CHAPTER 10

THE ADIABATIC APPROXIMATION

10.1 THE ADIABATIC THEOREM

10.1.1 Adiabatic Processes

Imagine a perfect pendulum, with no friction or air resistance, oscillating back and forth in a vertical plane. If I grab the support and shake it in a jerky manner, the bob will swing around in a wild chaotic fashion. But if I *very gently and steadily* move the support (Figure 10.1), the pendulum will continue to swing in a nice, smooth way, in the same plane (or one parallel to it) with the same amplitude. This *gradual change in the external conditions* characterizes an **adiabatic** process. Notice that there are two characteristic times involved: T_i, the "internal" time, representing the motion of the system itself (in this case the period of the pendulum's oscillations), and T_e, the "external" time, over which the parameters of the system change appreciably (if the pendulum were mounted on an oscillating platform, for example, T_e would be the period of the *platform's* motion). An adiabatic process is one for which $T_e \gg T_i$.[1]

The basic strategy for analyzing an adiabatic process is first to solve the problem with the external parameters held *fixed*, and only at the *end* of the calculation allow them to change with time. For example, the classical period of a pendulum of (constant) length L is $2\pi\sqrt{L/g}$; if the length is now gradually *changing*, the

[1] For an interesting discussion of classical adiabatic processes, see Frank S. Crawford, *Am. J. Phys.* **58**, 337 (1990).

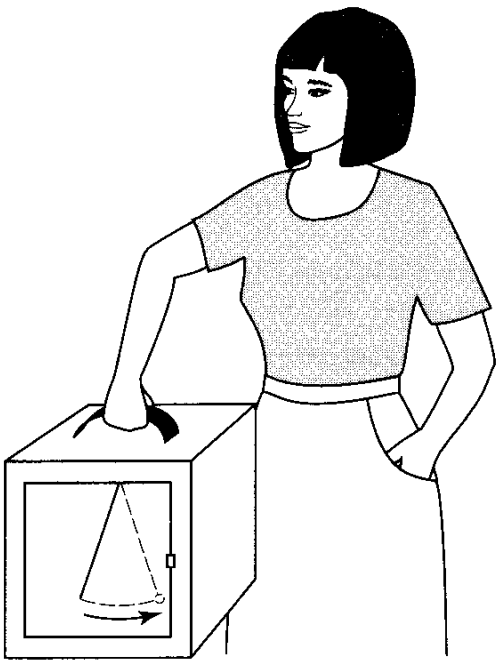

Figure 10.1: Adiabatic motion: If the case is transported very gradually, the pendulum inside keeps swinging with the same amplitude, in a plane parallel to the original one.

period will presumably be $2\pi\sqrt{L(t)/g}$. When you stop to think about it, we actually *use* the adiabatic approximation (implicitly) all the time without noticing it. A case in point is our discussion of the hydrogen molecule ion (Section 7.3). We began by assuming that the nuclei were *at rest*, a fixed distance R apart, and we solved for the motion of the electron. Once we had found the ground state energy of the system as a function of R, we located the equilibrium separation and from the curvature of the graph we obtained the frequency of vibration of the nuclei (Problem 7.10). In molecular physics this technique (beginning with nuclei at rest, calculating electronic wave functions, and using these to obtain information about the positions and—relatively sluggish—motion of the nuclei) is known as the **Born-Oppenheimer approximation**.

In quantum mechanics, the essential content of the **adiabatic approximation** can be cast in the form of a theorem. Suppose that the Hamiltonian changes *gradually* from some initial form H^i to some final form H^f (Figure 10.2). The **adiabatic theorem** states that if the particle was initially in the nth eigenstate of H^i, it will be

