HH0134 - Energy Quantization

Time-Independent Schrödinger equation

Since the Schrödinger equation is first-order in time, its time dependence can be solved easily

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} + V\psi$$

educated guess !!

$$\psi(x,t) = \Phi(x)\, e^{-i\omega t}$$

$$i\hbar(-i\omega)\,\Phi\, \cancel{e^{-i\omega t}}$$

$$= \left[-\frac{\hbar^2}{2m}\frac{\partial^2 \Phi}{\partial x^2} + V\Phi\right] \cancel{e^{-i\omega t}}$$

, note that $E = \hbar\omega$

$$\Rightarrow \quad -\frac{\hbar^2}{2m}\frac{d^2\Phi}{dx^2} + V\Phi = E\Phi$$

should always keep in mind the t dependence !!

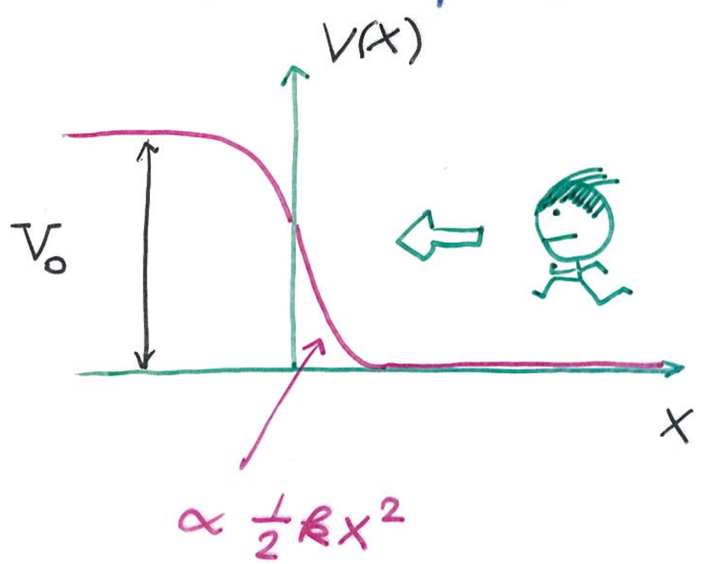
Or, sometimes in the form of

$$\frac{d^2\Phi}{dx^2} + \frac{2m}{\hbar^2}(E - V)\Phi = 0$$

$\boxed{\text{Q: Is } E \text{ arbitrary? Or .... NOT....}}$

Potential Wall.

Consider a particle and a wall at $x=0$. However, to simplify the problem, it is often approximated by the so-called hard-wall condition.



$$V(x) = \begin{cases} 0 & x > 0 \\ \infty & x \leq 0 \end{cases}$$

From linear superposition, the general solution with energy $E = \frac{(\hbar k)^2}{2m}$ takes the form:

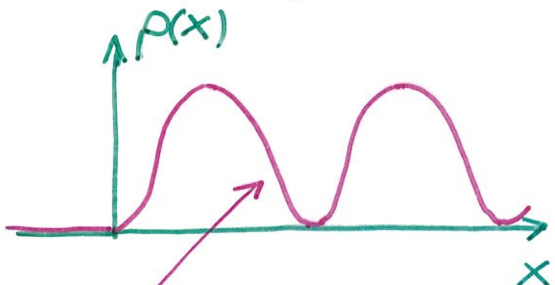
$$\psi(x) = A\, e^{ikx} + B\, e^{-ikx}$$

Since the wave function vanishes at $x=0$, we need to enforce to boundary condition $\psi(0)=0$.

$\psi(0) = 0 \quad \Rightarrow \quad A + B = 0 \qquad B = -A.$

Thus, $\psi(x) = A e^{ikx} - A e^{-ikx} = 2iA \sin kx = C \sin kx$

We can plot the probability density $\rho(x,t)$.



not uniform anymore!!

(1) $\rho(x,t)$ is not uniform anymore.

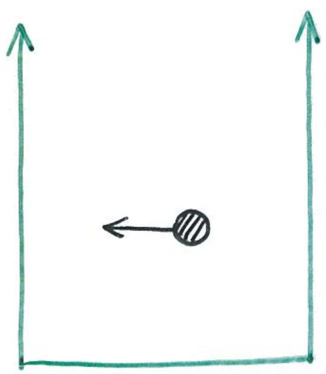
(2) $\rho(x,t)$ is static (not like the usual standing wave).

