QUANTUM CHEMISTRY

LECTURE-5

The Schrödinger equation

The wave-like nature of small particles means that they do not follow the well-defined trajectories inherent to classical mechanics. Instead, quantum mechanics uses wavefunctions to describe particles and their motions. A wavefunction describes a probability amplitude and the square of a wavefunction tells us something about the probability of a particle being at a certain point in space and time. We must abandon a description in terms of particle trajectories, or – as conceived of in the path integral formulation of quantum mechanics – all trajectories are potentially possible for the particle, but they are not equally probable. We need to learn how to calculate the probabilities and to understand the implications of particle dynamics being described by a probability amplitude that contains both magnitude and phase information.

The *Schrödinger equation* was proposed by Schrödinger[10] in 1926. His argument for what was at the time a very preposterous idea – that we really do have to take this wave-particle duality of de Broglie seriously when discussing the dynamics of subatomic particles – was to state that geometrical optics (treating light as rays) and physical optics (treating light as waves) emerge from one another in different limits. Furthermore, William Hamilton used as an analogy the theory of the propagation of light in a nonhomogeneous medium to derive theories in pure mechanics, most notably the Hamilton function of action and how it is used to describe the evolution of a mechanical system. It was left to Schrödinger to reverse engineer from Hamilton's work the implications for atomic-scale systems. In doing so he would derive the Planck relation of energy $E = \hbar\omega$, Bohr's energy level structure of the H atom $E_n = -2\pi^2 me^4/h^2n^2$, and both the intensities and polarizations of spectral lines observed in the Stark effect as natural consequences of these dynamics. Something this good just could not be wrong, so he forged ahead without a clear conception about the nature of the wavefunction.

For a particle of mass m moving in one dimension x with a possibly time-dependent potential described by $V(x,t)$, the *time-dependent Schrödinger equation* has the form

$$-\frac{\hbar}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} + V(x,t)\Psi(x,t) = \mathrm{i}\hbar\frac{\partial\Psi(x,t)}{\partial t}. \qquad (20.11)$$

The time-dependent wavefunction $\Psi(x,t)$ is the solution to this equation and $\hbar = h/2\pi$ is the reduced Planck constant. In many of our applications, the potential is independent of time. This allows us to factor the wavefunction into a spatial component and a time-dependent component,

$$\Psi(x, t) = \psi(x)\phi(t) \tag{20.12}$$

The function $\psi(x)$ is the spatial part of the wavefunction. These functions are also called the *stationary states* of the system.

Upon substitution of the factored wavefunction back into Eq. (20.11), the time-dependent Schrödinger equation becomes

$$\frac{1}{\psi(x)}\left[-\frac{\hbar}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + V(x)\,\psi(x)\right] = \frac{1}{\phi(t)}\mathrm{i}\hbar\frac{\mathrm{d}\phi(t)}{\mathrm{d}t} \tag{20.13}$$

Each side of Eq. (20.13) is a function of one variable only: x for the LHS and t for the RHS. They can only be equal to each other if they are both equal to the same constant. We call this constant E, and we will discover that it is equal to the total energy of the state described by the wavefunction. Setting the RHS equal to E, we obtain,

$$i\hbar\frac{\mathrm{d}\phi(t)}{\mathrm{d}t} = E\phi(t). \tag{20.14}$$

The solution to this differential equation is the exponential function,

$$\phi(t) = \exp(Et/\mathrm{i}\hbar), \tag{20.15}$$

which describes a sinusoidally oscillating wave with angular frequency $\omega = E/\hbar$. For a potential that does not vary in time, the total energy $E = \hbar\omega$ is constant and the time-dependent wavefunction has the form

$$\Psi(x, t) = \psi(x)\exp(Et/\mathrm{i}\hbar). \tag{20.16}$$

From the Born interpretation, we learn that the wavefunction is a probability amplitude, the absolute square of which gives the probability of finding the particle. However, to take the absolute square, we must take into consideration that the wavefunction is a complex function; thus, the square of the function is taken by multiplying the complex conjugate of the wavefunction by the wavefunction,

$$|\Psi(x, t)|^2 = \Psi^*(x, t)\Psi(x, t). \tag{20.17}$$

The complex conjugate is taken by switching the sign of each term involving an imaginary number i → −i; hence,

$$|\Psi(x, t)|^2 = \psi^*(x)\exp(Et/(-\mathrm{i}\hbar))\psi(x)\exp(Et/\mathrm{i}\hbar) = |\psi(x)|^2. \tag{20.18}$$

