Quantum Theory: techniques & applications

Application to translational motion

Reading: Atkins, ch. 9 (7판 ch. 12)

Schrödinger equations for three basic types of motion: translation, vibration, rotation $\rightarrow$ “quantization”

1. **Translational motion**

(1) Free motion

(2) Particle in a box

(3) Tunnelling

(1) Free motion

$V = 0$,
$H\Psi = E\Psi$, $H = (\hbar^2/2m)(d^2\Psi/dx^2)$

General solutions, $\Psi_k = Ae^{ikx} + Be^{-ikx}$, $E_k = k^2\hbar^2/2m$
$\Rightarrow H_k\Psi_k = E_k\Psi_k$

- all values of k, all values of the energy are permitted $\rightarrow$ the translational energy of a free particle is not quantized

- e^{ikx} is an eigenfunction of operator p_x with eigenvalue $+k\hbar$: motion toward +x
  e^{-ikx} is an eigenfunction of the operator p_x with eigenvalue $-k\hbar$: motion toward -x
$\Rightarrow |\Psi|^2$ is independent of x

$\rightarrow$ the position of the particle is completely unpredictable
(uncertainty principle, x, p_x do not commute)

(2) Particle in a box in 1-D

- a particle of mass m is confined between two walls at $x = 0$ and $x = L$
- Infinite square wall: $V(x) = 0$ inside the box, infinity at the walls

e.g., a gas phase molecule in 1-D container
π-electrons in a linear conjugated hydrocarbon

Schrödinger equation $$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi$$

i) $0 \le x \le L$, $V(x) = 0$ $$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0 \quad , \text{put } \frac{2mE}{\hbar^2} = k^2$$

$$\psi = Ae^{ikx} + Be^{-ikx} = A(\cos kx + i\sin kx) + B(\cos kx - i\sin kx)$$
$$= (A+B)\cos kx + (A-B)i\sin kx = C\sin kx + D\cos kx, \quad E = \frac{k^2\hbar^2}{2m}$$

ii) $x < 0$, $x > L$, $V = \infty$

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

curvature

$\downarrow$

∞

Boundary conditions

- physically impossible for the particle to be found with an infinite potential energy $\rightarrow$ the wavefunction must be zero ($\Psi = 0$) at $x < 0$, $x > L$

- wavefunction should be continuous

$\Rightarrow \Psi_k(0) = 0$, $\Psi_k(L) = 0$

$x = 0 \Rightarrow \Psi_k(0) = 0 = D = 0$, $\therefore D = 0$

$x = L \Rightarrow \Psi_k(L) = C\,\mathit{sin}\,kL$

if $C = 0$, $\Psi = 0$ for all x: no particle $\rightarrow$ the particle must be somewhere

$\Rightarrow \therefore \sin kL = 0$

$\rightarrow kL = n\pi$, $n = 1,2,3\ldots.$ ($n \neq 0$ since if $n = 0 \rightarrow \Psi = 0$ everywhere)

$\therefore \Psi_n(x) = C\,\mathit{sin}\,(n\pi x/L)$, $n = 1, 2 \ldots.$

- Normalization

$$\int_0^L \psi^2 dx = C^2 \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx$$

$$= C^2 \left[\frac{1}{2} \int_0^L \left(1 - \cos\frac{2n\pi}{L} x\right) dx \right] \quad \left(\because \int \sin^2 ax\, dx = \frac{1}{2}x - \frac{1}{4a}\sin 2ax \right)$$

$$= \frac{C^2}{2}[L - 0] = \frac{C^2}{2} L = 1$$

$$\therefore C = \left(\frac{2}{L}\right)^{1/2} \text{ for all } n$$

$$\therefore \psi_n(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right) \text{ for } 0 \le x \le L$$

$$E_n = \frac{(n\pi/L)^2 \hbar^2}{2m} = \frac{n^2 h^2}{8mL^2}, \quad n = 1, 2, \cdots$$

n: “quantum number” (integer, in some case, a half-integer)

