

## 13.7 The Eigenfunctions of a Quantum Mechanical Operator Form a Complete Set

The eigenfunctions of a quantum mechanical operator have another very important property that is frequently used. The eigenfunctions of a quantum mechanical operator form a **complete set**. The idea of a complete set should be familiar to you from the three-dimensional Cartesian coordinate system. Because the three mutually perpendicular unit vectors **x**, **y**, and **z** form a complete set, any three-dimensional vector can be expressed as a linear combination of **x**, **y**, and **z**.

**Completeness** is defined similarly in function space. The eigenfunctions of any quantum mechanical vector form a complete set. This means that any well-behaved function,  $f(x)$  (that is, a wave function), can be expanded in the eigenfunctions of any of the quantum mechanical operators of interest to us defined in the same space,  $x$  in this case:

$$f(x) = \sum_{n=1}^{\infty} b_n \psi_n(x) \quad (13.32)$$

Equation (13.32) should look familiar to you because this is exactly the same formalism used in Fourier sine and cosine series. See the Math Supplement for a more detailed discussion of Fourier series.

To illustrate the usefulness of a complete set of functions, we expand a function,  $f(x)$  that is periodic over a length  $2b$ , in a linear combination of the orthogonal functions  $\sin(n\pi x/b)$  and  $\cos(n\pi x/b)$ . These functions form a complete set if all values of  $n$  are included. Expanding quantum mechanical wave functions in a set of functions is something that we will do often in later chapters, particularly in Chapter 27 in which we discuss computational chemistry. Because the sine and cosine functions form a complete set, the degree to which our approximation resembles the exact function depends only on how many terms we are willing to include in our sum. Because we are interested in knowing how good our approximation is, we start with a known function, approximate it by a sum, and evaluate how well we succeed.

We take the periodic function

$$f(x) = \left\{ 2\left(\frac{x}{b}\right)^2 - 1 \right\} e^{-x^2/2b^2} \quad \text{for } -1 \leq \frac{x}{b} < 1 \quad (13.33)$$

$$f(x) = f(x - 2) \quad \text{for all } x$$

and approximate it by a Fourier series, which is a linear combination of sine and cosine functions:

$$f(x) = d_0 + \sum_{n=1}^m \left[ c_n \sin\left(\frac{n\pi x}{b}\right) + d_n \cos\left(\frac{n\pi x}{b}\right) \right] \quad (13.34)$$

## 14.4 The Expectation Value

**POSTULATE 4:** If the system is in a state described by the wave function  $\Psi(x, t)$ , and the value of the observable  $a$  is measured once each on many identically prepared systems, the average value (also called the expectation value) of all of these measurements is given by

$$\langle a \rangle = \frac{\int_{-\infty}^{\infty} \Psi^*(x, t) \hat{A} \Psi(x, t) dx}{\int_{-\infty}^{\infty} \Psi^*(x, t) \Psi(x, t) dx} \quad (14.4)$$

For the special case in which  $\Psi(x, t)$  is normalized, the denominator in this expression has the value one. Wave functions are usually normalized and in Equations (14.5) through (14.8), this is assumed to be the case. This postulate requires some explanation. As we know, two cases apply with regard to  $\Psi(x, t)$ : it either is or is not an eigenfunction of the operator  $\hat{A}$ . These two cases need to be examined separately.

In the first case,  $\Psi(x, t)$  is a normalized eigenfunction of  $\hat{A}$ , for example,  $\phi_j(x, t)$ . Because  $\hat{A}\phi_j(x, t) = a_j\phi_j(x, t)$ ,

$$\begin{aligned} \langle a \rangle &= \int_{-\infty}^{\infty} \phi_j^*(x, t) \hat{A} \phi_j(x, t) dx = a_j \int_{-\infty}^{\infty} \phi_j^*(x, t) \phi_j(x, t) dx \\ &= a_j \end{aligned} \quad (14.5)$$

If  $\Psi(x, t)$  is  $\phi_j(x, t)$ , all measurements will give the same answer, namely,  $a_j$ .

