elements connecting  $k$  to all other states are the same. Actually, of course, the matrix elements can, and do, exert a strong selective effect over and above the basic resonance effects. The matrix elements

$\int \psi_m^{0*} H' \psi_k^0 d\tau$  are the source of the selection rules of atomic and nuclear transitions for harmonic perturbations.)

Again, after  $H'$  has been on for  $\Delta t$  seconds, the half-width of each peak is  $\Delta W$ , where, by [10-21c],  $\Delta W \Delta t = h$ .

This case is very similar to that in which an atom is excited by the application of external radiation. Suppose an atom is in its ground state, and an electromagnetic wave of frequency  $\omega_0$  is applied, with some definite direction of propagation and polarization. There is no state at the lower of the two resonance regions, but if there is a state whose characteristic energy lies  $\hbar\omega_0$  ergs above the ground state, and if the matrix element of the electromagnetic field "connects" the two states—that is,  $H'_{jk}$  is not zero—then this state will experience a steady build-up in amplitude.

If one shines monochromatic light on a group of atoms for a definite (short) time, many atoms will be found in whatever excited states occur near the resonance level. (Generally, they re-radiate this energy as "resonance radiation.")

An almost perfect macroscopic model of the process of resonance excitation by a harmonic perturbation starting at  $t = 0$ , is provided by a bank of reed filters. Figure 10.4 shows photographs, taken at intervals of 1/16th second, of a bank of filters (each 2 cps wide) centered at 180 cps. The input signal is coupled uniformly to each of the filters (each state has the same "matrix element"). At  $t = 0$ , the first photograph (upper left) shows the small square "flags" on the ends of the unexcited reeds at  $t = 0$  when the constant-amplitude 180-cps signal is initiated. At  $t = 1/16$  second, very little change has occurred, but by  $t = 2/16$  second, a broad band of excitation, which is centered at 180 cps but has nulls at 168 and at 192 cps, is observed. This picture corresponds to either of the two resonance regions sketched in Figure 10.3b. As time passes, the reeds near 180 cps continue to increase in amplitude (limited, unfortunately, by mechanical constraints), but the off-resonance reeds fluctuate in their state of excitation. For example, at  $t = 5/16$  second (lower left) the reeds at 184 cps and at 176 cps are seen to have no vibration, whereas at earlier and later times they had observable excitation. At  $t = 5/16$  second, moreover, a small but definite peak of intensity is observed at 186 cps, and also at 174 cps. This picture corresponds to Figure 10.3c. Finally, in the last picture ( $t = 11/16$  second) only the one reed at 180 cps has appreciable excitation although, due to mechanical constraints, the excitation is much smaller than would be expected in a perfect system. In Figure 10.4 the steady narrowing of the region of excitation, with time, is very apparent.

Due to friction, the reeds have a natural decay time constant of about 1/2 second, so that they lose energy in proportion to their state of vibration. This too is analogous to the behavior of atoms which, while in the process of absorbing energy (from a light wave, for example) may also at the same time be re-radiating energy. If resonance radiation partially excites a hydrogen atom

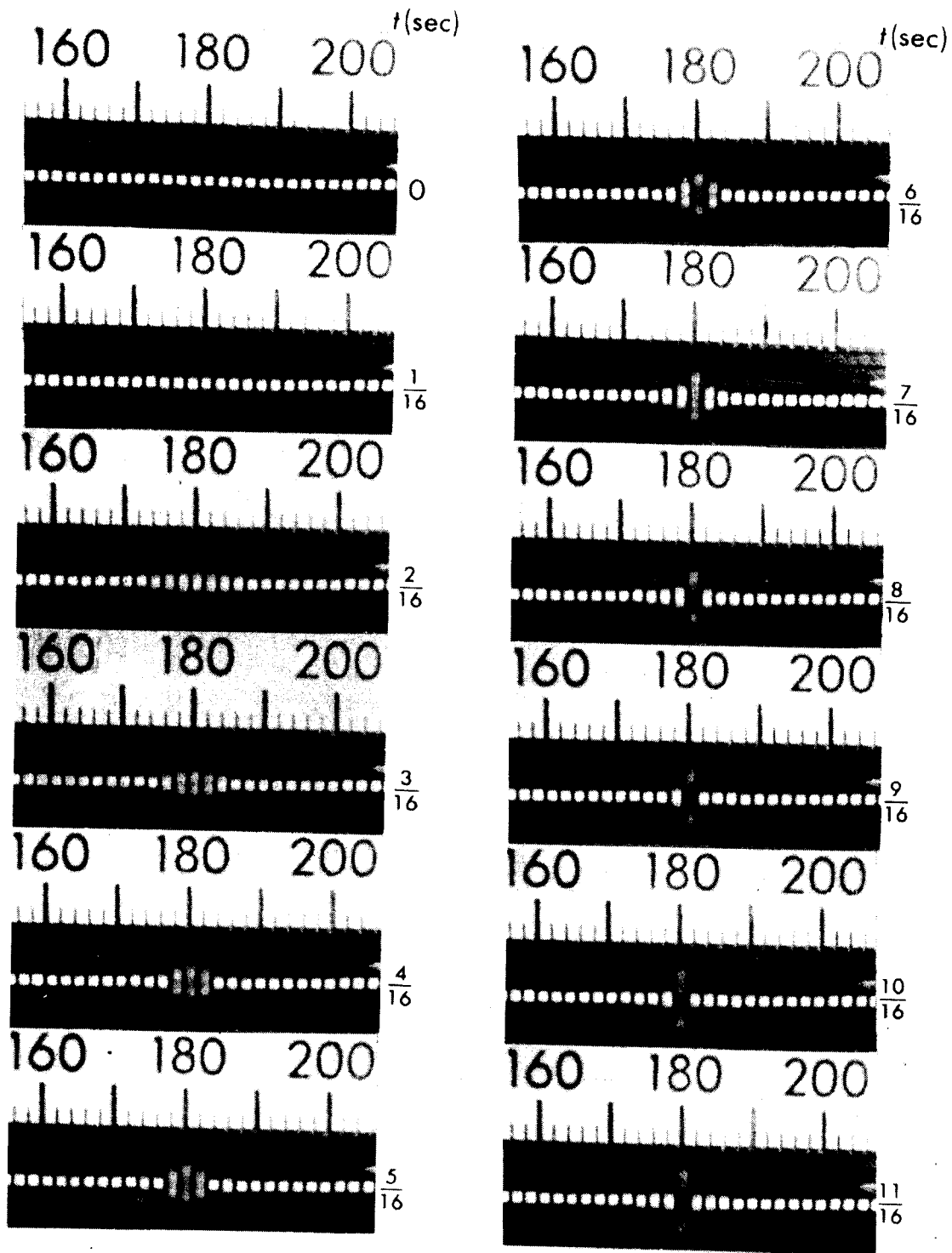


Fig. 10.4. Sequential photographs of a bank of reed filters. At  $t = 0$ , a constant-amplitude 180 cps signal is coupled equally to each of the reeds.

into its first excited state and then the perturbation is stopped, the excitation of the atom is observed to decay with a time constant of the order of  $10^{-8}$  second. However, when atoms radiate light waves whose wavelength is thousands of times their diameter (as is the case for hydrogen) they lose only a small fraction of their energy in any one cycle. They require a total of about  $10^7$  cycles to lose an appreciable fraction of their energy (time constant  $\simeq 10^{-8}$  second, and period of vibration  $\simeq 10^{-15}$  second). A quantitative treatment of radiation from atomic-sized systems will not be attempted here since, for adequate analysis, one needs relativistic quantum theory for both particles and fields. We do consider, however, in the next section, the manner in which an externally applied, time-varying electric field can both excite and de-excite atoms.

The model with the vibrating reeds can help interpret the constant, or “step-function” perturbation of Section 10.2 and Figure 10.2. The equipment could be prepared so that just one reed is excited, for example, the one at 180 cps. At  $t = 0$  very weak springs, all identical, are connected from the excited reed to each of the other reeds in the array. (This corresponds to the uniform-magnitude matrix elements which “connect” the  $k$ th state to each of the other states.) As time progresses, some excitation will be transferred to all the other reeds, at the expense, of course, of a decrease in amplitude of vibration of the original reed at 180 cps. Shortly after the connections occur at  $t = 0$ , there will be a broad region of excitation in the neighbourhood of 180 cps, but as time progresses the region of excitation will narrow, as in Figure 10.2. The two reeds, on either side of 180 will eventually develop the largest amplitudes, since they are most closely in resonance with the 180-cps driving signal coming through the very weak springs, but even they will eventually reach a maximum value and then decrease to zero, increase to a maximum once again, decrease to zero, etc., as *all* off-resonance reeds must do. During this whole process we assume that the amplitude of the reed at 180 cps has not changed appreciably, and that there are no decay-effects associated with energy loss.