- the properties of the solutions

(i) Energy is quantized

$$E_n \propto n^2$$

$\rightarrow$ only certain wavefunctions are acceptable

(ii) ψ vs. n

$\Psi_1(x) = (2/L)^{1/2}\,\mathit{sin}\,(\pi x/L)$
$\Psi_2(x) = (2/L)^{1/2}\,\mathit{sin}\,(2\pi x/L)$
……………

$\rightarrow$ same amplitude $(2/L)^{1/2}$, different wavelength

- n$\uparrow\rightarrow\lambda\downarrow$, $E_k = p^2/2m$, $p = h/\lambda$, $\lambda\downarrow$, $p\uparrow$, $E_k\uparrow$
- n$\uparrow\rightarrow\lambda\downarrow\rightarrow E_k\uparrow$
- n$\uparrow\rightarrow$ number of nodes$\uparrow \Rightarrow \Psi_n$ has n-1 nodes

(iii) linear momentum

$<p_x> =$

However, each wavefunction is a superposition of momentum eigenfunctions

$\Psi_n = (2/L)^{1/2}\, \mathit{sin}\, (n\pi x/L) = 1/2i\, (2/L)^{1/2}\, (e^{ikx} - e^{-ikx})$

$\Rightarrow$ $+k\hbar$ for half, $-k\hbar$ for half

$\Rightarrow$ equal probability for opposite directions

(iv) $E_{min} \neq 0$
cf) C.M. allow zero energy (stationary particle)

$n \neq 0$, "zero-point energy"

$$E_1 = h^2/8mL^2 \neq 0$$

uncertainty principle: non zero momentum $\rightarrow$ kinetic energy

curvature in a wavefunction $\rightarrow$ possession of kinetic energy

(v) $E_{n+1} - E_n = (h^2/8mL^2)(2n + 1)$

$L\uparrow \quad \Delta E \rightarrow 0$:
not quantized for complete free particles

(vi) probability

$\Psi^2(x) = (2/L)\, sin^2\, (n\pi x/L)$

low n $\rightarrow$ nonuniformity
n $\rightarrow \infty$, uniform $\Rightarrow$ classical mechanics
(independent of position)

"correspondence principle"

(vii) orthogonality

$\int \Psi_n^* \Psi_{n'} d\tau = 0$, $n' \neq n$: orthogonal

wavefunctions corresponding to different energies are orthogonal

ex. Ψ_1 Ψ_3

$\langle n | n' \rangle = 0$ ($n' \neq n$): Dirac bracket notation

$\langle n |$ "bra" $\Rightarrow \Psi_n^*$, $| n' \rangle$ "ket" $\Rightarrow \Psi$

normalized, $\langle n | n \rangle = 1$

$\langle n | n' \rangle = \delta_{nn'}$: kronecker delta, $n = n' \Rightarrow 1$

$n \neq n' \Rightarrow 0$

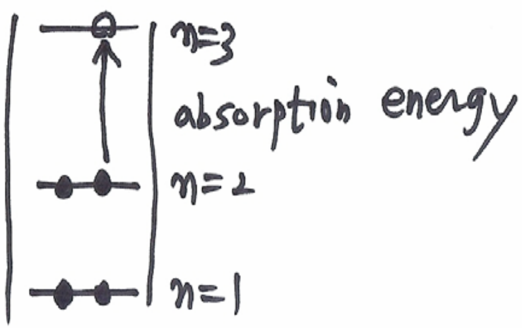
Orthogonality: important in Q.M.: eliminate a large number of integrals $\rightarrow$ central role in the theory of chemical bonding and spectroscopy e.g.) model of 1-D particle in a box: π electrons in linear conjugated hydrocarbons

butadiene (assume linear molecule) ⇒ absorption energy?