Now consider the second case, in which  $\Psi(x, t)$  is not an eigenfunction of the operator  $\hat{A}$ . Because the eigenfunctions of  $\hat{A}$  form a complete set,  $\Psi(x, t)$  can be expanded in terms of these eigenfunctions:

$$\Psi(x, t) = \sum b_n \phi_n(x, t) \quad (14.6)$$

Because  $\Psi(x, t)$  is normalized,  $\sum_m b_m^* b_m = \sum_m |b_m|^2 = 1$ . The expression for  $\Psi(x, t)$  in Equation (14.6) can be inserted in Equation (14.4), giving

$$\begin{aligned} \langle a \rangle &= \int \Psi^*(x, t) \hat{A} \Psi(x, t) dx \\ &= \int \left[ \sum_{m=1}^{\infty} b_m^* \phi_m^*(x, t) \right] \left[ \sum_{n=1}^{\infty} a_n b_n \phi_n(x, t) \right] dx \\ &= \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} b_m^* b_n a_n \int \phi_m^*(x, t) \phi_n(x, t) dx \end{aligned} \quad (14.7)$$

This complicated expression can be greatly simplified. At this point, we make use of the property that the eigenfunctions of a quantum mechanical operator are orthogonal. Because the eigenfunctions of  $\hat{A}$  form an **orthonormal set**, the only terms in this double sum for which the integral is nonzero are the terms for which  $m = n$ . The integral has the value one for these terms, because the eigenfunctions of  $\hat{A}$  are normalized. Therefore,

$$\langle a \rangle = \sum_{m=1}^{\infty} a_m b_m^* b_m = \sum_{m=1}^{\infty} |b_m|^2 a_m \quad (14.8)$$

What are the  $b_m$ ? They are the **expansion coefficients** of the wave function in the complete set of the eigenfunctions of the operator  $\hat{A}$ . They are a measure of the extent to which the wave function “looks like” the  $m$ th eigenfunction of the operator  $\hat{A}$ . To illustrate this point, consider the case in which  $\Psi(x,t) = \Psi_n(x,t)$ . In this case, all of the  $b_m$  except the one value corresponding to  $m = n$  are zero and  $\langle a \rangle = a_n$ . So if  $\Psi(x,t)$  is one of the eigenfunctions of  $\hat{A}$ , only one of the  $b_m$  is nonzero and the average value is just the eigenvalue corresponding to that eigenfunction. If three of the  $b_m$  are nonzero,  $\langle a \rangle$  will be determined by the eigenvalues corresponding to those three eigenfunctions. However,  $\langle a \rangle$  is not simply an average of these three eigenvalues; instead, it is a **weighted average**. The weighting factor  $|b_m|^2$  is simply related to the contribution of each eigenfunction to the wave function  $\Psi(x,t)$ .

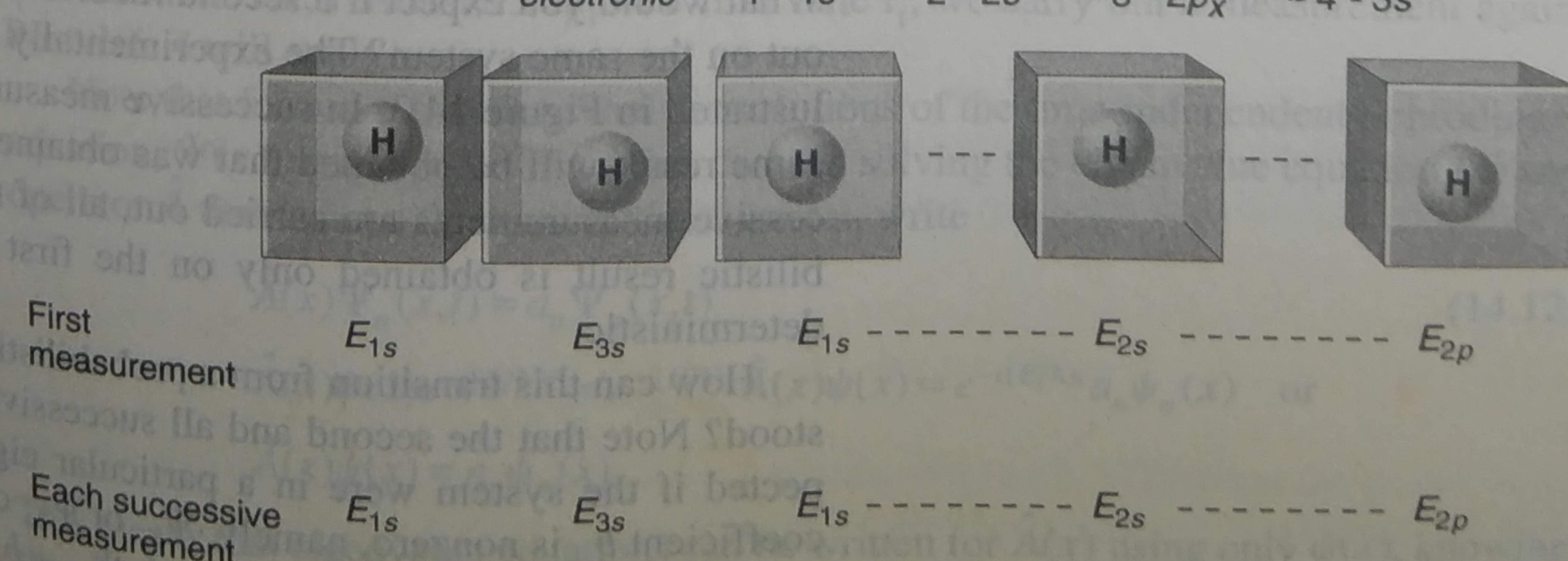
The fourth postulate states what will be measured in a large number of measurements, each carried out only once on a large number of identically prepared systems. What will be measured in each of these individual measurements? The third postulate says that the only possible result of a single measurement is one of the eigenvalues  $a_n$ . However, it does not tell us which of the  $a_n$  will be measured. The answer is that there is no way of knowing the outcome of an **individual measurement**, and that the outcomes from identically prepared systems are not the same. This is a sharp break with the predictability we have come to depend on in classical mechanics.

