【Chapter 5 Quantum Mechanics】

- limitation of Bohr theory:

1. Can not explain why certain spectral lines are more intense than others.
2. many spectral lines actually consist of several separate lines whose λ differ slightly.
3. an understanding of how individual atoms interact with one another to from macroscopic matters→ Quantum mechanics(1925~1926)

【5.1 Quantum Mechanics】

Classical mechanics $\rightarrow$ future history of a particle is completely determined by its initial position & momentum together with force.

Quantum Mechanics $\rightarrow$ suggest the nature of an observable quantity $\rightarrow$ uncertainty principle $\rightarrow$ probabilities

classical mechanics is an approximate version of quantum mechanics

Wave function φ.

$|\varphi|^2 \rightarrow$ probability of finding the body for complex φ $\rightarrow$

$|\varphi|^2=\varphi*\varphi^*$ (φ^*: complex conjugate)

$\varphi=A+iB$ $\quad \varphi^*=A-iB \rightarrow \varphi^*\varphi=A^2+B^2$

- "well behaved" wave function

(1)φmust be continuous & single-valued everywhere

(2) $\partial\varphi/\partial x, \partial\varphi/\partial y, \partial\varphi/\partial z$ must be single valued & continuous(for momentum consideration)

(3)φmust be normalization, which means thatφ must go to 0 as x $\rightarrow \pm\infty$ $\quad$ y $\rightarrow \pm\infty$ $\quad$ z $\rightarrow \pm\infty$

$\because \int|\varphi|^2 dv$ needs to be a finite constant

- $|\varphi|^2$ = probability density P

$$\int_{-\infty}^{\infty} p dv = 1 \Rightarrow \int_{-\infty}^{\infty} |\varphi|^2 dv = 1$$ normalization

probability $p_{x_1 x_2} = \int_{x_1} |\varphi|^2 dx$

- A particle in a box, φ=0 outside the box but in real case, never happen.

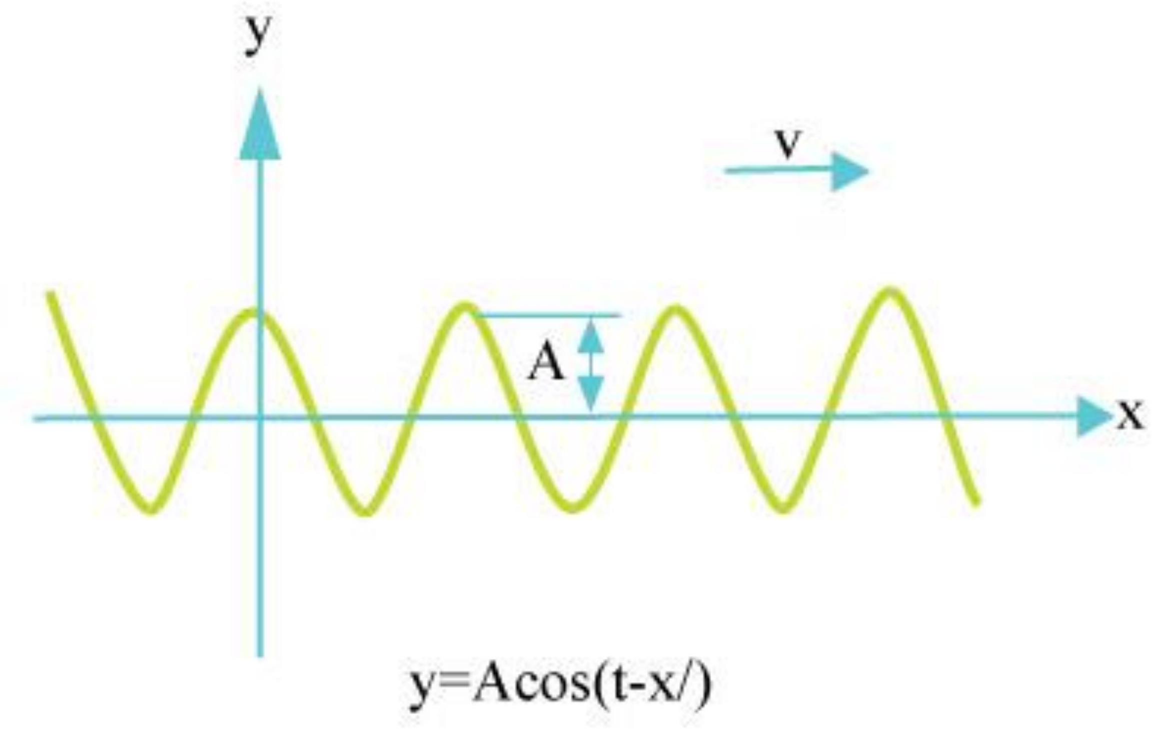

Figure 5.1 Waves in the *xy* plane traveling in the +*x* direction along a stretched string lyingon the *x* axis.

【5.2 wave equation】

$\frac{\partial^2 y}{\partial^2 x} = \frac{1}{v^2}\frac{\partial^2 y}{\partial^2 t}$ solution: $y=F(t \pm x/v)$

consider a wave equivalent of free particles.

$\longrightarrow$ $Y=Ae^{-i\omega(t-x/v)}$ {undamped(constant amplitude A),

monochromatic(const ω), harmonic}

$Y=A\cos\omega(t-x/v)-iA\sin\omega(t-x/v)$

For a strenched string, only real part has significance.

