

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^{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 ω_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-

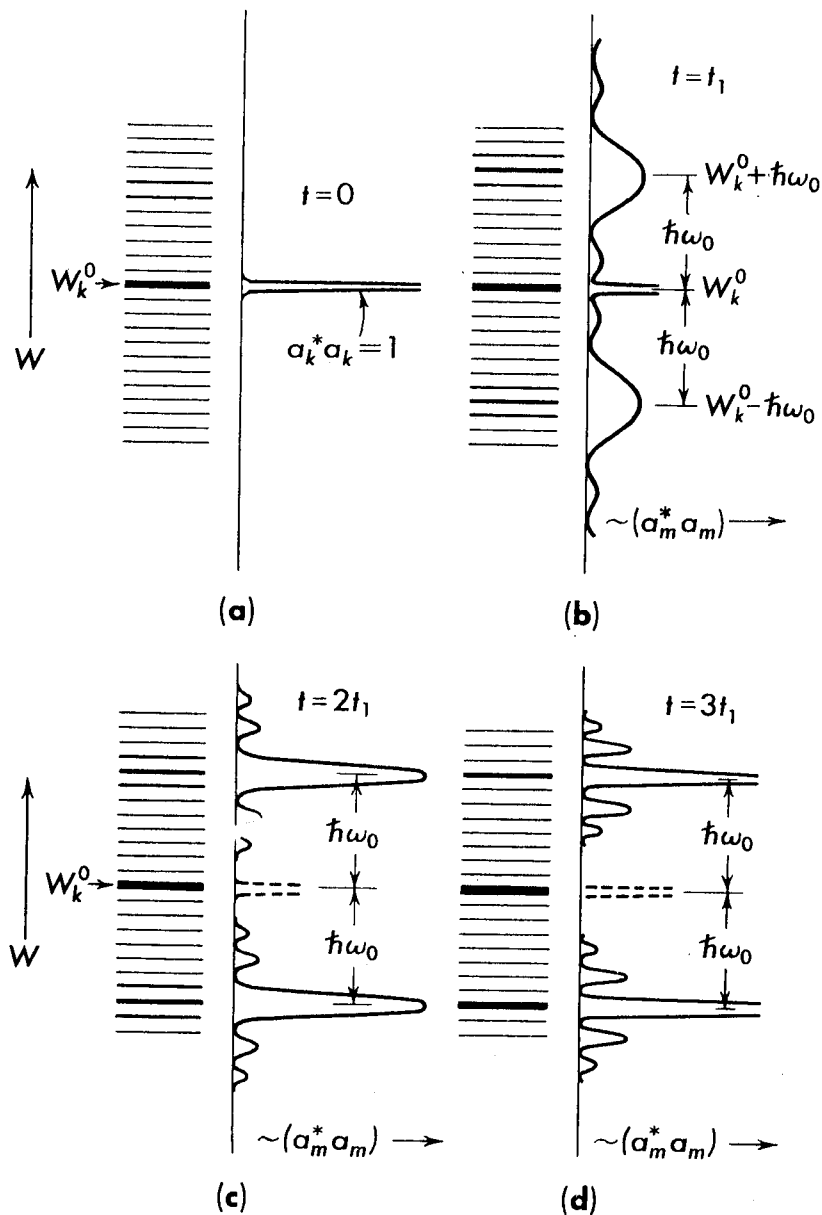


Fig. 10.3. The time variation of the excitation of the proper vibrations caused by a harmonic perturbation, starting at $t = 0$. The density of the horizontal lines indicates qualitatively the degree of excitation of the level or state.

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 Δt seconds, the half-width of each peak is ΔW , 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 ω_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

