

# Transitions Between Energy States

We have seen that the Schrödinger equation leads to energy quantization for bound systems. The existence of these energy levels is determined experimentally by observation of the energy emitted or absorbed when the system makes a transition from one level to another. In this section, we will consider some aspects of these transitions in one dimension. The results will be readily applicable to more complicated systems.

In classical physics, a charged particle radiates when it is accelerated. If the charge oscillates, the frequency of the radiation emitted equals the frequency of oscillation. A stationary charge distribution does not radiate.

Consider a particle with charge  $q$  in a quantum state  $n$  described by the wave function

$$\Psi_n(x,t) = \psi_n(x)e^{-iE_n t/\hbar}$$

where  $E_n$  is the energy and  $\psi_n(x)$  is a solution of the time-independent Schrödinger equation for some potential energy  $V(x)$ . The probability of finding the charge in  $dx$  is  $\Psi_n^* \Psi_n dx$ . If we make many measurements on identical systems (i.e., particles with the same wave function), the average amount of charge found in  $dx$  will be  $q\Psi_n^* \Psi_n dx$ . We therefore identify  $q\Psi_n^* \Psi_n$  with the *charge density*  $\rho$ . As we have pointed out, the probability density is independent of time if the wave function contains a single energy, so the charge density for this state is also independent of time:<sup>12</sup>

$$\rho_n = q\Psi_n^*(x,t)\Psi_n(x,t) = q\psi_n^*(x)\psi_n(x) = q\psi_n^*\psi_n$$

We should therefore expect that this stationary charge distribution would not radiate. (This argument, in the case of the hydrogen atom, is the quantum-mechanical explanation of Bohr's postulate of nonradiating orbits.) However, we do observe that systems make transitions from one energy state to another with the emission or absorption of radiation. The cause of the transition is the interaction of the electromagnetic field with the charged particle. A detailed treatment of this interaction is necessary in order to obtain rates of emission and absorption. Such a treatment is too difficult for us to consider in this text; however, we can learn a great deal from a combined classical/quantum argument, which goes as follows.

Let us write the wave function for a particle that is making a transition from state  $n$  to state  $m$  as a mixture of the two states  $\Psi_n$  and  $\Psi_m$ :

$$\Psi_{nm}(x,t) = a\Psi_n(x,t) + b\Psi_m(x,t) \qquad \mathbf{6-52a}$$

We need not be concerned with the numbers  $a$  and  $b$ . We want only to show that if neither  $a$  nor  $b$  is zero, the probability density and charge density oscillate with the angular frequency  $\omega_{nm}$ , given by the Bohr relation  $hf = \hbar\omega_{nm} = E_n - E_m$ , or

$$\omega_{nm} = \frac{E_n - E_m}{\hbar} \quad 6-52b$$

To simplify the notation, we will assume that the time-independent functions  $\psi_n(x)$  and  $\psi_m(x)$  are real. The probability density for the wave function  $\Psi_{nm}(x, t)$  is then

$$\Psi_{nm}^* \Psi_{nm} = a^2 \Psi_n^* \Psi_n + b^2 \Psi_m^* \Psi_m + ab (\Psi_n^* \Psi_m + \Psi_m^* \Psi_n) \quad 6-52c$$

The first two terms are independent of time. The third term in Equation 6-52c contains the quantities

$$\begin{aligned} \Psi_n^*(x, t) \Psi_m(x, t) &= \psi_n^* e^{iE_n t/\hbar} \psi_m e^{-iE_m t/\hbar} \\ &= \psi_n^* \psi_m e^{i\omega_{nm} t} \end{aligned}$$

and

$$\begin{aligned} \Psi_m^*(x, t) \Psi_n(x, t) &= \psi_m^* e^{iE_m t/\hbar} \psi_n e^{-iE_n t/\hbar} \\ &= \psi_m^* \psi_n e^{i\omega_{nm} t} \end{aligned}$$

where  $\omega_{nm}$  is the Bohr angular frequency given by Equation 6-52b. Adding these and using

$$e^{i\omega_{nm} t} + e^{-i\omega_{nm} t} = 2 \cos \omega_{nm} t$$

we see that the probability density is now time dependent and is given by

$$|\Psi_{nm}(x, t)|^2 = a^2 \psi_n^2 + b^2 \psi_m^2 + 2ab \psi_n \psi_m \cos \omega_{nm} t \quad 6-52d$$