Thus, “constant perturbation” merely means that the  $k$ th state is suddenly “connected” to one or more of the other states of the system with a constant, that is, a time-independent, coupling, with the result that a part of the vibration of the  $k$ th state is transferred to the other states. Since none of the other states is assumed to be *exactly* in resonance with the  $k$ th state, their amplitudes of vibration do not continuously increase, but each fluctuates periodically as required by [10–19].

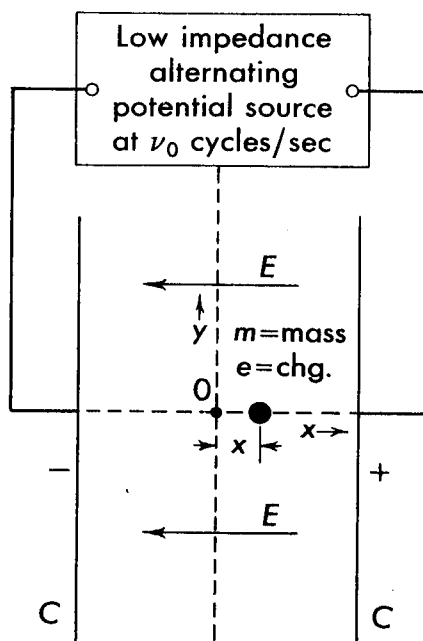
#### 10.4. The harmonic oscillator in a periodic electric field

As a simple example of how a time-varying electric field can cause a system to make a “transition to a higher energy state” or, alternatively, “to increase the amplitude,  $a_m$ , of the matter-wave vibrations characteristic of a higher energy state,” we consider the system in Figure 10.5a. A sinusoidally varying potential source of frequency  $\omega_0$  is connected to the two parallel plate con-

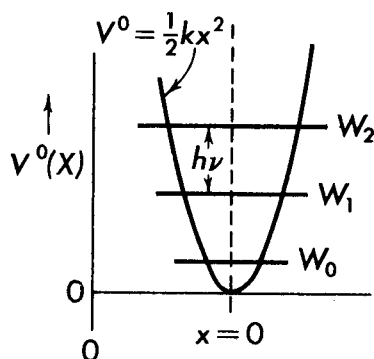
ductors  $C$  causing, therefore, a time-varying electric field<sup>9</sup> along the  $x$ -axis,

$$E_x(t) = E_x^0 \sin \omega_0 t; \quad \omega_0 = 2\pi\nu_0 \quad [10-28]$$

At any time  $t$  the electric field is everywhere constant in the region where the



(a) Harmonic oscillator in a time-varying electric field



(b) Energy levels of oscillator (zero-order)

mass  $m$ , of charge  $e$ , is executing harmonic motion along the  $x$ -axis, about  $0$ , as shown in the figure. (That is, over the region where  $\Psi^*\Psi$  has any appreciable

<sup>9</sup> The operators belonging to the electromagnetic radiation field are discussed in advanced textbooks on quantum mechanics. See, for example, H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry* (1944, John Wiley & Sons, Inc., New York): p. 108. For our purposes here the essential feature of an electromagnetic wave is its time-dependence—it produces a *periodic* variation in the total energy of any charged particle, or magnetic moment (current loop), present in its fields (see Section 10.5).

magnitude,  $E_x$  is independent of  $x$ .) Without  $E_x$ , the perturbing field, the harmonic oscillator is governed by the constant (in time) potential,

$$V^0 = (1/2) kx^2$$

where  $k$  is the “spring constant” of the oscillator. We assume that this constant potential is derived (indirectly) from an electric charge, fixed at 0, of opposite sign to  $e$ , the vibrating charge. Thus the harmonic oscillator is electrically neutral. In the potential  $V^0$ , the oscillator has the zero-order energy levels shown in Figure 10.5b since for

$$H^0 = \frac{p^2}{2m} + \frac{1}{2} kx^2,$$

the energy levels are equally spaced (Section 3.2).

In a spatially uniform electric field a charge  $e$  has at any time,  $t$ , the potential energy

$$V(t) = \underbrace{e E_x^0(t)}_{\text{force}} \underbrace{(x - x_0)}_{\text{distance}} \quad [10-29]$$

where  $V$  is defined to be zero at  $x = x_0$ . Since the zero value for the potential energy can be arbitrarily chosen, we shall define the perturbing potential energy to be zero when  $x = 0$ , that is, we chose  $x_0 = 0$ . (In Problem 10.5 we see that any constant value for  $x_0$  is equally satisfactory.) Thus, the perturbation  $H'$  is given by<sup>10</sup>

$$H' = exE_x^0 \sin \omega_0 t \quad [10-30]$$

This new  $H'$  has the same time dependence as the perturbation [10-22] which we discussed in the previous section. Now, however, *there is present a new factor,  $x$ , which causes the perturbation to have a particular spatial dependence*, even though  $E_x$  is itself uniform throughout the spatial extent of the oscillator. (The same situation occurs when the wavelength of a light wave is large compared to the physical dimensions of the atom which it is perturbing, so that the electric field in the wave is, at any instant, substantially constant throughout the atom.) The term  $ex$  is the classical dipole moment of a charge  $e$ , displaced a distance  $x$  from an equal charge of opposite sign. For this reason, the oscillator transitions caused by the perturbation [10-30] are called “electric dipole transitions.”

If we use the perturbation [10-30], we obtain the same results as given in [10-27] through [10-31], except that now the matrix element [10-24] has the particular form

$$H'_{mk} = e E_x^0 \int_{-\infty}^{+\infty} \psi_m^{0*} x \psi_k^0 dx \quad [10-31]$$

<sup>10</sup>  $H'$  is in ergs if  $x$  is in cm,  $e$  is in esu, and  $E_x^0 = E_x^0$  (volts/cm)/300.  $H'$  is in joules if  $x$  is in meters,  $e$  is in coulombs, and  $E_x^0$  is in volts/m or nt/coulomb.

The time-dependent part of the calculation is unchanged. If  $\omega_{mk} = \pm \omega_0$ , there will be a continuous growth proportional to  $t^2$  (see [10-21b]), in the magnitude of the amplitude  $a_m$  of the  $m$ th state. (We assume, again, that the system is initially in the pure state,  $\psi_k^0$ .) As before, if  $\omega_{mk} \neq \omega_0$  the “final state”  $\psi_m^0$  will, at most, develop a small, fluctuating amplitude. It is “off-resonance.”

The growth of the intensity of the  $m$ th state, measured by  $(a'_m)^*$  ( $a'_m$ ) [10-26] and [10-27], is, as before, dependent upon  $H'_{mk}{}^* H'_{mk}$ , the square of the matrix element. If the perturbation  $H'$  is given by [10-31] we find that certain transitions are allowed and certain ones are forbidden. As an example of these “section rules for dipole transitions” we will calculate two simple cases for the harmonic oscillator. Let the oscillator be initially in its zero-point state, that is,  $k$  (the quantum number) = 0. The zero-order wave function  $\psi_0^0$  belonging to this state is plotted in Figure 10.6, and below it is plotted  $x = x$ , and also  $x \psi_0^0$ . We wish to calculate

$$H'_{10} = e E_x^0 \int_{-\infty}^{+\infty} \psi_1^0{}^* x \psi_0^0 dx$$

With the aid of the graph of  $\psi_1^0$ , also given in Figure 10.6, we can see at once that the integral  $\int \psi_1^0 x \psi_0^0 dx$  is not zero, since the integrand is everywhere positive. In contrast to this,

$$H'_{20} = e E_x^0 \int_{-\infty}^{+\infty} \psi_2^0{}^* x \psi_0^0 dx = 0$$

since the contribution to the integral from the positive- $x$  region exactly cancels the contribution from the negative- $x$  region. Thus, if  $n$  is the quantum number of the initial state of the harmonic oscillator, we find (for these two special cases) that  $\Delta n = 1$  is allowed, and  $\Delta n = 2$  is forbidden. That is, if the system of Figure 10.5 is originally in its lowest states,  $n = 0$ , the oscillating electric field can cause it to “jump” to the state  $n = 1$  or, alternatively, the intensity of the vibrations characteristic of  $n = 1$  will increase but will *not* cause the system to “jump” to the state for which  $n = 2$  (or, the intensity of the vibrations characteristic of  $n = 2$  will *not* increase).