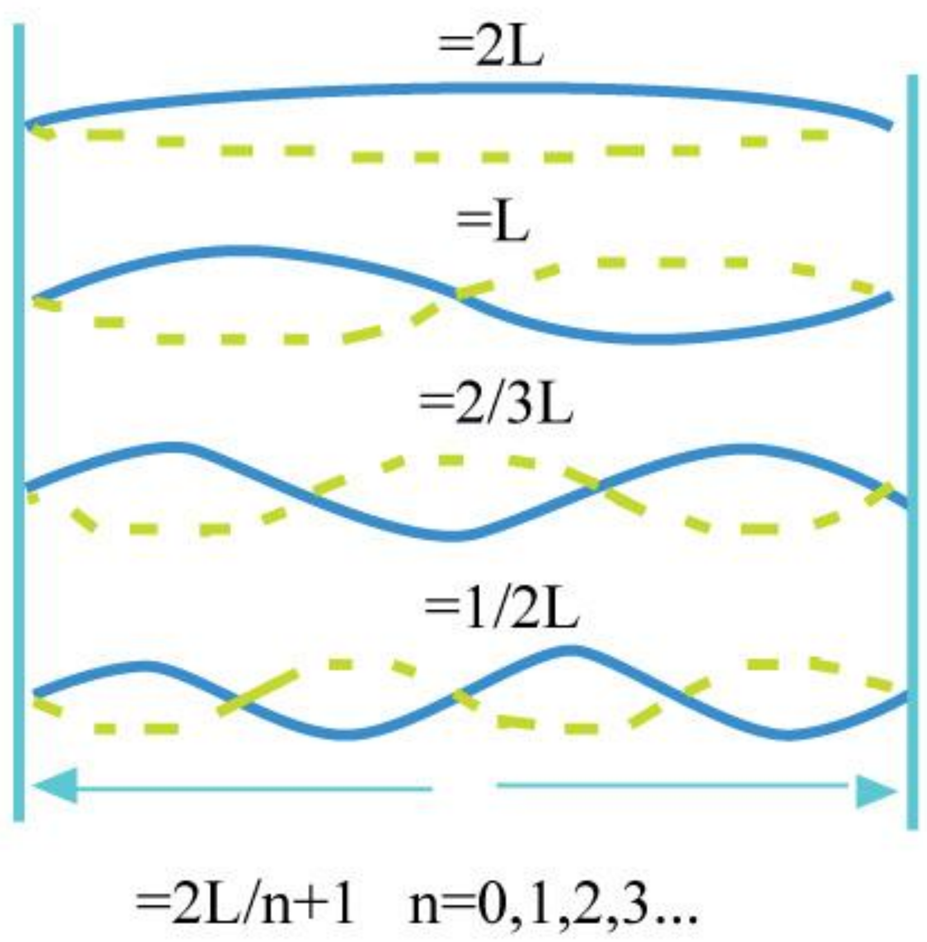

Figure 5.2 Standing waves in a stretched string fastened at both ends.

【5.3 Schrodinger's equation : time dependent form】

- for a free particle $\varphi = Ae^{-i\omega(t-x/v)} = Ae^{-2\pi i(\nu t - x/\lambda)}$

$$\because E = h\nu = 2\pi\hbar\nu, \lambda = \frac{h}{p} = \frac{2\pi\hbar}{p}$$

$$\Rightarrow \varphi = Ae^{-i/\hbar(Et-px)} \text{............}(A)$$

unrestricted particle of energy E & momentum P moving in +x direction

(1)differentiating eq(A) for φ twice with respect to x

$$\frac{\partial^2\varphi}{\partial x^2} = \frac{-p}{\hbar^2}\varphi$$

$$p^2\varphi = -\hbar^2\frac{\partial^2\varphi}{\partial x^2}$$

(2)differentiating eq(A) forφwith respect to t

$$\frac{\partial\varphi}{\partial t} = \frac{-iE}{\hbar}\varphi$$

$$E\varphi = \frac{-\hbar}{i}\frac{\partial\varphi}{\partial t}$$

for v<<c

$$E = \frac{p^2}{2m} + U(x,t)$$

$$\Rightarrow E\psi = \frac{p^2\varphi}{2m} + U\varphi$$

$$\Rightarrow i\hbar\frac{\partial\varphi}{\partial t} = \frac{-\hbar^2}{2m}\frac{\partial^2\varphi}{\partial x^2} + U\varphi \Rightarrow$$

$$restriction \leftrightarrow U$$

Derived from free particle, but it is a general case. If U known

⟶ φcan be solved.

【5.4 Expectation value】

calculated the expectation value <x>

$\Rightarrow$ The value of x we would obtain if we measure the positions of a great many particles described by the same wave function at time t and then average the results.

- The average position $\bar{x}$ of a number of identical particles distributed along x axis.

N_1 at x_1 , N_2 at x_2 ;……………

$$\bar{x} = \frac{N_1x_1 + N_2x_2 + N_3x_3 + ...}{N_1 + N_2 + N_3 + ...} = \frac{\sum N_i x_i}{\sum N_i}$$

- If along with a single particle,

$\Rightarrow$replaced N_i by probability P_i

$$p_i = |\varphi_i|^2 dx$$

$$\Rightarrow \langle x \rangle = \frac{\int_{-\infty}^{\infty} x|\varphi|^2 dx}{\int_{-\infty}^{\infty} |\varphi|^2 dx}$$

If φ is a normalized function

$$\Rightarrow \int_{-\infty}^{\infty} |\varphi|^2 dx = 1$$

$\Rightarrow$Expectation value of position

$$\langle x \rangle = \int_{-\infty}^{\infty} x|\varphi|^2 dx$$

$$\langle G(x) \rangle = \int_{-\infty}^{\infty} G(x)|\varphi|^2 dx$$

【5.5 Schrodinger's equation: steady-state form】

for one-dimensional wave function Ψ of an unrestricted particle may be written

$$\psi = Ae^{-\left(i/\hbar\right)(Et-px)} = Ae^{-\left(iE/\hbar\right)t}e^{+\left(ip/\hbar\right)x} = \varphi e^{-\left(iE/\hbar\right)t}$$

Ψ is the product of a time-dependent function $e^{-\left(iE/\hbar\right)t}$ and a position-dependent functionψ

If Ψ=F(x)×F'(t)

The time variations of all wave functions of particles acted on by stationary forces have the same form as that of an unrestricted particle.