Thus, the wave function consisting of a mixture of two energy states does lead to a charge distribution that oscillates with the Bohr frequency.

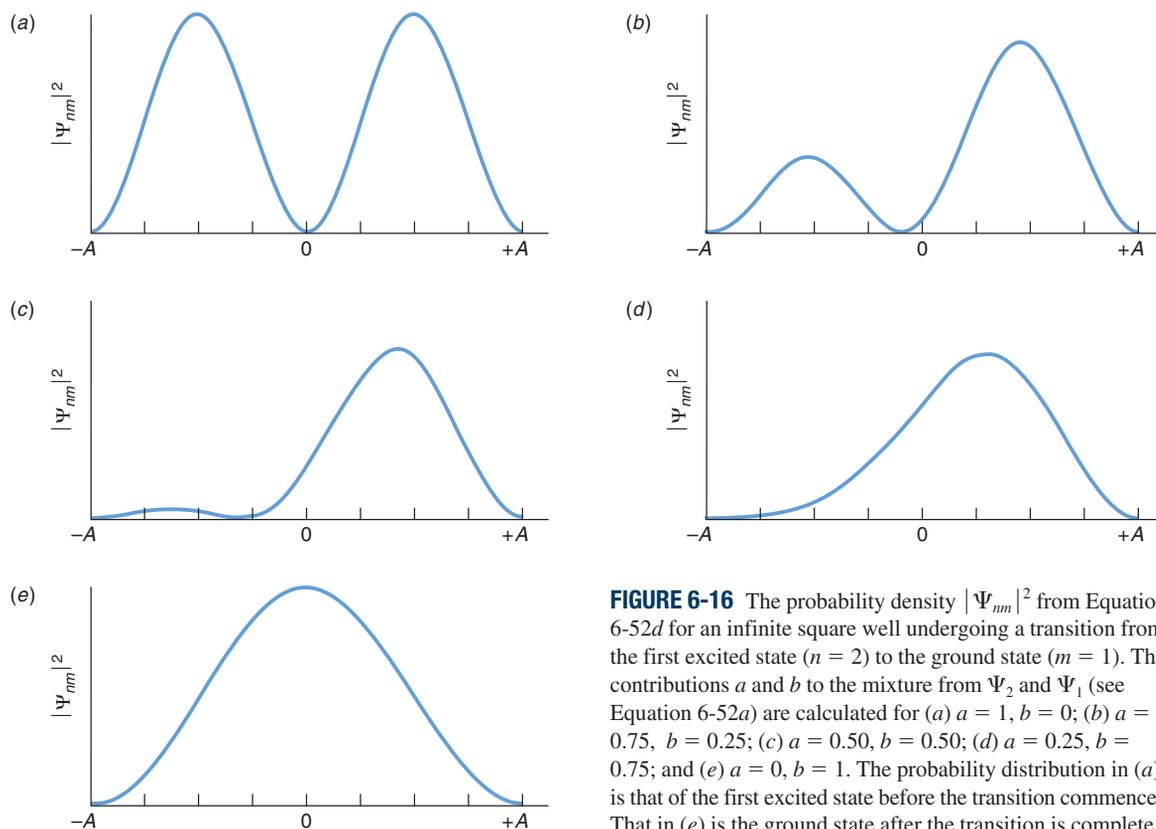
We can describe the radiation of the system somewhat loosely as follows. At some time, the system is in an excited state  $n$  described by Equation 6-52a with  $a = 1$  and  $b = 0$ . Because of an interaction of the system with the electromagnetic field (which we have not included in the Schrödinger equation),  $a$  decreases and  $b$  is no longer zero. At this time the charge density oscillates with angular frequency  $\omega_{nm}$ . The system does not, however, radiate energy continuously, as predicted by classical theory. Instead, the oscillating charge density implies a *probability* that a photon of energy  $\hbar\omega_{nm} = E_n - E_m$  will be emitted, after which the system will be in the state  $m$  with  $a = 0$ ,  $b = 1$ . The emission of an individual photon is a statistical process. Figure 6-16 illustrates how  $|\Psi_{nm}|^2$  changes during a transition from the first excited state to the ground state of an infinite square well.