The two examples we have just been discussing are included in the general rule for electric dipole transitions for the harmonic oscillator,  $\Delta n = \pm 1$ . This general rule can be derived from the properties of the Hermite functions. Specifically, it can be shown<sup>11</sup> that

$$\begin{aligned} H'_{k-1,k} &= e E_x^0 \sqrt{k/2a} \text{ (downward transitions)} \\ H'_{k+1,k} &= e E_x^0 \sqrt{(k+1)/2a} \text{ (upward transitions)} \\ H'_{m,k} &= 0 \text{ for all other values of } m. \end{aligned} \quad [10-32]$$

<sup>11</sup> See, for example, L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (1935, McGraw-Hill Book Co., Inc., New York): pp. 77 and 306.

$a = 2\pi m\nu/\hbar$ . (For  $k = 0$ , of course, there can be no downward transition.) The initial state (by convention, the right-hand subscript on a matrix element symbol) is  $k$ .

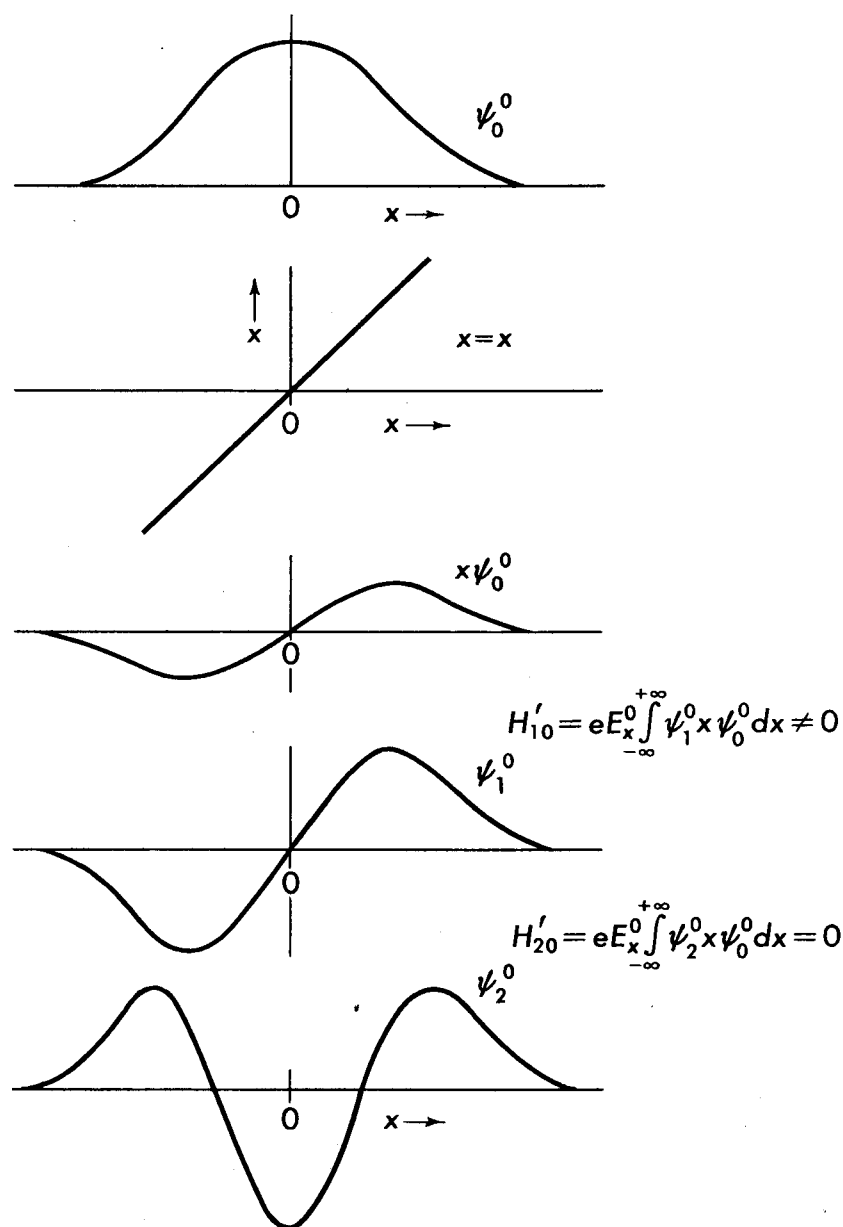


Fig. 10.6. Electric dipole transitions of the harmonic oscillator.

Suppose that the oscillator in Figure 10.5 is initially in an excited state,  $k$ . The periodic electric field now causes the amplitudes of *both* the  $k + 1$  and the  $k - 1$  states to increase (if  $\nu = \nu_0$ ). Since, by [10-32], the higher energy state  $k + 1$  will increase in amplitude more rapidly than the lower state, the expecta-



tion value of the energy of the oscillator will increase with time. (See Problem 10.6, where this effect is calculated for a specific case.)

We are using first-order perturbation theory and must, therefore, always require that the amplitude of initial state  $a_k$  remains (essentially) at unity. For a system with only two states involved in the resonance, it is possible to solve the time-dependent wave equation exactly<sup>12</sup> and, given the amplitudes of the two states at any initial time, find (without restriction) the new amplitudes at any later (or earlier) time. It is found that if one state alone is initially excited, the other state gradually increases in amplitude until it finally has all of the excitation—the system is now certain to be found in the second state. If the perturbation is continued, the second-state vibrations die down and the original-state vibrations build up. The shift of excitation from one state to the other is sinusoidal. (The  $t^2$ -dependence of the build-up of the intensity of a resonant state [10-21a] is just the beginning of this process, starting from the case where one state has all of the excitation.) Transitions of this type are encountered in “nuclear resonance,” where an external harmonic perturbation causes the relative population of two spin states to shift continuously.

The calculation of the  $x$ -component of the dipole moment matrix element [10-31] is intimately related to the already familiar calculation of the expectation value of  $ex$ , using Postulate V, for the case where the system is in a superposition of two pure states,  $\Psi_m$  and  $\Psi_k$ . As a simple example, let

$$\Psi = a_m \psi_m e^{-i\omega_m t} + a_k \psi_k e^{-i\omega_k t}, \quad a_m^2 + a_k^2 = 1, \quad \omega_m = \frac{W_m}{\hbar}, \quad \omega_k = \frac{W_k}{\hbar} \quad [10-33]$$

where the  $a$ 's and the  $\psi$ 's are both real. Using this superposition for the wave function, we find by Postulate V (see Problem 10.8)

$$\overline{ex} = \text{constant} \cdot H'_{mk} \cdot 2 \cos(\omega_k - \omega_m)t + (\text{const.})[\bar{x}_m + \bar{x}_k] \quad [10-34]$$

where  $H'_{mk}$  is exactly the matrix element of [10-31]. In other words, a system in certain mixed states but *without* an external perturbation may possess, quite naturally, a time-varying expectation value of its dipole moment. Classically, this means that electric charge is being accelerated, so that radiation will occur at the frequency  $(\omega_k - \omega_m)$ . We may expect, therefore, for those mixed states which possess a time-varying electric dipole moment,<sup>13</sup> that energy should be radiated away, and the system should have a continually increasing probability of being found in the state of lower energy. We will not discuss “spontaneous radiation” any further here. It can be adequately treated only with more advanced theory. We see once again, however, that  $H'_{mk}$  is intimately associated with transitions from one state to another.

<sup>12</sup> L. D. Landau and E. M. Lifschitz (tr. by J. B. Sykes and J. S. Bell), *Quantum Mechanics, Non-Relativistic Theory* (1958, Pergamon Press & Addison Wesley Press, Reading, Mass.): p. 143.

<sup>13</sup> For a *pure* state,  $\overline{ex} = \text{constant}$  in time.

Returning to our oscillator problem, we note that we have considered only the effect of the electric field on the oscillator. From Maxwell's equations, in a region of space where  $\mathbf{E}$  is uniform spatially but varying in time, we know that there must be an associated magnetic field,  $\mathbf{B}$ ,  $B = E/c$ , perpendicular to  $\mathbf{E}$ , and also varying in time with the same frequency.

