3.012 Fund of Mat Sci: Bonding – Lecture 2

THINK OUT OF THE BOX

Last time: Wave mechanics

1. Classical harmonic oscillator
2. Kinetic and potential energy
3. De Broglie relation $\lambda \bullet p = h$
4. "Plane wave"
5. Time-dependent Schrödinger's equation
6. A free electron satisfies it

Homework for Wed 14

- Study: 15.1, 15.2
- Read: 14.1-14.4

- Office Hours – Monday 4-5 pm

Time-dependent Schrödinger's equation

(Newton's 2nd law for quantum objects)

- An electron is fully described by a wavefunction – all the properties of the electron can be extracted from it
- The wavefunction is determined by the differential equation

WAVEFUNCTION

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

$$\nabla^2 = \frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$$

Stationary Schrödinger's Equation (I)

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

ANSATZ: $\Psi(\vec{r},t)=\varphi(\vec{r})\,f(t)$

$$-\frac{\hbar^2}{2m}\nabla^2(\varphi f)+V\varphi f=i\hbar\frac{\partial(\varphi f)}{\partial t}$$

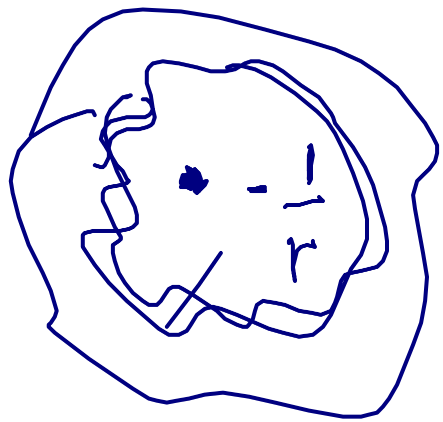
$$-\frac{\hbar^2}{2m}f\,\nabla^2\varphi+V\varphi f=i\hbar\,\varphi\frac{\partial f}{\partial t}\qquad /\,\varphi f$$

$$\underbrace{-\frac{\hbar^2}{2m}\frac{\nabla^2\varphi}{\varphi}+V}_{\text{FUNCTION OF }\vec{r}}=i\hbar\underbrace{\frac{1}{f}\frac{\partial f}{\partial t}}$$

DEPENDS ON TIME

Stationary Schrödinger's Equation (II)

$$-\frac{\hbar^2}{2m}\frac{1}{\varphi}\nabla^2\varphi + V = \text{CONSTANT} = E$$



$$\boxed{\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\varphi(\vec{r}) = E\varphi(\vec{r})}$$

Stationary Schrödinger's Equation (III)

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\varphi(\vec{r}) = E\varphi(\vec{r})$$

1. It's not proven – it's postulated, and it is confirmed experimentally
2. It's an "eigenvalue" equation: it has a solution only for certain values (discrete, or continuum intervals) of E
3. For those eigenvalues, the solution ("eigenstate", or "eigenfunction") is the complete descriptor of the electron in its equilibrium ground state, in a poteniitial V(r).
4. As with all differential equations, boundary conditions must be specified
5. Square modulus of the wavefunction = probability of finding an electron

From classical mechanics to operators

- Total energy is T+V (Hamiltonian is kinetic + potential)

$$T = \frac{1}{2} m v^2 = (p = mv) = \frac{p^2}{2m}$$

- classical momentum $\vec{p}$ $\rightarrow$
  $\rightarrow$ gradient operator $-i\hbar\vec{\nabla}$

$$\left(-i\hbar\vec{\nabla}\right)^2 / 2m = -\frac{\hbar^2}{2m}\vec{\nabla}\cdot\vec{\nabla} = -\frac{\hbar^2}{2m}\nabla^2$$

- classical position $\vec{r}$ $\rightarrow$
  $\rightarrow$ multiplicative operator $\hat{r}$

