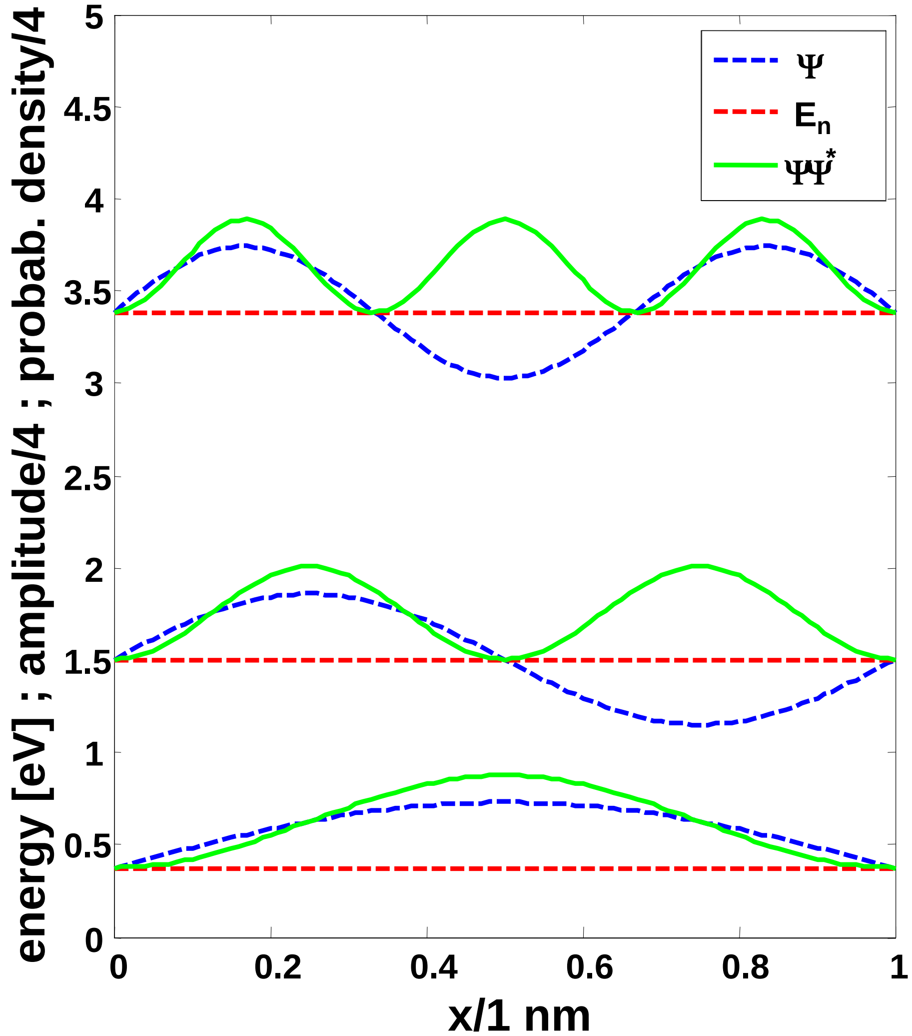
# Lecture 13: 02/16/09

- Stationary States
  - Properties
  - time-independent Schrödinger equation
- Superposition of stationary states
  - General solution



## Recap:

Time-dependent Schrödinger equation: $i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi(x,t)$

$\hat{H}$: Hamiltonian operator: $\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x,t)$

## $\mathrm{II}_{1,4}$ Physical Significance of the Wave Function $\Psi(x,t)$:

$$\int_a^b |\Psi|^2 dx = \int_a^b \underbrace{\Psi^* \Psi}_{=P(x,t)} dx = \left\{ \begin{array}{l} \text{probability of finding the} \\ \text{particle between a and b} \\ \text{at time t} \end{array} \right\}$$

$= P(x,t)\,dx$: probability density

## $\mathrm{II}_{1,5}$ Expectation Values

$$\langle Q \rangle = \int_{-\infty}^{+\infty} \Psi^* \hat{Q}\left(x, \frac{\hbar}{i}\frac{\partial}{\partial x}\right) \Psi \, dx$$

quantity Q ($\langle Q \rangle$) ; ← operator ($\hat{Q}$)

position x $\longleftrightarrow$ operator $\hat{x} = x$

momentum p $\longleftrightarrow$ operator $\hat{p} = \frac{\hbar}{i}\frac{\partial}{\partial x}$

