6.3 Translational, vibrational and rotational motion

important for molecular physics since big molecules can store energy in these modes of motion!

Translational Motion:

$$H\psi = E\psi \qquad H = -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} \quad \text{(free motion}$$

$\Rightarrow$ General solution $\quad \psi_k = Ae^{ikx} + Be^{-ikx}$

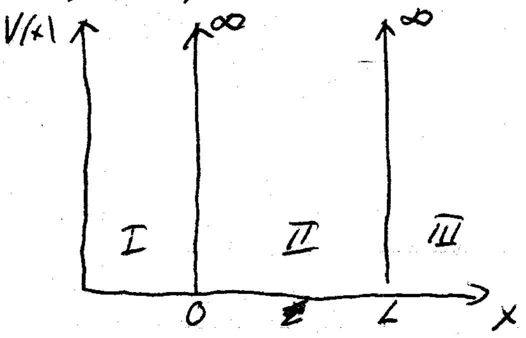
$$\Rightarrow \frac{\hbar^2 k^2}{2m}\left(Ae^{ikx} + Be^{-ikx}\right) = E\left(Ae^{ikx} + Be^{-ikx}\right)$$

Eigenvalues $\Rightarrow E_k = \dfrac{\hbar^2 k^2}{2m}$

k: arbitrary, free motion is not quantized

$$\psi_k = \underbrace{A\, e^{ikx}}_{\substack{\text{particle/wave}\\ \text{moving to the right}\\ p_x^+ = \hbar k}} + \underbrace{B\, e^{-ikx}}_{\substack{\text{particle/wave}\\ \text{moving to the left}\\ p_x^- = -\hbar k}}$$

Confine particle:



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

$\Rightarrow$ quantum dots, electrons in metals, etc

I and III: $-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + \underset{\to\infty}{V}\psi = E\psi$

$$\Rightarrow \psi \to 0$$

II: $-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} = E\psi$ ($\equiv$ free particle)

boundary conditions: $\psi_I(x=0) = \psi_{II}(x=0) = 0$
$\psi_{II}(x=L) = \psi_{III}(x=L) = 0$

$$\Rightarrow \psi_k(x) = C\sin kx + D\cos kx \qquad E_k = \frac{k^2\hbar^2}{2m}$$

$\psi(0) = C\sin k\cdot 0 + D\cos k\cdot 0 = D = 0$

$\psi(L) = C\sin kL = 0 \Leftrightarrow kL = n\pi \quad (n = 1, 2, \ldots)$

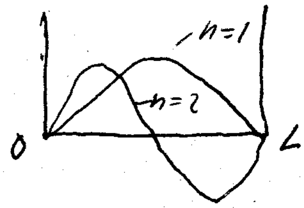
$\Rightarrow k = \frac{n\pi}{L}$

$$\Rightarrow \psi_n(x) = C\sin\left(\frac{n\pi x}{L}\right)$$

$$\boxed{E_n = \frac{k^2\hbar^2}{2m} = \frac{n^2h^2}{8mL^2}} \sim n^2$$

$$1 = \int_0^L \psi^2 dx = C^2\int_0^L \sin^2\frac{n\pi x}{L}dx = C^2\frac{L}{2}$$

$$\Rightarrow C = \sqrt{2/L} \quad \Rightarrow \boxed{\psi_n(x) = \sqrt{2/L}\sin\left(\frac{n\pi x}{L}\right)}$$



$$\psi_n(x) = \sqrt{2/L}\sin\frac{n\pi x}{L} = \frac{1}{2i}\sqrt{2/L}\left(e^{ikx} - e^{-ikx}\right)$$

$$\langle p\rangle = \int \psi^* \frac{d}{dx}\psi\, dx =$$

$$= \frac{ik}{2L}\left[-\frac{1}{2ik}\left(e^{-2ikL} - 1\right) - \frac{1}{2ik}\left(e^{2ikL} - 1\right)\right]$$

$$= -\frac{2}{4L}\left(e^{-\frac{2in\pi}{L}L} - 1\right) = 0$$

orthogonality: $n \neq n'$

$$\int_0^L \psi_n^* \psi_{n'}\, dx = \frac{2}{L}\int_0^L \sin\frac{n\pi x}{L}\sin\frac{n'\pi x}{L}\, dx$$

$$= \frac{2}{L}\left[\frac{\sin(n-n')\pi x}{2\pi(n-n')} - \frac{\sin(n+n')\pi x}{2\pi(n+n')}\right]_0^L = 0$$