## Electric Dipole Transitions

The most elementary classical radiation system is an oscillating electric dipole. The dipole moment  $qx$  for a particle with wave function  $\Psi$  has the expectation value

$$q\langle x \rangle = q \int \Psi^* x \Psi dx$$

It can be seen from the previous discussion that, if the wave function corresponds to a stationary state containing a single energy, the expectation value of the dipole moment will be independent of time. However, if  $\Psi$  is the mixture given by Equation 6-52a,  $q\langle x \rangle$  will have time-dependent terms that oscillate with the Bohr frequency. Using Equation 6-52d, we can write the dipole moment



**FIGURE 6-16** The probability density  $|\Psi_{nm}|^2$  from Equation 6-52d for an infinite square well undergoing a transition from the first excited state ( $n = 2$ ) to the ground state ( $m = 1$ ). The contributions  $a$  and  $b$  to the mixture from  $\Psi_2$  and  $\Psi_1$  (see Equation 6-52a) are calculated for (a)  $a = 1$ ,  $b = 0$ ; (b)  $a = 0.75$ ,  $b = 0.25$ ; (c)  $a = 0.50$ ,  $b = 0.50$ ; (d)  $a = 0.25$ ,  $b = 0.75$ ; and (e)  $a = 0$ ,  $b = 1$ . The probability distribution in (a) is that of the first excited state before the transition commences. That in (e) is the ground state after the transition is complete.

$$q\langle x \rangle = 2qab \cos \omega_{nm}t \int \psi_n x \psi_m dx + \text{stationary terms} \quad \mathbf{6-52e}$$

The integral in Equation 6-52e is called a *matrix element*. There are many cases for which this integral is zero. For example, if  $\psi_n$  and  $\psi_m$  are wave functions for the infinite square well, a direct calculation shows that the matrix element in Equation 6-45 is zero if  $n$  and  $m$  are both odd numbers or both even numbers. For these cases, electric dipole transitions are forbidden between these states. The absence of a transition between two states due to the fact that the matrix element is zero is usually described by a *selection rule*. For example, a selection rule for the infinite square well is that the quantum number  $n$  must change by 1, 3, 5, . . . (and not by 2, 4, 6, . . .). We will give other, more important examples of selection rules in the next section when we study the simple harmonic oscillator and in Chapter 7 when we consider transitions between stationary states of atoms. The transitions we have been discussing—those resulting from a perturbation of a charged system caused by interaction with the system's own electromagnetic field—are called spontaneous transitions. If a system (such as an atom) is in its ground state and exposed to external radiation of frequency  $\omega_{nm}$  corresponding to the Bohr frequency for a transition to an excited state, it can make such a transition by absorbing a photon from the external radiation. If such a system is in an excited state and exposed to external radiation of frequency corresponding to the Bohr frequency for a transition to a lower energy state, the system can be stimulated to make such a transition and emit a photon of exactly the same energy as those in the external radiation. Such stimulated emission, which occurs in masers and lasers, is important because the emitted photons are coherent and in phase with those stimulating the transition. Lasers will be discussed in more detail in Chapter 9.