The Schrödinger Equation

CHEM 361B: Introduction to Physical Chemistry

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Lecture 6

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Learning Objective: Solve the Schrödinger Equation for the Particle in a Box problem and apply its solutions to real molecules.

References:

- McQuarrie §3.1 - 3.7

Time Independent Schrödinger Equation

The separable nature of the wave equation allows us to examine the spatial part (x component) and ignore the temporal part (t component). For instance, let

$$u(x,t) = \psi(x)\cos(\omega t)$$

where $\psi(x)$ is the spatial amplitude of the wave equation. Evaluating this solution with the wave equation yields

$$\frac{d^2\psi}{dx^2} + \frac{\omega^2}{v^2}\psi(x) = 0$$

Using the de Broglie relation and assuming the total energy of a particle is the sum of its kinetic and potential energy yields

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + U(x)\psi(x) = E\psi(x)$$

which describes the steady state of a system.

What is $\psi(x)$?

$\psi(x)$ is the amplitude of a particle in some sense. The 'intensity of the particle' is

$$I \propto \psi(x)^* \psi(x)$$

where the asterix denotes the complex conjugate. Max Born interpreted this intensity when multiplied by a spatial zone

$$\psi^*(x)\psi(x)dx$$

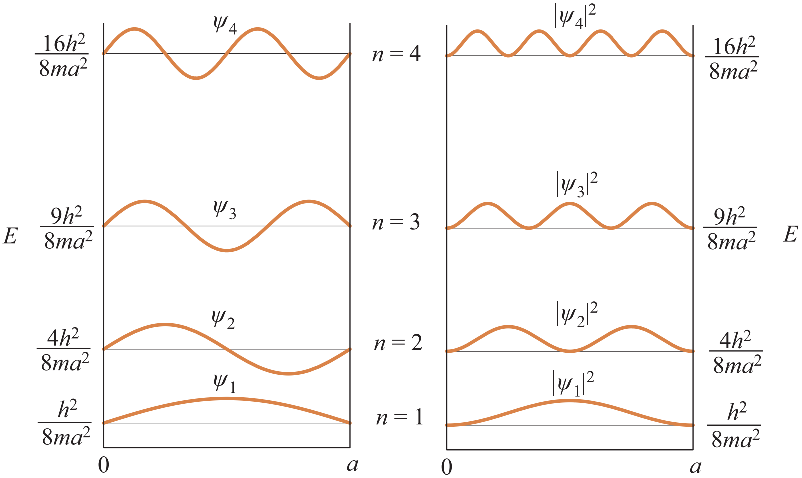
as the probability of finding the particle between x and $x + dx$. This is the widely accepted view.

Particle in a Box Example

Suppose that everywhere there is an infinite potential everywhere except for a small region ($0 \leq x \leq a$) where the potential is zero.

1. What are the boundary conditions for this system?
2. Show that the energy of the particle is discrete instead of continuous.
3. Find $\psi(x)$ for this system.

Particle in a Box Visualized



Quantization of Energy Emerges Naturally

- By simply employing the wave equation with boundary conditions to describe the particle, its energy is quantized.

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2ma^2} = \frac{h^2 n^2}{8ma^2}$$

- n in this case is can be called a quantum number.
- The emergence of quantization occurs naturally instead of forced when Planck and Bohr employed it.

Butadiene Example - Particle in a Box

Consider Butadiene ($H_2C{=}CH{-}CH{=}CH_2$) as a box:

- Assume that it is a linear molecule
- 4 π electrons moving across the four carbon atoms (trapped in the box)
- Total length between the two end carbon atoms is 5.78Å
- The energy of each electron can be described as

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

  but only two electrons can occupy any given energy level (Pauli exclusion principle).

Determine the lowest frequency of a photon required to excite the ground state of Butadiene.

Normalizing $\psi(x)$

According to the Born interpretation

$$\psi^*(x)_n \psi(x)_n dx = B^* B \sin^2\left(\frac{n\pi}{a}x\right) dx$$

is the probability of finding the particle between x and $x + dx$. If the particle is restricted to being between $0 \leq x \leq a$ then it must be found there. Therefore:

$$\int_0^a \psi^*(x)_n \psi(x)_n dx = 1$$

Using the normalization condition, determine B.

Particle Localization Example

Assume that the probability of finding a particle in a region of a box to be

$$Prob(x_1 \leq x \leq x_2) = \int_{x_1}^{x_2} \psi^*(x)\psi(x)dx$$

Determine the probability of finding a particle in the first half of our box ($0 \leq x \leq a/2$)

Summary

- The time-independent Schrödinger Equation represents the stationary state of a particle.
- The probabilistic interpretation of the wavefunction introduces a kind of indeterminacy. Quantum mechanics only provides statistical information on possible results.
- Quantization arises naturally from solving the Schrödinger Equation
- The particle in a box problem can be used to describe electrons on conjugated double bonds among other things