This explains why the $\psi(x)$ are called the stationary states – the probability distribution described by the square of the wavefunction is not time-dependent.

The LHS of Eq. (20.13) is also equal to the total energy E. This allows us to write the *time-independent Schrödinger equation*,

$$-\frac{\hbar}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} + V(x)\psi(x) = E\psi(x). \tag{20.19}$$

We introduce the *Hamiltonian operator* $\hat{H}$

$$\hat{H} = \frac{\hbar}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x) \tag{20.20}$$

which allows us to write the time-independent Schrödinger equation in the compact form

$$\hat{H}\psi(x) = E\psi(x). \tag{20.21}$$

Most of the questions we will try to answer will have their solution in the time-independent Schrödinger equation, which is why the short form in Eq. (20.21) has become so familiar. Essentially all of chemistry and physics is contained within the Schrödinger equation. This statement comes with the two very significant 'howevers.' The first is that we need to write down a complete Hamiltonian to describe *all* the interactions in our system. The kinetic energy term is easy, but the potential energy term requires detailed knowledge and a mathematical expression for every kind of interaction (electrostatic, magnetic, gravitational, chemical, van der Waals, etc.) experienced in the system. Once we can formulate all of the interactions, 'all' we have to do is find the wavefunctions. However – and this one is even tougher – the Schrödinger equation cannot be solved exactly for any atom or molecule containing more than one electron. Obviously, a major component of quantum mechanics is the pursuit of ever better approximations to the exact solution of the Schrödinger equation.

Example: particle in a one-dimensional box

The wavefunction for a particle confined in a one-dimensional box of length L, as we shall prove in the next chapter, is (in the range $0 \leq x \leq L$)

$$\psi_n(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right).$$

Take $L = 10.0$ nm. Now let's calculate the probability that a ground-state electron (that is, an electron in the $n = 1$ state) is (a) between $x = 4.95$ nm and 5.05 nm, and (b) in the left half of the box. (c) What is the probability of finding the particle at $x = 0$ or $x = 5$ nm?

The $n = 1$ wavefunction is $\psi = (2/L)^{1/2} \sin(\pi x/L)$. The probability is found by integration of the square of the wavefunction over the appropriate limits.

$$P = \int_a^b \psi^* \psi \, dx = \left(\frac{2}{L}\right) \int_a^b \sin^2\left(\frac{\pi x}{L}\right) dx = \left[\frac{x}{L} - \frac{1}{2\pi} \sin\left(\frac{2\pi x}{L}\right)\right]_a^b.$$

a In this case $a = 4.95$ nm and $b = 5.05$ nm.

$$P = \left[\frac{x}{L} - \frac{1}{2\pi} \sin\left(\frac{2\pi x}{L}\right)\right]_a^b = \frac{b-a}{L} - \frac{1}{2\pi}\left[\sin\left(\frac{2\pi b}{L}\right) - \sin\left(\frac{2\pi a}{L}\right)\right]$$

Substituting for a and b we find $P = 0.010$.

b In this case $a = 0$ and $b = L/2 = 5$. However, since the wavefunction is symmetric about the center of the box and the integral over the whole of the box is 1 (normalized wavefunction), the integral over half of the box is 0.5. Look back at Fig. 20.1. The $n = 4$ state is shown, which has four extrema and two full cycles of the sine function. The $n = 1$ state corresponds to just one half-cycle of the sine function.

