where

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

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

$$\psi_2 = \psi_2^0 + a_0\,\psi_0^0 + a_1\,\psi_1^0 + (0)\,\psi_2^0 + a_3\,\psi_3^0 + \cdots \qquad [10\text{–}42$$

Each of the a_j's is given by [7–13],

$$a_j = -\Big[\int_{-\infty}^{+\infty} \psi_j^{0*} f(x)\,\psi_2^0\,dx\Big] \Big/ \Big[W_j^0 - W_2^0\Big] \qquad [10\text{–}42a$$

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]).

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

We will obtain a non-zero result.[19] 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]

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

is also satisfied. ψ_2 and ψ_0 are the *true* wave functions belonging to the final state and the initial state respectively. *Neither* are exact harmonic oscillator eigenfunctions.

Since ψ_0 is the lowest state, however, it will be *nearly* the pure state,

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

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 ψ_1^0 and ψ_0^0. Thus,

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

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[19] A small amount of Ψ_1^0 present in Ψ_0 (the ground-state wave function) *also* contributes the $n = 0 \rightarrow n = 2$ transition. See Problem 10.11.

[20] 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 ν_0.

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

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

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

$$\psi_1^0 = [(1/2)(\sqrt{a/\pi})]^{\frac{1}{2}}\, (2\sqrt{a}\, x)\, e^{-ax^2/2},$$
$$\psi_2^0 = [(1/8)(\sqrt{a/\pi})]^{\frac{1}{2}}\, (4ax^2 - 2)\, e^{-ax^2/2} \qquad [10\text{–}47$$

Making use of the definite integral,

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

we have, using [10–40],

$$W_2 = W_2^0 + (49\, c)/(4a^2) \qquad [10\text{–}49$$

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 ψ_1^0 present in ψ_2,

$$a_1 = -(3b)/(a)^{3/2}\, (h\nu_0) \qquad [10\text{–}50$$

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

$$W_2 - W_0 = 2h\, \nu_0 + (49\, c)/(4a^2) \qquad [10\text{–}51$$

(since $W_2^0 = (5/2)\, h\nu_0$ and $W_0 \simeq W_0^0 = h\nu_0$) 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[21] gives the experimental value of the $n = 2$ energy level as 5668 cm^{-1} which is 1.8 per cent lower than twice the main resonance at 2886 cm^{-1}. If we assume that the latter value (converted to ergs and divided by h) is the characteristic frequency ν_0 of the ideal harmonic oscillator, we can use [10–51] to obtain the value of the constant c. Pauling and Wilson[22] 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,

$$v(t) = a_1 \cos (2\pi/T)\, t + a_2 \cos 2(2\pi/T)\, t + a_3 \cos 3(2\pi/T)\, t + \cdots \qquad [10\text{–}52$$

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,

$$F(t) = F_x^0 \cos 2(2\pi/T)\, t \qquad [10\text{–}53$$

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,

$$\text{work} = \int_0^T F(t)\, v(t)\, dt \qquad [10\text{–}54$$

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,

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

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

[22] 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 $a_2 \neq 0$*.[23] 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 vibraton 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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[23] Note: $1/T$ will in general differ slightly from ν_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.[24]

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,?"[25] 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 nonmathematical 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.

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[24] D. Bohm, *Quantum Theory* (1951, Prentice-Hall, Inc., New York): p. 583.

[25] 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

$$(H^0 + H')\Psi = -(\hbar/i)\,\partial\Psi/\partial t \qquad [10\text{–}5$$

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

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

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

$$\Psi(x, t_0) = \sum_n a_n(t_0)\,\Psi_n^0(x, t_0) \qquad [5\text{–}9$$

where

$$a_n(t_0) = \int \Psi_n^0(x, t_0)\,\Psi(x, t_0)\,dx \qquad [5\text{–}12$$

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,

$$\Psi(x, t) = \sum_n a_n(t)\,\Psi_n^0(x, t) \qquad [10\text{–}9$$

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

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

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 Ψ_m^{0*}, and performing the operation $\int d\tau$ on each term, [10–10] becomes the set of equations,

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

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

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

$$H = H^0 + \lambda H' \qquad [10\text{–}13$$

and

$$a_m(t) = a_m^0 + \lambda a_m' \qquad [10\text{–}14$$

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

$$-(\hbar/i)\, da_m'/dt = \sum_n a_n^0 \int \Psi_m^{0*} H' \Psi_n^0 \, d\tau, \qquad m = 1, 2, 3, \cdots \qquad [10\text{–}16$$

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

$$a_m(t) = -\frac{H_{mk}'}{\hbar} \frac{(e^{i\omega_{mk}t} - 1)}{\omega_{mk}} \qquad [10\text{–}18$$

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

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

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

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

and

$$H_{mk}' \equiv \int \psi_m^{0*} \mathrm{A}(x) \psi_k^0 \, dx$$

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 5×10^{-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 $2.8 \times 10^{+16}$ 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 ν_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 3.56×10^{-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.

(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 3×10^{-8} cm)?] [Note: NH_3 has a mode of vibration at about 3×10^{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 20×10^{-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 Ψ_m and Ψ_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 Ψ_1 and Ψ_2, one should expect radiation to occur.

(c) What would one expect if the system were in a superposition of Ψ_1 and Ψ_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 ν_0 be given by $h\nu_0 = 2886/(5 \times 10^{15})$ erg and let m, the reduced mass, be 1.6×10^{-24} gm.)

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

(a) Calculate an expression giving the correction to the energy of the $n = 0$ state.

(b) Calculate an expression for the amplitude $a_1^{(0)}$ of the $n = 1$ state which is "mixed" into ψ_0 by the perturbation above.

(c) Calculate the contribution to the absorption line located near $2h\nu_0$ of the term $a_1^{(0)}\psi_1^0$, present in ψ_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 ψ_1^0 present in the first-order wave function ψ_2, for which $n = 2$.)

Proplem 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,

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

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?