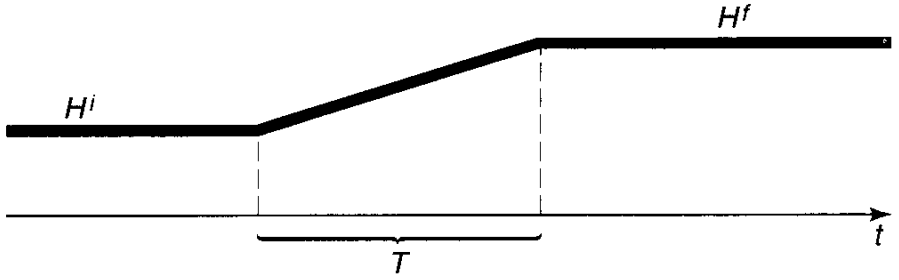

Figure 10.2: A model for adiabatic change in the Hamiltonian, from H^i to H^f.

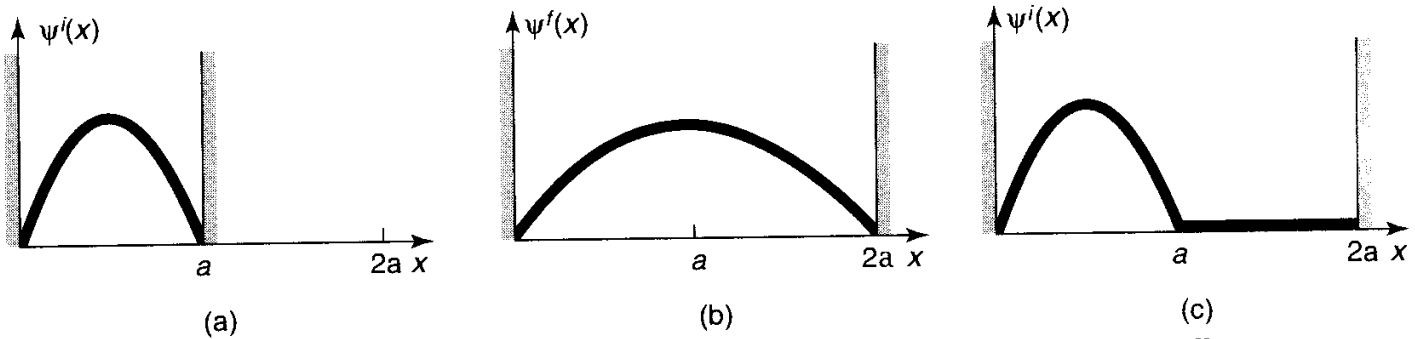

Figure 10.3: (a) Particle starts out in the ground state of the infinite square well. (b) If the wall moves *slowly*, the particle remains in the ground state. (c) If the wall moves *rapidly*, the particle is left (momentarily) in its initial state.

carried (under the Schrödinger equation) into the nth eigenstate of H^f. (I assume that the spectrum is discrete and nondegenerate throughout the transition from H^i to H^f, so there is no ambiguity about the ordering of the states; these conditions can be relaxed, given a suitable procedure for "tracking" the eigenfunctions, but I'm not going to pursue that here.)

For example, suppose we prepare a particle in the ground state of the infinite square well (Figure 10.3a):

$$\psi^i(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi}{a}x\right). \qquad [10.1]$$

If we now gradually move the right wall out to $2a$, the adiabatic theorem says that the particle will end up in the ground state of the expanded well (Figure 10.3b):

$$\psi^f(x) = \sqrt{\frac{1}{a}} \sin\left(\frac{\pi}{2a}x\right) \qquad [10.2]$$

(apart, perhaps, from a phase factor). Notice that we're not talking about a *small* change in the Hamiltonian (as in perturbation theory)—this one is a *huge* change. All we require is that it happen *slowly*. By contrast, if the well expands *suddenly*, the resulting state is still $\psi^i(x)$ (Figure 10.3c), which is a complicated linear combination of eigenstates of the new Hamiltonian (Problem 3.48).

