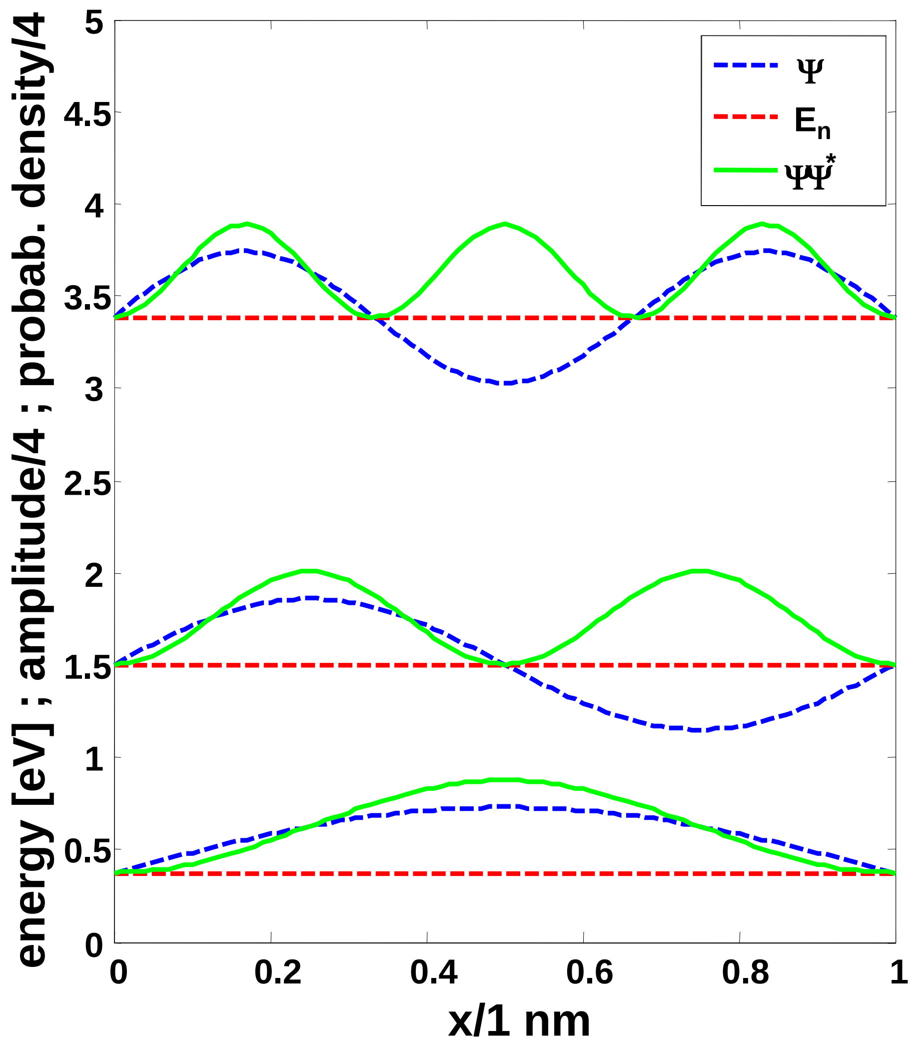
Lecture 14: 02/18/09

- The infinite square well
  - stationary states
  - Orthonormal wave functions
  - General solution



Recap

$II_{1,6}$ Stationary States

⇒ subset of solutions of Schrödingers equation:

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

- time indep. probability density
- time indep. expectation values
- definite total energy

time independent Schrödinger equation:

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

: eigenvalue equ.

solutions : $\psi_n(x)$ with associated E_n

$II_{1,7}$ General Solution of the time-dependent Schrödinger Equ.

$$\boxed{\Psi(x,t) = \sum_{n=1}^{\infty} c_n\, \psi_n(x)\, e^{-i\frac{E_n}{\hbar}t} = \sum_{n=1}^{\infty} c_n\, \Psi_n(x,t)}$$

Every solution of the time-dependent Schrödinger equation can be written as a linear combination of the stationary state wave functions for a given V(x)!

$$\boxed{\Psi(x,t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-i\frac{E_n}{\hbar}t} = \sum_{n=1}^{\infty} c_n \Psi_n(x,t)}$$

- This general solution is <u>not</u> a solution of the time-<u>in</u>dependent Schrödinger equation!
  $\Rightarrow$ no superposition principle for time <u>indep</u>. SE !
- It is the general solution for the time-dependent SE
- Every solution of the time-<u>dependent</u> Schrödinger equation can be written as a linear combination of the stationary state wave functions for a given $V(x)$!