$H_2C=CH-CH=CH_2$ total length $(L)=5.78\,\text{Å}$

4 π electrons

⇒ $4e^-$ exist in $5.78\,\text{Å}$ length



$$E_n=\frac{n^2h^2}{8mL^2},\quad n=1,2\cdots$$

transition $n=2\rightarrow n=3$

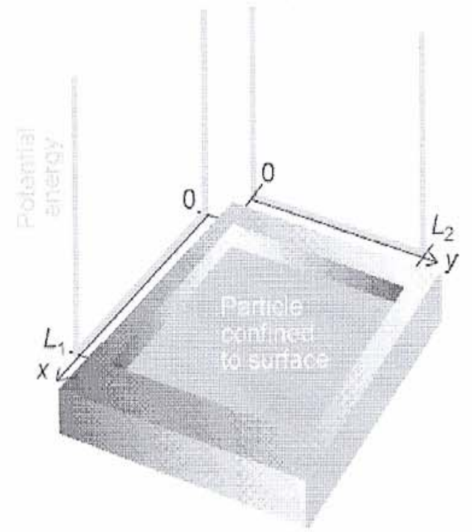
$$\Delta E=\frac{h^2}{8mL^2}(3^2-2^2)=\frac{(6.626\times10^{-34}\,J\cdot s)^2}{8\times(9.11\times10^{-31}\,kg)\times(5.78\times10^{-10}\,m)^2}\times5$$

$$=9.02\times10^{-19}\,J\Rightarrow\tilde{\nu}=\underline{\underline{4.54\times10^{4}\,cm^{-1}}}$$

$$\left(\because 1\,eV=8065.5\,cm^{-1}=1.602\times10^{-19}\,J\right)\qquad(\text{실험치}=4.61\times10^{4}\,cm^{-1})$$

(3) Particle in a box in 2-D

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



partial differential equations →
separation of variables techniques:
divide equation into two or more
ordinary differential equations

$$\psi(x,y)=X(x)\,Y(y)$$

$$\frac{\partial^2\psi}{\partial x^2}=\frac{\partial^2 XY}{\partial x^2}=Y\frac{d^2X}{dx^2}\,,\quad \frac{\partial^2\psi}{\partial y^2}=\frac{\partial^2 XY}{\partial y^2}=X\frac{\partial^2 Y}{\partial y^2}$$

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

divided by XY, $\dfrac{1}{X}\dfrac{d^2X}{dx^2}+\dfrac{1}{Y}\dfrac{d^2Y}{dy^2}=-\dfrac{2mE}{\hbar^2}$

$E = E_X + E_Y$, $\frac{1}{X}\frac{d^2X}{dx^2} = \frac{-2mE_x}{\hbar^2}$, $\frac{1}{Y}\frac{d^2Y}{dy^2} = -\frac{2mE_Y}{\hbar^2}$

$$-\frac{\hbar^2}{2m}\frac{d^2X}{dx^2} = E_X X, \quad -\frac{\hbar^2}{2m}\frac{d^2Y}{dy^2} = E_Y Y, \quad E = E_X + E_Y$$

$$X_{n_1}(x) = \left(\frac{2}{L_1}\right)^{1/2}\sin\left(\frac{n_1\pi x}{L_1}\right)$$

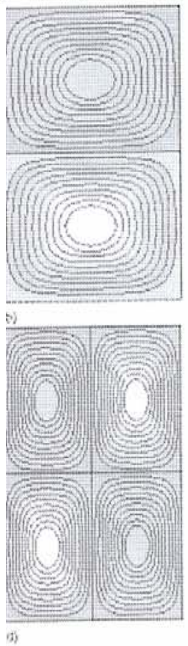
$$Y_{n_2}(y) = \left(\frac{2}{L_2}\right)^{1/2}\sin\left(\frac{n_2\pi y}{L_2}\right)$$

$$\psi = XY, \quad E = E_X + E_Y$$

$$\therefore \psi_{n_1,n_2}(x,y) = \frac{2}{(L_1L_2)^{1/2}}\sin\left(\frac{n_1\pi x}{L_1}\right)\sin\left(\frac{n_2\pi y}{L_2}\right)$$

$$E_{n_1,n_2} = \left(\frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2}\right)\frac{h^2}{8m}, \quad n_1 = 1, 2\cdots \quad n_2 = 1, 2\cdots$$

3-D: same, additional term, n_3 & L_3



The wavefunctions for a particle confined to a rectangular surface depicted as contours of equal amplitude. (a) $n_1 = 1$, $n_2 = 1$, the state of lowest energy, (b) $n_1 = 1$, $n_2 = 2$, (c) $n_1 = 2$, $n_2 = 1$, and (d) $n_1 = 2$, $n_2 = 2$.

