

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 5×10^{-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 40×10^{-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 27×10^{-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 ν_0 is 2.8×10^{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 ν_0 is still 2.8×10^{16} cps, the difference in characteristic frequency between the $n = 1$ and the $n = 2$ states.

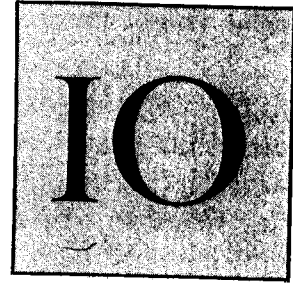
Let the above perturbation continue for 3.56×10^{-16} second, that is, for 10 complete cycles, and then be removed.

Find $|\text{amplitude}|^2$ 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 ν of Figure 10.4 is assumed to be initially in the pure state ψ_1^0 , and experiences an electric field, along the x -axis, whose frequency is equal to ν . 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.



TIME-DEPENDENT PERTURBATION THEORY

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 Ψ upon the four variables x, y, z , and t usually makes the direct solution of the equation very difficult.¹ 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 Ψ '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 Ψ_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*, ψ_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 ψ_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 Ψ_n^0 's,

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

¹ 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, Ψ must meet the requirements of the basic postulates. Let us suppose, as in Section 5.1, that at $t = t_0$, Ψ has some given form, $\Psi(x, t_0)$. Our objective is to find Ψ at some later time, where Ψ 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

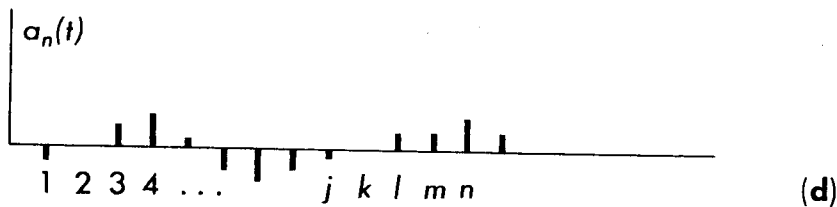
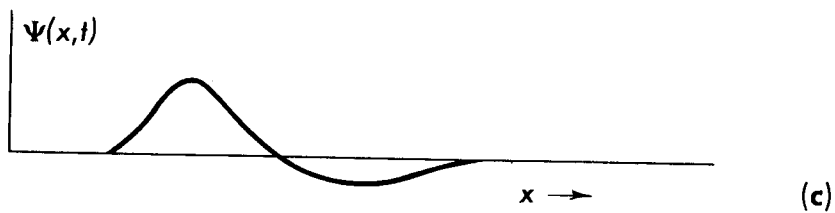
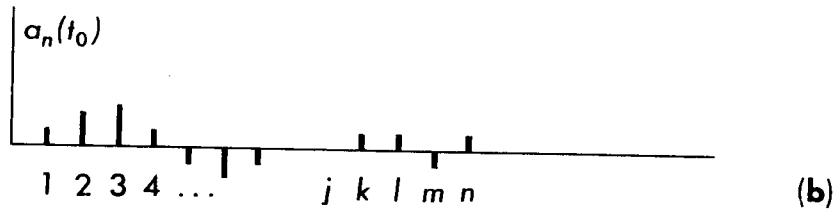
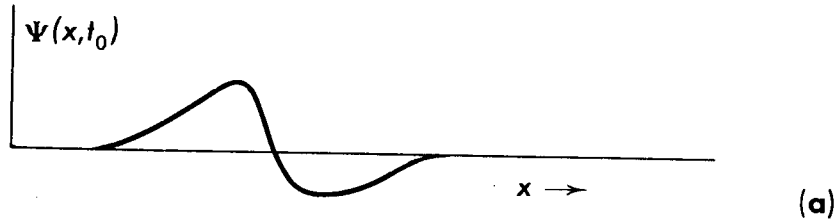


Fig. 10.1. The wave function of a system at two different times, $t = t_0$ and $t = t$, and the amplitude spectra of the eigenfunctions needed to synthesize each of the two different functions of x .

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 Ψ_n^0 's. Since it has a different shape it will, in general, have different amplitudes, $a_n(t)$, of the basic Ψ_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 Ψ is changing from moment to moment, and the amplitudes of the components that are needed to synthesize Ψ 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 Ψ in the complete wave equation [10-5], we have,²

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

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

The sum of terms on the extreme left equals, term by term, the sum of terms on the extreme right, so that these two parts of [10-10] cancel. Multiplying the rest of [10-10] by Ψ_m^{0*} , integrating with respect to the spatial coordinates $d\tau$, and using the orthogonality of the Ψ_m^0 's,

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

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 Ψ_m^0 with each of the other pure states Ψ_n^0 .³

We must visualize a vibrating system that has many modes or pure vibrations excited simultaneously. The time-dependent operator H' causes the amplitude of each of the pure vibrations to change in some definite manner. Some will increase with time and others must decrease—since at *all* times $\sum_n a_n^* a_n = 1$, and any amplitude can increase only at the expense of some, or all, of the others.