Furthermore, we can compute the probability current

$$j(x) = \frac{\hbar}{2mi}\left(\psi^* \frac{\partial\psi}{\partial x} - \frac{\partial\psi^*}{\partial x}\psi\right) = \frac{\hbar}{2mi}\left(\psi\frac{\partial\psi}{\partial x} - \frac{\partial\psi}{\partial x}\psi\right) = 0$$

- The probability current is zero as we expected.
- Hard wall gives rise to $k \to -k$ plus π shift !!

Potential Box



The Schrödinger eq reads $\frac{d^2\psi}{dx^2} + k^2\psi = 0$

where $k^2 = \frac{2mE}{\hbar^2}$. The general solution is

$$\psi(x) = A e^{ikx} + B e^{-ikx}$$

Now, needs to satisfy two boundary conditions

(1) $\psi(0) = 0$ (2) $\psi(L) = 0$ From the first B.C.

$$A + B = 0 \Rightarrow \psi(x) = A e^{ikx} - A e^{-ikx} = 2iA \sin kx$$
$$= C \sin kx$$

Now, ready to apply the 2nd B.C. $\psi(L) = 0$

$$\sin kL = 0 \Rightarrow k_n = \frac{n\pi}{L}$$

momentum is quantized !!

Energy Quantization

From the quantized momentum $p_n = \hbar k_n = \frac{n\pi\hbar}{L}$, it's easy to show that energy is also quantized.

$$E_n = \frac{p_n^2}{2m} = \frac{n^2\pi^2\hbar^2}{2mL^2} \qquad E_n \propto n^2 \quad \text{quantized!!}$$

We are NOT done yet.... $\psi_n(x) = C \sin(k_n x)$

Still need to figure out the const C ☺

$$\int dx\, |\psi(x)|^2 = 1 \quad \Rightarrow \quad \int_0^L dx\, C^2 \sin^2(k_n x) = 1$$

Recall that $\sin^2(k_n x) = \frac{1}{2}(1 + \cos 2k_n x)$

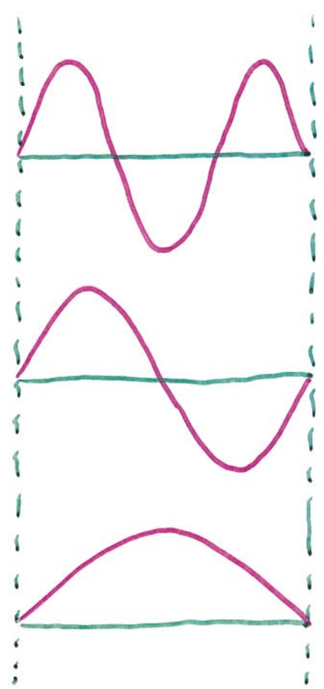
$$\int_0^L \sin^2(k_n x)\, dx = \int_0^L \frac{1}{2} + \frac{1}{2}\cos(2k_n x)\, dx = \frac{L}{2}$$

Thus, the wave function is $\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$

Wave Function

Just as in conventional standing waves, we see nodal structure in wave functions. Note that, except the ground state, all excited states have nodes.

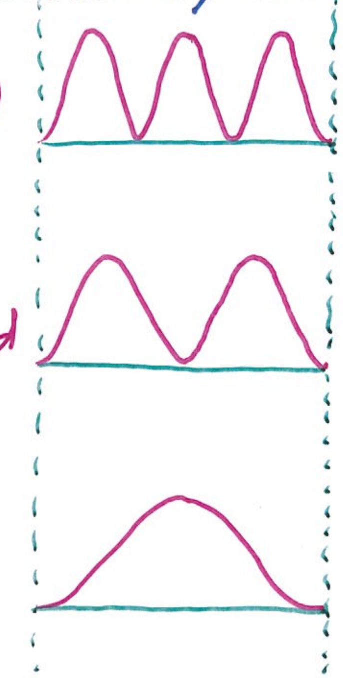
$$\boxed{\#\ \text{of nodes} = n-1}$$



$$\psi_3(x) = \sqrt{\frac{2}{L}}\,\sin\left(\frac{3\pi x}{L}\right)$$

$$\psi_2(x) = \sqrt{\frac{2}{L}}\,\sin\left(\frac{2\pi x}{L}\right)$$

$$\psi_1(x) = \sqrt{\frac{2}{L}}\,\sin\left(\frac{\pi x}{L}\right)$$



Uncertainty Principle.