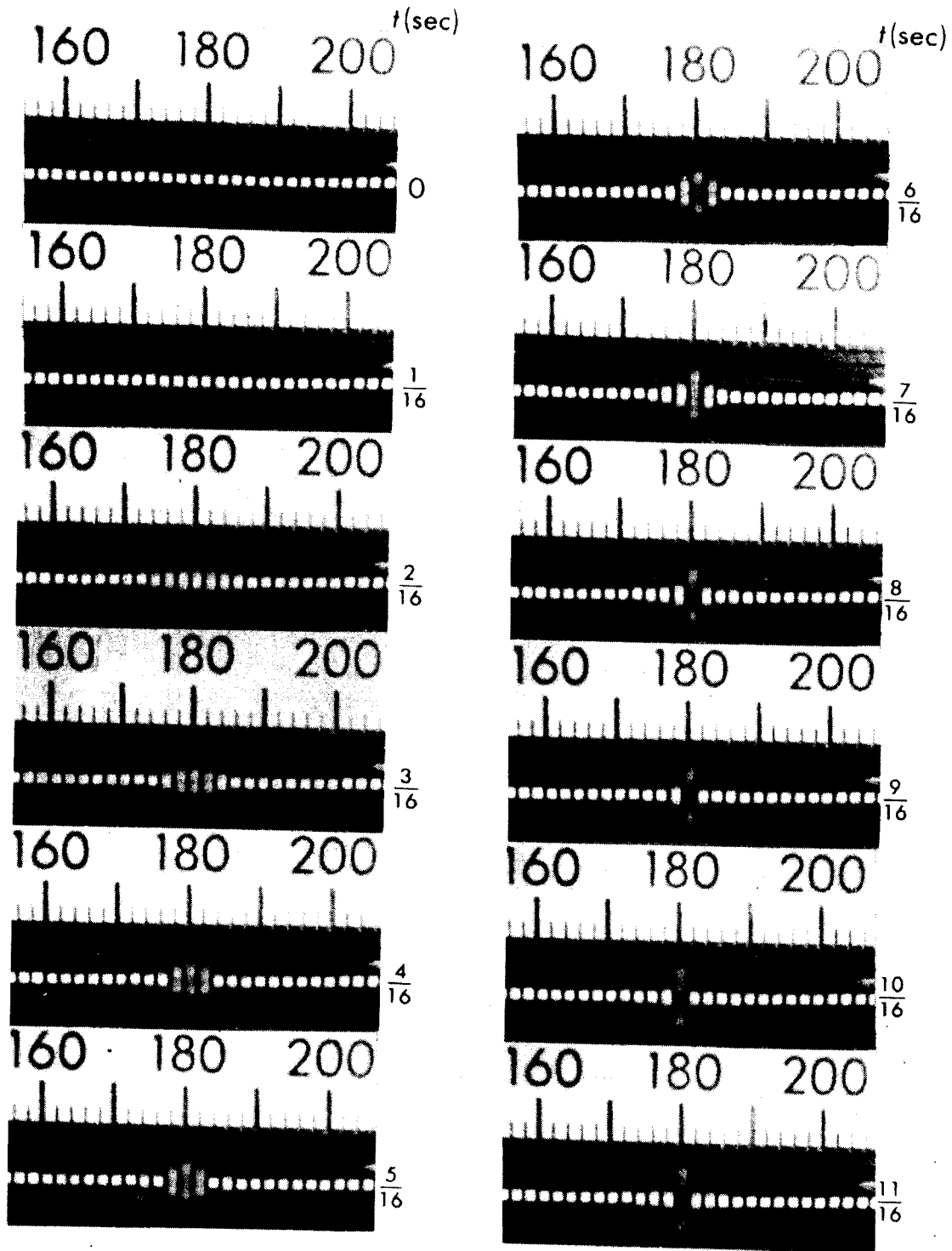


Fig. 10.4. Sequential photographs of a bank of reed filters. At $t = 0$, a constant-amplitude 180 cps signal is coupled equally to each of the reeds.

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].

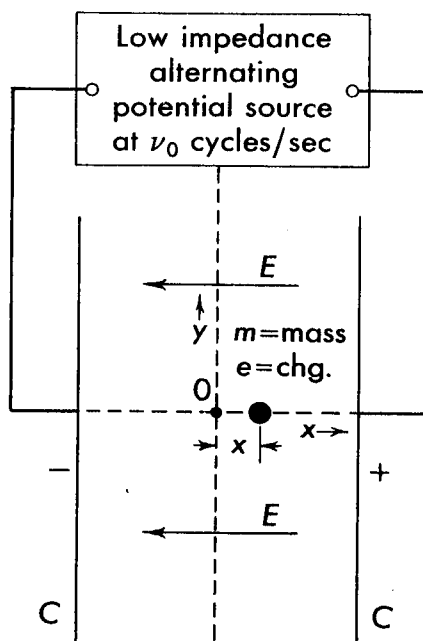
10.4. The harmonic oscillator in a periodic electric field