Consider a hypothetical example. Suppose that a single hydrogen atom could be isolated in a box and the electronic wave function prepared such that it is in a superposition of the ground state, in which the electron is in the  $1s$  orbital, and the excited states, in which the electron is in the  $2s$ ,  $2p_x$ , and  $3s$  orbitals. Assume that the wave function for this **superposition state** is

$$\Psi_{\text{electronic}} = b_1 \Psi_{1s} + b_2 \Psi_{2s} + b_3 \Psi_{2p_x} + b_4 \Psi_{3s} \quad (14.9)$$

An example of a superposition state is the particle in the double-slit experiment going through both slits simultaneously. We now prepare a large number of these systems, each of which has the same wave function, and carry out a measurement of the total energy of the atom. The results that would be obtained are illustrated in Figure 14.3. Even though the systems are identical, the same value is not obtained for the energy of the atom in each measurement.

More generally, the particular value observed in one measurement could be any one of the eigenvalues  $a_n$  for which the corresponding  $b_n$  is nonzero. This is a **probabilistic outcome**, similar to asking what the chance is of rolling a six with one throw of a die. In this more familiar case, there is no way to predict the outcome of a single throw. However, if the die is thrown a large number of times, the six will land facing up one-sixth of the time. The equivalent case to the die for our wave function is that each of the coefficients  $b_m$  is equal. In the particular case under consideration, we have only four nonzero coefficients and, therefore, we will only measure one of the



values  $E_{1s}$ ,  $E_{2s}$ ,  $E_{2p}$ , or  $E_{3s}$  in an individual measurement, but we have no way of knowing which of these values we will obtain. The certainty that we are familiar with from classical mechanics—that identically prepared systems all have the same outcomes in a measurement—is replaced in quantum mechanics by the probabilistic outcome just described.

More can be said about the outcome of a large number of measurements than about the outcome of a single measurement. Consider the more general result stated in Equation (14.8): the average number of a large number of measurements is given by a sum containing the possible eigenvalues of the operator weighted by  $|b_m|^2$ , the square of the expansion coefficient. The bigger the contribution of an eigenfunction  $\phi_m(x, t)$  of  $\hat{A}$  to  $\Psi(x, t)$  (larger  $|b_m|^2$ ), the more probable it is that the outcome of an individual measurement will be  $a_m$  and the more  $a_m$  will influence the average value  $\langle a \rangle$ . There is no way to predict which of the  $a_m$  will be found in an individual measurement. However, if this same experiment is repeated many times on identical systems, the **average value** can be predicted with very high precision. It is important to realize that this is not a shortcoming of how the “identical” systems were prepared. These systems are identical in every way and there is no reason to believe that we have left something out that resulted in this probabilistic result. Worked-out problems illustrating these concepts will be presented in the next chapter.