Let us consider a system (such as a hydrogen atom in an  $l = 1$  state) that has a magnetic moment  $\mu$ . (See the discussion in Problem 6.8.) In contrast to the harmonic oscillator, this system has motion in at least two dimensions, and has a magnetic moment. A current loop, or magnet, has, in a magnetic field, an orientation-dependent energy,<sup>14</sup>

$$H' = -\mu \cos \theta B = -\mu \cos \theta B^0 \sin \omega_0 t \quad [10-35]$$

where  $\theta$  is the angle between the direction of  $\mu$  and the direction of  $\mathbf{B}$ . In Problem 6.8 we found that a charge of  $e$  coulombs, moving in a circle of radius  $r_0$  meters with a velocity  $v$  m/sec, has, classically, a magnetic moment of magnitude  $\mu = evr_0/2$ ; so that

$$H' = (evr_0/2)[\cos \theta](E/c) \quad [10-36]$$

If we call  $er_0$  the electric dipole moment of the point charge  $e$  ( $r_0$  is a distance characteristic of the size of the structure), and if we consider  $\cos \theta$  and 2 to be approximately unity, we have,

$$H'(\text{magnetic}) \cong \left(\frac{v}{c}\right) \cdot H'(\text{electric dipole}) \quad [10-37]$$

Thus, since transition rates are proportional to  $|H'|^2$ , the effectiveness of the magnetic field on a rotating point charge is about  $(v/c)^2$  times that of the electric field. In typical atoms, electrons have energies of a few tens of electron volts, and therefore have velocities of less than .01 times the velocity of light, so that the "magnetic dipole transitions" which we have been discussing are, in general, about  $10^4$  times weaker than electric dipole transitions. The integration involved in the matrix elements for the magnetic perturbation is different from that for the electric dipole perturbation, so that the selection rules are different. Thus it often happens that  $H'_{mk}$  (electric) is zero, but  $H'_{mk}$  (magnetic)  $\neq 0$ . Thus, a "transition can proceed by a magnetic dipole perturbation" even though it is forbidden by the electric dipole matrix element.<sup>15</sup> For the transition to proceed rapidly, however, it needs (in addition to a favorable matrix element) a very powerful time-varying magnetic field, due to the inherent smallness of the magnetic force on a charge moving at velocities small compared to that of light.

In Figure 10.5 we considered the case where the perturbing electric field

<sup>14</sup> See Section 6.1.

<sup>15</sup> A classical model of this case would be a *uniform current loop* of magnetic moment  $\mu$ . Its  $H'$  (magnetic) would be  $\mu B \cos \theta$ , the same as above, while with respect to an origin in the center of the loop, the electric dipole moment—along any axis—is zero.

was produced with the aid of an alternating voltage source of fixed maximum amplitude. Let us consider a slightly different arrangement, in Figure 10.7, where the parallel plates are forming the capacitance  $C$ , connected to an (ideal) inductance  $L$ . The  $L$ - $C$  circuit is set into free oscillation. As before, the oscillating electric field is produced between the plates, the energy storage of the

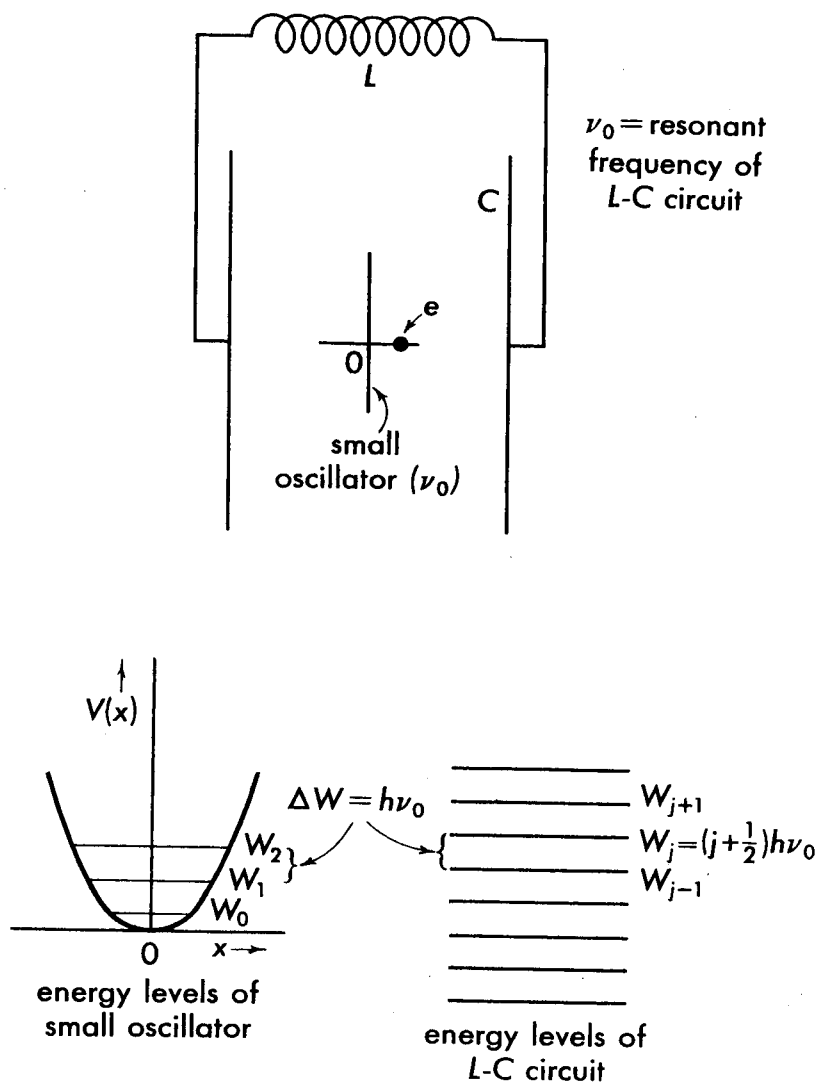


Fig. 10.7. The coupling of an atomic oscillator and a macroscopic oscillator by means of the electric field.

$L$ - $C$  circuit shifting rhythmically between the electric field of the capacitor and the magnetic field of the inductance. This has the basic features of a harmonic oscillator, so that we may expect the circuit to have similar energy levels—even though it is a macroscopic system. These levels are sketched in Figure 10.7 and, because the natural frequency of the  $L$ - $C$  circuit is the same as the small oscillator, the levels of the two systems are drawn equally spaced. If we regard

the  $L$ - $C$  circuit as being in a state (or a superposition of states) of high quantum number, then the small oscillator experiences the same perturbing electric field as before. Should the expectation value of the energy of the small system decrease, however, we must expect the energy so released to appear in the  $L$ - $C$  circuit by raising its energy. That is, the system as a whole maintains a constant energy. We can regard the energy  $H'$  [10-30] as being a perturbation on either system, and as being the mechanism for shifting the energy from one system to the other. We see that when macroscopic oscillators such as  $L$ - $C$  circuits or a resonant microwave cavity exchange energy with atomic systems, it is convenient to regard the circuits—along with their associated electric and magnetic fields—as being quantized.

A particularly interesting case (see Problem 10.7) is one in which an atomic system, known to be in its first excited state which is  $h\nu_0$  ergs above the ground state, is suddenly inserted into a microwave cavity, or  $L$ - $C$  circuit, in a state of high quantum number, resonating at  $\nu_0$  cycles per sec. The electric field causes the amplitude of the ground state (of the small oscillator) to increase. If the small system does *not* have another resonance  $h\nu_0$  ergs *above* the first excited state, the small system cannot make transitions to higher energy. The higher states that do exist are “off-resonance.” One speaks of the oscillating field in the cavity as “stimulating emission” in the atomic oscillators. Thus the oscillators “unload” their energy of excitation into the cavity which increases the amplitudes of its higher quantum number states. In this manner, atomic oscillators “drive” a macroscopic resonant circuit. If excited atomic oscillators are inserted into the cavity at a high enough rate, a stable, detectable oscillation can be maintained entirely from this source.<sup>16</sup> After being “unloaded” the atomic oscillators must be removed; otherwise, after reaching the ground state, they would start to develop excitation in the first excited state once again, and so take back the energy they had once given up.

Even in the simple system of Figure 10.7 we can see the inadequacy of the perturbation concept. We have regarded the small oscillator and the  $L$ - $C$  circuit as each having its “own” characteristic modes of vibration, whose amplitudes are shifted by the perturbation. In short, we have regarded each system as having a separate existence. Clearly, however, there is only *one* system—the small oscillator *plus* the circuit. If the zero-order wave equation [10-3] for the *complete* system is solved exactly, one finds a set of the *true* resonant modes [10-4] whose relative amplitudes shift in some exactly predictable and continuous manner according to [10-12], the *exact* time-dependent equation, from some given initial state. The conceptual problems of thinking about systems of this sort are discussed in a most interesting manner by Schrödinger in a reference given in Section 10.6.

