PC2232: Free Particle in Quantum Mechanics

~~(Lecture 7)~~ 22/03/2015

For a free non-relativistic particle with no spin, with mass m, wave-function $\psi(\vec{r},t)$ of its position $\vec{r} = x\hat{x} + y\hat{y} + z\hat{z}$ is given by Schrödinger equation:

$$j\hat{h}\frac{\partial \psi(\vec{r},t)}{\partial t} = -\frac{\hat{h}^2}{2m}\nabla^2\psi(\vec{r},t) \quad ---(1)$$

↳ different compared to Maxwell's equations

$\hat{h} = \frac{h}{2\pi}$, h = Plank's constant $= 6.626\times10^{-34}$ Js

A solution of (1) is the wave equation:

$$\psi(\vec{r},t) = \tilde{\psi}\, e^{-j(\omega t - \vec{k}.\vec{r})} \quad ---(2)$$

$\vec{k}$ = propagation vector $= k_x\hat{x} + k_y\hat{y} + k_z\hat{z}$, ω = ang. freq.

Substituting (2) in (1):

$$\text{L.H.S} = j\hat{h}\frac{\partial\psi(\vec{r},t)}{\partial t} = j\hat{h}\tilde{\psi}(-j\omega)e^{-j(\omega t-\vec{k}.\vec{r})}$$
$$= \hat{h}\omega\tilde{\psi}e^{-j(\omega t-\vec{k}.\vec{r})} \quad ---(3)$$

Now, $\vec{k}.\vec{r} = k_x x + k_y y + k_z z$. So, $\nabla[e^{-j(\omega t-\vec{k}.\vec{r})}]$

$$= jk_x e^{-j(\omega t-\vec{k}.\vec{r})}\hat{x} + jk_y e^{-j(\omega t-\vec{k}.\vec{r})}\hat{y} + jk_z e^{-j(\omega t-\vec{k}.\vec{r})}\hat{z}$$

Then,

$$\nabla^2[e^{-j(\omega t-\vec{k}.\vec{r})}] = -k_x^2 e^{-j(\omega t-\vec{k}.\vec{r})} - k_y^2 e^{-j(\omega t-\vec{k}.\vec{r})} - k_z^2 e^{-j(\omega t-\vec{k}.\vec{r})}$$

$= \nabla.\nabla$

$$= -(k_x^2+k_y^2+k_z^2)\,e^{-j(\omega t-\vec{k}.\vec{r})} = -k^2 e^{-j(\omega t-\vec{k}.\vec{r})}$$

where $k = |\vec{k}| \Rightarrow k^2 = k_x^2 + k_y^2 + k_z^2 \quad ---(4)$

So, R.H.S $= -\frac{\hat{h}^2}{2m}\nabla^2\psi(\vec{r},t) = -\frac{\hat{h}}{2m}\tilde{\psi}\nabla^2[e^{-j(\omega t-\vec{k}.\vec{r})}]$

$$= -\frac{\hat{h}^2}{2m}\tilde{\psi}[-k^2 e^{-j(\omega t-\vec{k}.\vec{r})}] = \frac{\hat{h}^2 k^2}{2m}\tilde{\psi}e^{-j(\omega t-\vec{k}.\vec{r})} \quad \text{---(5)}$$

using (1), (3) & (5):

$$\hat{h}\omega\tilde{\psi}e^{-j(\omega t-\vec{k}.\vec{r})} = \frac{\hat{h}^2k^2}{2m}\tilde{\psi}e^{-j(\omega t-\vec{k}.\vec{r})}$$

$$\Rightarrow \hat{h}\omega = \frac{\hat{h}^2k^2}{2m} \quad \text{--- (6)}$$

Now, using (6):

$$\hat{h}\omega = \frac{h}{2\pi}.2\pi f = hf = E = \frac{\hat{h}^2k^2}{2m} \quad \text{---(7)}$$

Where E is the energy of the particle (a definite classical value)

Now, $\hat{h}k = p$ ---(8)

where p is the momentum of the particle (a definite classical value)

using (7), (8) in (6):

$$E = \frac{p^2}{2m} \quad \text{---(9)}$$

is the Energy-momentum relationship of the particle which agrees with the classical equation.