c The wavefunction is zero at $x = 0$. The probability is also zero at $x = 0$. The wavefunction is a maximum at $x = 5$ nm; nonetheless, the probability of finding a particle at a point – any point – is zero. The integral of any *finite* function over a single point is zero.[9] Ponder that for a moment. The particle does not exist at any point in the box. Yet the particle is in the box. Ergo, the particle is not point-like. The probability of finding the particle in any region of space is nonvanishing. In the vicinity of a node, this probability is exceedingly small. The smaller we make the region, the smaller the probability, but it only goes uniquely to zero at a point. Thus, there is no difficulty for this non-point-like particle to move from one side of the box to the other, even though the wavefunction contains nodes in it.

Solving the Schrödinger equation

Postulate V tells us that solving the Schrödinger equation will provide us a complete description of the system and how it develops in time. Therefore, the following procedure should become very familiar to you.

- First, write out a complete Hamiltonian that accounts for all interactions in the system.
- Second, substitute the resulting Hamiltonian into the Schrödinger equation.
- Third, solve the Schrödinger equation for the wavefunctions.
- Fourth, brew coffee, interpret and publish results.[14]

You should note that practice can be much different than principle, and decidedly more difficult to execute than to plan. Nonetheless, let's see how this works by solving a few simple examples.

Postulate V: Unitarity

> To every physical system there corresponds a unique operator representing the total energy of the system. This operator, the Hamiltonian $\hat{H}$, and the observable physical states of the system are described by those wavefunctions that satisfy the time-dependent Schrödinger equation $\hat{H}\Psi = i\hbar(\partial\Psi/\partial t)$.

Free particle in one dimension

A free particle is a particle of mass m that is unconfined by a potential. This means that the potential energy is constant, so we are free to chose any value. In this example we choose $V(x) = 0$ everywhere. The Hamiltonian is the sum of kinetic and potential energy operators and in this case is given by

$$\hat{H} = \hat{T} + \hat{V} = \frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} \tag{20.29}$$

By inspection, a good candidate for a solution to this differential equation is

$$\psi = N e^{\mathrm{i}kx} \tag{20.30}$$

where both N and k are constants (k can be either positive or negative^{15}). Now prove that this is a solution to the Schrödinger equation,

$$\hat{H}\psi = E\psi, \tag{20.31}$$

by showing that operating on this function with the Hamiltonian returns a constant times the original function as required. Begin by taking the second derivative of ψ.

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = N\frac{\mathrm{d}}{\mathrm{d}x}(\mathrm{i}ke^{\mathrm{i}kx} = N(\mathrm{i}k)(\mathrm{i}ke^{\mathrm{i}kx}) = -k^2 N e^{\mathrm{i}kx} \tag{20.32}$$

Thus, the LHS of the Schrödinger equation is

$$\hat{H}\psi = \frac{-\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = \frac{-\hbar^2}{2m}(-k^2 N e^{\mathrm{i}kx}) = \frac{\hbar^2 k^2}{2m} N e^{\mathrm{i}kx} = \frac{\hbar^2 k^2}{2m}\psi. \tag{20.33}$$

Substituting this into Eq. (20.31) gives

$$\frac{\hbar^2 k^2}{2m}\psi = E\psi. \tag{20.34}$$

The result in Eq. (20.34) proves that our guess – or, in the parlance of the field, our *trial wavefunction* – was indeed a solution of the differential equation because application of the Hamiltonian operator led to a constant ($\hbar^2 k^2/2m$) times the wavefunction. The constant is equal to the energy,

$$E = (\hbar k)^2/2m. \tag{20.35}$$

Note that the normalization constant is irrelevant for the calculation of the energy.

Take a look at the resulting energy in Eq. (20.35). Is it quantized? No, as shown in Fig. 20.2. We have applied quantum mechanics but the result is that the energy can take on any value because there is no restriction on the value of k. This highlights two essential features of quantum mechanics. First, the methods of quantum mechanics are also valid in the region where classical results are obtained. Second, quantization of energy levels is *not* observed in the absence of confinement. The potential in the example was zero (actually it need only be constant). The particle is free. Only if the particle is confined by the potential to a region of space comparable to its de Broglie wavelength in at least one dimension will quantization be important.

