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CHEM 3420: Physical Chemistry II — Spring 2009

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Lecture 5: The Schrödinger Equation and the particle in a box (PIB)

References

1. Levine, *Physical Chemistry*, Sections 17.5–17.9

Key Concepts

- Schrödinger equation:
  - Solutions are called wavefunctions and given the symbol Ψ.
  - $\Psi(x, y, x)$ describes different possible behaviors (energy and positions) for an electron, i.e. orbitals.
  - The Schrödinger equation takes the sum of the kinetic and potential energies and sets it equal to the total energy.
  - The three dimensional Schrödinger wave equation:

$$\underbrace{-\frac{\hbar}{2m}\nabla^2\Psi(x,y,z)}_{\text{Kinetic Energy}} + \underbrace{V(x,y,z)\Psi(x,y,z)}_{\text{Potential Energy}} = \underbrace{E\Psi(x,y,z)}_{\text{Total Energy}}$$

  - What does it all mean?
    1. Describes the energy of the electron as the sum of the kinetic and potential energies.
    2. Is is a second-order partial differential equation (Yuck!)
    3. Solutions give us two things:
       (a) $\Psi(x, y, z)$ - wavefunctions that tell us where the electron is most likely to live
       (b) Energies of electrons in different possible states

- One of the classic applications of the SE is to solve the so-called particle in a box problem.
  - An electron is in a box of zero potential energy ($V = 0$ inside the box) with the potential being infinite everywhere else. This confines the electron to the box.
  - The boundary conditions for the wavefunction of the electron is it must be zero at the edges of the box.
  - We assumed a solution to the 1-D SE in the form:

$$\Psi = A\sin(kx) + B\cos(kx)$$

    and found that

$$k = \sqrt{\frac{2mE}{\hbar^2}}$$

  - Applying the boundary conditions meant that $B = 0$ (the cosine function doesn't work for these boundary conditions) and that

$$\sqrt{\frac{2mE}{\hbar^2}}a = n\pi$$

  - Rearranging this leads to an expression for the quantized energy of the electron wave

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

    where a is the length of the 1-D box.