<sup>16</sup> A system of this type (called a “Maser”), using excited  $\text{NH}_3$  molecules (selected by deflection in a molecular beam—the excited and non-excited molecules are deflected differently) has been constructed by J. P. Gordon, H. J. Zeiger, and C. H. Townes, *Phys. Rev.*, **99**: 1264, 1955.

The discussion here of the interaction of quantum-mechanical systems with electromagnetic fields is a very brief introduction to a very important subject. The electromagnetic field can be introduced into the classical Hamiltonian, and into the wave equation in a more general, although “semiclassical,” manner.<sup>17</sup> A more complete treatment, which involves the quantization of the electromagnetic field itself, requires, as a basis, the relativistic quantum theory.

### 10.5. An example: The vibration spectrum of the diatomic molecule

In Section 3.2 and Figure 3.6 it was shown that, in the vibration spectrum of the diatomic molecule, the energy levels are not exactly evenly spaced by the amount  $h\nu_0$  as in the perfect harmonic oscillator. Furthermore, the selection rule,  $\Delta n = \pm 1$  [10-32], is not exactly obeyed since molecules are observed to absorb energy directly from the ground state<sup>18</sup> ( $n = 0$ ) into the  $n = 2$ ,  $n = 3$ ,  $\dots$ , states. As an example of the application of both steady-state and time-dependent perturbation theory, we will show how both of these types of deviation may be explained.

The potential energy is

$$V(x) = (1/2) kx^2 + f(x); \quad x = r - r_0 \quad [10-38]$$

where  $r_0$  is the equilibrium separation of the two atoms. We will assume the perturbing term is

$$f(x) = bx^3 + cx^4 \quad [10-39]$$

and we will specifically consider the effects of this perturbation on the  $n = 2$  state. We will find, using first-order perturbation theory for the steady state, that not only is the energy level of this state shifted, but, in addition, the spatial form of the wave function is different from that of the zero-order eigenfunction  $\psi_2^0$ . Using the correct wave function, time-dependent perturbation theory will then show that dipole absorption and radiation is permitted, although at a reduced intensity, between the  $n = 0$  and the  $n = 2$  levels.

By [7-12] the first-order energy for the  $n = 2$  state is

$$W_2 = W_2^0 + \int_{-\infty}^{+\infty} \psi_2^{0*} f(x) \psi_2^0 dx \quad [10-40]$$

<sup>17</sup> An excellent introduction to the semiclassical treatment of radiation may be found in H. Eyring, J. Walter, and G. E. Kimball, *loc. cit.*

<sup>18</sup> For the HCl spectrum of Figure 3.6, the first excited state is  $2880 \text{ cm}^{-1}$ , or  $(2880)/(5 \times 10^{15}) = 3/5 \times 10^{-21}$  erg, above the zero-point state. At room temperature, the mean vibrational energy is  $kT = 1.36 \times 10^{-16} \times 300 = 0.04 \times 10^{-12}$  erg, which is  $\sim 15$  times smaller than the level spacing. Thus, using the Boltzmann factor,  $e^{-15} \cong 10^{-6}$ , we see that at room temperature only about 1 molecule in  $10^6$  will be found in the  $n = 1$  state, 1 in  $10^{12}$  in the  $n = 2$  state, etc.

where

$$W_2^0 = 2h \nu_0, \text{ and } \nu_0 = (1/2\pi)\sqrt{k/m} \quad [10-41]$$

The theory also gives the first-order wave function for the  $n = 2$  level,

$$\psi_2 = \psi_2^0 + a_0 \psi_0^0 + a_1 \psi_1^0 + (0) \psi_2^0 + a_3 \psi_3^0 + \cdots \quad [10-42]$$

Each of the  $a_j$ 's is given by [7-13],

$$a_j = - \left[ \int_{-\infty}^{+\infty} \psi_j^{0*} f(x) \psi_2^0 dx \right] / [W_j^0 - W_2^0] \quad [10-42a]$$

We are interested, however, in explaining the transition from  $n = 0$  to the  $n = 2$  state due to a time-varying electric field near the frequency  $2\nu_0$ . It is apparent that the presence of the  $a_1 \psi_1^0$  term in the first-order wave function belonging to the level at  $n = 2$  will explain the weak transition in question since

$$\int \psi_1^{0*} x \psi_0^0 dx \neq 0$$

and when we use time-dependent theory to calculate the normally forbidden transition from the  $n = 0$  state to the  $n = 2$  state (see [10-26] and [10-31]).

$$H'_{20} = eE_x^0 \int_{-\infty}^{+\infty} \psi_2^* x \psi_0 dx \quad [10-43a]$$

We will obtain a non-zero result.<sup>19</sup> Even if the matrix element [10-43a] is  $\neq 0$ , the amplitude  $a_2$  of the  $n = 2$  state will not grow steadily ( $\sim t^2$ ) unless, *in addition*, the resonance requirement [10-26]

$$E_x = E_x^0 \sin \omega_{20} t, \text{ where } \omega_{20} = (W_2 - W_0)/\hbar \quad [10-43b]$$

is also satisfied.  $\psi_2$  and  $\psi_0$  are the *true* wave functions belonging to the final state and the initial state respectively. *Neither* are exact harmonic oscillator eigenfunctions.

Since  $\psi_0$  is the lowest state, however, it will be *nearly* the pure state,

$$\psi_0^0 = (\sqrt{\alpha/\pi})^{1/2} e^{-\alpha x^2/2}; \quad \alpha = 2\pi \nu_0 m/\hbar \quad [10-44^{20}]$$

because  $f(x)$  is small at low vibrational amplitude. For simplicity, we assume that [10-44] is the exact form of the wave function for the ground state. When the first-order wave function [10-42] is used in the calculation of the matrix element  $H'_{20}$  of [10-43a], we see by [10-32] that only one term will be non-zero—the one involving  $\psi_1^0$  and  $\psi_0^0$ . Thus,

$$H'_{20} = eE_x^0 \int_{-\infty}^{+\infty} a_1^* \psi_1^{0*} x \psi_0^0 dx = a_1^* H'_{10} = eE_x^0 a_1^* \sqrt{1/\alpha} \quad [10-45]$$

<sup>19</sup> A small amount of  $\Psi_1^0$  present in  $\Psi_0^0$  (the ground-state wave function) *also* contributes the  $n = 0 \rightarrow n = 2$  transition. See Problem 10.11.

<sup>20</sup> See Appendix I.

Thus, the absorption line from  $n = 0$  to  $n = 2$  whose intensity is proportional to  $|H'_{20}|^2$ , is  $|a_1|^2$  times as intense as the main absorption line, which is proportional to  $|H'_{10}|^2$ , and since, in practice,  $a_1 \ll 1$ , the absorption line near  $2\nu_0$  is much weaker than the one at  $\nu_0$ .

By steady-state perturbation theory for a nondegenerate level [7-13],

$$a_1 = \frac{-\int \psi_1^{0*} f(x) \psi_2^0 dx}{W_1^0 - W_2^0} \quad \text{where } W_1^0 - W_2^0 = -h\nu_0 \quad [10-46]$$

Thus, if the deviation  $f(x)$  from a parabolic potential energy curve of the ideal harmonic oscillator has such a form that it "mixes" some of the  $n = 1$  state with the  $n = 2$  state (that is, if  $a_1$  is not zero), then the dipole transition from the  $n = 0$  to the  $n = 2$  state is no longer rigorously forbidden.

The same  $f(x)$ , used in [10-40], must explain the experimental fact that  $W_2$  is slightly smaller than the value  $2h\nu_0$  predicted for the case of the ideal oscillator.

From Appendix I, the zero-order wave functions for  $n = 1$  and  $n = 2$  are

$$\begin{aligned} \psi_1^0 &= [(1/2)(\sqrt{a/\pi})]^{1/2} (2\sqrt{a} x) e^{-ax^2/2}, \\ \psi_2^0 &= [(1/8)(\sqrt{a/\pi})]^{1/2} (4ax^2 - 2) e^{-ax^2/2} \end{aligned} \quad [10-47]$$

Making use of the definite integral,

$$\int_{-\infty}^{+\infty} x^{2n} e^{-ax^2} dx = \frac{1 \cdot 3 \cdot 5 \cdots (2n-1)}{2^n a^n} \sqrt{\frac{\pi}{a}}, \quad n = \text{a positive integer} \quad [10-48]$$

we have, using [10-40],

$$W_2 = W_2^0 + (49c)/(4a^3) \quad [10-49]$$

The  $bx^3$  term does not contribute, since it is odd with respect to  $x = 0$ , and  $\psi_2^{0*} \psi_2^0$  is even.

