Physics 570A Lecture 3

Wave mechanics

Planck: $E = h\nu = \hbar\omega$

$(\omega = 2\pi\nu)$
"angular frequency"

de Broglie: $p = \frac{h}{\lambda} = \hbar k$

$(k = \frac{2\pi}{\lambda})$
"wave number"

In terms of their complementary wave/particle properties, the photon and material particles, such as the electron, are quite similar. Thus, we will endeavor to write down a wave equation for electrons, similar to the E+M wave equation:

$$\left(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)\vec{A}(\vec{r},t) = 0,$$

in free space. Here $\vec{A}$ is the vector potential.

A plane-wave solution has the form:

$$\vec{A}(\vec{r},t) = \vec{\epsilon}\, e^{i(\vec{k}\cdot\vec{r}-\omega t)}$$

Plugging this into the wave

equation gives

$$\left(-\vec{k}^2 + \frac{\omega^2}{c^2}\right)\vec{E} = 0$$

or $\omega = c|\vec{k}|$. For a free particle of mass m, one has (neglecting relativistic effects)

$$E = \frac{\vec{p}^{\,2}}{2m}$$

$$\hbar\omega = \frac{\hbar^2\vec{k}^{\,2}}{2m}.$$

A plane wave

$$\psi(\vec{r},t) = A e^{i(\vec{k}\cdot\vec{r} - \omega t)}$$

for such a particle must

satisfy a different type of wave equation. Notice that

$$\nabla \psi = i\vec{k}\,\psi$$

$$\frac{\partial \psi}{\partial t} = -i\omega\,\psi$$

$$\vec{p}\,\psi = \hbar\vec{k}\,\psi = \frac{\hbar}{i}\nabla\psi$$

$$E\psi = \hbar\omega\psi = i\hbar\frac{\partial\psi}{\partial t}$$

$$\left(E - \frac{p^2}{2m}\right)\psi = 0$$

$$\left[i\hbar\frac{\partial}{\partial t} - \left(\frac{\hbar}{i}\nabla\right)^2\Big/2m\right]\psi = 0$$

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi$$

In general, for a particle in an external potential $V(\vec{r},t)$, one has

$$E = \frac{\vec{p}^{\,2}}{2m} + V(\vec{r},t).$$

We postulate that the quantum mechanical wave function $\psi(\vec{r},t)$ of a particle obeys the

Schrödinger equation (1)

$$\boxed{i\hbar \frac{\partial \psi(\vec{r},t)}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r},t) + V(\vec{r},t)\psi(\vec{r},t).}$$

The energy carried by an E&M wave is proportional to the time-average of the square of the field, and hence to $|\vec{A}|^2$.

Since $E = nh\nu$, this implies that the # of photons is proportional to $|\vec{A}|^2$. Indeed, the probability to find a photon at a given place and time is proportional to

$$P(\vec{r},t) \propto |\vec{A}(\vec{r},t)|^2.$$

By analogy, we assert, following Max Born, that the probability to observe a material particle is

$$P(\bar{r},t) \propto |\Psi(\bar{r},t)|^2.$$ (define $|z|^2$)

The total probability should be unity:

$$\boxed{1 = \int d^3r \, |\Psi(\bar{r},t)|^2.}$$

If $\Psi(\bar{r},t)$ satisfies this equation, it is said to be <u>normalized</u>.

Since the Schrödinger equation is linear in ψ, we have the important

Superposition principle:

If ψ_1 satisfies Eq. (1) and ψ_2 satisfies Eq. (1), then so does

$$\phi(\vec{r},t) = a\,\psi_1(\vec{r},t) + b\,\psi_2(\vec{r},t)$$

Normalization requires

$$1 = \int d^3r\, |\phi(\vec{r},t)|^2$$

$$= |a|^2 \int d^3r\, |\psi_1(\vec{r},t)|^2 + |b|^2 \int d^3r\, |\psi_2|^2$$

$$+ a^* b \int d^3r\, \psi_1^* \psi_2 + a b^* \int d^3r\, \psi_1 \psi_2^* .$$

Dirac notation for overlap integrals

$$\langle \psi_1 | \psi_2 \rangle = \langle 1|2 \rangle \equiv \int d^3r \; \psi_1^*(\vec{r}) \, \psi_2(\vec{r})$$