Dirac bracket notation

ψ_n^* $\langle n|$ bra

$\psi_{n'}$ $|n'\rangle$ ket

Motion in two or more dimensions

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2}\right) = E\psi$$

separation of variables $\Rightarrow$

Ansatz: $\psi(x,y) = X(x)\cdot Y(y)$

$$\Rightarrow \frac{\partial^2\psi}{\partial x^2} = Y\frac{d^2X}{dx^2} \qquad \frac{\partial^2\psi}{\partial y^2} = X\frac{d^2Y}{dy^2}$$

$$\Rightarrow -\frac{\hbar^2}{2m}\left(Y\frac{d^2X}{dx^2} + X\frac{d^2Y}{dy^2}\right) = EXY$$

$$\frac{1}{X}\frac{d^2X}{dx^2} + \frac{1}{Y}\frac{d^2Y}{dy^2} = -\frac{2mE}{\hbar^2} = -\frac{2m}{\hbar^2}(E_x + E_y)$$

$$\Rightarrow -\frac{\hbar^2}{2m}\frac{d^2X}{dx^2} = E_x X \qquad -\frac{\hbar^2}{2m}\frac{d^2Y}{dy^2} = E_y Y$$

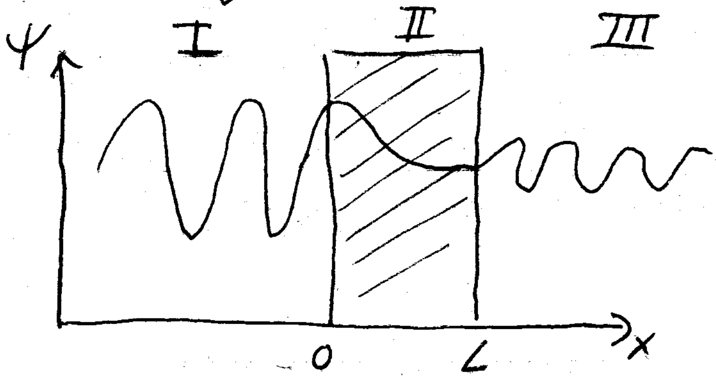
$$X_{n_1}(x) = \sqrt{\frac{2}{L_1}}\sin\frac{n_1\pi x}{L_1} \qquad Y_{n_2}(y) = \sqrt{\frac{2}{L_2}}\sin\frac{n_2\pi x}{L_2}$$

$$\Rightarrow \boxed{\begin{array}{ll} \psi_{n_1 n_2}(x,y) = \frac{2}{\sqrt{L_1 L_2}}\sin\frac{n_1\pi x}{L_1}\sin\frac{n_2\pi x}{L_2} & \begin{array}{l} 0 \le x \le L_1 \\ 0 \le y \le L_2 \end{array} \\ E_{n_1,n_2} = \left(\frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2}\right)\frac{h^2}{8m} & \end{array}}$$

<u>degeneracy:</u>

$L_1 = L_2 = L \Rightarrow \psi_{1,2}$ and $\psi_{2,1}$ are degenerate

<u>tunneling:</u>



I: $\psi = Ae^{ikx} + Be^{-ikx}$ (free particle)

$\hbar k = \sqrt{2mE}$

II: $-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V\psi = E\psi$ with $V > E$

$\psi = Ce^{Kx} + De^{-Kx}$

$\hbar K = \sqrt{2m(V-E)}$

III: $\psi = A'e^{ikx} + B'e^{-ikx}$

<u>boundary conditions:</u>

$\psi_I(0) = \psi_{II}(0)$: $A + B = C + D$

$\psi_{II}(L) = \psi_{III}(L)$: $Ce^{KL} + De^{-KL} = A'e^{ikL} + B'e^{-ikL}$

derivates continuous:

$\psi_I'(0) = \psi_{II}'(0)$: $ikA - ikB = KC - KD$

$\psi_{II}'(L) = \psi_{III}'(L)$: $KCe^{KL} - KDe^{-KL} = ikA'e^{ikL} - ikB'e^{-ikL}$

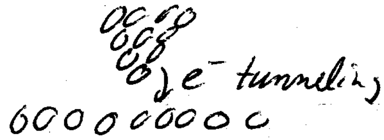
no particles to the left $\Rightarrow B' = 0$ $\Rightarrow$ 4 equation
in barrier exponential decay $\Rightarrow C = 0$ 4 unknowns

Transmission Probability

$$T = \frac{|A'|^2}{|A|^2} = \left\{ 1 + \frac{(e^{\kappa L} - e^{-\kappa L})^2}{16\varepsilon(1-\varepsilon)} \right\}^{-1} \neq 0$$

with $\varepsilon = E/V$

⇒ scanning tunneling microscopy (STM)
Rohrer, Binnig ⇒ Nobel prize



scanning with piezo
⇒ AFM, atomic force mic.
NSOM Near-field scanning optical microscope