***Problem 10.1** The case of an infinite square well whose right wall expands at a *constant* velocity (v) can be solved *exactly*.[2] A complete set of solutions is

$$\Phi_n(x,t) \equiv \sqrt{\frac{2}{w}} \sin\left(\frac{n\pi}{w}x\right) e^{i(mvx^2 - 2E_n^i at)/2\hbar w}, \qquad [10.3]$$

where $w(t) \equiv a + vt$ is the width of the well and $E_n^i \equiv n^2\pi^2\hbar^2/2ma^2$ is the nth allowed

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[2] S. W. Doescher and M. H. Rice, *Am. J. Phys.* **37**, 1246 (1969).

10.1.2 Proof of the Adiabatic Theorem

The adiabatic theorem is simple to state, and it *sounds* plausible, but it is not easy to prove.[3] Suppose the time-dependent part of the Hamiltonian can be written in the form[4]

$$H'(t) = Vf(t), \qquad [10.7]$$

where $f(t)$ is a function that starts out zero (at $t = 0$) and increases to 1 (at $t = T$), Figure 10.4. Assume that the particle starts out in the n^{th} eigenstate of the original Hamiltonian:

$$\Psi(0) = \psi_n^i \qquad [10.8]$$

and evolves into some state $\Psi(t)$. Our problem is to show that if the function $f(t)$ rises *very gradually*, then the probability that the particle, at time T, is in the nth eigenstate of the *final* Hamiltonian (ψ_n^f) is 1. More precisely, we must demonstrate that

$$|\langle \Psi(T)|\psi_m^f\rangle|^2 = \begin{cases} 1, & \text{if } m = n, \\ 0, & \text{if } m \neq n. \end{cases} \qquad [10.9]$$

(Of course, if the first of these is true, the second *has* to be, and vice versa. But it is not clear at this stage which condition will be easier to prove.)

Assume for the moment that V is *small*, so we can use first-order time-independent perturbation theory to determine ψ_m^f. From Equation 6.12,

$$\psi_m^f \cong \psi_m + \sum_{k \neq m} \frac{V_{km}}{E_m - E_k} \psi_k, \qquad [10.10]$$

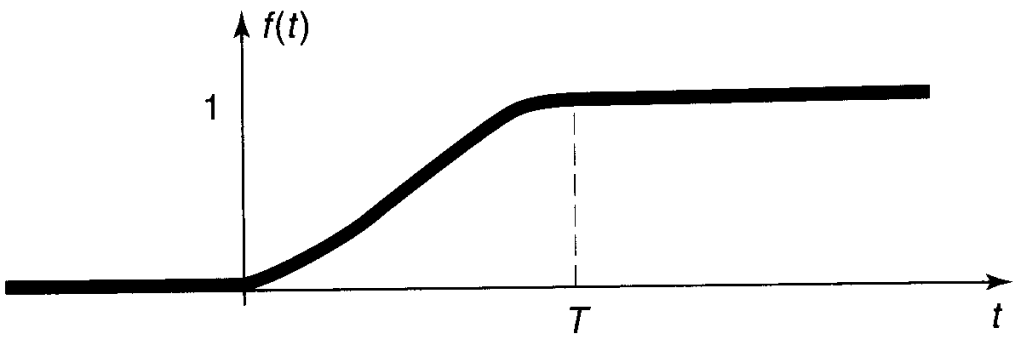

Figure 10.4: The function $f(t)$, in Equation 10.7.

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[3]The adiabatic theorem is usually attributed to Ehrenfest, who studied adiabatic processes in early versions of the quantum theory. The first proof in modern quantum mechanics was given by Born and Fock, *Zeit. f. Physik* **51**, 165 (1928). Other proofs will be found in Messiah, *Quantum Mechanics* (New York: John Wiley & Sons, 1962), Vol. II, Chapter XVII, Section 12, and J-T. Hwang and Philip Pechukas, *J. Chem. Phys.* **67**, 4640 (1977). The argument given here is suggested by Gasiorowicz, *Quantum Physics* (New York: John Wiley & Sons, 1974), Chapter 22, Problem 6.