From [10-46] we obtain for the amplitude of  $\psi_1^0$  present in  $\psi_2$ ,

$$a_1 = - (3b)/(a)^{3/2} (h\nu_0) \quad [10-50]$$

The  $cx^4$  term does not contribute here due to symmetry properties. Thus the absorption line whose energy is

$$W_2 - W_0 = 2h\nu_0 + (49c)/(4a^2) \quad [10-51]$$

(since  $W_2^0 = (5/2)h\nu_0$  and  $W_0 \cong W_0^0 = h\nu_0$ ) has a lower intensity than the main resonance, by the factor  $a_1^2$ .

We note that the  $bx^3$  term in the perturbation  $f(x)$  accounts for the  $n = 0$  to  $n = 2$  absorption line, while the  $cx^4$  term accounts for the energy shift in

the  $n = 2$  level. Since experimentally the correction to  $W_2$  is negative,  $c$  must be negative—that is, the  $x^4$  term “flattens out” the potential well.

From the experimental HCl spectrum of Figure 3.6 we see, using [10-45], that  $a_1$  is  $\sim \sqrt{60}$  and, using [10-50], we can find the constant  $b$ .

Hertzberg<sup>21</sup> gives the experimental value of the  $n = 2$  energy level as  $5668 \text{ cm}^{-1}$  which is 1.8 per cent lower than twice the main resonance at  $2886 \text{ cm}^{-1}$ . If we assume that the latter value (converted to ergs and divided by  $h$ ) is the characteristic frequency  $\nu_0$  of the ideal harmonic oscillator, we can use [10-51] to obtain the value of the constant  $c$ . Pauling and Wilson<sup>22</sup> derive a general formula for the energy level corrections, which depends only upon the constant  $c$ .

It has been found that quantum theory gives a consistent account of the vibration spectrum, including many other effects not mentioned here, such as the rotational energy levels, the influence of the nuclei (particularly when they are identical isotopes and show exchange-symmetry properties), etc.

We close this section by pointing out that it is also possible for a classical perturbed oscillator to absorb energy at about twice its (low-amplitude) resonance frequency. Suppose that the oscillator is vibrating at an appreciable amplitude. The mass point of an *ideal* oscillator will have its velocity proportional to an exact sinusoidal function such as  $\cos 2\pi\nu_0 t$ , but the nonideal potential will cause the velocity, although exactly periodic with period  $T$  near  $(1/\nu_0)$ , to deviate from a pure sinusoidal form, the deviation being expressible as a Fourier series,

$$v(t) = a_1 \cos(2\pi/T)t + a_2 \cos 2(2\pi/T)t + a_3 \cos 3(2\pi/T)t + \cdots \quad [10-52]$$

where, for small deformations of the potential from  $1/2 kx^2$ ,  $a_2$  and  $a_3$  are small compared to  $a_1$ . If a force along the  $x$ -axis,

$$F(t) = F_x^0 \cos 2(2\pi/T)t \quad [10-53]$$

which is periodic, with *twice* the basic frequency of the oscillator, is applied to the mass, work *may* be done on the mass. Over one complete period  $T$ ,

$$\text{work} = \int_0^T F(t) v(t) dt \quad [10-54]$$

where  $v dt = dx$ , the distance moved in the time  $dt$ .

If [10-53] is the force and [10-52] is the velocity, then the integral in [10-54] is non-zero for one term,

$$a_2 F_x^0 \int_0^T \cos^2 2(2\pi/T)t dt$$

<sup>21</sup> G. Hertzberg, *Molecular Spectra and Molecular Structure* (1939, Prentice-Hall, Inc., New York). I: Diatomic Molecules, p. 58.

<sup>22</sup> L. Pauling and E. B. Wilson, *op. cit.*, p. 160.



Thus, it is possible for the mass to absorb energy (or, release energy) at twice its basic frequency  $1/T$ , providing that its velocity is not purely sinusoidal in such a way that  $a_2 \neq 0$ .<sup>23</sup> For the HCl molecule, however, we have seen that at room temperature only one molecule in  $10^6$  has an energy equal to the first quantum level, and only one molecule in  $10^{12}$  has an energy equal to the second quantum level, so that, even if  $a_1 \cong a_2$  for molecules whose energy is in the range of  $h\nu_0$  (a *very* large nonlinearity), the classically predicted absorption line near  $2\nu_0$  is *much* weaker than the experimental value. In addition, the classical line should be broadened in frequency—due to the lack of quantization—in contrast to the sharp experimental value.

The diatomic molecule vibration spectrum provides an excellent example of the application of both stationary and time-dependent perturbation theory to a case of physical interest and, in addition, shows the distinctive differences between the (experimentally verified) quantum theory and the incorrect classical theory.

## 10.6. The importance of time-dependent perturbations

We see, then, that time-dependent perturbations can cause a system to change its wave function in a significant and observable manner. These perturbations can cause either increases or decreases in the expectation value of the energy of a system, implying either an inflow of energy to the system or an outflow of energy from the system.

Similarly, time-dependent perturbations can cause the expectation value of the magnitude of the angular momentum, or the magnitude of the z-component of the angular momentum, to change. In either case, the system is interchanging angular momentum with its environment, since the angular momentum vector is not constant in time.

Thus, it is through time-dependent perturbations that a system “interacts with its environment.” This, of course, is the realm of experiment and observation, so that the great importance of the theory is clear.

But what is the environment? Is it not another system with its own zero-order vibrations and resonant modes? If energy flows out of “the system under observation” which we have been analyzing, it must flow into the system making up the environment. The environmental system is usually large—for example, a box containing slits, an optical grating, and a photographic film—so that it generally has many, closely spaced resonant modes. As the amplitudes of vibration of two of the modes of the atomic wave functions shift, causing the expectation value of the energy of the atomic system energy to drop, we expect that there will be some corresponding shift among the amplitudes of the many modes of the environment, causing its energy to rise a corresponding

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<sup>23</sup> Note:  $1/T$  will in general differ slightly from  $\nu_0$ , the frequency of oscillation at very low amplitude.

amount. Suppose, for example, that there were many atoms, originally in a pure state with energy  $W_k^0$ . A perturbation causes these atoms to build up some finite amplitude of the state of energy,  $W_m^0$ , with a consequent loss (or gain) in the expectation value of the atomic energy. During this process, the electromagnetic vibrations in the environment of frequency,  $\omega_{km}/2\pi$ , will become more intense (or less intense). If the atoms are losing energy, the electromagnetic vibrations will interact with the grating, and finally result in a black line on the photographic plate at the place where the grating causes the electromagnetic waves to superimpose in phase. Once permanent, macroscopic changes are made (such as the exposed photographic film), the environmental system can be examined at will without altering it significantly. Thus, observation, considered carefully, is a very complex process.

This very brief outline of a typical experiment shows the many problems involved in a really complete quantum-mechanical theory of experiment. The student is referred to other sources for a further discussion of this important and interesting problem.<sup>24</sup>

There are many interesting discussions of the nature of measurement and the philosophical implications of quantum mechanics which the student is now in a position to appreciate. One of them is an extremely interesting article, "Are There Quantum Jumps,?"<sup>25</sup> by Erwin Schrödinger.

Some of the other founders of the theory of quantum mechanics explain their attitude toward the quantum phenomena in the following relatively non-mathematical articles and books:

Niels Bohr, "Discussion with Einstein on Epistemological Problems in Atomic Physics," Paul A. Schelpp (ed.), in *Albert Einstein, Philosopher-Scientist* (1949, The Library of Living Philosophers, Evanston, Illinois): p. 201.

Louis de Broglie, *The Revolution in Physics* (1953, The Noonday Press, New York).

Max Born, *Physics in my Generation* (1956, Pergamon Press, London).

There are two technical books of both historical and current interest:

E. Schrödinger, *Four Lectures on Wave Mechanics* (1929, Blackie and Son, Ltd., London).

W. Heisenberg (Tr. by C. Eckart & F. Hoyt), *The Physical Principles of Quantum Theory* (1930, University of Chicago Press, Chicago, Ill., also Dover Publications Inc., New York).

There are few subjects so fascinating and so puzzling as the interpretation of quantum phenomena, and it is clear that the last word has not yet been said. Now that the student has been introduced to what quantum mechanics *is*, he will find the study of what it *means* both stimulating and rewarding.

<sup>24</sup> D. Bohm, *Quantum Theory* (1951, Prentice-Hall, Inc., New York): p. 583.