∵ substituting $\psi = \varphi e^{-\left(iE/\hbar\right)t}$ into time-dependent eq

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

$$\Rightarrow E\psi e^{-\left(iE/\hbar\right)t} = \frac{-\hbar^2}{2m}e^{-\left(iE/\hbar\right)t}\frac{\partial^2\psi}{\partial x^2} + U\psi e^{-\left(iE/\hbar\right)t}$$

$$\Rightarrow \frac{\partial^2\psi}{\partial x^2} + \frac{2m}{\hbar^2}(E-U)\psi = 0$$

Steady-state Schrodinger eq in 1-D

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{2m}{\hbar^2}(E-U)\psi = 0$$ 3-D

** For Schrodinger's steady-state eq, if it has one or more solutions for a given system, each of these wave functions corresponds to a specific value of energy E. $\Rightarrow$ energy quantization

- Considering standing waves in a stretched string of length L that is fixed at both ends.

$\Rightarrow$these waves are subject to the condition(boundary condition) that y=0 at both ends.

$\because$ φ & $\frac{\partial \varphi}{\partial x}$ need to be continuous, finite, and single-value

$\Rightarrow$ λ_n=2L/n+1 , n=0,1,2,3……

$\Rightarrow$combination of wave eq & boundary condition.

$\Rightarrow$y(x,t) can exist only for certainλ_n

Eigenvalues & Eigenfunctions

The value of energy E_n for which Schrodinger's steady-state eq can be solved are called eigenvalues and the corresponding wave functions φ_n are called eigenfunctions.

- The discrete energy levels of H atom

$$E_n = \frac{-me^4}{32\pi^2 {\varepsilon_o}^2 \hbar^2}\left(\frac{1}{n^2}\right), n = 1,2,3,..........$$

are an example of a set of eigenvalues.

In addition to E, angular momentum L is also quantized. In H atom, the eigenvalues of the magnitude of the total angular momentum are $L = \sqrt{l(i+1)}\hbar, l = 0,1,2,3............(n-1)$

- A dynamic variable G may not be quantiaed.

$\Rightarrow$measurements of G made on a number of identical systems will not yield a unique result but a spread of values which average is expectation value.

$$\langle G \rangle = \int_{-\infty}^{\infty} G|\varphi|^2 dx$$

for example, in H atom, position x is not quantized.

【5.6 particle in a box】

- the motion of a particle is confined between x=0 & x=L by infinitely hard wall(it U(0)=U(L)=∞)
- A particle does not lose energy when it collides with hard walls.

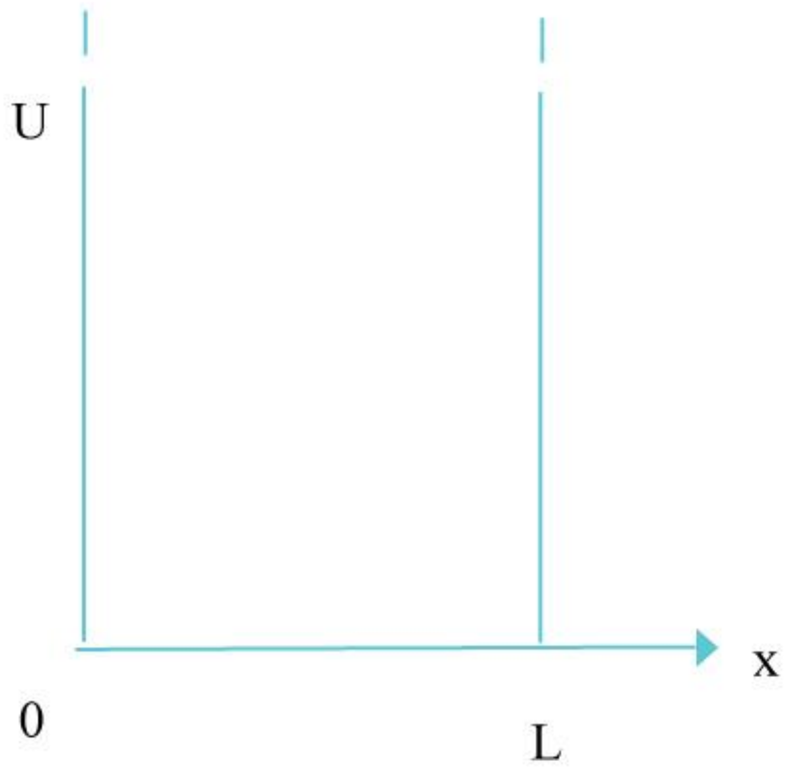

Figure 5.3 A square potential well with infinitely high barriers at each end

- φis 0 for x$\leq 0 \& x \geq L$

within the box: $\frac{d^2\varphi}{dx^2}+\frac{2m}{\hbar^2}E\varphi=0(\because U=0)$........(5.24)

eq(5.24) has the solution

$$\varphi = A\sin\frac{\sqrt{2mE}}{\hbar}x + B\cos\frac{\sqrt{2mE}}{\hbar}x$$

B.C. φ=0 at x=0 & x=L

∵cos0=1 B=0 (∵φ(x=0)=0)

$\varphi(x=L)=0 \Rightarrow \frac{\sqrt{2mE}}{\hbar}L = n\pi$ n=1,2,3,……….