[4]The assumption that H' is the *product* of an operator (V) and a (real) function of t is not necessary for the theorem itself, but it does make the proof less cumbersome. In Section 10.1.3 we will encounter a case in which the different matrix elements of H' have *different* (complex) time dependences. As long as the adiabatic approximation (in the form of Equation 10.15) holds for *each* of them, the adiabatic theorem itself is valid.

where

$$V_{km} \equiv \langle \psi_k | V | \psi_m \rangle. \tag{10.11}$$

(To simplify the notation, I'll drop the superscript i on eigenfunctions and eigenvalues of the initial Hamiltonian; these are the "unperturbed" states for the problem.)

Meanwhile, we use first-order time-*dependent* perturbation theory to determine $\Psi(T)$. From Equation 9.81,

$$\Psi(t) = \sum_l c_l(t) \psi_l e^{-iE_l t/\hbar}, \tag{10.12}$$

where (Equation 9.84)

$$c_n(t) \cong 1 - \frac{i}{\hbar} V_{nn} \int_0^t f(t')\, dt' \tag{10.13}$$

and (Equation 9.85)

$$c_l(t) \cong -\frac{i}{\hbar} V_{ln} \int_0^t f(t') e^{i(E_l - E_n)t'/\hbar}\, dt', \quad l \neq n. \tag{10.14}$$

This last integral can be evaluated using integration by parts. Note that

$$e^{i(E_l - E_n)t'/\hbar} = \frac{-i\hbar}{E_l - E_n} \frac{d}{dt'} \left[e^{i(E_l - E_n)t'/\hbar} \right],$$

so

$$c_l(t) \cong -\frac{V_{ln}}{E_l - E_n} \int_0^t f(t') \frac{d}{dt'} \left[e^{i(E_l - E_n)t'/\hbar} \right] dt'$$

$$= -\frac{V_{ln}}{E_l - E_n} \left\{ f(t) e^{i(E_l - E_n)t/\hbar} - \int_0^t \frac{df}{dt'} e^{i(E_l - E_n)t'/\hbar}\, dt' \right\}.$$

[I dropped the lower limit in the first term, because $f(0) = 0$.] Now comes the adiabatic approximation: We want $f(t)$ to be a *very gradual* function, so that df/dt is extremely small. Specifically, we assume that

$$\frac{df}{dt} \ll \frac{|E_l - E_n|}{\hbar} f; \tag{10.15}$$

then the last term makes a negligible contribution to $c_l(t)$, and we conclude that

$$\Psi(T) \cong \left[\left(1 - i \frac{V_{nn} A}{\hbar} \right) \psi_n - \sum_{l \neq n} \frac{V_{ln}}{E_l - E_n} \psi_l \right] e^{-iE_n T/\hbar}, \tag{10.16}$$

where A is the area under the graph of $f(t)$, from 0 to T.

Putting together Equations 10.10 and 10.16, and exploiting the orthonormality of the initial eigenfunctions, we find that

$$\langle \Psi(T)|\psi_n^f\rangle = \left[1 + i\frac{V_{nn}A}{\hbar} + \sum_{k\neq n}\frac{|V_{kn}|^2}{(E_n - E_k)^2}\right] e^{iE_nT/\hbar}, \qquad [10.17]$$

while, for $m \neq n$,

$$\langle \Psi(T)|\psi_m^f\rangle = \left\{\left[1 + i\frac{V_{nn}A}{\hbar}\right]\frac{V_{nm}}{E_m - E_n} - \frac{V_{nm}}{E_m - E_n} + \sum_{n\neq k\neq m}\frac{V_{nk}V_{km}}{(E_n - E_k)(E_m - E_k)}\right\} e^{iE_nT/\hbar}$$

$$= \left[\frac{iAV_{nn}V_{nm}}{\hbar(E_m - E_n)} + \sum_{n\neq k\neq m}\frac{V_{nk}V_{km}}{(E_n - E_k)(E_m - E_k)}\right] e^{iE_nT/\hbar}. \qquad [10.18]$$