Operators, eigenvalues, eigenfunctions

$$T = \frac{p^2}{2m} = -\frac{\hbar^2}{2m}\nabla^2$$

$$(T+V) \Rightarrow \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\varphi(\vec{r}) =$$

$$= E\varphi(\vec{r})$$

Free particle: $\Psi(x,t)=\varphi(x)f(t)$

$$-\frac{\hbar^2}{2m}\nabla^2\varphi(x)=E\varphi(x)$$

$\Rightarrow$ HOMEWORK

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

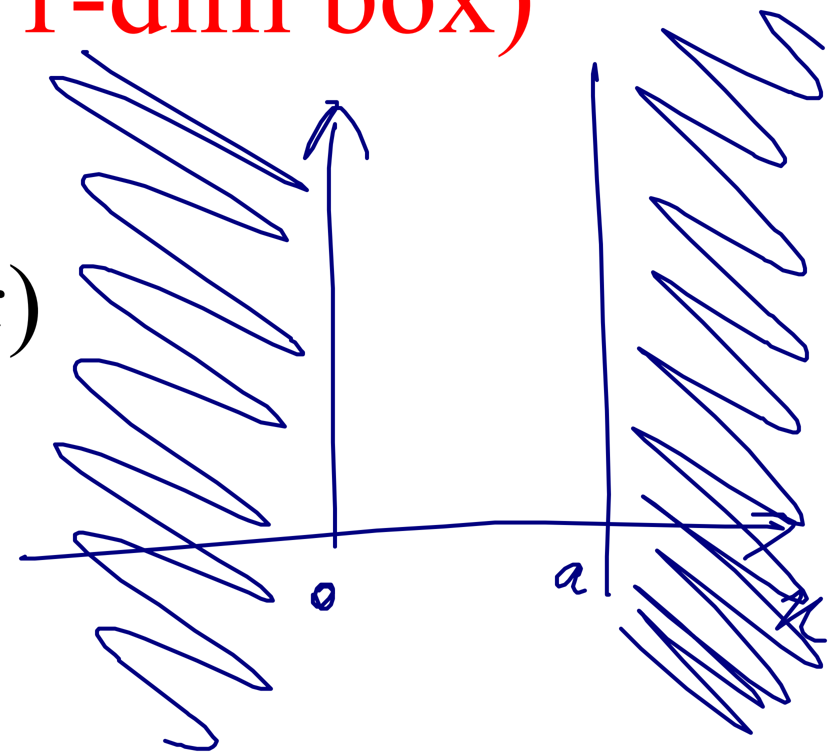
$\Rightarrow$

sin
cos
$\longleftrightarrow$ $\underbrace{e^{i\alpha}}$

$\cos\alpha + i\sin\alpha$

Infinite Square Well (I)
(particle in a 1-dim box)

$$-\frac{\hbar^2}{2m}\frac{d^2\varphi(x)}{dx^2} = E\varphi(x)$$



$\varphi(x) = 0 \quad \forall x < 0$

$\forall x > a$

$$\frac{d^2\varphi}{dx^2} = -\frac{2mE}{\hbar^2}\varphi(x) \Longrightarrow \varphi(x) = A\sin kx + B\cos kx$$

Infinite Square Well (II)