$\Rightarrow$ Once you have solved the time-indep. SE, you are done. Just need to find the constants $c_1, c_2, c_3, \ldots$ to fit the initial conditions.

Example:

$$\Psi(x,t) = \psi_1(x)\, e^{-i\frac{E_1}{\hbar}t} + \psi_2(x)\, e^{-i\frac{E_2}{\hbar}t}$$

$$\Rightarrow \underline{\hat{H}\,\Psi(x,t)} = \hat{H}\psi_1 e^{-i\frac{E_1}{\hbar}t} + \hat{H}\psi_2 e^{-i\frac{E_2}{\hbar}t}$$

time ind. S.E.

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

$$= E_1\psi_1 e^{-i\frac{E_1}{\hbar}t} + E_2\psi_2 e^{-i\frac{E_2}{\hbar}t}$$

$$\neq E\,\Psi(x,t)$$ $\Rightarrow \Psi$ is not a solution of the time-indep. SE

time dep. S.E.

$\hat{H}\Psi(x,t) = i\hbar\frac{\partial\Psi}{\partial t}$

$$= i\hbar\frac{\partial}{\partial t}\psi_1 e^{-i\frac{E_1}{\hbar}t} + i\hbar\frac{\partial}{\partial t}\psi_2 e^{-i\frac{E_2}{\hbar}t}$$

$$= \underline{i\hbar\frac{\partial}{\partial t}\Psi(x,t)}$$ $\Rightarrow \Psi$ is solution of the time-dependent SE

• given $V = V(x)$; starting wave function $\underline{\Psi(x, t=0)}$

$\Rightarrow$ Find $\Psi(x, \underline{t}) = ?$

<u>step 1:</u> Solve time-ind. S.E for $V = V(x) \rightarrow$ infinite collection of stationary state solutions $\psi_n(x)$ with associated E_n

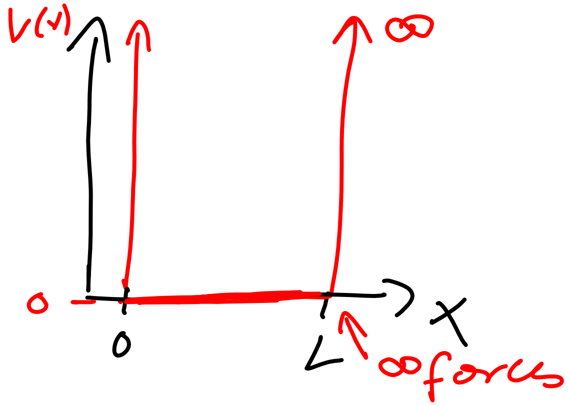
<u>step 2:</u> $$\Psi(x, t=0) = \sum_{n=1}^{\infty} c_n \psi_n(x) \qquad [\, t = 0 \rightarrow e^0 = 1 \,]$$

<u>step 3:</u> find constants c_n's from this (see later)

<u>step 4:</u> $$\underline{\Psi(x,t)} = \sum_{n=1}^{\infty} c_n \Psi_n(x,t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-i\frac{E_n}{\hbar}t}$$

II_2 Solutions of the 1-D Schrödinger Equations

$II_{2,1}$ Infinite Square Well – Particle in a Box:



⇒ particle confined to be between $x = 0$ and $x = L$ by potential

$$V(x) = \begin{cases} 0, & \text{if } 0 \le x \le L \\ \infty & \text{otherwise (infinite high walls)} \end{cases}$$

- outside the well: probability of finding the particle $= 0$

⇒ $\psi(x) = 0$, $x < 0$ or $x > L$

- inside the well: $V(x) = 0$ for $0 \le x \le L$

⇒ time indep. Schrödinger equ. gives:

$$-\frac{\hbar}{2m}\frac{d^2\psi(x)}{dx^2} + 0 = E\,\psi(x)$$ ⇒ solutions = stationary states

→ get differential equation:

$$\frac{d^2\psi(x)}{dx^2} = -\frac{2mE}{\hbar^2}\psi(x) = -k^2\psi(x) \quad \text{with } k \equiv \frac{\sqrt{2mE}}{\hbar}$$

⇒ general solutions:

$$\psi(x) = A\sin(kx) + B\cos(kx)$$

A, B: constants ⇒ fixed by boundary conditions!