But wait: These wave functions were only accurate to *first* order in V, so the *second*-order terms in Equations 10.17 and 10.18 are spurious (we have already thrown away quantities of comparable size). To *first* order, we have

$$\langle \Psi(T)|\psi_m^f\rangle = \begin{cases} \left[1 + i\frac{V_{nn}A}{\hbar}\right] e^{iE_nT/\hbar}, & m = n, \\ 0 & m \neq n. \end{cases} \qquad [10.19]$$

It follows that

$$|\langle \Psi(T)|\psi_n^f\rangle|^2 = 1, \qquad [10.20]$$

while (for $m \neq n$)

$$|\langle \Psi(T)|\psi_m^f\rangle|^2 = 0. \qquad [10.21]$$

Ostensibly, *either* of these would suffice to establish the desired result (Equation 10.9). However, Equation 10.20 is only accurate to *first* order (in V), whereas Equation 10.21 is accurate to *second* order (and for that matter to *third* order as well).[5] In truth, Equation 10.20 tells us *nothing* (it would be valid also for a *nonadiabatic* transformation); the *crucial* point is the cancellation of the first-order terms in Equation 10.18, for this tells us that there will be no transitions to other states.[6]

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[5] See Problem 9.15 for a discussion of the analogous situation in ordinary perturbation theory.

[6] In this context the word "*transition*" means from an eigenstate ψ_n^i of the *initial* Hamiltonian (H^i) to a different eigenstate ψ_m^f of the *final* Hamiltonian (H^f). The adiabatic theorem says that if the Hamiltonian changes *gradually* from H^i to H^f, there will be *no* such transitions. By contrast, in the previous chapter we were always dealing with eigenstates of the *same* (unperturbed) Hamiltonian. At the end of the process the perturbation was (explicitly or implicitly) turned off, and a "transition" meant from one eigenstate of the unperturbed Hamiltonian to another eigenstate of the unperturbed Hamiltonian. The transition amplitudes were of *first* order in H' (Equations 9.17 and 9.85) and the transition probabilities of *second* order (for example, Equations 9.28, 9.86, and 9.87). The essence of the adiabatic theorem (as we shall see in the next paragraph) is that the transition amplitudes are only *second* order, and the transition probabilities *fourth* order in the (small) perturbation.

This shows that if the change in the Hamiltonian is both adiabatic *and* very small (so that first-order perturbation theory can be applied), then there will be no transitions. But what if the change, though gradual, is *not* small? In that case we chop the interval T into N subintervals, so that the change in the Hamiltonian during a single subinterval (ΔV) is of order V/N; if N it large, then ΔV is small, and we can apply the previous argument to each subinterval. If the transition amplitude (Equation 10.18) were *first* order in the perturbation, then the *total* transition amplitude would go like

$$N\left(\frac{V}{N}\right) \to V \qquad [10.22]$$

(N steps, each making a contribution proportional to ΔV). The net result would be of order V, and if V is large, so too would be the transition amplitude. But in *fact* the transition amplitude is *second* order, so the total goes like

$$N\left(\frac{V}{N}\right)^2 \to \frac{V^2}{N} \qquad [10.23]$$

In the limit as $N \to \infty$, the transition amplitude goes to zero, *regardless* of the size of V. QED

Problem 10.2 In the beginning of this chapter, I characterized an adiabatic process informally as one for which $T_e \gg T_i$. How is this related to the precise condition (Equation 10.15) required in the proof (in other words, what are T_e and T_i here)?