To illustrate the preceding discussion, consider the three different normalized superposition wave functions shown in Figure 14.4. They are made of the normalized eigenfunctions  $\phi_1(x)$ ,  $\phi_2(x)$ , and  $\phi_3(x)$  of the operator  $\hat{A}$  with eigenvalues  $a_1$ ,  $4a_1$ , and  $9a_1$ , respectively. The superposition wave functions are the following combinations of  $\phi_1(x)$ ,  $\phi_2(x)$ , and  $\phi_3(x)$ :

$$\psi_1(x) = \frac{\sqrt{11}}{4} \phi_1(x) + \frac{1}{4} \phi_2(x) + \frac{1}{2} \phi_3(x) \quad (14.10)$$

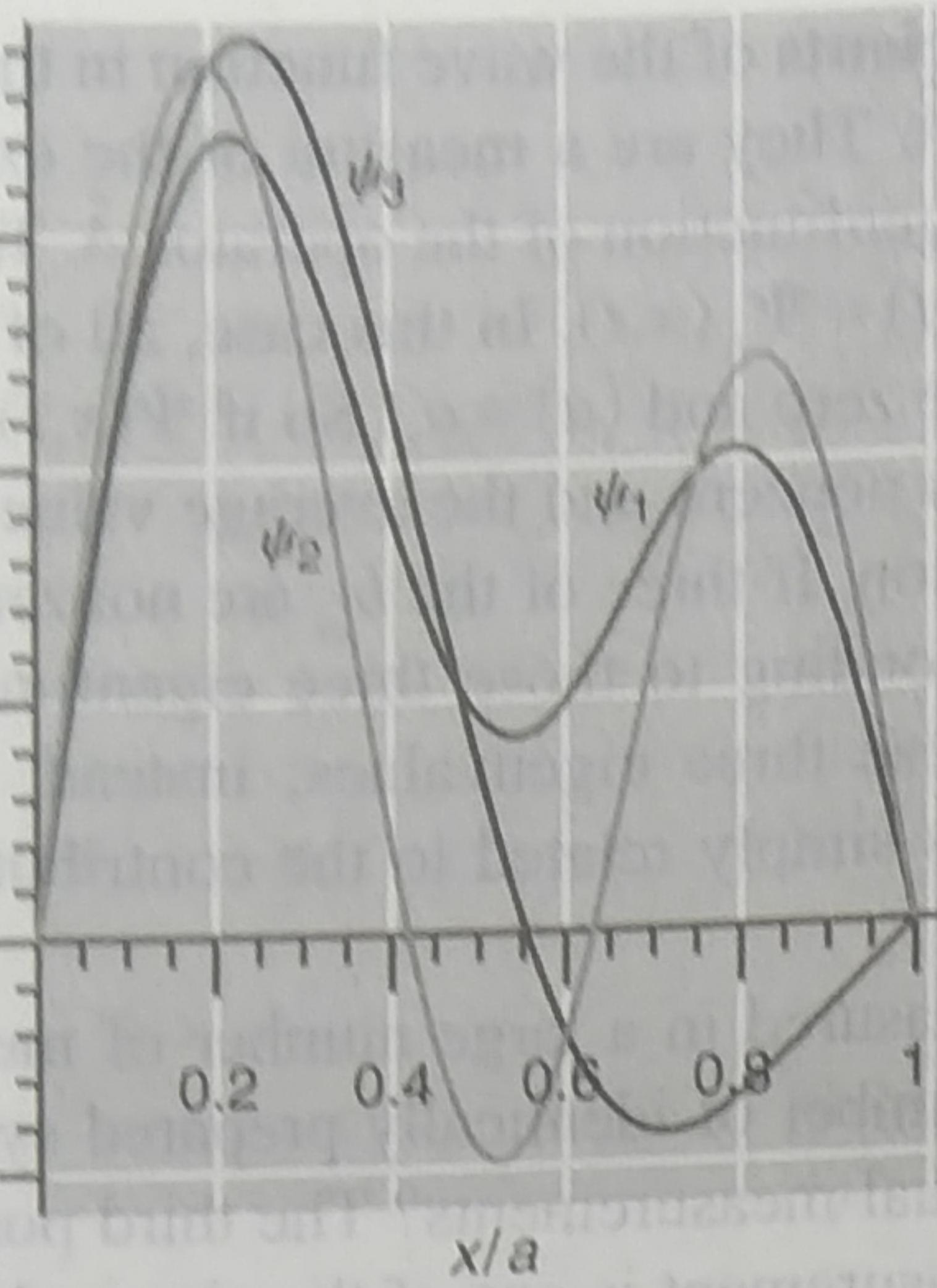
$$\psi_2(x) = \frac{1}{2} \phi_1(x) + \frac{1}{4} \phi_2(x) + \frac{\sqrt{11}}{4} \phi_3(x)$$

$$\psi_3(x) = \frac{1}{2} \phi_1(x) + \frac{\sqrt{11}}{4} \phi_2(x) + \frac{1}{4} \phi_3(x)$$

