Lecture 5

Schrodinger Equation

Sept. 22, 2007

States of Definite Energy and Momentum

State of definite energy and momentum.

$$\psi(x,t) = Ae^{i(kx-\omega t)} = Ae^{i(px-Et)/\hbar}$$

Probability of finding particle at x at time t given by:

$$|\psi(x,t)|^2 = \left(Ae^{i(px-Et)/\hbar}\right)\left(Ae^{-i(px-Et)/\hbar}\right) = A^2$$

This is independent of x and t. $\Rightarrow$ The particle has equal probability of being found at any place at any time.

More about this later.

Operators

If particle is in state of definite energy E and momentum p

$$\psi(x,t) = Ae^{i(px-Et)/\hbar}$$

$$i\hbar\,\frac{\partial}{\partial t}\,\psi(x,t) = E\,\psi(x,t) \qquad\qquad -i\hbar\,\frac{\partial}{\partial x}\,\psi(x,t) = p\,\psi(x,t)$$

Energy operator: $\hat{E} = i\hbar\,\frac{\partial}{\partial t}$

Momentum operator: $\hat{p} = -i\hbar\,\frac{\partial}{\partial x}$

Eigenfunctions and Eigenvalues

If $\hat{E}\psi(x,t) = E\psi(x,t)$ then

$\psi(x,t)$ is an eigenfunction of $\hat{E}$ with eigenvalue E.

If $\psi(x,t)$ is a state of definite energy then

$\Rightarrow$ $\psi(x,t)$ is an eigenfunction of $\hat{E}$.

$$\hat{E}\psi(x,t) = E\psi(x,t)$$

If $\psi(x,t)$ is a state of definite momentum then

$\Rightarrow$ $\psi(x,t)$ is an eigenfunction of $\hat{p}$.

$$\hat{p}\psi(x,t) = p\psi(x,t)$$

If $\psi(x,t)$ is <u>not</u> a state of definite energy then

$$\hat{E}\psi(x,t) \neq E\psi(x,t)$$

Free Particle Schrodinger Equation

For a non-relativistic particle in a state of definite energy and momentum, not subject to any forces, $V(x) = 0$

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

$$\Rightarrow \qquad \hat{E}\psi(x,t) = \frac{\hat{p}^2}{2m}\psi(x,t)$$

This will be true for any free-particle state

Free-particle Schrodinger equation

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

Schrodinger Equation

If particle is subjected to a force there will be a potential energy $V(x)$ such that $F = \mathrm{d}V(x)/\mathrm{d}x$. Then

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

$$\Rightarrow \qquad \hat{E}\psi(x,t) = \left(\frac{\hat{p}^2}{2m} + V(x)\right)\psi(x,t)$$

Schrodinger equation:

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

Note that this is a non-relativistic equation.

Separation of Variables

$$\psi(x,t) = u(x)T(t)$$

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

$$i\hbar u(x)\frac{\mathrm{d}}{\mathrm{d}t}T(t) = T(t)\left(-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x)\right)u(x)$$

$$i\hbar \frac{1}{T(t)}\frac{\mathrm{d}}{\mathrm{d}t}T(t) = \frac{1}{u(x)}\left(-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x)\right)u(x)$$

$$i\hbar \frac{1}{T(t)}\frac{\mathrm{d}}{\mathrm{d}t}T(t) = E = \frac{1}{u(x)}\left(-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x)\right)u(x)$$

$$i\hbar \frac{\mathrm{d}}{\mathrm{d}t}T(t) = ET(t) \qquad \left(-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x)\right)u(x) = Eu(x)$$

Solutions

$$i\hbar \frac{\mathrm{d}}{\mathrm{d}t} T(t) = E T(t) \qquad \Rightarrow \qquad T(t) = e^{-iEt/\hbar}$$

$$\boxed{\psi(x,t) = u_E(x) e^{-iEt/\hbar}}$$

We are left with solving:

$$\left(-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x)\right) u_E(x) = E u_E(x)$$

$$H u_E(x) = E u_E(x)$$

$$H = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x)$$ is the Hamiltonian

Example of Free Particle

$$V(x) = 0 \qquad \Rightarrow \qquad H = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}$$

$$H u_E(x) = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} u_E(x) = E u_E(x)$$

possible solution: $u_E(x) = Ae^{ipx/\hbar}$

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} u_E(x) = \frac{p^2}{2m} u_E(x) = E u_E(x)$$

$$\Rightarrow \qquad \frac{p^2}{2m} = E$$

$$\psi(x,t) = Ae^{i(px-Et)/\hbar}$$

Note that $u_E(x) = Ae^{-ipx/\hbar} \quad \Rightarrow \quad \psi(x,t) = Ae^{i(-px-Et)/\hbar}$

would also work

Example of infinite Well

$V(x) = 0$ for $0 < x < L$

$V(x) = \infty$ elsewhere

outside of $0 < x < L$ $u_E(x) = 0$

for $0 < x < L$

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}u_E(x) = Eu_E(x)$$

bouundary condition: $u_E(x) = 0$ at $x = 0$ and $x = L$

$u_E(x) = Ae^{\pm ipx/\hbar}$ doesn't work

try

$$u_E(x) = \frac{A}{2i}\left(e^{ipx/\hbar} - e^{-ipx/\hbar}\right) = A\sin\left(px/\hbar\right) = A\sin(kx)$$

