Organic Electronic Devices

Week 2: Electronic Structure

Lecture 2.2: The Schrödinger Equation

Bryan W. Boudouris
Chemical Engineering
Purdue University

Lecture Overview and Learning Objectives

- **Concepts to be Covered in this Lecture Segment**
  - Defining a Wavefunction with Temporal and Spatial Dependence
  - Solving the Time-independent Schrödinger Equation for Certain Situations

- **Learning Objectives**

  By the Conclusion of this Presentation, You Should be Able to:

  1. **Derive** the time-independent Schrödinger equation and **label** the kinetic, potential, and total energy terms in this equation.
  2. **Show** how discrete energy levels arise for the particle in an (infinite) box.

Derivation of the 1-Dimensional Schrödinger Equation

The State of an Electron can be Thought of In Terms of a Wavefunction

$$Wavefunction\ in\ 1-D: \quad \psi(x,t)$$

From the Classical Partial Differential Equations Result, We Know:

$$\frac{\partial^2}{\partial x^2}[\psi(x,t)] = \frac{1}{u^2}\frac{\partial^2}{\partial t^2}[\psi(x,t)]$$

Here, u^2 is the speed of the wave

Now, We Can Break the Function Into the Spatial and Temporal Parts

$$[\psi(x,t)] = [\psi(x)][\psi(t)] = [\psi(x)]\cos(\omega t)$$

The Second Equality of the Above Equation is Possible Because the Solution is Cyclic in Nature with a Given Period

Here, $\omega = 2 \pi \nu$, where ν is the frequency of the wave

Derivation of the 1-Dimensional Schrödinger Equation (Part II)

Substitution of the 2nd Equation into the 1st Equation of the Last Slide Yields:

$$\frac{\partial^2}{\partial x^2}\left[\psi(x,t)\right] = \frac{1}{u^2}\frac{\partial^2}{\partial t^2}\left[\psi(x)\cos(\omega t)\right]$$

Taking the Partial Derivative with Respect to Time Yields:

$$\frac{\partial^2}{\partial x^2}\left[\psi(x,t)\right] = \frac{\psi(x)}{u^2}\frac{\partial^2}{\partial t^2}\left[\cos(\omega t)\right] = \frac{-\psi(x)}{u^2}\omega^2$$

Now, The Expression is Solely a Function of Position

$$\frac{\partial^2}{\partial x^2}\left[\psi(x)\right] = \frac{-\psi(x)}{u^2}\omega^2 \quad or \quad \frac{\partial^2}{\partial x^2}\left[\psi(x)\right] + \frac{\psi(x)}{u^2}\omega^2 = 0$$

Derivation of the 1-Dimensional Schrödinger Equation (Part III)

Substitution of the Definition of ω Converts the Equation To:

$$\frac{\partial^2}{\partial x^2}\left[\psi(x)\right]+\frac{\psi(x)}{u^2}\omega^2=0=\frac{\partial^2}{\partial x^2}\left[\psi(x)\right]+\frac{4\pi^2\nu^2\psi(x)}{u^2}$$

But Frequency Times a Wavelength is Just a Velocity So:

$$\nu\times\lambda=u \quad or \quad \lambda=\frac{u}{\nu} \quad and \quad \frac{\nu^2}{u^2}=\frac{1}{\lambda^2}$$

Then the Equation Above Reduces to the Following

$$\frac{\partial^2}{\partial x^2}\left[\psi(x)\right]+\frac{4\pi^2\psi(x)}{\lambda^2}=0$$

Derivation of the 1-Dimensional Schrödinger Equation (Part IV)

Now, Two Properties of Waves Proposed by de Broglie Must Be Used

1. **The energy of the wave can be expressed in terms of kinetic and potential energy**

2. **Wavelength is related to momentum through Planck's constant (*h*)**

These Expressions Can Be Written Mathematically as the Following

$$E = \frac{p^2}{2m} + V(x)$$

Here, E is the energy, p is the momentum, m is the mass, and $V(x)$ is the potential energy with respect to position.

$$\lambda = \frac{h}{p}; \quad h = 6.626 \times 10^{-34} \frac{m^2}{kg - s}$$

Derivation of the 1-Dimensional Schrödinger Equation (Part V)

Solving for Momentum in Terms of Energy Yields the Following Two Equations

$$p = \left\{2m\left[E - V(x)\right]\right\}^{1/2}$$

$$\lambda = \frac{h}{\left\{2m\left[E - V(x)\right]\right\}^{1/2}}$$

Now, We Can Substitute This Expression for Wavelength into the PDE

$$\frac{\partial^2}{\partial x^2}\left[\psi(x)\right] + \frac{4\pi^2\psi(x)}{\left[\dfrac{h}{\left\{2m\left[E - V(x)\right]\right\}^{1/2}}\right]^2} = 0$$

Derivation of the 1-Dimensional Schrödinger Equation (Part VI)

Rearranging The Equation from the Previous Slide Yields:

$$\frac{\partial^2\psi(x)}{\partial x^2}+\frac{4\pi^2\psi(x)}{\dfrac{h^2}{2m[E-V(x)]}}=\frac{\partial^2\psi(x)}{\partial x^2}+\frac{2m[E-V(x)]}{\hbar^2}\psi(x)=0$$