$\Rightarrow$ energy of particle can have only certain values

→ eigenvalues → energy levels

En= $\frac{n^2\pi^2\hbar^2}{2mL^2}$ **n=1,2,3……….**

$$\varphi_n = A\sin\frac{\sqrt{2mE_n}}{\hbar}x$$

$$\because E_n = \frac{n^2\pi^2\hbar}{2mL} \Rightarrow \varphi_n = A\sin\frac{n\pi x}{L}(eigenfunctions)$$

→ these eigenfunction meet all requirements

φ_n is a finite, single-valued, and $\varphi_n \,\&\, \frac{\partial \varphi_n}{\partial x}$ continuous

(except at the ends of the box)

- To normalize φ

$$\Rightarrow \int_{-\infty}^{\infty} |\varphi_n|^2 dx = 1$$

$$\Rightarrow \int_0^L |\varphi_n|^2 dx = A^2 \int_0^L \sin^2\left(\frac{n\pi x}{L}\right)dx$$

$$= \frac{A^2}{2}\left[\int_0^L dx - \int_0^L \cos\left(\frac{2n\pi x}{L}\right)dx\right]$$

$$\left(\because \sin^2\theta = \frac{1}{2}(1-\cos 2\theta)\right)$$

$$= \frac{A^2}{2}\left[x - \left(\frac{L}{m\pi}\right)\sin\frac{2n\pi x}{L}\right]_0^L = A^2\left(\frac{L}{2}\right) = 1$$

$$\Rightarrow A = \sqrt{\frac{2}{L}}$$

$$\Rightarrow \varphi_n = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}, n = 1,2,3.........$$

$$*\ \varphi_n = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$$

φ_n may be "-" , but $|\varphi_n|^2$ is "+"

($\because$ $|\varphi_n|^2$ is probability density of finding the particle)

*when n=1 , the particle most likely to be in the middle of the box but when n=2 , $|\varphi_n|^2$ =0 in the middle of the box.

Ex 5.3

Find the probability that a particle trapped in a box L wide can be found between 0.45L & 0.55L

For n=1 & n=2

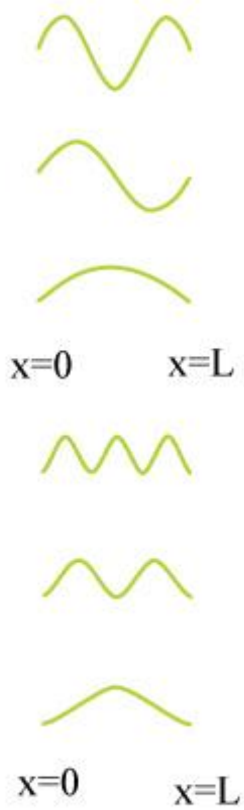

Figure 5.4 Wave function and probability densities of a particle confined to a box with rigid walls.

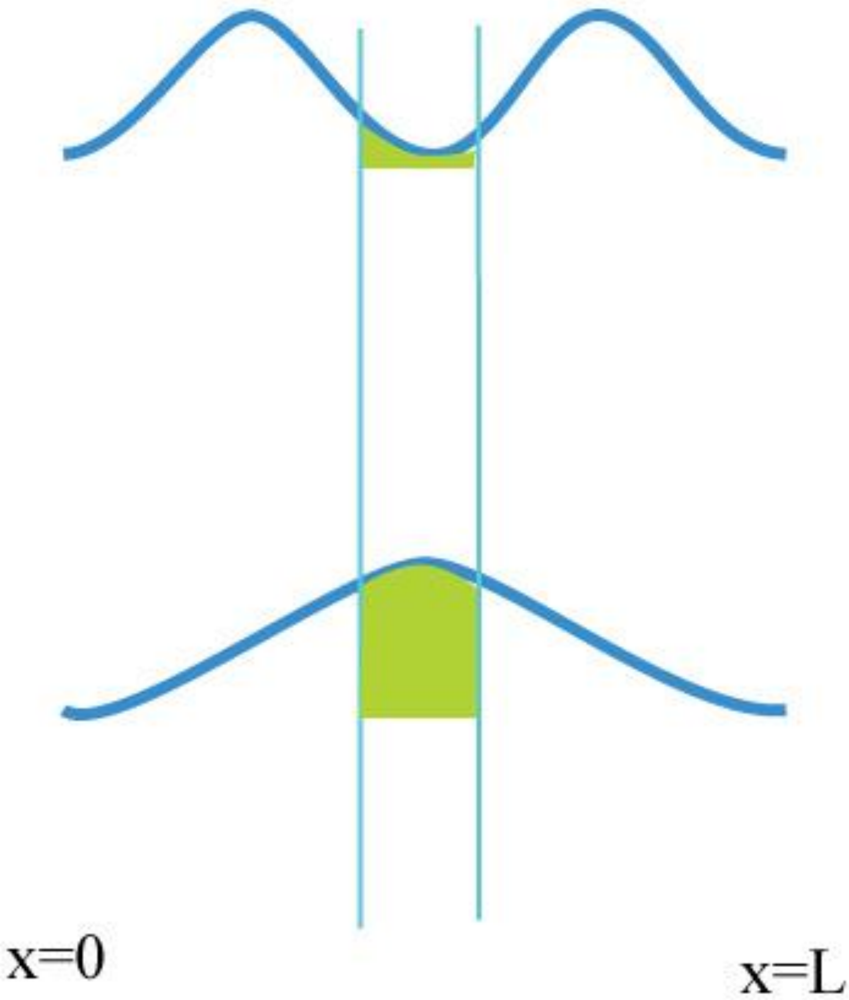

Figure 5.5 The probability P_{x1x2} of finding a particle in the box of Fig. 5.4 between $x_1 = 0.45L$ and $x_2 = 0.55L$ is equal to the area under the $|\Psi|^2$ curves between these limits.

Classically, we expect the particle to be in this region 10% of the time ($\because \frac{(0.55-0.45)L}{L} = 0.1$) but QM gives different prediction depending on n

$$P_{x_1,x_2} = \int_{x_1}^{x_2} |\varphi_n|^2 dx$$

$$= \frac{2}{L}\int_{x_1}^{x_2} \sin^2 \frac{2n\pi x}{L} dx$$

$$= \left[\frac{x}{L} - \frac{1}{2n\pi}\sin\frac{2n\pi x}{L}\right]_{x_1}^{x_2}$$

$\therefore$ for n=1 , $P_{x1\ x2}$=19.8%

n=2 , $P_{x1\ x2}$=0.65%

ex 5.4

Find <x> of the position of a particle trapped in a box L wide

$$\langle x \rangle = \int_{-\infty}^{\infty} x|\varphi|^2 dx = \frac{2}{L}\left[\frac{x^2}{4} - \frac{x\sin\left(\frac{2n\pi x}{L}\right)}{4n\pi/L} - \frac{\cos\left(2n\pi x/L\right)}{8\left(n\pi/L\right)^2}\right]_0^L$$

$$\Rightarrow \langle x \rangle = \frac{2}{L}\left(\frac{L}{4}\right)^2 = \frac{L}{2}$$

Middle of the box !!