The wave function $\psi_n(x) = \sqrt{\frac{2}{L}} \sin(k_n x)$. We can calculate the uncertainty in position.

$$\langle x \rangle \equiv \int_0^L dx\, \rho(x) \cdot x = \frac{L}{2} \quad \text{by symmetry.}$$

$$(\Delta x)^2 \equiv \langle (x - \langle x \rangle)^2 \rangle = \langle x^2 - 2x\langle x \rangle + \langle x \rangle^2 \rangle$$

$$= \langle x^2 \rangle - 2\langle x \rangle \langle x \rangle + \langle x \rangle^2 = \langle x^2 \rangle - \langle x \rangle^2$$

Only need to compute $\langle x^2 \rangle$ now.

$$\langle x^2 \rangle = \int_0^L dx\, \rho(x)\, x^2 = \frac{2}{L} \int_0^L dx\, x^2 \sin^2(k_n x)$$

The integral is elementary:

$$\int x^2 \sin^2 kx\, dx = \frac{x^3}{6} - \frac{x \cos(2kx)}{4k^2} - \frac{2k^2x^2 - 1}{8k^3} \sin(2kx)$$

$$\langle x^2\rangle = \int_0^L dx\, \frac{2}{L} \sin^2 k_n x \cdot x^2 = \frac{2}{L}\cdot\left[\frac{L^3}{6} - \frac{L}{4k_n^2}\right]$$

$$= \frac{1}{3}L^2 - \frac{1}{2k_n^2} \approx \frac{1}{3}L^2$$

Finally, the uncertainty in x is

$$(\Delta x)^2 = \langle x^2\rangle - \langle x\rangle^2 \approx \frac{1}{3}L^2 - \frac{1}{4}L^2$$

$$= \frac{1}{12}L^2$$

$$\Rightarrow \quad \Delta x \approx \frac{1}{2\sqrt{3}} L$$

On the other hand, the uncertainty in momentum is

$$\langle p^2\rangle = p_n^2$$

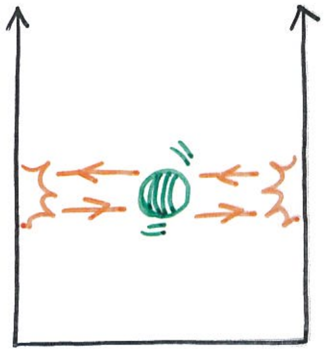
$$\langle p\rangle^2 = 0$$

$$\Rightarrow \quad \Delta p = \sqrt{\langle p^2\rangle - \langle p\rangle^2} = p_n = \frac{n\hbar\pi}{L}$$

One can easily see that $\Delta x\, \Delta p \approx \frac{1}{2\sqrt{3}} L \cdot \frac{n\hbar\pi}{L}$

$$\rightarrow \quad \Delta x\, \Delta p \approx n\hbar \quad !!$$

Bohr Quantization



View the stationary solution as multiple self constructive interference. The phase difference is

$$\delta = 2\pi\left(\frac{2L}{\lambda}\right) - \varphi_s \qquad \varphi_s = \pi + \pi$$

The constructive interference requires $\delta = 2n\pi$

$$2n\pi = 2\pi\left(\frac{2L}{\lambda}\right) - 2\pi \Rightarrow \frac{2L}{\lambda} = (n+1)$$

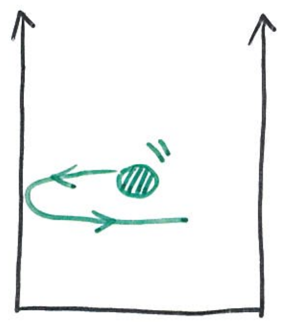
Using the relation $p = \frac{h}{\lambda}$ $\Rightarrow$ $2L\frac{h}{\lambda} = (n+1)h$

Finally, we arrive at $2pL = n'h$. OR, in more formal format

$$\oint p\,dx = \hbar\,(2n\pi + \varphi_s)$$

scattering phase.

Simple Applications.



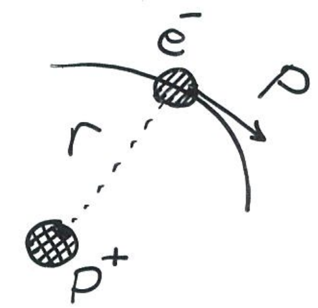
$$\oint p\,dx = \hbar\,(2n\pi + \varphi_s) \Rightarrow p \cdot 2L = \hbar\, 2n'\pi$$

$$p_n = \frac{2n'\pi\hbar}{2L} = \frac{n'\pi\hbar}{L}$$

Another example is Bohr's model for H atom. Somehow, the angular momentum is quantized ....