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 ω_0 is connected to the two parallel plate con-

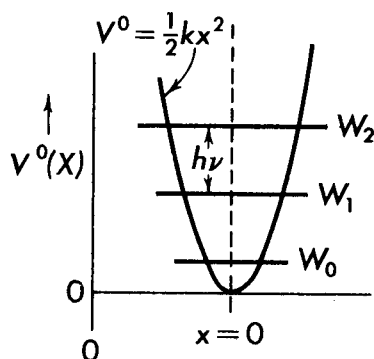
ductors C causing, therefore, a time-varying electric field⁹ along the x -axis,

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

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

⁹ 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 by¹⁰

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

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

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

¹⁰ 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, ψ_k^0 .) As before, if $\omega_{mk} \neq \omega_0$ the “final state” ψ_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 ψ_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 ψ_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 shown¹¹ that

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

¹¹ 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 .

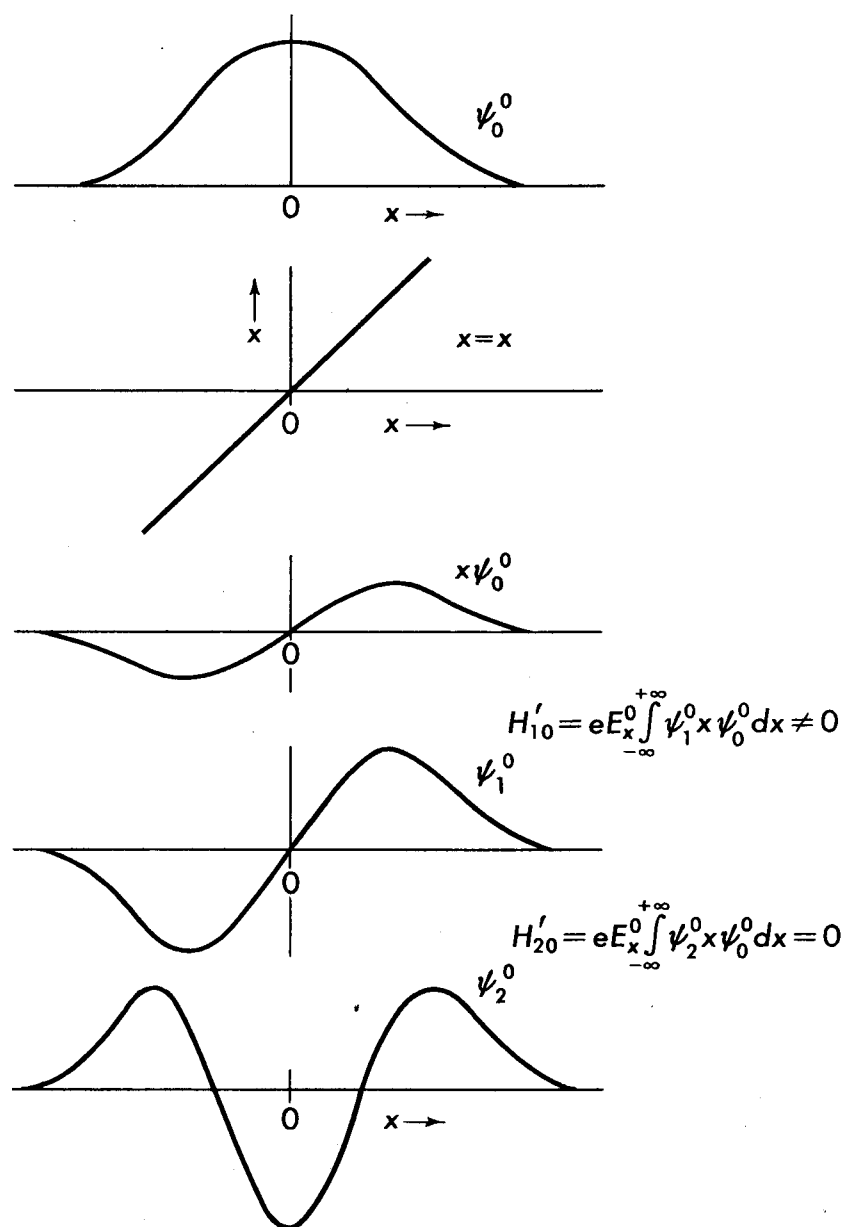


Fig. 10.6. Electric dipole transitions of the harmonic oscillator.