• Boundary conditions:

key idea: $\psi(x)$ needs to be continuous!

⇒ $\psi(x=0) = \psi(x=L) \stackrel{!}{=} 0$

⇒ $\psi(0) = A\sin(0) + B\cos(0) = \underline{B \stackrel{!}{=} 0}$

⇒ $\psi(L) = A\sin(kL) \stackrel{!}{=} 0$

⇒ $\underline{kL} = \pi, 2\pi, 3\pi \ldots = \underline{n\pi}$

⇒ distinct solutions: $k_n = \frac{n\pi}{L}$ $\quad n = 1, 2, 3, \ldots$

⇒ standing wave with $\lambda_n = 2\pi/k_n = 2L/n$

1) $\Rightarrow$ Possible energy values:

$$k_n \equiv \frac{\sqrt{2mE}}{\hbar} \overset{!}{=} \frac{n\pi}{L} \Rightarrow E_n = \frac{\hbar^2 \pi^2}{2mL^2} n^2 \quad n = 1, 2, 3 \ldots$$

Note: quantized energy! (as a consequence of the boundary conditions!)

- recall: confined particle $\rightarrow$ quantized energy levels!
- only certain energy values are allowed
- $L \approx 1\,nm \Rightarrow E_1 \approx 0.5\,eV$ for an electron in box

$\Rightarrow$ "zero point energy" $E_1 > 0$
Particle can not have zero energy!

2) Stationary state wave functions:

inside well $\left\{ \Psi_n(x,t) = \psi(x) e^{-i\frac{E_n}{\hbar}t} = A \sin\left(\frac{\pi n}{L}x\right) e^{-i\frac{\hbar\pi^2}{2mL^2}n^2 t} \right.$

$\uparrow$ find A by normalizing the wave function

outside well: $\Psi_n(x,t) = 0$

$\Rightarrow$ normalize Ψ_n

$$\int_{-\infty}^{+\infty} |\Psi|^2 dx \overset{!}{=} 1 = \int_0^L |A|^2 \sin^2(k_n x)\, dx$$

$$= |A|^2 \frac{1}{2} L \quad \Rightarrow \quad |A|^2 = \frac{2}{L}$$

$\Rightarrow$ pick positive root:

$$\underline{A = \sqrt{\frac{2}{L}}} \quad \text{for all } n$$

$\rightarrow$ <u>stationary state:</u>

$$\Psi_n(x,t) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L} x\right) e^{-i \underbrace{\frac{\hbar \pi^2}{2mL^2} n^2 t}_{}}$$

