The Richard Stockton College of New Jersey
Chemistry Program, School of Natural Sciences and Mathematics
PO Box 195, Pomoma, NJ

CHEM 3420: Physical Chemistry II — Spring 2009

January 28, 2008

Lecture 4: Uncertainty, Wave Equations

References

1. Levine, *Physical Chemistry*, Sections 17.1–17.6

Key Concepts

- The wave-like nature of particles (electrons) leads to an inherent uncertainty in their position and energy. This is quantified in the Heisenbery Unicertainty principle.

$$\Delta x \Delta P \geq \frac{\hbar}{2}$$

  where Δx is the uncertainty in the position of the electron and Δp is the uncertainty in the momentum (energy).

- The important conceptual point is that due to the wave properties we can not describe the position and energy of an electron exactly. If we know one exactly, we know nothing about the other.

- For classical waves (a vibrating string) the wave equation is a differential equation that when solved will yield a functional relationship describing the physical wave.

$$\frac{\partial^2 F}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 F}{\partial t^2}$$

  where x is the position variable, t is time, v is the wave velocity, and $F(x,t)$ is the solution (the wave!).

- Solutions to the classical wave equation can be determined using separation of variables: $F(x,t) = X(x)T(t)$. This converts the partial derivatives to full derivatives, allowing for a solution.

$$\frac{1}{X} \frac{d^2 X}{dx^2} = \frac{1}{v^2 T} \frac{d^2 T}{dt^2} = \text{constant} = -k^2$$

  - For the position part ($X(x)$), the general solution has the form:

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

    where A and B are constants that are determined using the physical boundary conditions for a particular situation.

  - The temporal portion ($T(t)$) has a similar looking general solution:

$$T(t) = E \sin kvt + G \cos kvt$$

    with E and G being constants that can be determined using the initial conditions.

- One possible solution has the form: $AE \sin kx \sin kvt$. If the solution is truly a wave, then the value of F must be the same at x and $x + \lambda$ (one wave length away). This leads to a restriction on k

$$k = \frac{2\pi}{\lambda} n$$

  which leads to the fundamental ($n = 1$) and higher harmonics ($n = 2, 3, 4...$).