$$\langle 2|1 \rangle = \langle 1|2 \rangle^*$$

inner product of two wave functions

normalization

$$\langle \psi | \psi \rangle = \int d^3r \, |\psi(\vec{r})|^2$$

$$\underline{1} = \langle \phi | \phi \rangle = |a|^2 \overbrace{\langle 1|1 \rangle}^{1} + |b|^2 \overbrace{\langle 2|2 \rangle}^{1}$$

$$+ a^* b \, \langle 1|2 \rangle + a \, b^* \langle 2|1 \rangle$$

$$1 = |a|^2 + |b|^2 + a^* b \, \langle 1|2 \rangle + a b^* \langle 2|1 \rangle$$

If $\langle 1|2 \rangle = 0$, ψ_1 and ψ_2 are said to be <u>orthogonal</u>. Then

$$1 = |a|^2 + |b|^2.$$

Conservation of probability

$$\rho(x,t) = \psi^*(x,t)\,\psi(x,t)$$

probability density (per unit length)

What is $\frac{\partial \rho}{\partial t}$?

$$\frac{\partial}{\partial t}\psi^*\psi = \psi^*\frac{\partial \psi}{\partial t} + \frac{\partial \psi^*}{\partial t}\psi$$

$$\psi^*\left[\, i\hbar\frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} + V\psi \,\right]$$

$$-\psi\left[\, -i\hbar\frac{\partial \psi^*}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi^*}{\partial x^2} + V\psi^* \,\right]$$

$(V^* = V)$

$$\frac{\partial \rho}{\partial t} = -\frac{\hbar}{2im}\left[\psi^*\frac{\partial^2 \psi}{\partial x^2} - \psi\frac{\partial^2 \psi^*}{\partial x^2}\right]$$

$$\frac{\partial \rho}{\partial t} = -\frac{\partial}{\partial x}\left[\frac{\hbar}{2im}\left(\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x}\right)\right]$$

Defining the probability current

$$j_x(x,t) \equiv \frac{1}{2m}\left[\psi^* \frac{\hbar}{i}\frac{\partial}{\partial x}\psi - \psi \frac{\hbar}{i}\frac{\partial}{\partial x}\psi^*\right],$$

we find

$$\boxed{\frac{\partial \rho}{\partial t} + \frac{\partial j_x}{\partial x} = 0}$$

$$P(a,b) = \int_a^b dx\, |\psi|^2$$

$$\frac{d\,P(a,b)}{dt} = \int_a^b dx\, \frac{\partial \rho}{\partial t} = -\int_a^b dx\, \frac{\partial j_x}{\partial x}$$

$$= \underbrace{j_x(a,t)}_{\text{in}} - \underbrace{j_x(b,t)}_{\text{out}}$$

In three dimensions,

$$\vec{J}(\vec{r},t) = \frac{1}{2m}\left[\psi^* \frac{\hbar}{i}\nabla\psi - \psi\frac{\hbar}{i}\nabla\psi^*\right]$$

and

$$\boxed{\frac{\partial \rho}{\partial t} + \nabla \cdot \vec{J} = 0 \qquad \text{continuity equation}}$$

What is the meaning of $\vec{J}$?

Electric current operator

$$\vec{J}_e = -\frac{e\hbar}{2im}\left[\psi^*\nabla\psi - \psi\nabla\psi^*\right] = -e\vec{J}$$

for electrons of charge $-e$.

The complexity of ψ

If ψ is real, then $\psi^* = \psi$.

$$\Rightarrow j_x = \frac{\hbar}{2im}\left(\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x}\right) = 0.$$

Thus a real wavefunction cannot describe a state with a flux or flow of particles. The complexity of ψ is not a mathematical convenience, but a necessity.

Amplitude and phase

Let $\psi(x,t) = A(x,t)\, e^{i\theta(x,t)}$

A, θ = real functions

$$A(x,t) = \sqrt{\rho(x,t)}$$

$$j_x = \frac{\hbar \rho}{m} \frac{\partial \theta(x,t)}{\partial x} \quad \text{or}$$

$$\vec{J} = \frac{\hbar \rho}{m} \nabla \theta \quad \text{in 3D}$$

Thus the probability current (flow of particles) is determined by the gradient of the phase of the wavefunction.

Ex. Plane wave $\psi(x) = Ae^{ikx}$

$$j_x = \rho \frac{\hbar k}{m} = \rho \frac{p_x}{m} = \rho v$$