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 exactly¹² 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, Ψ_m and Ψ_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 ψ '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,¹³ 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.

¹² 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.

¹³ 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 μ . (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,¹⁴

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

where θ is the angle between the direction of μ 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.¹⁵ 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

¹⁴ See Section 6.1.

¹⁵ A classical model of this case would be a *uniform current loop* of magnetic moment μ . 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

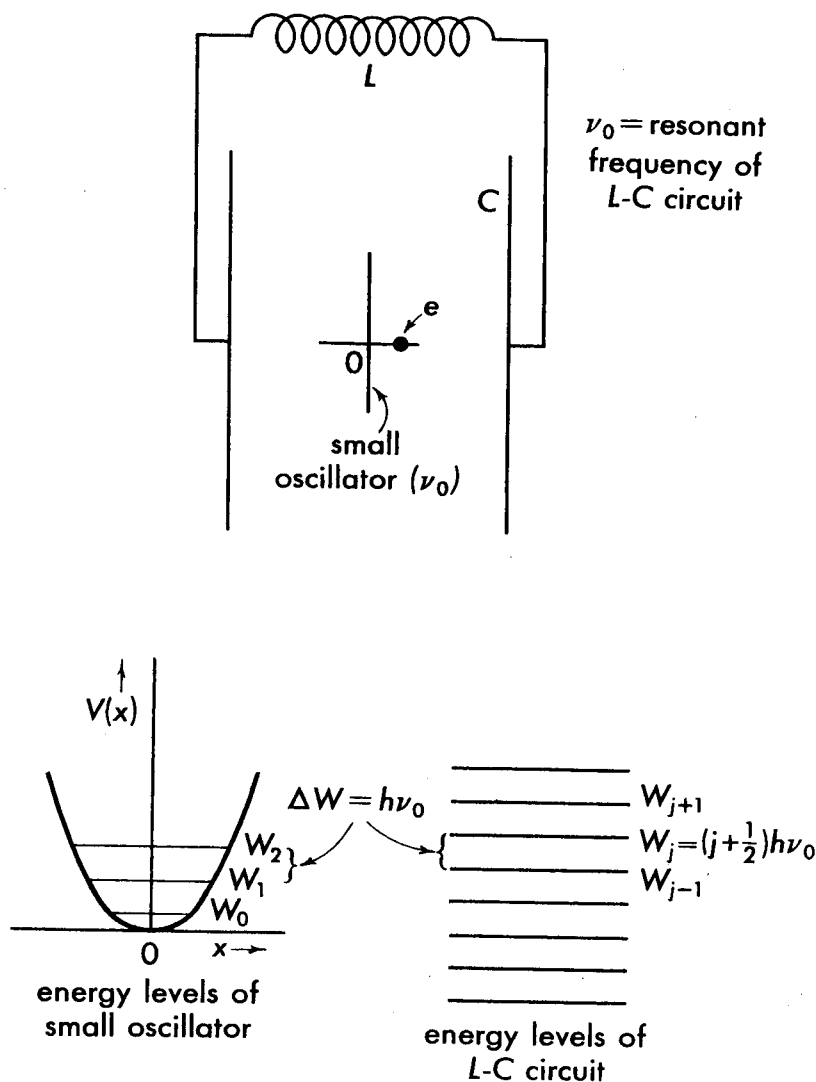


Fig. 10.7. The coupling of an atomic oscillator and a macroscopic oscillator by means of the electric field.

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 ν_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.¹⁶ 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.

¹⁶ A system of this type (called a “Maser”), using excited 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.¹⁷ 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 state¹⁸ ($n = 0$) 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 ψ_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

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

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

¹⁸ For the HCl spectrum of Figure 3.6, the first excited state is 2880 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 ~ 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.