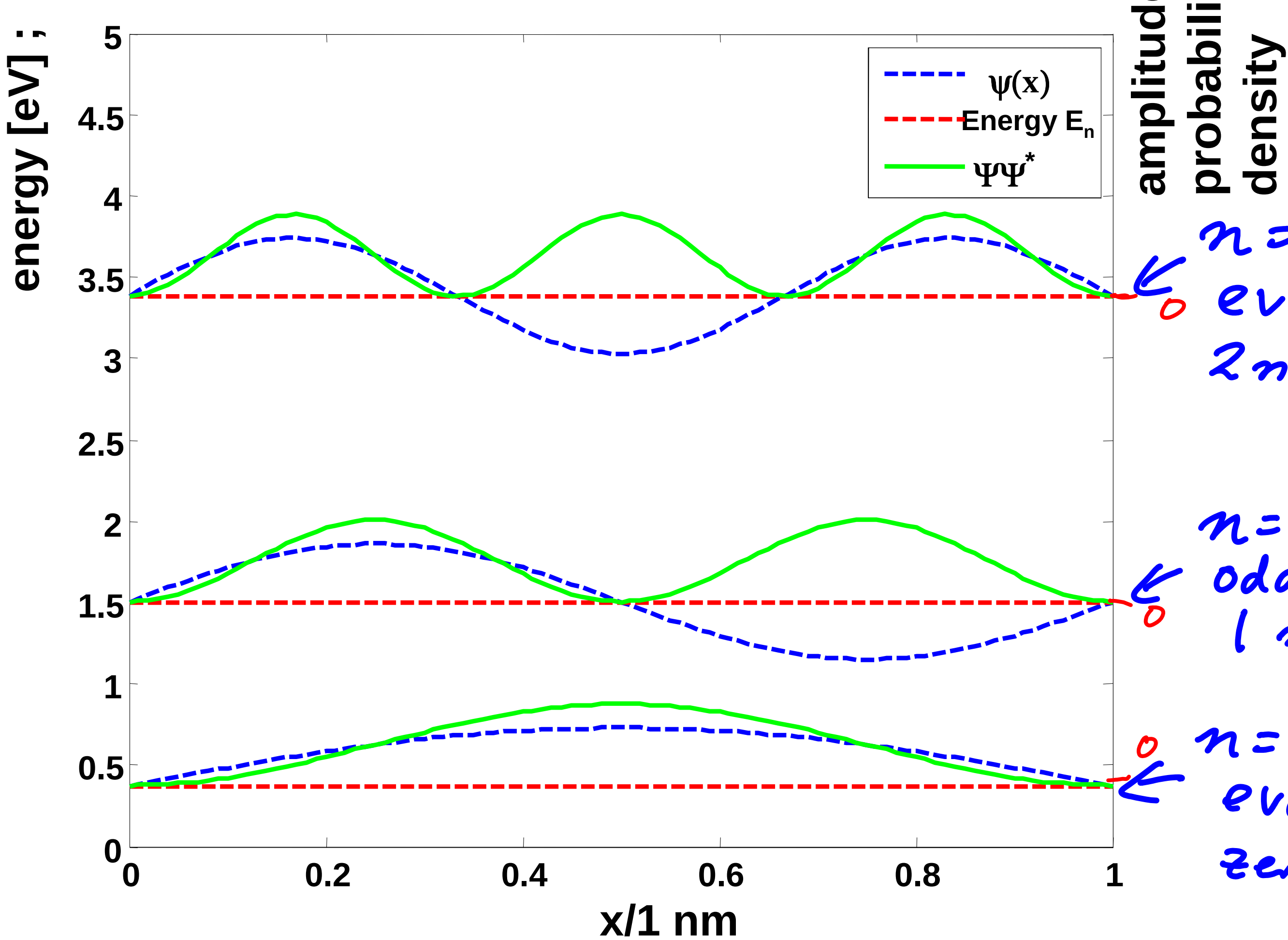
inside the well

oscillates with

$$\omega_n = \frac{E_n}{\hbar} = \frac{\hbar \pi^2}{2mL^2} n^2$$

Note:

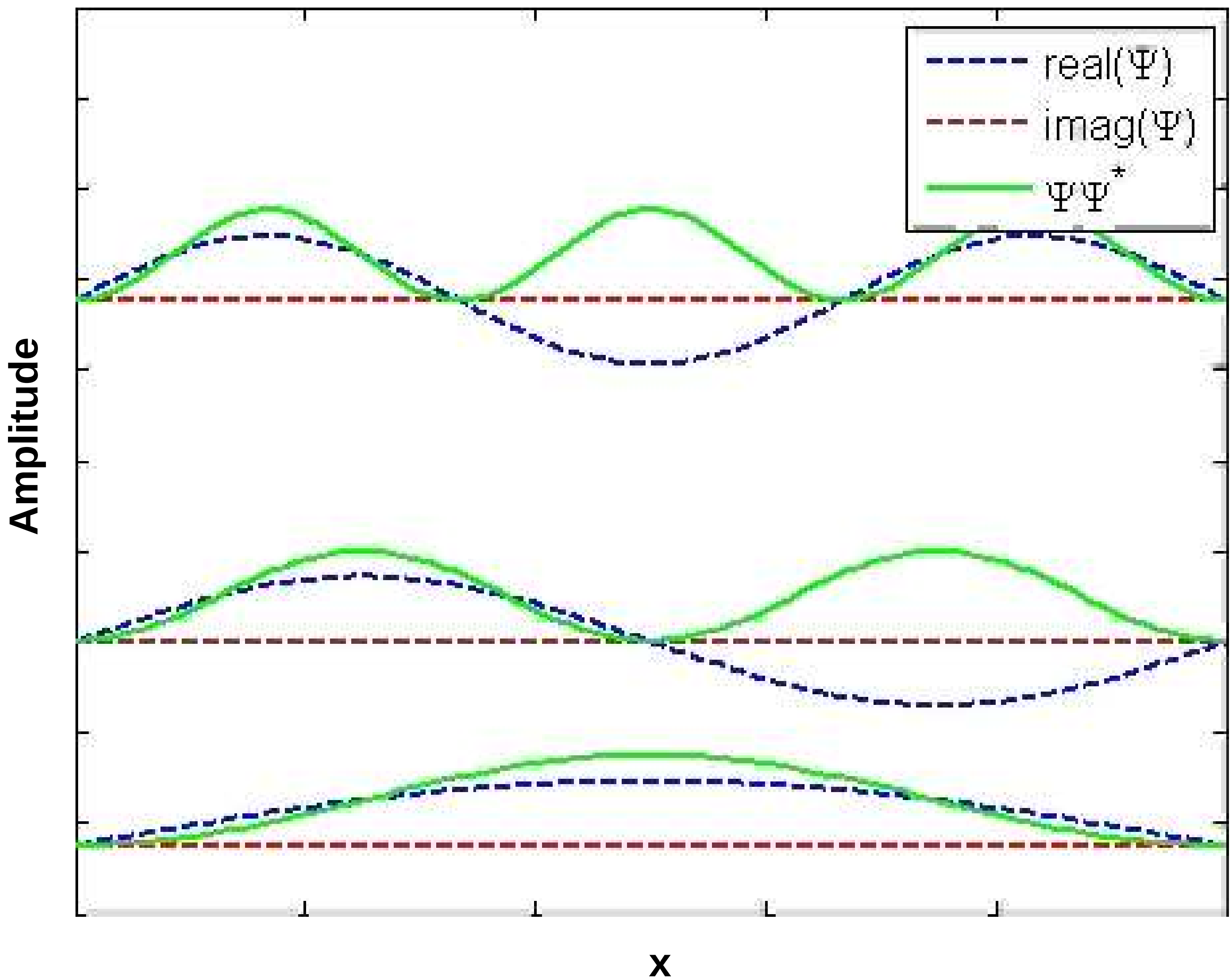
- infinite set of solutions
- $n=1$ state: "ground state"
- $n>1$ state: "excited states"
- probability density: $|\Psi_n(x,t)|^2 = \Psi_n^* \Psi_n$
  $= \frac{2}{L} \sin^2(k_n x)$ is time independent



$n=3$
even function
2 nodes

$n=2$
odd wave function
1 node

$n=1$:
even function
zero nodes


real(Ψ)
imag(Ψ)
ΨΨ*
Amplitude
x

- **Properties of the stationary state wave functions: $\psi(x)$**

1) They are alternately even and odd, wrt the center of the symmetric well.

2) Each successive state has one more node:

   # of nodes $= n-1$

3) They are orthonormal (orthogonal + normalized)

   which means: $$\int_{-\infty}^{+\infty} \psi_m^*(x)\,\psi_n(x)\,dx = \underbrace{\delta_{nm}}_{\text{Kronecker delta}}$$

$$\delta_{nm} = \begin{cases} 1, & \text{if } m=n \\ 0, & \text{if } m \neq n \end{cases}$$

- $m=n$: ψ_n is normalized $\Rightarrow \int = 1$

Proof for infinite square well states:

- for $m \neq n$

$$\int_{-\infty}^{+\infty} \psi_m^*(x)\,\psi_n(x)\,dx = \frac{2}{L}\int_0^L \sin\left(\frac{m\pi}{L}x\right)\sin\left(\frac{n\pi}{L}x\right)dx$$

$$= \frac{1}{L}\int_0^L \left[\cos\left(\frac{m-n}{L}\pi x\right) - \cos\left(\frac{m+n}{L}\pi x\right)\right]dx$$

$$= \left\{\frac{1}{(m-n)\pi}\sin\left(\frac{m-n}{L}\pi x\right) - \frac{1}{(m+n)\pi}\sin\left(\frac{m+n}{L}\pi x\right)\right\}\Bigg|_0^L$$

$$\underset{\sin(0)=0}{=} \frac{1}{\pi}\left\{\frac{\sin[(m-n)\pi]}{(m-n)} - \frac{\sin[(m+n)\pi]}{(m+n)}\right\}$$

$$= \text{if } \underline{\underline{m \neq n}} \checkmark$$