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.

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

³ 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 Ψ_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.⁴

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 Ψ_j^0 's as the set of functions used to synthesize the true wave function. The choice of the particular set of Ψ_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 λ . We therefore set

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

and allow λ to vary from 0 to 1.⁵ As this occurs, we expect each of the a 's to vary, but not necessarily in a purely linear manner, with λ . 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 ψ 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

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

⁴ 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 Ψ_j^0 's" is equivalent to "the Ψ_k^0 's", etc.

⁵ As in Chapter 7, λ 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 λ . 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 Ψ_m^0 of the complete wave function Ψ), 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 λ^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 Ψ_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 Ψ_k^0 "feeds amplitude" into the state Ψ_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 Ψ_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.⁶ 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 ψ_m^0 and ψ_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: $|a_k^0(t_1)| = 1$.)

⁶ 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 calculate⁷

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

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 levels⁸ 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

⁷ 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 $(1 - e^{ix})^*(1 - e^{ix}) = 4 \sin^2 \frac{x}{2}$.

⁸ 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 [10-21b] 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

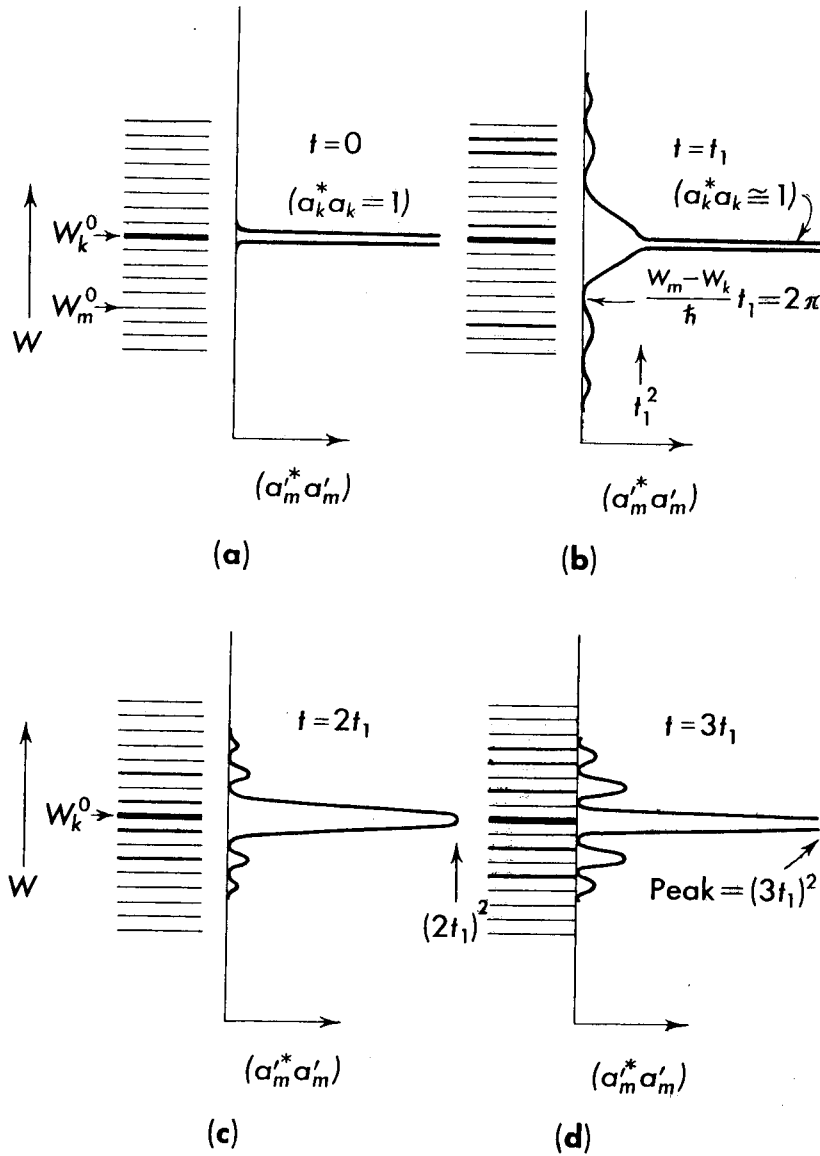


Fig. 10.2. The time variation of the excitation of the proper vibrations (eigenfunctions) caused by the constant perturbation, starting at $t = 0$. The density of the horizontal lines indicates the degree of excitation of the level or state.

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 ΔW . 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 Δt 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, Δt ,” there is a spread, ΔW , 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 ω_0 , and which