Then, the wavelength (de Broglie wave length) is:

using (7): $\lambda = \frac{2\pi}{k} = \frac{2\pi\hat{h}}{p} = \frac{h}{p}$ --- (10)

Schrodinger Equation with Potential

$$j\hat{h}\,\frac{\partial \psi(\vec{r},t)}{\partial t} = -\frac{\hat{h}^2}{2m}\nabla^2\psi(\vec{r},t) + \underbrace{u(\vec{r})}_{\text{potential of particle.}}\psi(\vec{r},t)$$

--- (11)

The following solution will be used: (standing wave solution)

$$\psi(\vec{r},t) = \underbrace{\tilde{\psi}(\vec{r})}_{\text{envelop}}\, e^{-j\omega t} \qquad \text{--- (12)}$$

Sub (12) in (11):

$$j\hat{h}(-j\omega)\,\tilde{\psi}(\vec{r})\,e^{-j\omega t} = -\frac{\hat{h}^2}{2m}e^{-j\omega t}\,\nabla^2\psi(\vec{r}) + u(\vec{r})\,\psi(\vec{r})\,e^{-j\omega t}$$

$$\Rightarrow \quad \hat{h}\omega\,\tilde{\psi}(\vec{r}) = -\frac{\hat{h}^2}{2m}\nabla^2\tilde{\psi}(\vec{r}) + u(\vec{r})\,\tilde{\psi}(\vec{r})$$

$$\Rightarrow \quad E\,\tilde{\psi}(\vec{r}) = -\frac{\hat{h}^2}{2m}\nabla^2\tilde{\psi}(\vec{r}) + u(\vec{r})\,\tilde{\psi}(\vec{r})$$

--- (13)

(13) is known as time-independent schrödinger equation.

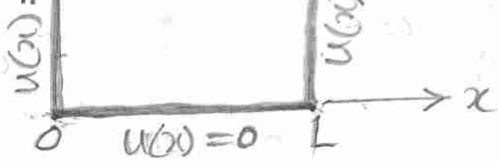
Considering 1-D case where $\vec{r} = x\hat{x}$, (3) reduces to:

$$E\,\tilde{\psi}(x) = -\frac{h^2}{2m}\cdot\frac{\partial^2\tilde{\psi}(x)}{\partial x^2} + u(x)\,\tilde{\psi}(x) \qquad \text{--- (14)}$$

Case-I Infinite square Potential Well:

$$u(x) = \begin{cases} 0 & 0 \le x \le L \\ \infty & x < 0 \text{ or } x > L \end{cases}$$

--- (15)



$$u(x) = \infty \Rightarrow \tilde{\psi}(x) = 0.$$

as probability of a particle having ∞ potential is 0.

So, $\tilde{\psi}(x) = 0$ for $x \le 0$ or $x \ge L$. --- (16)

[equality sign for continuity in $\tilde{\psi}(x)$]

For $0 \leq x \leq L$, using (14) and (15)

$$E \tilde{\psi}(x) = -\frac{h^2}{2m} \frac{\partial^2 \tilde{\psi}(x)}{\partial x^2}$$

$$\Rightarrow \frac{\partial \tilde{\psi}(x)}{\partial x^2} + E . \frac{2m}{h^2} \tilde{\psi}(x) = 0$$

$$\Rightarrow \frac{\partial \tilde{\psi}(x)}{\partial x^2} + \frac{\hat{h}^2 k^2}{2m} . \frac{2m}{\hat{h}^2} \tilde{\psi}(x) = 0 \quad \text{using (7)}$$

$$\Rightarrow \frac{\partial^2 \tilde{\psi}(x)}{\partial x^2} + k^2 \tilde{\psi}(x) = 0 . \quad --- (17)$$

The general solution for (16) is

$$\tilde{\psi}(x) = A \sin(kx) + B \cos(kx) \quad --- (18)$$

Now, using boundary condition $\psi(0) = 0$ from (16)