An individual measurement of the observable  $a$  gives only one of the values  $a_1$ ,  $4a_1$ , and  $9a_1$ , regardless of which wave function describes the system. However, the probability of observing these values depends on the system wave function. For example, the probability of observing the value  $9a_1$  is given by the square of the magnitude of the coefficient of  $\phi_3(x)$  and is  $1/4$ ,  $11/16$ , and  $1/16$ , respectively, depending on whether the state is described by  $\psi_1(x)$ ,  $\psi_2(x)$ , or  $\psi_3(x)$ .

You may have noticed that the postulate specified that the measurement was to be carried out only once on a large number of identically prepared systems. What lies behind this requirement? We have just learned that the first measurement will give one of the eigenvalues of the operator corresponding to the observable being measured. We have also learned that we have no way to predict the outcome of a single measurement. What would you expect if a second measurement of the same observable were carried out on the same system? The experimentally established answer to this question is illustrated in Figure 14.3. In successive measurements on the same system, exactly the same result will be obtained that was obtained in the first experiment. If further successive measurements are carried out, all of the results will be the same. The probabilistic result is obtained only on the first measurement; after that, the result is deterministic.

How can this transition from a probabilistic to a **deterministic outcome** be understood? Note that the second and all successive results are exactly what would be expected if the system were in a particular eigenstate of the operator for which the coefficient  $b_m$  is nonzero, namely,  $\Psi_{1s}$  or  $\Psi_{2s}$  or  $\Psi_{2p_x}$  or  $\Psi_{3s}$ , and not in the original superposition state  $\Psi_{\text{electronic}} = b_1 \Psi_{1s} + b_2 \Psi_{2s} + b_3 \Psi_{2p_x} + b_4 \Psi_{3s}$ . In fact, this is the key



**FIGURE 14.4**  
The three normalized wave functions  $\psi_1(x)$ ,  $\psi_2(x)$ , and  $\psi_3(x)$  (blue, yellow, and black curves, respectively) are defined over the interval  $0 \leq x \leq a$ . The amplitude of the wave functions is zero at both ends of the interval.

understanding this very puzzling result. The act of carrying out a quantum mechanical measurement appears to convert the wave function of a system to the eigenfunction of the operator corresponding to the measured quantity! We are accustomed to thinking of our role in carrying out a measurement in classical mechanics as being passive. We simply note what the system is doing and it in turn takes no notice of us. The **measurement process** in quantum mechanics is radically different. In fact, the standard interpretation of quantum mechanics attributed to the school of Niels Bohr gives the measurement process a central role in the outcome of the experiment. This has vexed many scientists, most notably Albert Einstein. Applying this reasoning to the macroscopic world, he remarked to a colleague "Do you really think that the moon is not there when we are not looking at it?" However strange this may all seem, no one has devised an experiment to show that the view of the measurement process in quantum mechanics stated in this postulate is incorrect.

Assume now that the superposition state that describes the system is not known. This is generally the case for a real system. Can we determine the wave function from measurements like those shown in Figure 14.3? By measuring the frequency with which a particular eigenvalue is measured, the various  $|b_m|^2$  can be determined. However, this only allows  $b_m$  to be determined to within a multiplicative factor  $e^{i\theta}$  in which  $0 < \theta < 2\pi$ . Unfortunately, this does not provide enough information to reconstruct the wave function from experimental measurements. This is a general result; the wave function of a superposition state cannot be determined by any experimental means.

## 14.5 The Evolution in Time of a Quantum Mechanical System

**POSTULATE 5:** The evolution in time of a quantum mechanical system is governed by the time-dependent Schrödinger equation:

$$\hat{H}\Psi(x,t) = i\hbar \frac{\partial\Psi(x,t)}{\partial t} \quad (14.11)$$

In this case, the total energy operator is given by  $\hat{H} = (-\hbar^2/2m)(\partial^2/\partial x^2) + V(x,t)$ . This looks like more familiar territory in that the equation has a unique solution for a set of given initial conditions. We call this behavior *deterministic* (like Newton's second law in contrast to the probabilistic nature of Postulate 4. The fourth and fifth postulates are not contradictory. If a measurement is carried out at time  $t_0$ , Postulate 4 applies. If we as what st