$$Where:\hbar=\frac{h}{2\pi}$$

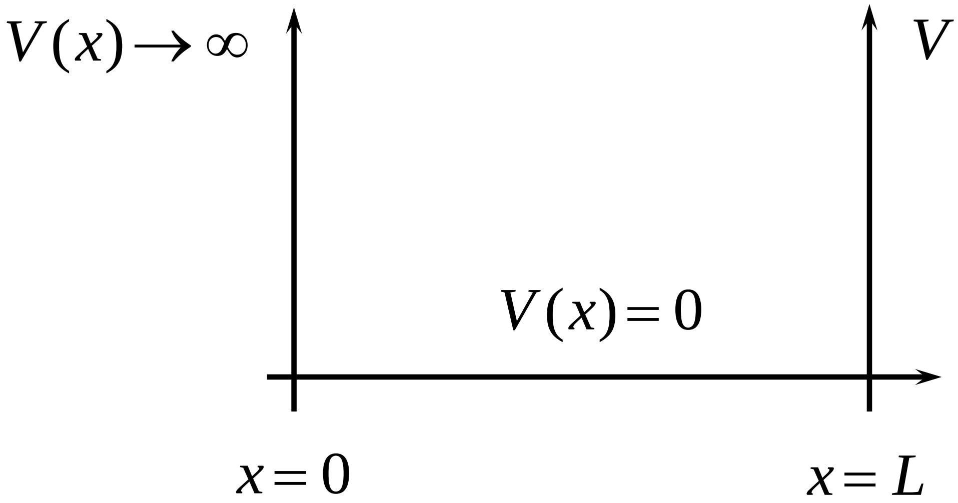
This Can Be Rewritten as the Time-Independent Schrödinger Equation

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2}+V(x)\psi(x)=E\psi(x)$$

Kinetic Energy Term | **Potential Energy Term** | **Total Energy Term**

Solving the Problem of the Free Electron in a Box

Here, We Are Given a Free Electron (*i.e.*, V(x) = 0) Confined to a Box



Because of the infinite potential energy outside of the box (x < 0, x > L), the electron is confined to the box where the potential energy is 0 everywhere.

This Causes the Schrödinger Equation To Be Reduced to the Following

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2mE}{\hbar^2}\psi(x) = 0$$

The Two Boundary Conditions Are:

$$\psi(x = 0) = \psi(x = L) = 0$$

Solving the Problem of the Free Electron in a Box (Part II)

The General Solution to the Equation on the Previous Slide Is:

$$\psi(x) = A\cos(kx) + B\sin(kx)$$

$$Where: k = \frac{(2mE)^{1/2}}{\hbar}$$

We Can Solve for *A* and *B* by Implementing the Boundary Conditions

$$\psi(x=0) = A\cos[k(0)] + B\sin[k(0)] = 0$$

$$\psi(x=0) = A(1) + 0 = 0$$

$$\therefore A = 0 \ and$$

$$\psi = B\sin[k(x)]$$

Solving the Problem of the Free Electron in a Box (Part III)

Applying the Second Boundary Condition Yields the Following

$$\psi(x = L) = B\sin[k(L)] = 0$$

If We Exclude the Trivial Solution (*i.e.*, *B* = 0), Then:

$$\psi(x = L) = B\sin[k(L)] = 0, \; if \; k(L) = n\pi$$

Then the Expression for the Wavefunction Reduces To (If B = 1):

$$\psi_n(x) = \sin\left[\frac{n\pi}{L}(x)\right]$$

Also, This Means That:

$$\frac{\partial^2\psi(x)}{\partial x^2} = \frac{-n^2\pi^2}{L^2}\sin\left[\frac{n\pi}{L}(x)\right] = \frac{-n^2\pi^2}{L^2}\psi(x)$$

Solving the Problem of the Free Electron in a Box (Part IV)

We Can Then Apply This to the Original Equation

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2mE}{\hbar^2}\psi(x) = 0$$

Substituting the Result from the Previous Slide and Rearranging Yields:

$$\frac{-n^2\pi^2}{L^2}\psi_n(x) + \frac{2mE_n}{\hbar^2}\psi_n(x) = 0, or$$

$$\frac{-n^2\pi^2}{L^2} + \frac{2mE_n}{\hbar^2} = 0$$

Solving for the Energy with Respect to Different Integer Values Yields:

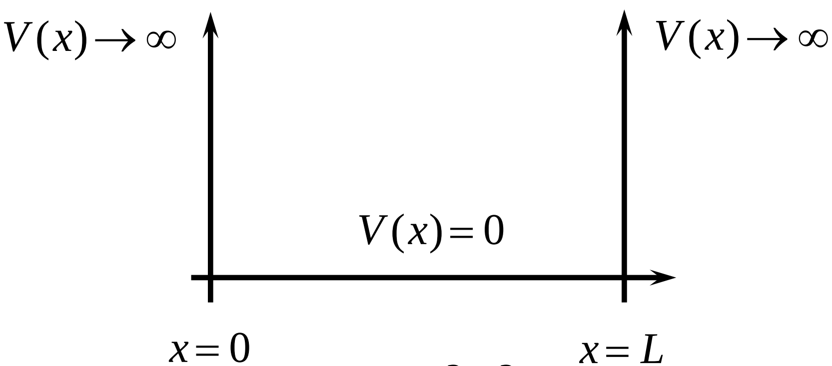
$$E_n = \frac{n^2h^2}{8mL^2}$$

Prove This to Yourself

Summary and Preview of the Next Lecture

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2}+V(x)\psi(x)=E\,\psi(x)$$

The solution to solving for a mathematical description for the description of an electron was presented by Erwin Schrödinger. If reduced to a form that is more simple than the initial equation, one can derive the one-dimensional, time-independent equation in a straightforward manner. While this equation does not encompass all of the reality of true electron systems, it provides an excellent guide for simple molecular systems.



$$E_n=\frac{n^2h^2}{8mL^2}$$

The one-dimensional time-independent Schrödinger equation was solved for the special case of a free electron in a box with infinite potential energy walls. The solution to this equation was defined both in terms of the wavefunction and the quantized energy levels. In future efforts, we will see how these different states correspond to transitions in real organic molecules.

Next Time: Application of These Equations and Expansion to 3 Dimensions