Organic Electronic Devices

Week 2: Electronic Structure
Lecture 2.3: Application of the Schrödinger Equation

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Lecture Overview and Learning Objectives

• Concepts to be Covered in this Lecture Segment
  • Implementation of the Time-independent Schrödinger Equation in Order to Solve for Transition Energies
  • Derivation of the Three-Dimensional Time-independent Schrödinger Equation
  • Extension of the Three-Dimensional Time-independent Schrödinger Equation to Wavevector Surfaces

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

  1. **Solve** for the transition energy values in simple organic molecule systems using the Time-independent Schrödinger Equation.
  2. **Derive** the three-dimensional, time-independent Schrödinger equation using the separation of variables method.
  3. **Convert** between real space and wavevector space.
The Energy of the Electron is a Function of the Quantum Number

Recall from the Previous Lecture That the Following Holds for a Free Electron Contained within a Well with Walls at Infinite Potential Energy

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

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

Note that as the Quantum Number \((n)\) increases, the energy increases. Furthermore, the “length of the box” plays an important role in the calculated energy.
Estimating Energetic Transitions in Molecules Using This Model

Example: The HOMO to LUMO Transition Energy in 1,3-Butadiene

1,3-Butadiene
4 Carbons with sp² Hybridized Orbitals

Assume that the Molecule is Linear (i.e., Do Not Consider Bond Angles)

2 C=C Double Bonds (0.135 nm): 0.270 nm
1 C-C Single Bond (0.154 nm): 0.154 nm
2 Carbon Radii (0.077 nm): 0.154 nm

Summing These Values Gives L

\[ L = 0.578 \text{ nm} \]

\[ E_n = \frac{n^2 \hbar^2}{8mL^2} \quad \text{or} \]

\[ \Delta E_{i \rightarrow j} = \frac{(j^2 - i^2)\hbar^2}{8m_eL^2} \]

Further Reading: Physical Chemistry: A Molecular Approach by Donald A. McQuarrie and John D. Simon
Estimating the HOMO to LUMO Transition Energy in 1,3-Butadiene

Example: The HOMO to LUMO Transition Energy in 1,3-Butadiene

\[
\Delta E_{HOMO \rightarrow LUMO} = \Delta E_{2 \rightarrow 3} = \frac{(3^2 - 2^2)\hbar^2}{8m_e L^2}
\]

\[
\Delta E_{2 \rightarrow 3} = \frac{(3^2 - 2^2)\hbar^2}{8m_e L^2} = \frac{(9 - 4) \times (6.626 \times 10^{-34} \text{ } J \cdot \text{s})^2}{8 \times (9.109 \times 10^{-31} \text{ } \text{kg}) \times (0.578 \times 10^{-9} \text{ } \text{m})^2}
\]

\[
\Delta E_{2 \rightarrow 3} = 9.02 \times 10^{-19} \text{ } J = 5.63 \text{ } eV
\]

Measured Transition Energy: 5.71 eV; Difference: 1.4%

For Simple Systems, Such as the One Used Here, This Simple Model Works

Further Reading: Physical Chemistry: A Molecular Approach by Donald A. McQuarrie and John D. Simon
Extension of the Schrödinger Equation to 3 Dimensions

Recall the Time-Independent Schrödinger Equation in 1 Dimension

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

If the Case of the Free Electron ($V = 0$), Then the Equation Can be Transformed

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(x, y, z) = -\frac{\hbar^2}{2m} \left[ \frac{\partial^2 \psi(x, y, z)}{\partial x^2} + \frac{\partial^2 \psi(x, y, z)}{\partial y^2} + \frac{\partial^2 \psi(x, y, z)}{\partial z^2} \right] = E \psi(x)$$

The Dimensions of the Box Are Now: $0 \leq x \leq L_x$; $0 \leq y \leq L_y$; $0 \leq z \leq L_z$

And the Boundary Conditions for the Box Are:

$$\psi(x = 0, y, z) = \psi(x = L_x, y, z) = 0 \text{ for all } y \text{ and } z$$

$$\psi(x, y = 0, z) = \psi(x, y = L_y, z) = 0 \text{ for all } x \text{ and } z$$

$$\psi(x, y, z = 0) = \psi(x, y, z = L_z) = 0 \text{ for all } x \text{ and } y$$
Separation of Variables Can Be Used to Solve for the Energy

We Can Rewrite the 3-dimensional Wavefunction As:

\[ \psi(x, y, z) = X(x) Y(y) Z(z) \]

This Form Can Now Be Substituted Into the Equation on the Previous Slide

\[
-\frac{\hbar^2}{2m} \left[ \frac{\partial^2 \psi(x, y, z)}{\partial x^2} + \frac{\partial^2 \psi(x, y, z)}{\partial y^2} + \frac{\partial^2 \psi(x, y, z)}{\partial z^2} \right] = E \psi(x, y, z)
\]

\[
= -\frac{\hbar^2}{2m} \left[ \frac{\partial^2 X(x)Y(y)Z(z)}{\partial x^2} + \frac{\partial^2 X(x)Y(y)Z(z)}{\partial y^2} + \frac{\partial^2 X(x)Y(y)Z(z)}{\partial z^2} \right] = E \psi(x, y, z)
\]

\[
= -\frac{\hbar^2}{2m} \left[ Y(y)Z(z) \frac{d^2 X(x)}{dx^2} + X(x)Z(z) \frac{d^2 Y(y)}{dy^2} + X(x)Y(y) \frac{d^2 Z(z)}{dz^2} \right] = E \psi(x, y, z)
\]

\[
= -\frac{\hbar^2}{2m} \left[ Y(y)Z(z) \frac{d^2 X(x)}{dx^2} + X(x)Z(z) \frac{d^2 Y(y)}{dy^2} + X(x)Y(y) \frac{d^2 Z(z)}{dz^2} \right] = E X(x) Y(y) Z(z)
\]