<sup>25</sup> E. Schrödinger, "What Is Life," and *Other Scientific Essays* (1956, Doubleday Anchor Co., Garden City, New York): p. 132. (Originally published in the *Brit. J. Phil. Sci.*, 3: nos. 10 & 11, 1952.)

## 10.7. Summary

The complete time-dependent wave equation is

$$(H^0 + H')\Psi = -(\hbar/i)\partial\Psi/\partial t \quad [10-5]$$

where  $H'$  may depend upon space, momentum, and time, and where the time-independent part of the equation is

$$H^0\psi_n^0 = -(\hbar/i)\partial\Psi_n^0/\partial t = W_n^0\Psi_n^0, \text{ since } \Psi_n^0 = \psi_n^0 e^{-iW_n^0 t/\hbar} \quad [10-3a]$$

In order to solve the wave equation [10-5] when  $H'$  is time-dependent, it is necessary to be given the wave function  $\Psi(x, t_0)$  at some time  $t = t_0$ . Any reasonable form of  $\Psi(x, t_0)$  can be synthesized by the orthogonal series

$$\Psi(x, t_0) = \sum_n a_n(t_0)\Psi_n^0(x, t_0) \quad [5-9]$$

where

$$a_n(t_0) = \int \Psi_n^0(x, t_0)\Psi(x, t_0) dx \quad [5-12]$$

The complete list of  $a_n$ 's, at  $t = t_0$ , gives an exact description of the wave function at  $t = t_0$ .

At any time  $t$  the (well-behaved and bounded) wave function may be characterized by some particular set of  $a_n$ 's which will synthesize  $\Psi(x, t)$  at that instant,

$$\Psi(x, t) = \sum_n a_n(t)\Psi_n^0(x, t) \quad [10-9]$$

The objective of the calculation is this: Given a set of  $a_n$ 's at  $t_0$ , find the *new* set of  $a_n$ 's at any arbitrary time  $t$ . To find the  $a_n$ 's at  $t$ , we substitute [10-9] into the true wave equation [10-5], giving

$$\sum_n a_n(t)H^0\Psi_n^0 + \sum_n a_n(t)H'\Psi_n^0 = -\frac{\hbar}{i}\sum_n \left[ \frac{d}{dt} a_n(t) \right] \Psi_n^0 - \frac{\hbar}{i}\sum_n a_n(t) \frac{\partial\Psi_n^0}{\partial t} \quad [10-10]$$

The sums on the extreme left and the extreme right cancel term by term (by the zero-order equation [10-3a]). Multiplying the remainder of [10-10] from the left by  $\Psi_m^{0*}$ , and performing the operation  $\int d\tau$  on each term, [10-10] becomes the set of equations,

$$\frac{d}{dt} a_m(t) = -\frac{i}{\hbar} \sum_n a_n(t) \int \Psi_m^{0*} H' \Psi_n^0 d\tau \quad [10-11]$$

$$m = 1, 2, 3, \dots$$

There is one equation [10-11] for each value of  $m$ , and for each equation,  $n$  ranges over all the values needed to identify each member of the complete set

of eigenfunctions of the time-independent equation [10-3a]. There is no approximation in the set of equations [10-11]. It is fully equivalent to the wave equation [10-5]. The set is written out in more detail in [10-12]. Given all the  $a_n$ 's at  $t = 0$ , it is possible to integrate the set of differential equations [10-11] from  $t = 0$  to  $t$ , obtaining, thereby, each of the  $a_n$ 's at  $t$ . In practice this operation is difficult mathematically, and so we turn to a first-order perturbation calculation.

If we substitute

$$H = H^0 + \lambda H' \quad [10-13]$$

and

$$a_m(t) = a_m^0 + \lambda a'_m \quad [10-14]$$

in [10-11] or [10-12], we obtain, equating the coefficients of  $\lambda^0$ , the result that all the  $a_m^0$ 's are constant in time. Equating the coefficients of  $\lambda$ , we obtain the set of first-order equations,

$$-(\hbar/i) da'_m/dt = \sum_n a_n^0 \int \Psi_m^{0*} H' \Psi_n^0 d\tau, \quad m = 1, 2, 3, \dots \quad [10-16]$$

which are written out more fully in Section 10.1. This set of approximate equations may be most easily solved for the case where, at  $t = 0$ ,  $a_k^0 = 1$  and all the other  $a_m^0$ 's are zero. For one dimension,  $d\tau = dx$ . Since at  $t = 0$  all the  $a_m^0$ 's (except  $a_k$ ) are zero,  $a'_m(t) = a_m(t)$ , and the integral of [10-16] is:

$$a_m(t) = \int_0^t \left[ -\frac{i}{\hbar} \int_{\text{space}} \psi_m^{0*} e^{iW_m^0 t/\hbar} H' \left( x, \frac{\partial}{\partial x}, t \right) \psi_k^0 e^{-iW_k^0 t/\hbar} dx \right] dt$$

where  $H'$  may depend upon  $x$ ,  $\partial/\partial x$  (i.e., momentum) or  $t$ . There is the usual first-order restriction  $|a_m(t)| \ll 1$ .

$a_m(t)$  is calculated for two different forms for  $H'$ :

(a)  $H' = f(x)$ , a constant perturbation, starting at  $t = 0$ , then

$$a_m(t) = -\frac{H'_{mk}}{\hbar} \frac{(e^{i\omega_{mk}t} - 1)}{\omega_{mk}} \quad [10-18]$$

$$m = 1, 2, 3, \dots, m \neq k, \omega_{mk} = (W_m^0 - W_k^0)/\hbar, H'_{mk} \equiv \int \psi_m^{0*} f(x) \psi_k^0 dx$$

(b)  $H' = A(x) \sin \omega_0 t$ , starting at  $t = 0$ , then

$$a_m(t) = -\frac{H'_{mk}}{2\hbar} \left[ \frac{(e^{i(\omega_{mk} + \omega_0)t} - 1)}{\omega_{mk} + \omega_0} - \frac{(e^{i(\omega_{mk} - \omega_0)t} - 1)}{\omega_{mk} - \omega_0} \right] \quad [10-25]$$

$$m = 1, 2, 3, \dots, m \neq k, \omega_{mk} = (W_m^0 - W_k^0)/\hbar,$$

and

$$H'_{mk} \equiv \int \psi_m^{0*} A(x) \psi_k^0 dx$$

## PROBLEMS

*Problem 10.1.* A particle of mass  $= 9 \times 10^{-28}$  gm is trapped in an infinite-wall, one-dimensional box of width  $a = 1 \times 10^{-8}$  cm. The lowest state of this system ( $n = 1$ ) has a characteristic energy  $W_1^0 = 38$  e.v. Also,  $W_2^0 = 152$  e.v.,  $W_3^0 = 342$  e.v., and  $W_4^0 = 608$  e.v.

At  $t = 0$ , the particle is known to be in the state for which  $n = 1$ .

- (a) At  $t = 0$ , a rectangular potential well,  $V_0 = -10^4$  e.v., centered at  $a/2$  and of width  $10^{-12}$  cm, is suddenly introduced into the well and kept there for  $5 \times 10^{-18}$  second, at which time it is removed. After removal of the perturbation, what is the chance that the system will be found in each of the states  $n = 2$ ,  $n = 3$ , and  $n = 4$ ? (The height and width of the potential well is characteristic of a neutron interacting with an electron.)
- (b) Let the above perturbation continue for a sequence of different time intervals, ranging up to  $30$  or  $40 \times 10^{-18}$  sec. Plot the  $|\text{amplitude}|^2$  of the  $n = 3$  state over this interval. What would be the result of an experiment designed to identify the presence of the  $n = 3$  state, if it were performed about  $27 \times 10^{-18}$  sec after the onset of the perturbation?

*Problem 10.2*

- (a) Using the identity,  $2 \cos x = e^{ix} + e^{-ix}$ , show that the cross terms, neglected in both [10-26] and [10-27] (time-dependent part, only), are equal to

$$(-2) \frac{\cos 2\omega_0 t_1 + 1 - \cos(\omega_{mk} - \omega_0)t_1 - \cos(\omega_{mk} + \omega_0)t_1}{(\omega_{mk} - \omega_0)(\omega_{mk} + \omega_0)}$$

- (b) Show that when  $\omega_{mk} - \omega_0 \ll 1$ , the cross terms become, approximately,

$$-\frac{(\omega_{mk} - \omega_0)}{(\omega_{mk} + \omega_0)} t_1^2$$

- (c) Under what conditions, therefore, are [10-26] and [10-27] good approximations?

