Chemistry 3P51 – Fall 2013
Quantum Chemistry

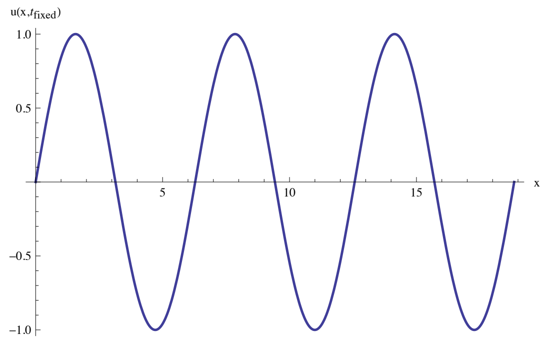
Lecture No. 3
Sep 9th, 2013

Objectives

- To introduce the mathematical description of standing and traveling waves.
- To introduce the wave equation of classical waves.
- To motivate the one-dimensional time-independent Schrödinger equation as the matter wave equation for obtained from the De Broglie relationship.

Mathematical description of waves

- A wave is a **disturbance** of the medium. The magnitude $u(x,t)$ of the displacement (disturbance) relative to equilibrium is called **amplitude of the wave**



Snapshot of harmonic wave at $t = t_{fixed}$

- There are two types of waves: **traveling** and **standing.** The former is a disturbance that progresses in some direction. The latter is disturbance that repeats itself in time but has no net translational motion

Standing and traveling waves

- Standing waves in one-dimension have the form

$$u_{\text{stand}}(x,t) = X(x)T(t) = (\text{function of } x) \times (\text{function of } t)$$

- Traveling waves in one-dimension have the form

$$u_{\text{travel}}(x,t) = f(kx - \omega t)$$

- Using the trigonometric identity

$$\sin\alpha\cos\beta = \frac{1}{2}\sin(\alpha+\beta) + \frac{1}{2}\sin(\alpha-\beta)$$

- It is possible to write a **standing wave** as a superposition of two **traveling waves of the same frequency traveling in opposite direction**

$$u_{\text{stand}}(x,t) = A\sin(kx)\cos(\omega t)$$
$$= \frac{1}{2}A\sin(kx+\omega t) + \frac{1}{2}A\sin(kx-\omega t)$$

Classical wave equation

- The amplitude $u(x,t)$ of every one-dimensional (1D) wave satisfies a partial differential equation known as the **classical wave equation**

$$\boxed{\frac{\partial^2 u}{\partial x^2}(x,t) = \frac{1}{\mathrm{v}^2}\frac{\partial^2 u}{\partial t^2}(x,t)}$$

where v is the speed with which the wave propagates. This equation can be derived from general physics principles

- The former equation can be extended from 1D to 3D (three dimensions). In 3D the amplitude depends on three spatial coordinates and time. In this case the equation looks like

$$\boxed{\nabla^2 u(x,y,z,t) = \frac{1}{\mathrm{v}^2}\frac{\partial^2 u}{\partial t^2}(x,y,z,t)}$$

∇^2.– Laplacian

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General form of solutions of the classical wave equation

- The general form $u(x,t)$ of a solution to the wave equation has the form

$$u(x,t) = f(kx \mp \omega t)$$

f is any given function
- is for a wave propagating to the right
+ Is for a wave propagating to the left

k and ω are variables characterizing the wave motion

$\nu = \frac{1}{T} = \frac{\mathrm{v}}{\lambda}$ is the **frequency**

$k = \frac{2\pi}{\lambda}$ is the **wave number**

$\omega = 2\pi\nu$ is the **angular frequency**

v is the **speed**

T is the **period**

λ is the **wave length**

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Searching for a differential equation for matter waves

- Let us propose a solution to the wave equation

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

- We would like to find what is the equation that ψ should satisfy so that *u* is a solution to the classical wave equation
- In order to do so, we substitute the former expression into the classical wave equation. After doing so and simplifying, we obtain the following equation

$$\psi''(x)=-\frac{\omega^2}{\mathrm{v}^2}\psi(x) \qquad (3.1)$$

- From the De Broglie equation we know that

$$\lambda=\frac{h}{p} \qquad (3.2)$$

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Searching for a differential equation for matter waves

- From the relations presented in slide 5, it is possible to conclude that

$$\frac{\omega}{\mathrm{v}}=\frac{2\pi}{\lambda}$$

which from equation (3.2) can be re-expressed as

$$\frac{\omega}{\mathrm{v}}=\frac{2\pi p}{h} \qquad (3.3)$$

- We also know that the **total mechanical energy** for a classical particle is the sum of the **kinetic energy** and **potential energy**

$$E=T+V(x)=\frac{p^2}{2m}+V(x) \qquad (3.4)$$

- From (3.3) and (3.4) we obtain

$$\frac{\omega^2}{\mathrm{v}^2}=\frac{8\pi^2 m}{h^2}\left[E-V(x)\right] \qquad (3.5)$$

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The time-independent Schrödinger equation

- Substitution of (3.5) into (3.1) leads, after some manipulations, to

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

- The former equation is the one-dimensional (1D) time-independent **Schrödinger equation.**

- This **partial differential equation** determines the matter wave $\psi(x)$ for a particle moving along the *x* axis in the presence of a time-independent potential *V(x)*

- This equation was first deduced in 1926 by Erwin Schrödinger, an Austrian physicist.

- Solutions of the Schrödinger equation are called **wave-functions** because they represent de Broglie waves of a particle.

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