Particle in a Box

Skills to Develop

- Derive Schrodinger's Equation (optional)
- Verbalize the solution of Schrodinger's Equation (optional)

Many introductory chemistry textbooks introduce the Schrodinger Equation, but students don't understand what it means. This section is optional; if you want to know where orbitals come from, it can help you understand. It will be easier to follow this section if you know a little calculus (basically, what a derivative is).

The Schrodinger Equation is the starting point for describing the motions of electrons as waves. De Broglie suggested that their stable "orbits" in the Bohr model were standing waves analogous to those in a guitar string. Schrodinger extended this theory using the wave equation and wavefunction. Instead of circular orbits, Schrodinger's waves were 3D and took up the whole space of the atom, more like vibration of air in a spherical flute than the vibration of a circular string. The wavefunction Ψ(x, y, z, t) describes the amplitude of the electron vibration at each point in space and time. Oddly, Schrodinger seems to have proposed the wavefunction without fully understanding what it means, but it worked! Here we will describe the time-independent Schrodinger equation for simplicity, which describes the standing waves. We will also consider only a 1-dimensional system, such as a particle that only moves linearly, also for simplicity. Thus, we will find Ψ(x) for a very simple situation.

Schrodinger proposed that a standing wave is described by the wavefunction Ψ when the it fits the following differential equation

$$H\Psi = E\Psi \tag{1}$$

where H is the Hamiltonian operator, which finds the total energy of the system E. (This approach uses the linear algebra concept of an eigenfunction and eigenstate, but don't worry if you don't know what these are.) Kinetic energy KE is given by

$$KE = \frac{p^2}{2m} \tag{2}$$

where p is the momentum (p = mv). For a particle moving in 1D (along x) Schrodinger assumed that a permissible general form of Ψ is

$$\Psi(x,\ t) = Ae^{\frac{i(px\ -\ Et)}{\hbar}} \tag{3}$$

where A is a constant and i is the imaginary number (i^2 = -1). (This comes from the equations E = hv and the de Broglie relationship λ = h/p. These equations connect energy to time and distance to momentum through Planck's constant. These are also the quantities that are mutually limited by the Uncertainty Principle.) If this is true, the derivative of the wavefunction with respect to x is

$$\frac{d\Psi}{dx} = \frac{ip}{\hbar}\Psi \tag{4}$$

Notice that this is kind of like the equation HΨ = EΨ in that we get the original wavefunction multiplied by some important quantity, like energy or momentum. So the momentum operator **p** (like the Hamiltonian operator, which gives the energy) gives the momentum p, and can be written like this:

$$\mathbf{p}\Psi(x,\ t) = -i\hbar\frac{d\Psi}{dx} \tag{5}$$

We can write the Schrodinger equation using this Hamiltonian (which gives total energy, KE + PE)

$$H\Psi(x) = -\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} + V(x)\Psi(x) = E\Psi(x) \tag{6}$$

The potential energy is given by V(x), which just depends on the position. The kinetic energy is calculated using the equation above, using the square of the momentum operator (thus, the first derivative in the momentum operator becomes a second derivative when the operator is squared). Now, if we choose a function V(x) we can find the wavefunctions that fit! We will use a simple example: a particle in a box (in 1-D). The potential is 0 inside the box and infinite outside the box. So we will just know that the particle has to be inside the box, but use V = 0. Then our Schrodinger Equation looks like this

$$H\Psi(x) = -\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} = E\Psi(x) \tag{7}$$

or basically the second derivative of Ψ is a constant times Ψ. There are different forms of the solution, but we'll just choose a simple one.

$$\frac{d}{dx}\, sin(ax) = a\; cos(ax) \tag{8}$$

$$\frac{d}{dx}\, cos(ax) = -a\; sin(ax) \tag{9}$$

Thus,

$$\frac{d^2}{dx^2}\, sin(ax) = -a^2\; sin(ax) \tag{10}$$

So we can pick sin(ax) or cos(ax) or a sum of these for the wavefunction:

$$\Psi(x) = sin(ax) + cos(bx) \tag{11}$$

So far, there is no quantization! The coefficient a can have any value. But just like a string on a guitar, the amplitude of Ψ has to be 0 at the edges of the box. If we just use Ψ(x) = sin(ax), then if the box is from x = 0 to x = L, we need to have an integer number of half-wavelengths in the box. So

$$a = \frac{n\pi}{L} \tag{12}$$

so that

$$\Psi(0) = \Psi(L) = 0 \tag{13}$$

To summarize,

$$\Psi = sin\left(\frac{n\pi x}{L}\right) \tag{14}$$

is a solution of the Schrodinger Equation for the 1-D particle-in-a-box system. Try putting this in and see what the energy is! You should get:

$$E_n = \frac{n^2\hbar^2\pi^2}{2mL^2} \tag{15}$$

There are an infinite number of solutions, or wavefunctions that satisfy the Schrodinger Equation, corresponding to n = 1, 2, 3... and any sum of these wavefunctions is also a solution. What do they mean? The amplitude of the particle wave is given by Ψ. The next section explains the meaning of the wavefunction in more detail, now that you have been introduced to the math.

Contributors and Attributions

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