$$\tilde{\psi}(0) = 0 = A \sin(0) + B \cos(0)$$

Then $B = 0$

Then particular solution of (17) is

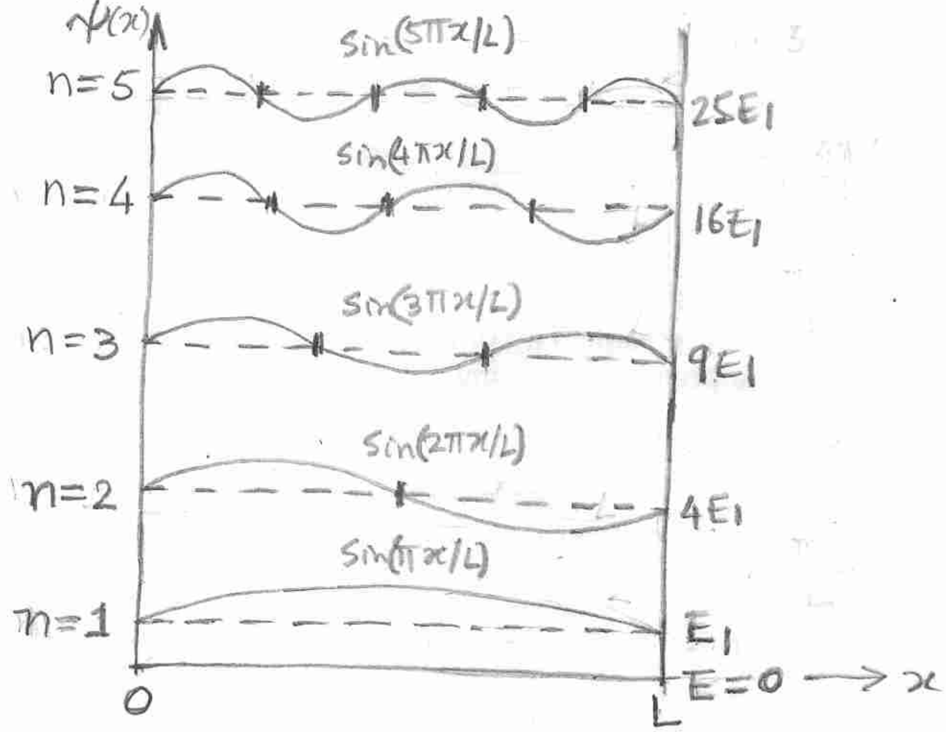
$$\tilde{\psi}(x) = A \sin(kx) \quad ---- (19)$$

using boundary condition $\tilde{\psi}(L) = 0$ from (16)

$$\tilde{\psi}(L) = 0 = A \sin(kL)$$

$$\left.\begin{array}{l} \Rightarrow kL = n\pi \Rightarrow k = \dfrac{n\pi}{L} \\ \qquad n = 1, 2, 3 \end{array}\right\} \quad ..... (20)$$

Eqn (20) says there can only be discrete values of k for standing wave solutions in 'infinite square potential well'.

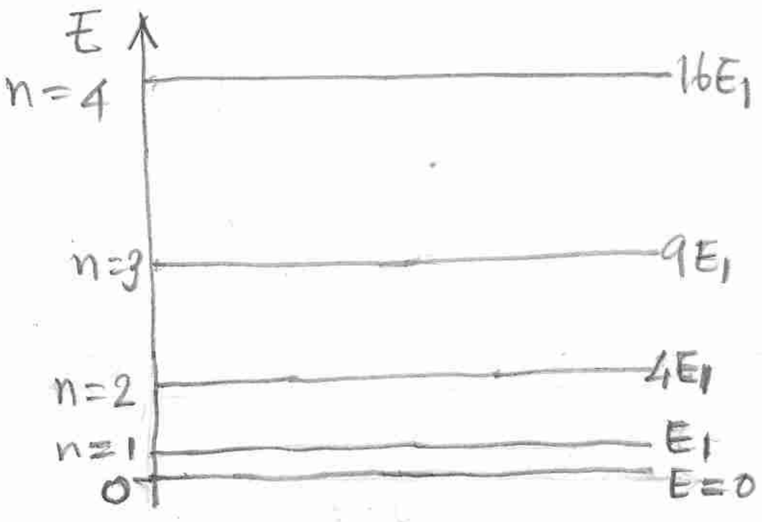


Using (8) and (20), the momentum is also quantized:

$$p = \frac{n\pi\hbar}{L} \quad n = 1, 2, 3 \ldots \qquad \text{--- (21)}$$

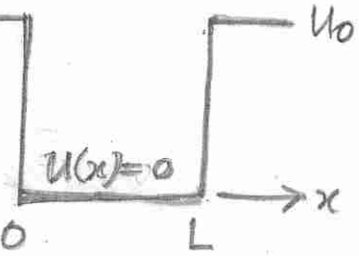
Using (7) and (20), the energy is also quantized:

$$E = \frac{n^2\pi^2\hbar^2}{2mL^2} \quad n = 1, 2, 3 \ldots \qquad \text{--- (22)}$$



