CHEMISTRY 163A

HEURISTIC "MOTIVATIONS" FOR SCHRÖDINGER WAVE EQUATION

I. Schrödinger *time independent* wave equation

Start with time-independent classical wave equation for **standing wave** (section 3-1 McQ.)

$$u(x, t) = \psi(x) \cos 2\pi\nu t$$

This can be written as sum of two traveling waves

$$u(x,\ t) = \frac{\psi(x)}{2\cos\left(\frac{2\pi x}{\lambda}\right)}\left\{\cos\left[2\pi\left(\frac{x}{\lambda} - \nu t\right)\right] + \cos\left[2\pi\left(\frac{x}{\lambda} + \nu t\right)\right]\right\}$$

$$u(x, t) = \psi(x) \cos 2\pi\nu t = \psi(x) \cos \omega t$$

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

Substituting $u(x, t)$ into C.W.E. (eq 3.1, McQ):

$$\frac{d^2\psi}{dx^2} + \frac{\omega^2}{\mathrm{v}^2}\psi = 0$$

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda^2}\psi$$

Make DeBroglie connection using

$$\lambda \text{ of particle} \rightarrow m\mathrm{v} \rightarrow E$$

$$p\lambda = h$$

$$E = \frac{1}{2}m\mathrm{v}^2 + U = \frac{p^2}{2m} + U$$

$$E = \frac{h^2}{2m\lambda^2} + U$$

$$\frac{1}{\lambda^2} = \frac{2m}{h^2}[E - U]$$

Using this in time independent equation for ψ

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{h^2} 2m[E - U]\psi$$

$$\frac{-\hbar^2}{2m}\frac{d^2\psi}{dx^2} = [E - U]\psi$$

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

as we will
see this is
time independent Schrödinger Eqn.

II. Second "heuristic"—Time dependence for "free" (no particle energy) particle wave

A *general* (complex) time dependent wave is

$$a(x,t) = a_o e^{2\pi i\left(\frac{x}{\lambda} - \nu t\right)}$$

Get relationship between space and time derivatives via $E = h\nu \quad p\lambda = h$

$$\frac{\partial^2 a(x,t)}{\partial x^2} = a_o\left(\frac{-2\pi i}{\lambda}\right)^2 e^{2\pi i\left(\frac{x}{\lambda} - \nu t\right)}$$

$$= \frac{-4\pi^2}{\lambda^2} a(x,t)$$

using $p\lambda = h$

$$= \frac{-4\pi^2}{h^2} p^2 a(x,t)$$

Since $E = \frac{p^2}{2m}$ for *free* particle

$$\frac{\partial^2 a(x,t)}{\partial x^2} = \frac{-4\pi^2}{h^2} 2mEa(x,t)$$

$$-\frac{\hbar^2}{2ma(x,t)}\frac{\partial^2 a(x,t)}{\partial x^2} = E$$

taking *time* derivative

$$\frac{\partial a(x,t)}{\partial t} = (-2\pi i\nu)a(x,t)$$

using $E = h\nu$

$$-\frac{\hbar^2}{2m}\frac{1}{a(x,t)}\frac{\partial^2 a(x,-t)}{\partial x^2} = -\frac{\hbar}{i}\frac{1}{a(x,t)}\frac{\partial a(x,t)}{\partial t}$$

$-\frac{\hbar^2}{2m}\frac{\partial^2 a(x,t)}{\partial x^2} = i\hbar\frac{\partial a(x,t)}{\partial t}$	suggestive of time dependent Schrödinger equation