- Degeneracy

ket $|n_1\ n_2>$

if $L_1 = L_2 = L$ (square)

$\Psi_{n1,n2}(x, y) = (2/L)\ \mathit{sin}\ (n_1\pi x/L)\ \mathit{sin}\ (n_2\pi y/L)$

$E_{n1,n2} = (n_1^2 + n_2^2)\ (h^2/8mL^2)$

if $n_1 = 1$, $n_2 = 2$ and $n_1 = 2$, $n_2 = 1$

$\Psi_{1,2}(x, y) = (2/L)\ \mathit{sin}\ (\pi x/L)\ \mathit{sin}\ (2\pi y/L)$, $E_{1,2} = 5h^2/8mL^2$

$\Psi_{2,1}(x, y) = (2/L)\ \mathit{sin}\ (2\pi x/L)\ \mathit{sin}\ (\pi y/L)$, $E_{1,2} = 5h^2/8mL^2$

$\Rightarrow$ Different wavefunctions, same energy $\Rightarrow$ "degeneracy"

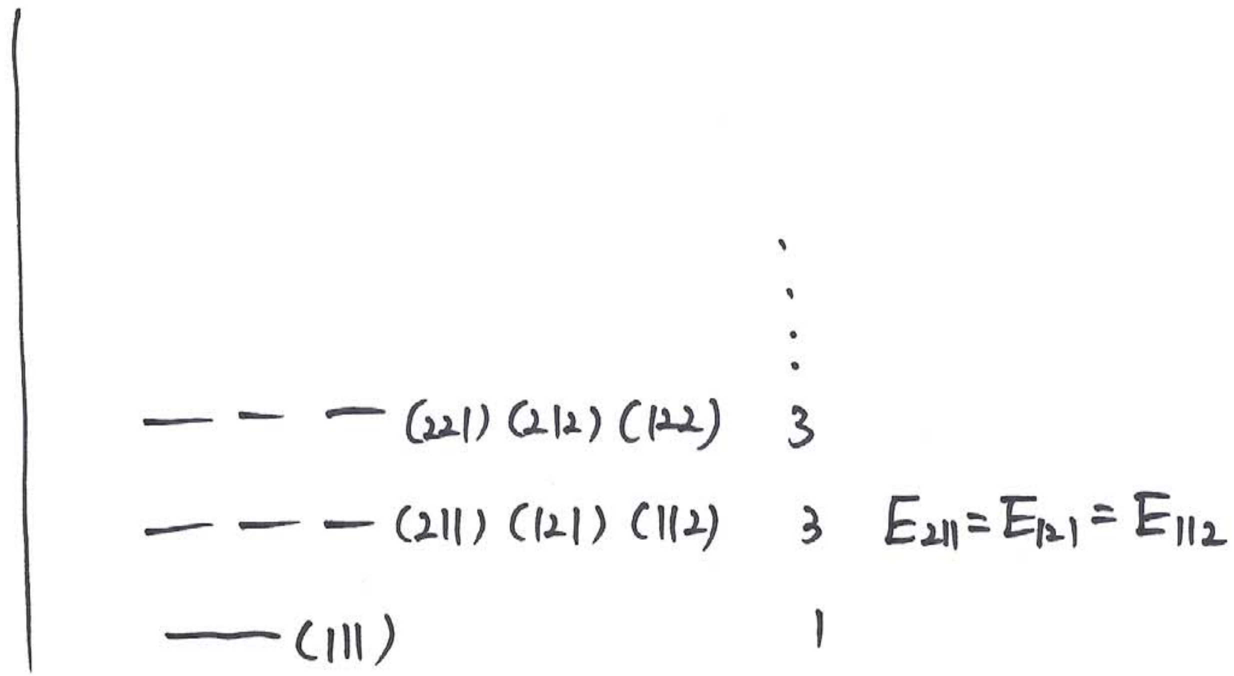
energy level $5h^2/8mL^2$ is doubly degenerate