【5.7 finite potential well】

*Potential energies are never ∞ consider potential wells with barriers of finite height

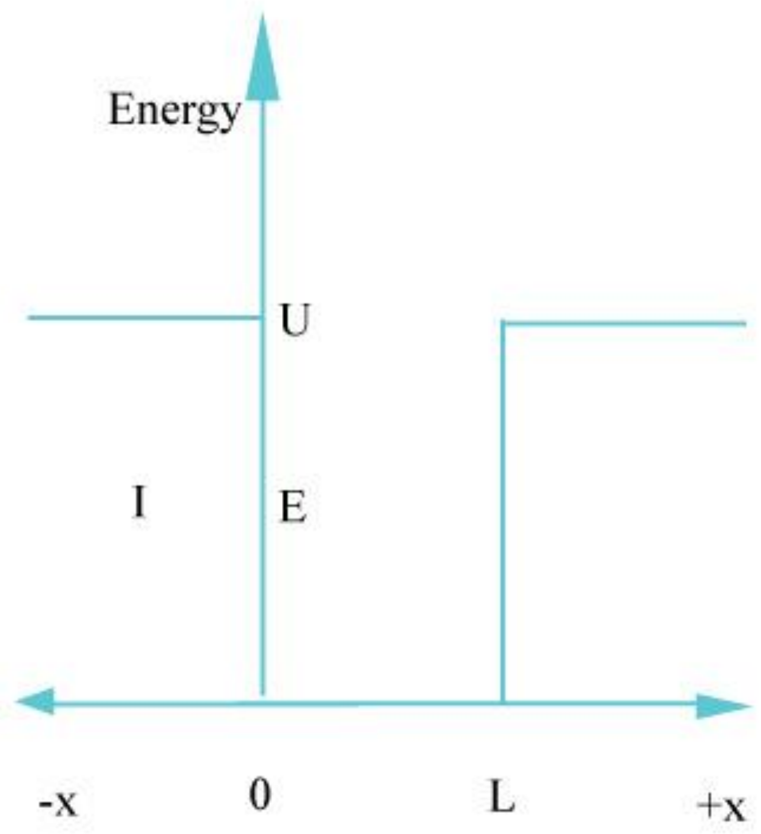

Figure 5.6 A square potential well with finite barriers. The energy *E* of the trapped particle is less than the height *U* of the barriers.

*Particle energy E<U

classical mechanics: when particle strikes the side of the well, it bounces off without entering regions In QM, it has a certain probability of penetrating into regions Ⅰ&Ⅲ

*In Ⅰ&Ⅲ

$$\frac{\partial^2\varphi}{\partial x^2}+\frac{2m}{\hbar^2}(E-U)\varphi=0$$

$$\frac{d^2\varphi}{dx^2}-a^2\varphi=0 \qquad x<0\ ,\ x>L$$

$$a=\frac{\sqrt{2m(U-E)}}{\hbar}$$

$$\Rightarrow \varphi_{\mathrm{I}}=Ae^{ax}+Be^{-ax}$$

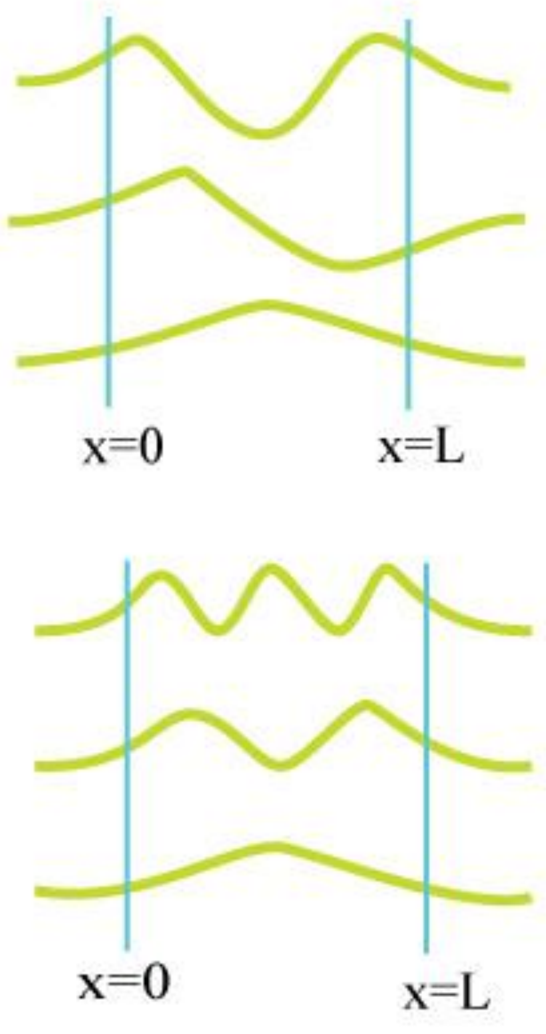

Figure 5.7 Wave functions and probability densities of a particle in a finite potential probability of being found outside the wall.