10.1.3 An Example

Imagine an electron (charge $-e$, mass m) at rest at the origin, in the presence of a magnetic field whose *magnitude* (B_0) is constant but whose *direction* sweeps out a cone, of opening angle α, at constant angular velocity ω (Figure 10.5):

$$\mathbf{B}(t) = B_0[\sin\alpha\cos(\omega t)\hat{\imath} + \sin\alpha\sin(\omega t)\hat{\jmath} + \cos\alpha\hat{k}. \qquad [10.24]$$

The Hamiltonian (Equation 4.158) is

$$H(t) = \frac{e}{m}\mathbf{B}\cdot\mathbf{S} = \frac{e\hbar B_0}{2m}[\sin\alpha\cos(\omega t)\sigma_x + \sin\alpha\sin(\omega t)\sigma_y + \cos\alpha\sigma_z]$$

$$= -\frac{\hbar\omega_1}{2}\begin{pmatrix} \cos\alpha & e^{-i\omega t}\sin\alpha \\ e^{i\omega t}\sin\alpha & -\cos\alpha \end{pmatrix}, \qquad [10.25]$$

where

$$\omega_1 \equiv -\frac{eB_0}{m}. \qquad [10.26]$$

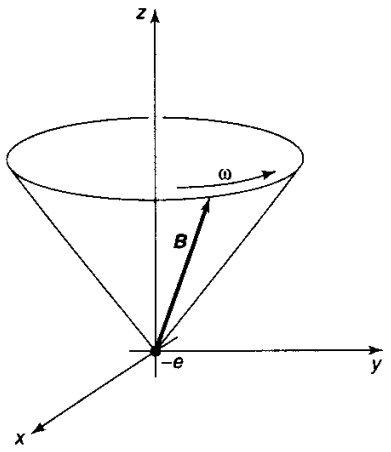

Figure 10.5: Magnetic field sweeps around on a cone, at angular velocity ω, Equation 10.24.

The normalized eigenspinors of $H(t)$ are

$$\chi_+(t) = \begin{pmatrix} \cos(\alpha/2) \\ e^{i\omega t}\sin(\alpha/2) \end{pmatrix} \quad [10.27]$$

and

$$\chi_-(t) = \begin{pmatrix} \sin(\alpha/2) \\ -e^{i\omega t}\cos(\alpha/2) \end{pmatrix}; \quad [10.28]$$

they represent spin up and spin down, respectively, *along the instantaneous direction of* $\mathbf{B}(t)$ (see Problem 4.31). The corresponding eigenvalues are

$$E_\pm = \mp\frac{\hbar\omega_1}{2}. \quad [10.29]$$

Suppose the electron starts out with spin up, along $\mathbf{B}(0)$:

$$\chi(0) = \begin{pmatrix} \cos(\alpha/2) \\ \sin(\alpha/2) \end{pmatrix}. \quad [10.30]$$

The exact solution to the time-dependent Schrödinger equation is (Problem 10.3)

$$\chi(t) = \begin{pmatrix} \left[\cos(\lambda t/2) + i\frac{(\omega_1+\omega)}{\lambda}\sin(\lambda t/2)\right]\cos(\alpha/2)e^{-i\omega t/2} \\ \left[\cos(\lambda t/2) + i\frac{(\omega_1-\omega)}{\lambda}\sin(\lambda t/2)\right]\sin(\alpha/2)e^{i\omega t/2} \end{pmatrix}, \quad [10.31]$$

where

$$\lambda \equiv \sqrt{\omega^2 + \omega_1^2 + 2\omega\omega_1\cos\alpha}, \quad [10.32]$$

or, writing it as a linear combination of χ_+ and χ_-,

$$\chi(t) = \left[\cos\left(\frac{\lambda t}{2}\right) + i\frac{(\omega_1 + \omega\cos\alpha)}{\lambda}\sin\left(\frac{\lambda t}{2}\right)\right]e^{-i\omega t/2}\chi_+(t)$$
$$+ i\left[\frac{\omega}{\lambda}\sin\alpha\sin\left(\frac{\lambda t}{2}\right)\right]e^{-i\omega t/2}\chi_-(t). \quad [10.33]$$

Evidently the (exact) probability of a transition to spin down (along the current direction of **B**) is

$$|\langle\chi(t)|\chi_-(t)\rangle|^2 = \left[\frac{\omega}{\lambda}\sin\alpha\sin\left(\frac{\lambda t}{2}\right)\right]^2. \qquad [10.34]$$