$$\oint p\,dx = \hbar\,(2n\pi + \varphi_s)$$

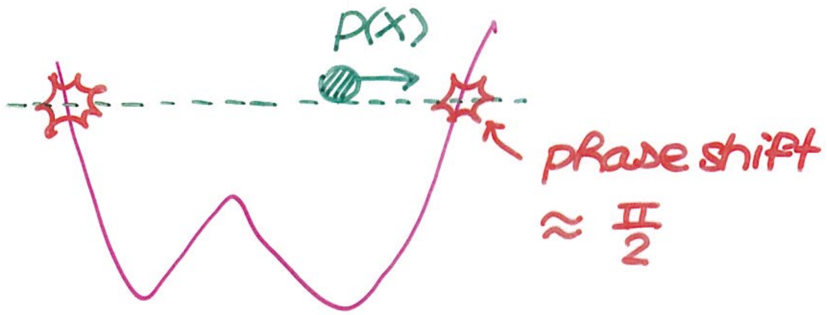
$\varphi_s = 0$ in this case !!



$$p \cdot \cancel{2\pi} r = \cancel{2} n \cancel{\pi} \hbar$$

$\Rightarrow \quad L = n\hbar \qquad$ the angular momentum is quantized in unit of $\hbar$.

Semiclassical Approximation

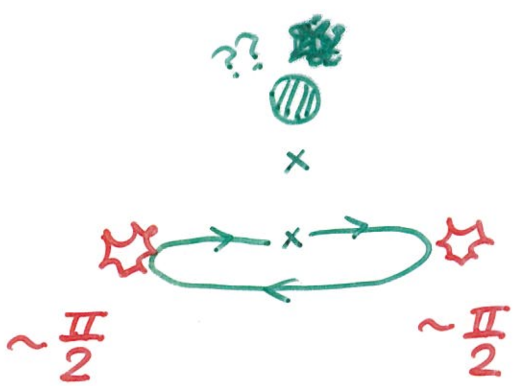


The first cute notion is $p(x)$ — the position-dependent momentum.

$$\frac{p^2}{2m} + V(x) = E, \qquad \text{smooth } V(x).$$

$$p^2(x) = 2m\left[E - V(x)\right] > 0 \quad \Rightarrow \quad p(x) = \pm\sqrt{2m\left[E - V(x)\right]}$$

The second cute notion is constructive self interference.



$$\frac{1}{\hbar}\oint p(x)\,dx - \varphi_s = 2n\pi, \quad \varphi_s = \text{scattering phase}$$

$$\frac{1}{\hbar}\oint p(x)\,dx = 2n\pi + \varphi_s$$

$$\oint \sqrt{2m\left[E - V(x)\right]}\,dx = \hbar\,(2n\pi + \varphi_s)$$

$$\varphi_s \approx \frac{\pi}{2} + \frac{\pi}{2} = \pi$$

$$\Rightarrow \quad \oint \sqrt{2m\left[E - V(x)\right]} = 2\pi\hbar\left(n + \tfrac{1}{2}\right)$$

9.

A simple check.....

Does the semiclassical approximation make~~s~~ sense at all ?

Let's check.... The position-dependent momentum $p(x)$ implies the wave function takes the form,

$$\psi(x,t) \approx e^{i[k(x)x - \omega t]} \qquad p(x) = \hbar k(x) = \sqrt{2m(E-V)}$$

check. ✓ $\dfrac{\partial\psi}{\partial t} = (-i\omega)\, e^{i(kx-\omega t)} = (-i\omega)\,\psi$

$$\frac{\partial\psi}{\partial x} = i\left(k + \frac{dk}{dx}x\right) e^{i(kx-\omega t)} = i\left(k+\frac{dk}{dx}x\right)\psi$$

$$\frac{\partial^2\psi}{\partial x^2} = i\left(\frac{dk}{dx} + \frac{d^2k}{dx^2}x + \frac{dk}{dx}\right) e^{i(kx-\omega t)} + (i)^2\left(k+\frac{dk}{dx}x\right)^2 e^{i(kx-\omega t)}$$

$$= \left[-\left(k+\frac{dk}{dx}x\right)^2 + i\left(2\frac{dk}{dx} + \frac{d^2k}{dx^2}x\right)\right]\psi$$

Note that $\dfrac{dk}{dx} = \dfrac{1}{\hbar}\dfrac{dp}{dx} = \dfrac{1}{\hbar}\dfrac{-2m\frac{dV}{dx}}{2\sqrt{2m(E-V)}} \propto \dfrac{dV}{dx}$!! Thus, for smooth potential, we can drop all derivatives ☺

After dropping all spatial derivatives ....

$$\frac{\partial \psi}{\partial t} = (-i\omega)\psi \qquad \text{plug in the Schrödinger equation} \;\Rightarrow\; i\hbar\frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} + V\psi$$

$$\frac{\partial^2 \psi}{\partial x^2} \approx -k^2 \psi$$

$$\text{left} = i\hbar\frac{\partial \psi}{\partial t} = (i\hbar)(-i\omega)\psi = \hbar\omega\,\psi = E\,\psi.$$