$\varphi_{III} = Ce^{ax}+De^{-ax}$ $\because e^{-ax} \longrightarrow \infty$ when $x \longrightarrow -\infty$

$e^{ax} \longrightarrow \infty$ when $x \longrightarrow \infty$

$\therefore$ B=C=0 $\Rightarrow$ $\varphi_{I} = Ae^{ax}$, $x<0$ $\varphi_{III} De^{-ax}$, $x>L$

** these wave functions decrease exponentially inside the barrier.

Within the well

$$\Rightarrow \varphi_{II} = E\sin\frac{\sqrt{2mE}}{\hbar}x + F\cos\frac{\sqrt{2mE}}{\hbar}x$$

$\because \varphi$ is continuous

$\therefore \varphi_{I}(x=0)=\varphi_{II}(x=0)$ $\varphi_{II}(x=L)=\varphi_{III}(x=L)$

$\therefore$ A=F $= De^{-aL}$

$\Rightarrow$ solve E ($E\neq 0$)

$\frac{\partial \varphi}{\partial x}$ at x=0 & x=L is continuous

Combining these B.C. $\Rightarrow$ solve complete wave function

**Because the wavelengths that fit into the well are longer than for an infinite well of the same width $\Rightarrow$ particle momentum are lower ($\because P=h/\lambda$) $\Rightarrow$ En are lower than they are for a particle in an infinite well $\Rightarrow$ The wave function penetrates the walls, which lowers the energy levels.

【5.8 Tunnel effect】

Particle strikes a potential U(E<U) the barrier has finite width (see Fig 5.8) $\Rightarrow$ particle has non-zero probability to pass through the barrier & emerge on the other side.

Ex: tunnel diode: e' pass through potential barrier even though their KE<barrier height

- In region Ⅰ&Ⅲ U=0

$$\frac{d^2\varphi_{\mathrm{I}}}{dx^2}+\frac{2m}{\hbar^2}E\varphi_{\mathrm{I}}=0$$

$$\frac{d^2\varphi}{dx^2}+\frac{2m}{\hbar^2}E\varphi=0$$

$$\varphi_{\mathrm{I}}=Ae^{ik_1x}+Be^{-ik_1x}$$

$$\varphi=Fe^{ik_1x}+Ge^{ik_1x} \qquad k_1=\frac{\sqrt{2mE}}{\hbar}=\frac{p}{\hbar}=\frac{2\pi}{\lambda} \qquad \text{(eq 5.43)}$$

$$\because e^{i\theta}=\cos\theta+i\sin\theta$$

$$e^{-i\theta}=\cos\theta-i\sin\theta$$

$\therefore$ eq 5.43 the same as particle in a box

$\varphi_{1\div}=Ae^{ik_1x}$ represents incoming wave

$\varphi_{1-}=Be^{-ik_1x}$ represents reflected wave

Figure 5.8 When a particle of energy $E<U$ approaches a potential barriers, according to classical mechanics the particle must be reflected. In quantum mechanics, the de Broglie waves that correspond to the particle are partly reflected and partly transmitted, which means the particle has a finite chance of penetrating the barrier.

Figure 5.9 At each wall of the barrier, the wave functions inside and outside it must match u perfectly, which means that they must have the same values and slopes there.

- $\varphi_{\mathrm{I}} = \varphi_{\mathrm{I}+} + \varphi_{\mathrm{I}-}$

$\varphi_{\mathrm{III}+} = Fe^{ik_1x}$ represented transmitted wave in region Ⅲ nothing could reflect the wave

$\therefore G = 0 \Rightarrow \varphi_{\mathrm{III}} = \varphi_{\mathrm{III}+} = Fe^{ik_1x}$

- $v_{1=}$ is the group velocity of incoming wave (equal to v of particles)

  $\Rightarrow S = |\varphi_{1+}|^2 v_{\mathrm{I}+}$

  is the flux of particles that arrives at the barrier,

  S= # of particles/m^{2}sec ($\frac{\#}{m^3}\frac{m}{\sec}$)

- Transmission probability

  $$T = \frac{|\varphi^+|^2 v^+}{|\varphi_{\mathrm{I}}^+|^2 v_{\mathrm{I}}^+} = \frac{FF^* v^+}{AA^* v_{\mathrm{I}}^+}$$

  classically T=0 ∵E<U

  In region Ⅱ Sch. Eq.

$$\frac{d^2\varphi_{\mathrm{II}}}{dx^2} + \frac{2m}{\hbar^2}(E-U)\varphi_{\mathrm{II}} = 0$$

$$\varphi_{\mathrm{II}} = Ce^{-k_2x} + De^{k_2x}, k_2 = \frac{\sqrt{2m(E-U)}}{\hbar}$$

(same as finite potential well)

∵exp are real quantities$\Rightarrow \varphi_{\mathrm{II}}$ does not oscillate and $|\varphi_{\mathrm{II}}|^2$ is not zero

$\Rightarrow$ particle may emerge into Ⅲ or return to Ⅰ

Applying B.C. $\frac{\partial\varphi}{\partial x}$ & φ need to be continuous

$$\varphi_{\mathrm{I}} = \varphi_{\mathrm{II}}$$

at x=o $\frac{d\varphi_{\mathrm{I}}}{dx} = \frac{d\varphi_{\mathrm{II}}}{dx}$ (see Fig 5.9)

at x=L $\varphi_{\mathrm{II}} = \varphi_{\mathrm{III}}$

$d\varphi_{\mathrm{II}}/dx = d\varphi_{\mathrm{III}}/dx$

$\Rightarrow$ A+B=C+D

$$ik_1A - ik_1B = -k_2C + k_2D$$
$$Ce^{-k_2L} + De^{k_2L} = Fe^{ik_1L}$$
$$-k_2Ce^{-k_2L} + k_2De^{k_2L}$$

$$\Rightarrow \left(\frac{A}{F}\right) = \left[\frac{1}{2} + \frac{i}{4}\left(\frac{k_2}{k_1} - \frac{k_1}{k_2}\right)\right]e^{(ik_1+k_2)L} + \left[\frac{1}{2} - \frac{i}{4}\left(\frac{k_2}{k_1} - \frac{k_1}{k_2}\right)\right]e^{(ik_1-k_2)L}$$