$|1\ 2>$ and $|2\ 1>$ are degenerate

degeneracy: many examples in atoms, symmetry properties

3-D: same, additional term, n_3 & L_3

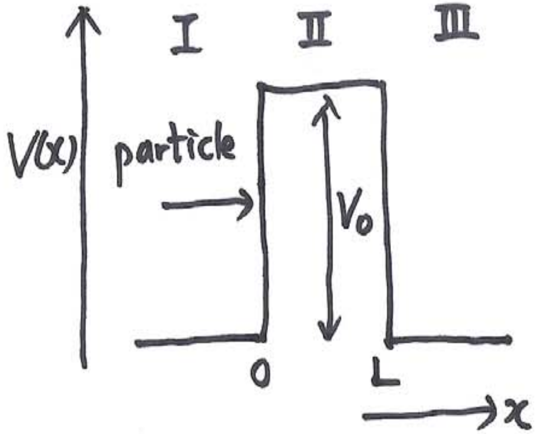
if $L_1 = L_2 = L_3 = L$, $E = \dfrac{h^2}{8mL^2}(n_1^2 + n_2^2 + n_3^2)$, $n_1, n_2, n_3 = 1, 2 \ldots$



(4) Tunnelling

- if the potential energy of a particle does not rise to infinite in the wall & $E < V \rightarrow \Psi$ does not decay abruptly to zero
- if the walls are thin $\rightarrow \Psi$ oscillate inside the box & on the other side of the wall outside the box $\rightarrow$ particle is found on the outside of a container: leakage by penetration through classically forbidden zones "tunnelling"

cf) C.M.: insufficient energy to escape



$$-\frac{\hbar^2}{2m}\psi'' + V\psi = E\psi$$

(I) x < 0, V = 0, $\psi_{I} = Ae^{ikx} + Be^{-ikx}$, $k\hbar = (2mE)^{1/2}$

(II) 0 ≤ x ≤ L , E < L → $E < V \rightarrow V - E > 0$

$$\psi_{II} = Ce^{ik_2x} + De^{-ik_2x} \quad \underset{k_2 = i\kappa}{\Longrightarrow} \quad \psi_{II} = Ce^{-\kappa x} + De^{+\kappa x}$$

$$k_2 = \frac{\sqrt{2m(E-V)}}{\hbar}$$

↑ imaginary!

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

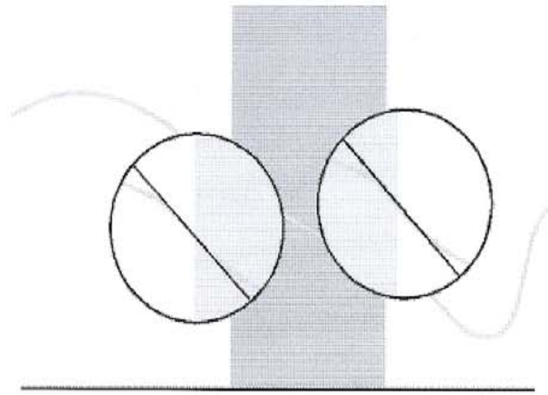
(카파) real

(III) X > 0, V = 0

$$\psi_{III} = \underset{+\text{direction}}{A'e^{ikx}} + \underset{-\text{direction}}{B'e^{-ikx}}, \quad k = \frac{(2mE)^{1/2}}{\hbar}$$