Case II Finite square Potential Well

$$U(x) = \begin{cases} 0 & 0 \leq x \leq L \\ U_0, & x < 0 \text{ or } x > L \\ E < U_0 & \end{cases} \quad \text{---(23)}$$



Consider $x < 0$ or $x > 0$:

$$E\tilde{\psi}(x) = -\frac{h^2}{2m} \cdot \frac{\partial^2 \tilde{\psi}(x)}{\partial x^2} + U_0 \tilde{\psi}(x)$$

$$\Rightarrow (E - U_0)\tilde{\psi}(x) = -\frac{h^2}{2m} \cdot \frac{\partial^2 \psi(x)}{\partial x^2}$$

$$\Rightarrow \frac{\partial^2 \tilde{\psi}(x)}{\partial x^2} + \frac{2m}{h^2}(E - U_0)\tilde{\psi}(x) = 0$$

$$\Rightarrow \frac{\partial^2 \psi(x)}{\partial x^2} - \alpha^2 \tilde{\psi}(x) = 0 \quad \text{---(24)}$$

where $\alpha^2 = -\frac{2m}{h^2}(E - U_0)$

Then general solution for (24) is:

$$\tilde{\psi}(x) = Ce^{\alpha x} + De^{-\alpha x} \quad \text{---(25)}$$

Now since $\tilde{\psi}(x)$ must $\to 0$ as $x \to \pm\infty$,

$$\left.\begin{aligned} \tilde{\psi}(x) &= Ce^{\alpha x} \quad \text{for } x < 0 \\ \text{and } \tilde{\psi}(x) &= De^{-\alpha x} \quad \text{for } x > L \end{aligned}\right\} \alpha^2 = -\frac{2m}{\hbar^2}(E - U_0) \quad \text{----(26)}$$

Consider $0 \leq x \leq L$:

The solution is as before with A, B nonzero:

$$\tilde{\psi}(x) = A\sin(kx) + B\cos(kx) \quad \text{---(27)}, \qquad k^2 = \frac{2m}{\hbar^2}E$$

Now, (26) and (27) need to be combined considering continuity of $\tilde{\psi}(x)$ and $\frac{d\tilde{\psi}(x)}{dx}$ at $x=0$ & $x=L$.

(i) Continuity of $\tilde{\psi}(x)$ at $x=0$:

$$\left.\begin{aligned} &\text{From (26)}\quad \tilde{\psi}(0) = C \\ &\text{From (27)}\quad \tilde{\psi}(0) = B \end{aligned}\right\} \text{ Then, } B = C \quad \text{---(28)}$$

(ii) Continuity of $\frac{d\tilde{\psi}(x)}{dx}$ at $x=0$:

$$\left.\begin{aligned} &\text{From (26):}\quad \frac{d\tilde{\psi}(0)}{dx} = \alpha C \\ &\text{From (27):}\quad \frac{d\tilde{\psi}(0)}{dx} = kA \end{aligned}\right\} \text{ Then, } A = \frac{\alpha}{k} C \quad \text{---(29)}$$

Sub (28) & (29) in (27):

$$\tilde{\psi}(x) = \frac{\alpha}{k} C \sin(kx) + C\cos(kx) \quad \text{...(30)}$$

(iii) Continuity of $\tilde{\psi}(x)$ at $x=L$:

$$\left.\begin{aligned} &\text{From (26)}\quad \tilde{\psi}(L) = De^{-\alpha L} \\ &\text{From (30)}\quad \tilde{\psi}(L) = \frac{\alpha}{k} C \sin(kL) + C\cos(kL) \end{aligned}\right\}$$

Then, $$D = e^{\alpha L}\left[\frac{\alpha}{k}\sin(kL) + \cos(kL)\right]C \quad \text{---(31)}$$

(iv) Continuity of $\frac{d\tilde{\psi}(x)}{dx}$ at $x=L$:

$$\left.\begin{aligned} &\text{From (26)}\quad \frac{d\tilde{\psi}(L)}{dx} = -\alpha De^{-\alpha L} \\ &\text{From (30)}\quad \frac{d\tilde{\psi}(L)}{dx} = [\alpha\cos(kL) - k\sin(kL)]C \end{aligned}\right\}$$