Let's assume U>>E

$$k_1 = \frac{\sqrt{2mE}}{\hbar} \quad \Rightarrow \quad \frac{k_2}{k_1} >> \frac{k_1}{k_2}$$

$$k_2 = \frac{\sqrt{2m(E-U)}}{\hbar} \Rightarrow \frac{k_2}{k_1} - \frac{k_1}{k_2} \approx \frac{k_2}{k_1}$$

also assume L is wide enough $\Rightarrow$ $k_2L>>1$

$$e^{k_2L} >> e^{-k_2}$$
$$\Rightarrow \left(\frac{A}{F}\right) \cong \left(\frac{1}{2} + \frac{ik_2}{4k_1}\right)e^{(ik_1+k_2)L}$$
$$\therefore \left(\frac{A}{F}\right)^* = \left(\frac{1}{2} + \frac{-ik_2}{4k_1}\right)e^{(-ik_1+k_2)L}$$

Here $v_{\mathrm{III}}^{+} = v_{\mathrm{I}}^{-}$ $\therefore v_{\mathrm{III}}^{+}/v_{\mathrm{I}}^{-} = 1$

$$\Rightarrow T = \frac{FF^* v^+}{AA^* v_{\mathrm{I}}^+} = \left(\frac{AA^*}{FF^*}\right)^{-1} = \left[\frac{16}{4 + \left({k_2}\big/{k_1}\right)^2}\right] e^{-2k_2 L}$$

$$\because \left(\frac{k_2}{k_1}\right)^2 = \frac{2m(U-E)/\hbar^2}{2mE/\hbar^2} = \frac{U}{E} - 1$$

$$approximation[\ \ ] \approx 1$$

$$\Rightarrow T = e^{-2k_2 L}$$

【5.9 Harmonic oscillator】

Harmonic motion: the presence of a restoring force that acts to return the system to its equilibrium configuration when it is disturbed.

In the special case, the restoring force F follow Hook's law $\Rightarrow$

F=-kx $\Rightarrow$ -kx= $m\dfrac{d^2x}{dt^2} \Rightarrow \dfrac{d^2x}{dt^2} + \dfrac{k}{m}x = 0$

$\Rightarrow x = A\cos(2\pi\nu t + \phi)$

$\nu = \dfrac{1}{2\pi}\sqrt{\dfrac{k}{m}}$ frequency of harmonic oscillator

A: amplitude

Φ: phase angle depends on what x is at t=0

In most of cases, restoring forces do not follow Hook's low, but when only consider a small displacement of x $\longrightarrow$ restoring force can be exercised by Hook's low.

$\Rightarrow$ Any system in which something executes small vibrations about an equilibrium (eqm) position behaves like a simple harmonic oscillator.

.Maclaurin's series

$F(x)=F_{x>0} + (\frac{dF}{dx})_{x=0}\, X + 1/2(\frac{d^2F}{dx^2})_{x=0}\, X^2 + 1/6(\frac{d^3F}{dx^3})_{x=0}\, X^3 + \ldots\ldots$

$\because$ x=0 is eqm position $\Rightarrow F_{x=0}=0$

for small x $\Rightarrow x^2, x^3$ is much smaller than x $\Rightarrow F(x)=(dF/dx)_{x=0}\, X$

for restoring force $(dF/dx)_{x=0}$ is negative $\Rightarrow$ Hook's law

.potential energy $U(x)=-\int_0^x F(x)dx=\ k\int_0^x xdx=1/2kx^2$

.Sch. eq.

$\frac{\partial^2\varphi}{\partial y^2}$ + $2m/\hbar^2(E-1/2kx^2)\varphi=0$……(5.75)

let $c=(1/\hbar\sqrt{km})^{1/2}$, $y=(1/\hbar\sqrt{km})^{1/2}x=cx$

$$\frac{\partial^2\varphi}{\partial y^2}=\frac{\partial}{\partial x}\left(\frac{\partial\varphi}{\partial y}\frac{\partial y}{\partial x}\right)=\frac{\partial}{\partial x}\left(\frac{\partial\varphi}{\partial y}\bullet c\right)$$

$$=c\left[\frac{\partial}{\partial y}\left(\frac{\partial\varphi}{\partial y}\frac{\partial y}{\partial x}\right)\right]=c^2\frac{\partial^2\varphi}{\partial y^2}$$

$\Rightarrow$eq5.75 $\Rightarrow c^2\ \frac{\partial^2\varphi}{\partial y^2}+2m/\hbar^2(E-1/2kx^2)\varphi=0$

$\Rightarrow\ \frac{\partial^2\varphi}{\partial y^2}+2E/\hbar(\sqrt{m/k}\,\varphi)-\sqrt{mk}/\hbar\ \times\ x^2\varphi=0$

$\Rightarrow$ let $\alpha=2E/\hbar(\sqrt{m/k})$

$\therefore$Sch eq (5.75) $\Rightarrow \frac{\partial^2\varphi}{\partial y^2}+(\alpha-y^2)\varphi=0$......(5.74)

for this eq, when $y\to\infty \Rightarrow \varphi\to 0$

for $\int_{\infty}^{\infty}|\varphi|^2 dy=1$

*for(5.78) only when $\alpha=2n+1$ n=1,n=2,n=3……

can satisfy all conditions

$\because \alpha=2E/\hbar(\sqrt{m/k})=2E/h\nu$ & $\alpha=2n+1$

$\therefore E_n=(n+1/2)h\nu$ n=0,n=1,n=2……

energy levels of Harmonic oscillator

Zero point energy $E_0=1/2(h\nu)$ $\therefore$ when T 0 $\Rightarrow$ E E_0 not

0

Figure 5.10 The potential energyof a harmonic oscillator is pro-portional to x2, where x is the displacement from the equilib-rium position. The amplitude Aof the motion is determined by the total energy E of the oscilla-tor, which classically can haveany value.

Figure 5.11 Potential wells andenergy levels of (a) a hydrogenatom, (b) a particle in a box, and (c) a harmonic oscillator. In eachcase the energy way on the quantumnumber n. Only for the levels equallyspaced. The symbol means "isroportional to".

Figure 5.12 The first six harmonic-oscillator wave functions. The vertical lines show the limits -A and +A between which a classical oscillator with the same energy will vibrate.