## Expectation Values: Examples

- position: $\langle x \rangle = \int_{-\infty}^{+\infty} \Psi^*(x,t)\, x\, \Psi(x,t)\, dx$

- particle momentum: $\langle p \rangle = \int_{-\infty}^{+\infty} \Psi^* \left( \frac{\hbar}{i} \frac{\partial}{\partial x} \right) \Psi \, dx$

- kinetic energy: $\langle KE \rangle = \int_{-\infty}^{+\infty} \Psi^* \left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \right) \Psi \, dx$

- total energy: $\langle E \rangle = \langle KE \rangle + \langle V \rangle = \int_{-\infty}^{+\infty} \Psi^* \left( \underbrace{-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x,t)}_{\hat{H}} \right) \Psi \, dx$

$\hat{H}$: Hamiltonian operat.

$$\Rightarrow \langle E \rangle = \langle H \rangle = \int_{-\infty}^{+\infty} \Psi \left( i\hbar \frac{\partial}{\partial t} \right) \Psi \, dx$$

$\hat{H}\Psi = i\hbar \frac{\partial}{\partial t} \Psi$ : Schrödinger equ.

$\Rightarrow i\hbar \frac{\partial}{\partial t}, \hat{H} \longleftrightarrow$ represent energy in QM

## $II_{1,6}$ Stationary States

concider special case: $V = V(x)$ indep. of time

$\Rightarrow$ use separation of variables to find special subset of solutions of time-dep. Schrödinger equ.

(1) $$\Psi(x,t) = \psi(x) \cdot f(t)$$

"capital psi"

"lowercase" function of x alone

function of time alone

$\Rightarrow$ at every point x, time dependency is the same

$\Rightarrow$ Analogous to standing waves in classical physics

$\Rightarrow$ Insert (1) into time-dependent Schrödinger Equ:

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

$$\Rightarrow i\hbar\,\psi(x)\frac{d\varphi(t)}{dt} = -\frac{\hbar^2}{2m}\varphi(t)\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x)\varphi(t)$$

$$\Rightarrow \underbrace{i\hbar\frac{1}{\varphi(t)}\frac{d\varphi(t)}{dt}}_{\text{depends on time only}} = \underbrace{-\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{d^2\psi(x)}{dx^2} + V(x)}_{\text{depends on position only since } V = V(x) \text{ here}} = E$$

$\Rightarrow$ "$=$" must be true for all $x, t$

$\Rightarrow$ both sides must be constant!

$\Rightarrow$ call constant $=$ "$E$"

$\Rightarrow$ look at left and right side of this equation separately!

- **left side:**

$$i\hbar \frac{1}{f(t)} \frac{d f(t)}{dt} = E$$

$\Rightarrow$ $$\frac{d f(t)}{dt} = -\frac{iE}{\hbar} f(t)$$ : differential equ.

Solution: $$f(t) \propto e^{-iE/\hbar \cdot t}$$

$\Rightarrow$ oscillates with definite $\underline{\omega} = 2\pi\nu = \underline{E/\hbar}$

$\Rightarrow$ get $\underline{\underline{E}} = \underline{\hbar\omega}$ = energy of particle (according to Einstein, de Broglie!)

$\Rightarrow$ stationary states always have definite energy $E$!

$\Rightarrow$ $$\boxed{\Psi_n(x,t) = \psi_n(x)\, e^{-i\frac{E_n}{\hbar}t} \text{ for stationary states (only!)}}$$

• right side: (multipl. by $\psi(x)$)

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

time independent Schrödinger equation

has $\psi_n(x)$ as solution

$\rightarrow$ $\Psi(x,t) = \psi(x)e^{-iE/\hbar\, t}$ is solution of time-dep. S.E.

$\Rightarrow$ short form:

$$\hat{H}\psi_n(x) = E_n\psi_n(x) \iff \hat{H}: \text{"total energy operator"}$$

operator, eigenvalue, eigenfunction

This type equ. is called an eigenvalue equation

$\Rightarrow$ $\psi_n(x)$, $E_n$ : solutions of eigenvalue equation for operator $\hat{H}$

Why is $\Psi(x,t)=\psi(x)e^{-i\frac{E}{\hbar}t}$ called a "stationary state"?