Vibrational Motion

harmonic potential $V = \frac{1}{2}kx^2 \Rightarrow F = -kx$ Hooke's law

$$\Rightarrow -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}kx^2\psi = E\psi \quad \text{with } \psi = 0 \text{ for } x \to \pm\infty$$

⇒ Energy Eigenvalues: $E_v = (v + \frac{1}{2})\hbar\omega$

$$\omega = \sqrt{\frac{k}{m}} \qquad v = 0, 1, 2, 3, \ldots$$

Eigenfunctions: normalization constant

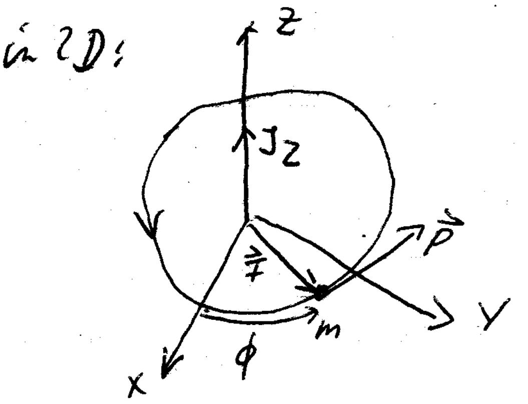
$$\psi_v(x) = N_v H_v(y) e^{-y^2/2} \quad \text{with } y = \frac{x}{\alpha},\ \alpha = \left(\frac{\hbar^2}{mk}\right)^{1/4}$$

Hermite polynomial

$$H_0 = 1, \quad H_1 = 2y \quad H_2 = 4y^2 - 2$$

Rotational Motion:

in 2D:



$V = 0$

$E = E_{kin} = \frac{p^2}{2m}$

$\vec{J} = \vec{r} \times \vec{p}$ angular momentum

$J_z = \pm rp$

$\Rightarrow E = \frac{J_z^2}{2mr^2} = \frac{J_z^2}{2I}$

$\underset{=}{!} mr^2$ (moment of inertia)

quantization of angular momentum

$J_z = \pm pr$ and $p = \frac{h}{\lambda}$ (de Broglie)

$= \pm \frac{hr}{\lambda}$

quantization $\lambda = \frac{2\pi r}{m_l}$ $m_l = 0, \pm 1, \pm 2$

$J_z = \pm \frac{hr}{\lambda} = \frac{m_l hr}{2\pi r} = m_l \frac{h}{2\pi}$

$$\boxed{J_z = m_l \hbar \quad \text{with } m_l = 0, \pm 1, \pm 2, \ldots}$$

$$\Rightarrow \boxed{E = \frac{J_z^2}{2I} = \frac{m_l^2 \hbar^2}{2I}}$$

wavefunction:

$H = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)$

$x = r\cos\phi \quad y = r\sin\phi$

$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \phi^2}$

$r = \text{const} \Rightarrow$ drop $\frac{\partial}{\partial r}$ term

$$H = -\frac{\hbar^2}{2mr^2}\frac{d^2}{d\phi^2} = -\frac{\hbar^2}{2I}\frac{d^2}{d\phi^2}$$

$$\frac{d^2\psi}{d\phi^2} = -\frac{2IE}{\hbar^2}\psi$$

$$\Rightarrow \psi_{m_l}(\phi) = \frac{e^{im_l\phi}}{\sqrt{2\pi}} \qquad m_l = \pm\frac{\sqrt{2IE}}{\hbar}$$

$$\psi(\phi+2\pi) = \psi(\phi)$$

$$\psi_{m_l}(\phi+2\pi) = \frac{1}{\sqrt{2\pi}}e^{im_l(\phi+2\pi)} = \frac{1}{\sqrt{2\pi}}e^{im_l\phi}e^{2\pi i m_l} = \psi_{m_l}(\phi)e^{2\pi i m_l}$$
$$= (-1)^{2m_l}\psi(\phi)$$

$$\Rightarrow (-1)^{2m_l} = 1 \Rightarrow m_l = 0, \pm 1, \pm 2, \ldots$$

<u>Formal derivation of angular momentum quantization</u>

$$\vec{L} = \vec{r}\times\vec{p} \qquad L_z = xp_y - yp_x$$

$$\hat{L} = \hat{r}\times\hat{p} \qquad L_z = \frac{\hbar}{i}\left(\hat{x}\frac{\partial}{\partial y} - \hat{y}\frac{\partial}{\partial x}\right)$$
$$= \frac{\hbar}{i}\frac{\partial}{\partial\phi}$$

$$\hat{L}_z\psi_{m_l} = \frac{\hbar}{i}\frac{d\psi_{m_l}}{d\phi} = im\frac{\hbar}{i}e^{im\phi} = \underline{m_l\hbar\psi_{m_l}}$$