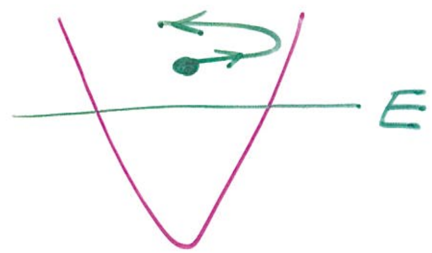
$$\text{right} = -\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} + V\psi = \left[-\frac{\hbar^2}{2m}(-k^2) + V\right]\psi = \left[\frac{p^2}{2m} + V\right]\psi$$

$$= \left[\frac{\left(\sqrt{2m(E-V)}\right)^2}{2m} + V\right]\psi = \left[(E-V) + V\right] = E\,\psi.$$

The left = right $\Rightarrow$ Schrödinger equation is satisfied.
Thus, as long as the potential is smooth, one can use the semiclassical approximation to compute the discrete bound-state energy.

Q: How "smooth" is smooth? Huh?

Try a simple example.



Consider a parabollic potential $V(x) = \frac{1}{2}kx^2$.

The Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + \frac{1}{2}kx^2\psi = E\psi$$

The above differential equation certainly looks unfriendly. At least, to freshman....

Let's try to solve it by the semiclassical approach.

$$\oint p(x)\,dx = \hbar\,(2n\pi + \varphi_s) \quad \Rightarrow \quad \oint \sqrt{2m(E-V)}\,dx = 2\pi\hbar\,(n+\tfrac{1}{2})$$

How nice !! We only need to compute a simple integral.

$$\oint p(x)\,dx = 2\int_{-x_c}^{x_c} \sqrt{2mE - mkx^2}\,dx\,, \qquad \pm x_c : \text{turning points}$$

12.

Some algebra....

$$2\int_{-x_c}^{x_c}\sqrt{2mE-mkx^2}\,dx = 2\sqrt{mk}\int_{-x_c}^{x_c}\sqrt{\frac{2E}{k}-x^2}\,dx$$

$\frac{1}{2}kx_c^2 = E$

$x_c^2 = \frac{2E}{k}$

$$=2\sqrt{mk}\int_{-x_c}^{x_c}\sqrt{x_c^2-x^2}\,dx$$

change variabe

$x = x_c\sin\theta$

$$\begin{cases} x = x_c \rightarrow \theta = \frac{\pi}{2} \\ x = -x_c \rightarrow \theta = -\frac{\pi}{2} \end{cases}$$

$dx = x_c\cos\theta\,d\theta$

$$=2\sqrt{mk}\int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} x_c\sqrt{1-\sin^2\theta}\,(x_c\cos\theta\,d\theta)$$

$$=2\sqrt{mk}\,x_c^2\int_{-\frac{\pi}{2}}^{\frac{\pi}{2}}\cos^2\theta\,d\theta = 2\sqrt{mk}\,\frac{2E}{k}\cdot(\text{integral})$$

$$=\sqrt{\frac{m}{k}}\cdot 4E\cdot(\text{integral}) = \frac{4E}{\omega}\int_{-\frac{\pi}{2}}^{\frac{\pi}{2}}\cos^2\theta\,d\theta$$

Now the integral ...  a piece of cake 

$$\int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \cos^2\theta \, d\theta = \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \frac{1+\cos 2\theta}{2} \, d\theta = \frac{\theta}{2}\Big|_{-\frac{\pi}{2}}^{\frac{\pi}{2}} + \cancelto{0}{\frac{1}{4}\sin 2\theta\Big|_{-\frac{\pi}{2}}^{\frac{\pi}{2}}} = \frac{\pi}{2}$$

Finally, combine every pieces together....

$$\frac{\cancelto{2}{4}E}{\omega} \cdot \frac{\cancel{\pi}}{\cancel{2}} = \cancel{2\pi}\hbar\left(n+\frac{1}{2}\right) \Rightarrow \quad E_n = \hbar\omega\left(n+\frac{1}{2}\right)$$

☆ For a simple harmonic oscillator, the "allowed" energy is no longer continuous. In fact, the energy is quantized in unit of $\hbar\omega = h\nu$ — very similar to Einstein's notion for photons !!

☆ The residual $\frac{1}{2}$ comes from.....

— Heisenberg uncertainty principle !!

charged particle

$$\text{EM wave} = \underbrace{\hbar\omega + \hbar\omega + \cdots + \hbar\omega}^{N \text{ photons}} = N\hbar\omega$$

The End