A. Because the probability density does not change with time

B. Because all expectation values do not change with time

C. Because they have definite total energies

D. All of the above

E. None of the above

- Why is $\Psi(x,t) = \psi(x)\, e^{-iE/\hbar\, t}$ called a "stationary state"?

1) Probability density:

$$|\Psi(x,t)|^2 = \Psi^* \Psi = \psi^*(x)\, e^{+i\frac{E}{\hbar}t}\, \psi(x)\, e^{-i\frac{E}{\hbar}t}$$

$$= |\psi(x)|^2 \cdot 1 = |\psi(x)|^2 \text{ time independent}$$

$\Rightarrow$ stationary state have stationary probability densities!

normalization requires: $\int_{-\infty}^{+\infty} |\psi(x)|^2 dx = 1$ as before

2) Expectation values:

$\Rightarrow$ time dependence cancels out

Example:

$$\langle x\rangle = \int_{-\infty}^{+\infty} \psi^*(x)\, e^{+i\frac{E}{\hbar}t} \times \psi(x)\, e^{-i\frac{E}{\hbar}t} = \int_{-\infty}^{+\infty} \psi(x)^* x\, \psi\, dx$$

$$\boxed{\Rightarrow \text{Every expectation value is constant in time for stationary states}}$$

Note: $\langle x\rangle = \text{const} \Rightarrow \langle p\rangle = m\dfrac{d\langle x\rangle}{dt} = 0$ for all stationary states!

3) Total Energy:

$\hat{H}\psi = E\psi$

$$\langle E\rangle = \langle H\rangle = \int_{-\infty}^{+\infty} \psi^*(x)\, \hat{H}\, \psi(x)\, dx = E \underbrace{\int_{-\infty}^{+\infty} |\psi(x)|^2 dx}_{=1 \text{ (normalized)}} = E$$

$\langle H^2\rangle$

$$\hat{H}^2\psi(x) = \hat{H}(\hat{H}\psi) = \hat{H}(E\psi) = E(\hat{H}\psi) = E^2\psi$$

$$\Rightarrow \langle H^2\rangle = E^2$$

$\Rightarrow$ variance of energy: $\sigma_H^2 = \langle H^2\rangle - \langle H\rangle^2 = E^2 - E^2 = 0$

$\Rightarrow$ stationary states have definite total energy! i.e. measurement of energy on ensemble of identical particles always gives same $E$.

## $II_{1,7}$ General Solution of the time-dependent Schrödinger Equation

- for a given $V = V(x)$

time indep S.E ⟹ infinite collection of solutions $\psi_1, \psi_2, \psi_3 \dots$ each with its associated energy values $E_1, E_2, E_3 \dots$

⟹ wave functions for stationary states (energy states)

$$\Psi_n(x,t) = \psi_n(x) e^{-i\frac{E_n}{\hbar} \cdot t}$$

⟹ The linear combination of these stationary states gives a much more general solution of the time dep. S.E. for a given $V(x)$: (recall that the time dep. S.E. is linear in $\Psi(x,t)$!)

$$\Psi(x,t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-iE_n/\hbar\, t} = \sum_{n=1}^{\infty} c_n \Psi_n(x,t)$$

$c_n$ ↑ constant

**Is the linear combination (superposition) of stationary states:**

$$\Psi(x,t) = \sum c_n \Psi_n(x,t)$$

**also a solution of the <u>time independent</u> <u>Schrödinger equation</u>?**

- **A. Yes**
- **B. No**
- **C. Who knows**

time indep. S.E.

$$\hat{H}\psi_n = E_n \psi_n$$

Example: if

$$\left.\begin{array}{l}\hat{H}\psi_1 = E_1\psi_1 \\ \hat{H}\psi_2 = E_2\psi_2\end{array}\right\} E_1 \neq E_2$$

$$\Rightarrow H(\psi_1 + \psi_2) = E_1\psi_1 + E_2\psi_2$$

$$\neq E(\psi_1 + \psi_2)$$