Dividing Each Side of the Equation by the Wavefunction Yields:

\[
E = -\frac{\hbar^2}{2m} \left[ \frac{1}{X(x)} \frac{d^2 X(x)}{dx^2} + \frac{1}{Y(y)} \frac{d^2 Y(y)}{dy^2} + \frac{1}{Z(z)} \frac{d^2 Z(z)}{dz^2} \right]
\]
Separation of Variables Can Be Used to Solve for the Energy (Part II)

Each Term on the Right Side of the Equation is a Function of a Single Variable

\[ E = E_x + E_y + E_z \quad \text{where:} \]

\[
E_x = -\frac{\hbar^2}{2m} \frac{1}{X(x)} \frac{d^2 X(x)}{dx^2}; \quad E_y = -\frac{\hbar^2}{2m} \frac{1}{Y(y)} \frac{d^2 Y(y)}{dy^2}; \quad E_z = -\frac{\hbar^2}{2m} \frac{1}{Z(z)} \frac{d^2 Z(z)}{dz^2}
\]

The Transformation of Variables Yields The Following Boundary Conditions:

\[
X(x = 0) = X(x = L_x) = 0 \\
Y(y = 0) = Y(y = L_y) = 0 \\
Z(z = 0) = Z(z = L_z) = 0
\]

Using the Same Mathematical Logic As for the 1-Dimensional Case Yields:

\[
X(x) = A_x \sin \left( \frac{n_x \pi x}{L_x} \right); \quad Y(y) = A_y \sin \left( \frac{n_y \pi y}{L_y} \right); \quad Z(z) = A_z \sin \left( \frac{n_z \pi z}{L_z} \right)
\]
Separation of Variables Can Be Used to Solve for the Energy (Part III)

If One Normalizes the Probability of Finding the Electron Over Space to 1 Then:

\[ A_x A_y A_z = \left( \frac{8}{L_x L_y L_z} \right)^{1/2} \]

Combining These Equations with the Original Wavefunction Definition Yields:

\[ \psi(x, y, z) = X(x) Y(y) Z(z) \]

\[ \psi_{n_x, n_y, n_z}(x, y, z) = \left( \frac{8}{L_x L_y L_z} \right)^{1/2} \sin \left( \frac{n_x \pi x}{L_x} \right) \sin \left( \frac{n_y \pi y}{L_y} \right) \sin \left( \frac{n_z \pi z}{L_z} \right) \]

Inserting This Form of the Wavefunction Into the Energy Expression Yields:

\[ E_{n_x, n_y, n_z} = \frac{\hbar^2}{8m} \left[ \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right] \]

This Is Very Similar to the 1-Dimensional Solution
The Presence of Symmetry Leads to Energy Level Degeneracy

Even for an Equal-Sided Box, Added Dimensions Yield Added Complexity

\[ E_{n_xn_yn_z} = \frac{\hbar^2}{8m} \left[ \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right] \]

where \( L_x = L_y = L_z = L \)

\[ E_{n_xn_yn_z} = \frac{\hbar^2}{8mL^2} \left[ n_x^2 + n_y^2 + n_z^2 \right] \]

For a Given Length of a Side and a Given Mass, Different Combinations of the Quantum Numbers Can Lead to the Same (Degenerate) Energy Values

\[
\begin{array}{c|c|c}
\text{Degeneracy} & (n_x, n_y, n_z) & \text{Count} \\
\hline
14 & (3,2,1);(3,1,2);(2,3,1) & 6 \\
& (1,3,2);(1,2,3);(2,1,3) & \\
12 & (2,2,2) & 1 \\
11 & (3,1,1);(1,3,1);(1,1,3) & 3 \\
9 & (2,2,1);(2,1,2);(1,2,2) & 3 \\
6 & (2,1,1);(1,2,1);(1,1,2) & 3 \\
3 & (1,1,1) & 1 \\
\end{array}
\]

In Quantum Mechanics, Degeneracy is Considered an Underlying Sign of Symmetry in the System
The Energy Equation Can Be Expanded to Surfaces

Recall from Last Lecture the Definition of the Wavevector \((k)\)

\[ k_i = \frac{n_i \pi}{L_i} \]

Therefore, the Energy Equation Can be Written As:

\[ E_{n_x n_y n_z} = \frac{\hbar}{8m} \left[ \frac{k_x^2}{\pi^2} + \frac{k_y^2}{\pi^2} + \frac{k_z^2}{\pi^2} \right] \]

\[ E_{n_x n_y n_z} = \frac{\hbar}{2m} \left[ k_x^2 + k_y^2 + k_z^2 \right] \]

This 3-Dimensional Description Can Be Converted to a Sphere with a Surface at a Distance \((k_F)\) from the \((0,0,0)\) Point in Space. This is Known as the Fermi Surface.
Applying the concepts of the 1-dimensional Schrödinger equation allows for the calculation of energy levels in model systems. In some instances, if the architecture of the molecule is simple enough, it provides a high-quality estimate of the actual transition energies observed experimentally. Corrections to the equation and the addition of a temporal component of the equation make it even more powerful, but will not be described in this course.

The three-dimensional time-independent Schrödinger equation can be solved in a ready manner using the separation of variables technique. Furthermore, solving for the energy of the system when implemented into a “particle in a box” type of scenario is rather straightforward. If the lengths of all of the 3 sides of the box are equivalent, degenerate energy levels appear as a natural consequence of quantum mechanics.

Next Time: The Fermi Energy and the Density of States