Figure Probability densities for the n = 0 and n = 10 states of a quantum-.mechanical harmonic oscillator. The probability densities for classical harmonic oscillators with the same energies are shown in white. In the n = 10 state, the wavelength is shortest at x = 0 and longest at x = -A.

Operators, eigenfunctions & eigenvalues

Is $\langle p\rangle = \int_{-\infty}^{\infty} p|\varphi|^2 dx$??

$\langle E\rangle = \int_{-\infty}^{\infty} E|\varphi|^2 dx$??

$\because$ φ=φ(x,t), In order to carry out the integrations

$\Rightarrow$ we need to express P&E as functions of x,t

but $\Delta p \Delta x \geq \frac{\hbar}{2}$ & $\Delta E \Delta x \geq \frac{\hbar}{2}$

$\therefore$ no function as p(x,t)&E(x,t)

$\Rightarrow$ Integration form is not suitable for <P> <E>

for free particle $\varphi = Ae^{-\left(i/\hbar\right)(Et-px)}$

$$\frac{\partial\varphi}{\partial x} = \frac{i}{\hbar}p\varphi \Rightarrow p\varphi = \frac{\hbar}{i}\frac{\partial}{\partial x}\varphi$$

$$\frac{\partial\varphi}{\partial t} = \frac{-i}{\hbar}E\varphi \Rightarrow E\varphi = i\hbar\frac{\partial}{\partial t}\varphi$$

$$\Rightarrow P \to \left(\frac{\hbar}{i}\right)\frac{\partial}{\partial x}$$

operator

$$E \to (i\hbar)\frac{\partial}{\partial t}$$

$$E = KE + U$$

$$KE = \frac{p^2}{2m} \Rightarrow KE = \frac{1}{2m}\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)^2 = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

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

$$\Rightarrow i\hbar\frac{\partial\varphi}{\partial t} = \frac{-\hbar^2}{2m}\frac{\partial^2\varphi}{\partial x^2} + U\varphi \to$$ Sch. Eq.

$$\langle p\rangle = \int_{-\infty}^{\infty}\varphi * p\varphi dx = \int_{-\infty}^{\infty}\varphi *\left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)\varphi dx$$

$$= \frac{\hbar}{i}\int_{-\infty}^{\infty}\varphi *\frac{\partial\varphi}{\partial x}dx$$

$$\langle E\rangle = \int_{-\infty}^{\infty}\varphi * E\varphi dx = \int_{-\infty}^{\infty}\varphi *\left(i\hbar\frac{\partial}{\partial t}\right)\varphi dx$$

$$= i\hbar\int_{-\infty}^{\infty}\varphi *\frac{\partial\varphi}{\partial t}dx$$

expectation value

of an operator $\langle G(x,p)\rangle = \int_{-\infty}^{\infty} \varphi * G\varphi dx$

eigenvalue eq. $G\varphi_n = G_n\varphi_n$

Hamiltonian operator $H = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U$

$\Rightarrow H\varphi_n = E_n\varphi_n$

$*$Particle in a box

$$\varphi * = \varphi_n = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L} \qquad \frac{d\varphi}{dx} = \sqrt{\frac{2}{L}}\frac{n\pi}{L}\cos\frac{n\pi x}{L}$$

$$\langle p\rangle = \int_{-\infty}^{\infty} \varphi * p\varphi dx = \int_{-\infty}^{\infty} \varphi * \left(\frac{\hbar}{i}\frac{d}{dx}\right)\varphi dx$$

$$= \frac{\hbar}{i}\frac{2}{L}\frac{n\pi}{L}\int_0^L \sin\frac{n\pi x}{L}\cos\frac{n\pi x}{L}dx$$

$$= 0$$

$\because E = p^2/2m \Rightarrow p_n = \pm\sqrt{2mE_n} = \pm\frac{n\pi\hbar}{L} \Leftarrow$ momentum

eigenvalue

$\pm$ means that the particle is moving back & forth

$\longrightarrow$ average $p_{av} = \frac{\left(n\pi\hbar/L - -n\pi\hbar/L\right)}{L} = 0$

$*$ Find momentum eigenfunction

$$p\varphi_n = p_n\varphi_n \qquad p = \frac{\hbar}{i}\frac{d}{dx} \qquad \varphi_n = \sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}$$

φ_n is not momentum eigenfunction

$$\because \frac{\hbar}{i}\frac{d}{dx}\left(\sqrt{\frac{2}{L}}\sin\frac{n\pi x}{L}\right) = \frac{\hbar}{i}\frac{n\pi}{L}\sqrt{\frac{2}{L}}\cos\frac{n\pi x}{L} \neq p_n\varphi_n$$

$$\sin\theta = \frac{e^{i\theta} - e^{-i\theta}}{2i} = \frac{1}{2i}e^{i\theta} - \frac{1}{2i}e^{-i\theta}$$

$$\left.\begin{aligned} \varphi_n^+ &= \frac{1}{2i}\sqrt{\frac{2}{L}}e^{in\pi x/L} \\ \varphi_n^- &= \frac{1}{2i}\sqrt{\frac{2}{L}}e^{-in\pi x/L} \end{aligned}\right\} \text{momentum eigenfunction}$$

Varity $\varphi_n^+ \,\&\, \varphi_n^-$ are eigenfunction

$$p\varphi_n^+ = p_n^+\varphi_n^+$$

$$\frac{\hbar}{i}\frac{d}{dx}\varphi_n^+ = \frac{\hbar}{c}\frac{1}{2i}\sqrt{\frac{2}{L}}\frac{in\pi}{L}e^{in\pi x/L} = \frac{n\pi\hbar}{L}\varphi_n^+ = p_n{}^+\varphi_n{}^+$$

$$p_n{}^+ = \frac{n\pi\hbar}{L}$$

and $\varphi_n{}^+$ can be $\frac{1}{2i}\sqrt{\frac{2}{L}}e^{in\pi x/L}$

similar $p_n{}^- = \frac{-n\pi\hbar}{L}$