In region III, no reflected wave, B′ = 0

Conditions



at x = 0 and x = L, must be continuous

1. $\Psi_I(0) = \Psi_{II}(0)$, $\Psi_{II}(L) = \Psi_{III}(L)$

slope (1st derivatives) must also be continuous

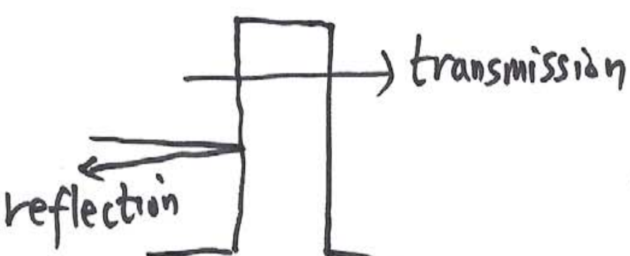
2. $\Psi'_I(0) = \Psi'_{II}(0)$, $\Psi'_{II}(L) = \Psi'_{III}(L)$

1. $A+B=C+D$, $Ce^{-\kappa L}+De^{+\kappa L}=A'e^{ikL}$

2. $ikA-ikB=-\kappa C+\kappa D$, $-\kappa Ce^{\kappa L}+\kappa De^{-\kappa L}=ikA'e^{ikL}$

4 equations, 5 unknown

Transmission probability: probability that the particle passes the barrier



$$T=\frac{|A'|^2}{|A|^2}$$

reflection probability, $R=\frac{|B|^2}{|A^2|}$

$$R+T=1$$

$$\Rightarrow \quad T = \left\{ 1 + \frac{(e^{\kappa L} - e^{-\kappa L})^2}{16\,\varepsilon(1-\varepsilon)} \right\}^{-1}, \quad \varepsilon = \frac{E}{V}$$

(유도)

$$A + B = C + D \quad \cdots\cdots ①$$

$$Ce^{\kappa L} + De^{-\kappa L} = A' e^{ik} \quad \cdots\cdots ②$$

$$ikA - ikB = \kappa C - \kappa D \quad \cdots\cdots ③$$

$$\kappa Ce^{\kappa L} - \kappa De^{-\kappa L} = ikA' e^{ikL} \quad \cdots\cdots ④$$

$① + \frac{1}{ik} \times ③$ $\quad 2A = \left(1 + \frac{\kappa}{ik}\right)C + \left(1 - \frac{\kappa}{ik}\right)D \quad \cdots\cdots ⑤$

$② + \frac{1}{ik} \times ④$ $\quad 2A' e^{ikL} = \left(1 + \frac{\kappa}{ik}\right)Ce^{\kappa L} + \left(1 - \frac{\kappa}{ik}\right)De^{-\kappa L} \quad \cdots\cdots ⑥$

$② - \frac{1}{ik} \times ④$ $\quad \left(1 - \frac{\kappa}{ik}\right)C \cdot e^{\kappa L} + \left(1 + \frac{\kappa}{ik}\right)De^{-\kappa L} = 0 \quad \cdots\cdots ⑦$

$$\longrightarrow \quad D = \frac{-\left(1 - \frac{\kappa}{ik}\right)}{\left(1 + \frac{\kappa}{ik}\right)} \cdot Ce^{2\kappa L} \quad \cdots\cdots ⑧$$

⑧ → ⑤ and ⑥

⑧ → ⑤

$$2A = \left(1+\frac{K}{ik}\right)C - \frac{\left(1-\frac{K}{ik}\right)}{\left(1+\frac{K}{ik}\right)} C e^{2KL}$$

$$= \left[\frac{\left(1+\frac{K}{ik}\right)^2 - \left(1-\frac{K}{ik}\right)^2 e^{2KL}}{\left(1+K/ik\right)}\right] C$$

$$\Rightarrow A = \left[\frac{\left(1-\frac{K^2}{k^2}\right)\left(1-e^{2KL}\right) - \frac{2iK}{k}\left(1+e^{2KL}\right)}{2\left(1+\frac{K}{ik}\right)}\right] C$$