Quantized Energies

$$u_E(x) = A\sin(kx) \qquad \Rightarrow \qquad u_E(0) = 0$$

$u_E(L) = 0$ requires $kL = n\pi$ where $n = 1, 2, \cdots$

$$k = \frac{n\pi}{L} \qquad \Rightarrow \qquad p = \frac{n\pi\hbar}{L} \qquad \Rightarrow \qquad E = \frac{n^2\pi^2\hbar^2}{2mL}$$

$$\boxed{\begin{gathered} \psi_n(x,t) = A\sin(k_n x)e^{-iE_n t/\hbar} \\ k_n = \frac{n\pi}{L} \qquad\qquad E_n = \frac{n^2\pi^2\hbar^2}{2mL} \end{gathered}}$$

Normalization

Probability density for particle to be at x at time t:

$$P(x,t) = |\psi(x,t)|^2 = \psi^*(x,t)\,\psi(x,t)$$

Normalize $\psi(x,t)$ (multiply by a constant) so that the particle has unit probability of being found somewhere.

$$\int_{-\infty}^{\infty} |\psi(x,t)|^2 \,\mathrm{d}x = 1$$

$$\langle x \rangle = \int_{-\infty}^{\infty} x\,P(x,t)\,\mathrm{d}x = \int_{-\infty}^{\infty} \psi^*(x,t)\,x\,\psi(x,t)\,\mathrm{d}x$$

Normalization of Infinite Well Solutions

$$\int_{-\infty}^{\infty} |\psi_n(x,t)|^2 \,\mathrm{d}x = \int_{-\infty}^{\infty} \psi_n^*(x,t)\,\psi_n(x,t)\,\mathrm{d}x$$

$$\int_0^L A\sin\left(\frac{n\pi x}{L}\right) e^{iE_nt/\hbar} A\sin\left(\frac{n\pi x}{L}\right) e^{-iE_nt/\hbar}\,\mathrm{d}x$$

$$= A^2 \int_0^L \sin^2\left(\frac{n\pi x}{L}\right)\,\mathrm{d}x = A^2\,\frac{L}{2} = 1$$

$$A = \sqrt{\frac{2}{L}}$$

$$\psi_n(x,t) = \sqrt{\frac{2}{L}}\,\sin(k_n x) e^{-iE_nt/\hbar}$$

Expectation Values

- Any observable (e.g., energy, momentum, position, angular momentum) is represented by a corresponding operator.
- For a particle in a given state, in general, we can't make exact predictions for what value of an observable will be measured. We can only give the probability distribution for the observable.
- The expectation value of an observable is the average value of the observable that will be observed for a particle in a given state.

$$\boxed{\langle A \rangle = \int_{-\infty}^{\infty} \psi^*(x,t)\, \hat{A}\, \psi(x,t)\, \mathrm{d}x}$$

Examples of Expectation Values

$$\langle E\rangle = \int_{-\infty}^{\infty} \psi^*(x,t)\,\hat{E}\,\psi(x,t)\,\mathrm{d}x \;=\; i\hbar \int_{-\infty}^{\infty} \psi^*(x,t)\,\frac{\partial}{\partial t}\,\psi(x,t)\,\mathrm{d}x$$

$$\langle p\rangle = \int_{-\infty}^{\infty} \psi^*(x,t)\,\hat{p}\,\psi(x,t)\,\mathrm{d}x \;=\; -i\hbar \int_{-\infty}^{\infty} \psi^*(x,t)\,\frac{\partial}{\partial x}\,\psi(x,t)\,\mathrm{d}x$$

$$\langle p^2\rangle = \int_{-\infty}^{\infty} \psi^*(x,t)\,\hat{p}^2\,\psi(x,t)\,\mathrm{d}x \;=\; -\frac{\hbar^2}{2m} \int_{-\infty}^{\infty} \psi^*(x,t)\,\frac{\partial^2}{\partial x^2}\,\psi(x,t)\,\mathrm{d}x$$

$$\langle x\rangle = \int_{-\infty}^{\infty} \psi^*(x,t)\,\hat{x}\,\psi(x,t)\,\mathrm{d}x \;=\; \int_{-\infty}^{\infty} \psi^*(x,t)x\psi(x,t)\,\mathrm{d}x$$

Summary of Main Points

- Operators

$$\hat{x} = x \qquad \hat{p} = -i\hbar\,\frac{\partial}{\partial x} \qquad \hat{E} = -\hbar\,\frac{\partial}{\partial t} \qquad \hat{E} = \frac{\hat{p}}{2m}$$

- Schrodinger Equation

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

$$\psi(x,t) = T(t)u(x)$$

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\,T(t) = ET(t) \qquad T(t) = e^{-iEt/\hbar}$$

$$Hu_E(x) = \left(-\frac{\hbar^2}{2m}\,\frac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x)\right)\,u_E(x)$$