$\psi(0) = 0 \Rightarrow B = 0$

$\psi(x) = A \sin(kx)$

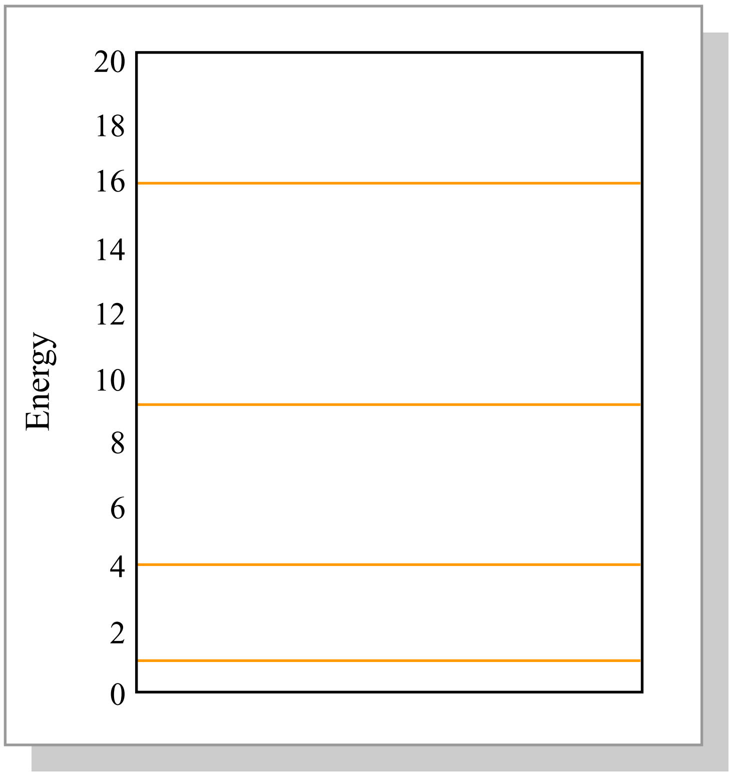
$\psi(a) = 0 \Rightarrow A \sin(\underbrace{ka}) = 0$

$\Downarrow$

$ka = n\pi \Leftarrow ka = 0, \pi, 2\pi, 3\pi, \ldots$

$\hookrightarrow k = \frac{n\pi}{a}$

Infinite Square Well (III)



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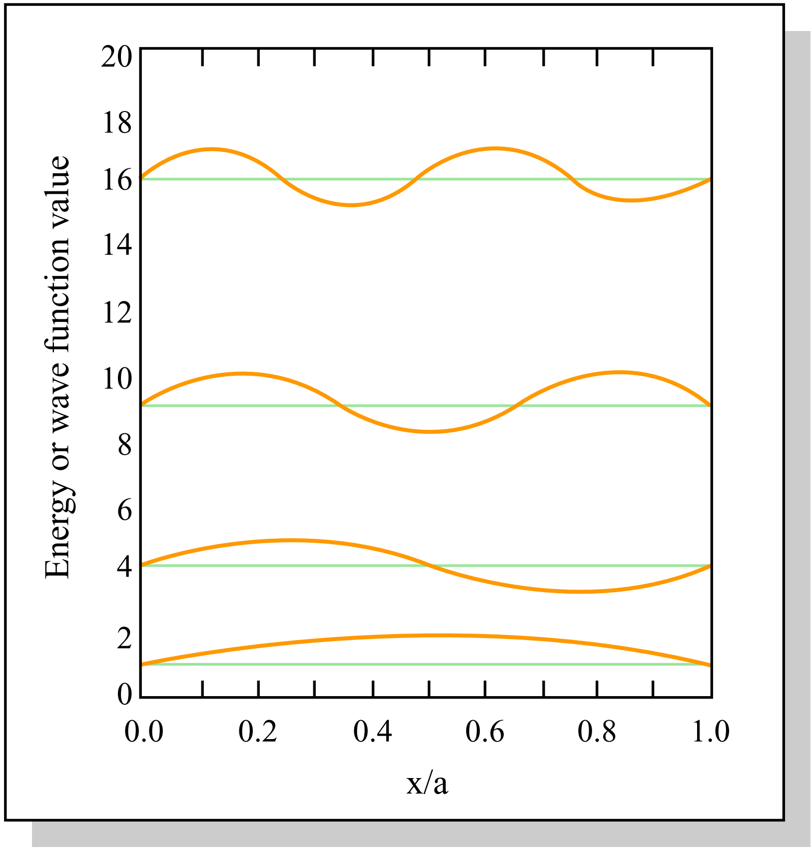

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