*Problem 10.3.* Consider, once again, the system of Problem 10.1 where the particle is known to be initially in the state  $n = 1$ . Now, however, the potential well is perfectly flat from  $x = 0$  to  $x = a$ . Add a perturbation,  $H' = A \sin \omega_0 t$ , from  $t = 0$  to  $t = t_1$ , where  $A$  is a constant, equal to 1 e.v. ( $= 1.60 \times 10^{-12}$  erg), independent of both  $x$  and  $t$ . This causes the entire bottom of the well to be raised

and lowered sinusoidally with the frequency  $\nu_0 = \omega_0/2\pi$ . Assume that the frequency  $\nu_0$  is  $2.8 \times 10^{16}$  cps [so that  $h\nu_0 = 114$  e.v., the energy needed to reach the first excited state at ( $n = 2$ )]. Show that no excitation will occur either for  $n = 2$  or for any other level.

*Problem 10.4.* Change the perturbation of Problem 10.3 into the following,

$$H' = A(x) \sin \omega_0 t$$

where

$$A(x) = -1 \text{ e.v. from } x = 0 \text{ to } x = a/2$$

$$A(x) = +1 \text{ e.v. from } x = a/2 \text{ to } x = a$$

and where  $\nu_0$  is still  $2.8 \times 10^{16}$  cps, the difference in characteristic frequency between the  $n = 1$  and the  $n = 2$  states.

Let the above perturbation continue for  $3.56 \times 10^{-16}$  second, that is, for 10 complete cycles, and then be removed.

Find |amplitude|<sup>2</sup> of vibration of (a) the  $n = 2$  state, (b) the  $n = 3$  state, and (c) the  $n = 4$  state.

*Problem 10.5.* Equation [10-29] gives the potential energy of a charge  $e$  in an electric field  $E_x$ , as  $eE_x(x - x_0)$ , where  $x_0$  is a constant. In Section 10.4 we set  $x_0 = 0$ , but suppose that this had not been done, so that  $H' = e(x - x_0) E_x^0 \sin \omega_0 t$ , rather than [10-30]. Show in the two cases discussed in Figure 10.4 that the presence of  $x_0$  in  $H'$  does not change the predictions regarding the shifts in excitation of the states of the oscillator.

*Problem 10.6.* The harmonic oscillator of natural frequency  $\nu$  of Figure 10.4 is assumed to be initially in the pure state  $\psi_1^0$ , and experiences an electric field, along the  $x$ -axis, whose frequency is equal to  $\nu$ . According to [10-32], the vibrations in the upper state, for which  $m = 2$ , should grow more rapidly than those in the ground state  $m = 0$ .

- (a) Using the harmonic oscillator eigenfunctions given in Section 3.5, show, for this case, that [10-32] is correct. (The integrals involved are composed of the gamma functions,  $\Gamma(n + \frac{1}{2})$ , which can be found in a table of definite integrals.)
- (b) Let  $\nu = \nu_0 = 10^{10}$  cycles per second,  $e = 1.6 \times 10^{-19}$  coulomb,  $m = 20 \times 10^{-27}$  kg (the approximate mass of a nitrogen atom), and  $E_x^0 = 100$  volt/m, or nt/coulomb. Calculate the time needed for the most strongly excited of the two states to build up to an intensity of 1 per cent of the excitation of the initial state.

- (c) Show that in this problem  $H'(\text{max.}) \ll h\nu$ , that is, the maximum value of the perturbation energy is small compared to the energy difference between levels. [Suggestion: estimate the maximum value of  $x$  from the harmonic oscillator wave function (see Figure 3.10). Does this value of  $x(\text{max.})$  agree with the known size of small molecules ( $2$  or  $3 \times 10^{-8}$  cm)?] [Note:  $\text{NH}_3$  has a mode of vibration at about  $3 \times 10^{10}$  cps—referred to at the end of Section 3.3 in connection with barrier penetration. The N atom vibrates from one side of the triangular  $H_3$  structure to the other, through a barrier, so it is not a harmonic oscillator, but it does have an electric dipole moment and can, therefore, react with the electric field of the cavity. It is used in Townes's "Maser" (see footnote in Section 10.4).]

**Problem 10.7.** We consider a particle of mass  $20 \times 10^{-27}$  kg and charge  $e = 1.6 \times 10^{-19}$  coulombs to be in an infinite-wall, one-dimensional box of length  $L$ .

- (a) What must be the value of  $L$  in order that the first excited state lie an amount  $h\nu$  above the ground state, where  $\nu = 10^{10}$  cps?
- (b) This system, initially in its first excited state, is introduced, at  $t = 0$ , into a microwave cavity which is resonating at  $10^{10}$  cps. In the region occupied by the small system, the electric field (assumed to be parallel to the  $x$ -axis of the small system) has the amplitude  $E_x^0 = 100$  volt/m. How long will it take for the ground-state vibrations to attain an intensity of 1 percent of the initial state vibrations? (Suggestion: It is convenient, although not essential, to let  $x = 0$  in the center of the one-dimensional box and re-write the eigenfunctions accordingly.)
- (c) At the time calculated in (b), what is the intensity of vibration of the *second* excited state? (Assume that [10-26] holds, although it cannot be strictly correct owing to the distance from resonance.) What must be happening to the expectation value of the system energy for the small oscillator?

**Problem 10.8**

- (a) Show that a system whose wave function is the superposition of two pure states  $\Psi_m$  and  $\Psi_k$ , given in [10-33], has the periodically varying electric dipole moment given in [10-34].
- (b) Show that if a charged particle in a one-dimensional infinite-

wall box is in a superposition of  $\Psi_1$  and  $\Psi_2$ , one should expect radiation to occur.

- (c) What would one expect if the system were in a superposition of  $\Psi_1$  and  $\Psi_3$ ? (Suggestion: Place the origin in the center of the box.)

*Problem 10.9.* In Chapter 9 it was mentioned that any system which originally has a given exchange symmetry must keep it always. Let the perturbation  $H'$  be unchanged by the interchange of  $x_1$  and  $x_2$ , the coordinates of two identical particles. Let the initial state of the system be  $\Psi_k(x_1, x_2)$ , and the final state be  $\Psi_m(x_1, x_2)$ . Assume that one of these states is symmetrical to interchange of  $x_1$  and  $x_2$ , while the other is antisymmetrical. Show that if this is true,

$$H'_{mk} = \iint \Psi_m(x_1, x_2) H' \Psi_k(x_1, x_2) dx_1 dx_2$$

must equal zero, that is, transitions between states of different exchange symmetry do not occur. (Hints: Interchange of variables in a definite integral cannot change its value. When a number equals its own negative, it must be zero.)

*Problem 10.10.* Using the theory in Section 10.5, calculate the numerical values of  $b$  and  $c$  for the HCl molecule. (Let  $\nu_0$  be given by  $h\nu_0 = 2886/(5 \times 10^{15})$  erg and let  $m$ , the reduced mass, be  $1.6 \times 10^{-24}$  gm.)

*Problem 10.11.* Using the perturbation  $f(x) = bx^3 + cx^4$  for the harmonic oscillator:

- Calculate an expression giving the correction to the energy of the  $n = 0$  state.
- Calculate an expression for the amplitude  $a_1^{(0)}$  of the  $n = 1$  state which is "mixed" into  $\psi_0$  by the perturbation above.
- Calculate the contribution to the absorption line located near  $2h\nu_0$  of the term  $a_1^{(0)} \psi_1^0$ , present in  $\psi_0$ . (Note: The  $a_1$ , used in Section 10.5, should more properly be written  $a_1^{(2)}$ , since it refers to the amplitude of  $\psi_1^0$  present in the first-order wave function  $\psi_2$ , for which  $n = 2$ .)

*Problem 10.12.* A particle of mass  $m = 10^{-27}$  gm and charge,  $e = 4.8 \times 10^{-10}$  esu forms a harmonic oscillator whose resonant frequency is  $\nu_0 = 1.0 \times 10^{14}$  cps. At  $t = 0$ , the oscillator is known to be in the state  $n = 0$ , and an electric field,

$$E = E_0 \sin 2\pi ft, f = 1.1 \times 10^{14} \text{ cps}$$



parallel to the axis of vibration of the oscillator, is applied to the system.  $E_0 = 100$  stat-volts/cm. (Note: stat-volts times esu = ergs.)

- (a) At  $t = 5 \times 10^{-14}$  sec, what is the probability that the system will be found in the state  $n = 1$ ?
- (b) At  $t = 10 \times 10^{-14}$  sec, what is the probability that the system will be found in the state  $n = 1$ ?
- (c) On the average, how much energy does this "off-resonance" system absorb from the electric radiation field?