Then, $$D = e^{\alpha L}\left[\frac{k}{\alpha}\sin(kL) - \cos(kL)\right]C \quad \text{---(32)}$$

Equivalent to one equation

From (31) & (32):

$$\frac{\alpha}{k}\cdot\sin(kL) + \cos(kL) = \frac{k}{\alpha}\sin(kL) - \cos(kL)$$

$$\Rightarrow \quad 2\cos(kL) = \left(\frac{k}{\alpha} - \frac{\alpha}{k}\right)\sin(kL)$$

$$\Rightarrow 2\cot(kL) = \left(\frac{k}{\alpha} - \frac{\alpha}{k}\right) \quad \text{--- (33)}$$

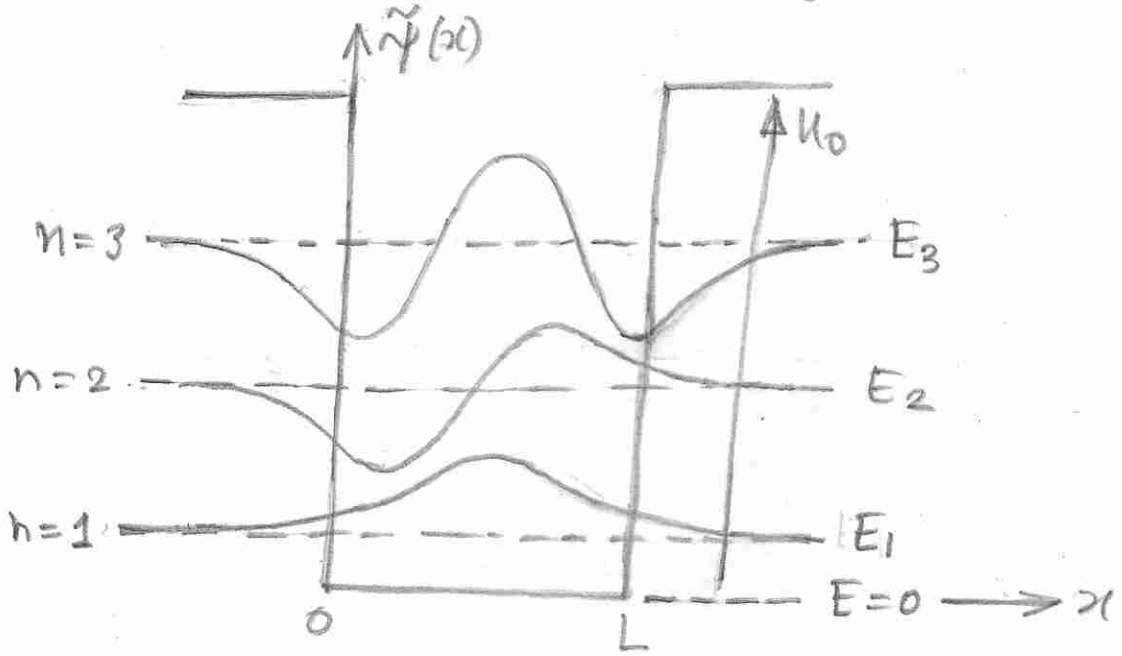
From (26), $\alpha = \dfrac{\sqrt{2m(U_0 - E)}}{\hbar}$

From (27), $k = \dfrac{\sqrt{2mE}}{\hbar}$

Sub. above in (33):

$$2\cot\left(\frac{\sqrt{2mE}}{\hbar}L\right) = \sqrt{\frac{E}{U_0 - E}} - \sqrt{\frac{U_0 - E}{E}} \quad \text{--- (34)}$$

(34) is not possible to solve analytically. But solutions can be found numerically. It has several discrete solutions $E_1, E_2, E_3 \ldots$ corresponding to $n = 1, 2, 3, \ldots$



For $\alpha \to \infty$, (26) gives $\psi(x) \to 0$ for $x < 0$ & $x > L$. This is the same case as infinite square potential well. Then (33) gives $k = \frac{n\pi}{L}$ and (27) gives $\tilde{\psi}(x) = A\sin(kx)$ as obtained before for the same case.

From (28), (29), (31), (32) it can be seen that only one constant is unknown. This can be decided based one some other constraint.