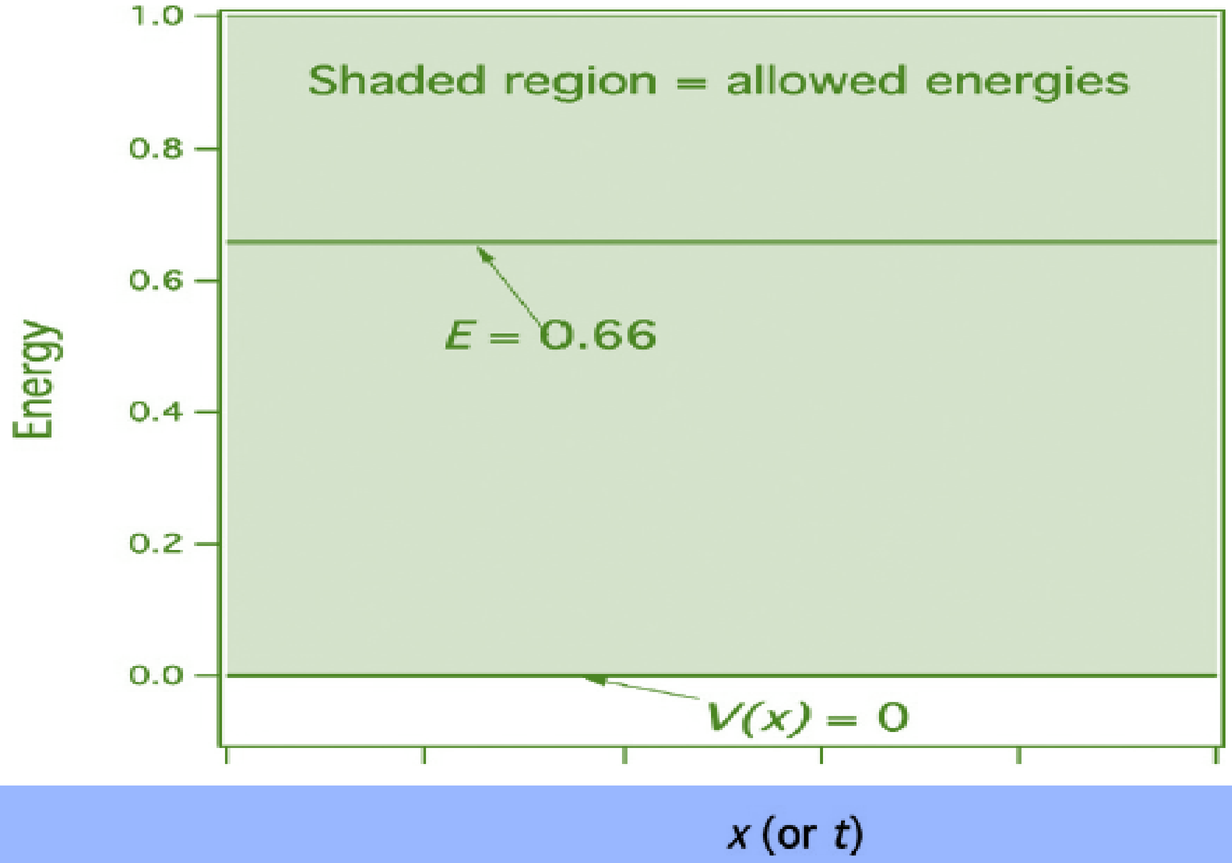

Figure 20.2 A particle moving in a potential that is constant both in space and time. Since the potential is constant, we are free to choose the value of the potential as zero. With no other interactions in the system, the energy of the particle is constant. The energy of one particular particle that has an energy of 0.66 (in units where 1 is the maximum allowed) is depicted. The shaded region, which is continuous, represents the energies that the particle may have.