The adiabatic theorem says that this transition probability should vanish in the limit $T_e \gg T_i$, where T_e is the characteristic time for changes in the Hamiltonian (in this case, $1/\omega$) and T_i is the characteristic time for changes in the wave function [in this case, $\hbar/(E_+ - E_-) = 1/\omega_1$]. Thus the adiabatic approximation means $\omega \ll \omega_1$: The field rotates slowly, in comparison with the phase of the (unperturbed) wave functions. In the adiabatic regime $\lambda \cong \omega_1$, and therefore

$$|\langle\chi(t)|\chi_-(t)\rangle|^2 \cong \left[\frac{\omega}{\omega_1}\sin\alpha\sin\left(\frac{\lambda t}{2}\right)\right]^2 \to 0, \qquad [10.35]$$

as advertised. The magnetic field leads the electron around by its nose, with the spin always pointing in the direction of **B**. By contrast, if $\omega \gg \omega_1$ then $\lambda \cong \omega$, and the system bounces back and forth between spin up and spin down (Figure 10.6).

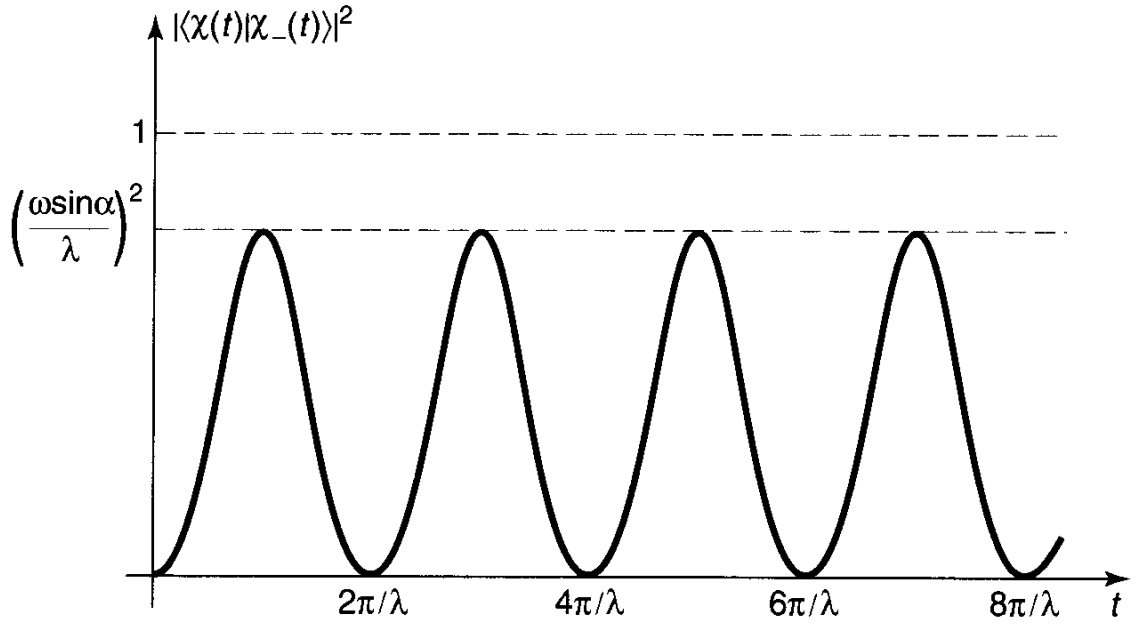

Figure 10.6: Plot of the transition probability, Equation 10.34, in the *nonadiabatic* regime ($\omega \ll \omega_1$).

****Problem 10.3** Check that Equation 10.31 satisfies the time-dependent Schrödinger equation for the Hamiltonian (Equation 10.25). *Note*: This is the same as Problem 9.19(b), except that now the electron starts out with spin up along **B**, whereas in Equation 9.90 it started out with spin up along z. Also confirm Equation 10.33, and show that the sum of the squares of the coefficients is 1, as required for proper normalization.