⑧ → ⑥

$$2A' e^{ikL} = \left(1+\frac{K}{ik}\right) C e^{KL} - \frac{\left(1-\frac{K}{ik}\right)}{\left(1+\frac{K}{ik}\right)} C e^{KL}$$

$$= \left[\frac{\left(1+\frac{K}{ik}\right)^2 - \left(1-\frac{K}{ik}\right)^2}{\left(1+\frac{K}{ik}\right)}\right] C e^{KL} = \frac{\frac{4K}{ik} \cdot e^{KL}}{\left(1+\frac{K}{ik}\right)} C$$

$$\Rightarrow A' = \left[\frac{\frac{2K}{ik} e^{KL} \cdot e^{-ikL}}{\left(1+K/ik\right)}\right] C$$

$$T = \frac{|A'|^2}{|A|^2} = \frac{A' \cdot A'^*}{A \cdot A^*}$$

$$A'A'^* = \frac{4K^2}{k^2} e^{2KL} = 4(\varepsilon^{-1} - 1) e^{2KL} \quad \left(\because \frac{K^2}{k^2} = \frac{\frac{2m(V-E)}{\hbar^2}}{\frac{2mE}{\hbar^2}} = \frac{V-E}{E}, \ \varepsilon = \frac{E}{V} \right)$$

$$AA^* = \frac{\left[\left(1 - \frac{K^2}{k^2}\right)\left(1 - e^{2KL}\right) \right]^2 + \frac{4K^2}{k^2}\left(1 + e^{2KL}\right)^2}{4}$$

$$= \frac{\left[(2 - \varepsilon^{-1})(1 - e^{2KL}) \right]^2 + 4(\varepsilon^{-1} - 1)(1 + e^{2KL})^2}{4}$$

$$= \frac{1}{4}\left(-16 e^{2KL} + 16 \varepsilon^{-1} e^{2KL} + \varepsilon^{-2} - 2\varepsilon^{-2} e^{2KL} + \varepsilon^{-2} e^{4KL} \right)$$

$$\therefore T = \frac{A'A'^*}{AA^*} = \frac{16(\varepsilon^{-1} - 1)e^{2KL}}{-16 e^{2KL} + 16\varepsilon^{-1} e^{2KL} + \varepsilon^{-2}(1 - 2e^{2KL} + e^{4KL})}$$

$$= \frac{16(\varepsilon^{-1} - 1)}{16(\varepsilon^{-1} - 1) + \varepsilon^{-2}(e^{-2KL} - 2 + e^{2KL})} = \frac{16(\varepsilon^{-1} - 1)}{16(\varepsilon^{-1} - 1) + \varepsilon^{-2}(e^{KL} - e^{-KL})^2}$$

$$= \frac{1}{1 + \frac{(e^{KL} - e^{-KL})^2}{16\varepsilon(1 - \varepsilon)}} = \left[1 + \frac{(e^{KL} - e^{-KL})^2}{16\varepsilon(1 - \varepsilon)} \right]^{-1} \quad //$$

The transition probabilities for passage through a barrier. The horizontal axis is the energy of the incident particle expressed as a multiple of the barrier height. The curves are labelled with the value of $L(2mV)^{1/2}/$. The graph on the left is for $E<V$ and that on the right for $E>V$. Note that $T = 0$ for $E<V$ whereas classically T would be zero. However, $T<1$ for $E>V$, whereas classically T would be 1.

enhanced reflection (antitunnelling)

- high, wide barrier $\kappa L >> 1$

$\Rightarrow$ T decrease exponentially with thickness of the barrier, with $m^{1/2}$

$\Rightarrow$ low mass particle $\rightarrow$ high tunnelling *tunnelling is important for electron

e.g) proton transfer reaction
STM (scanning tunnelling microscopy)
AFM (atomic force microscopy)

Application to vibrational motion

Schrödinger equations for three basic types of motion: translation, vibration, rotation $\rightarrow$ "quantization"

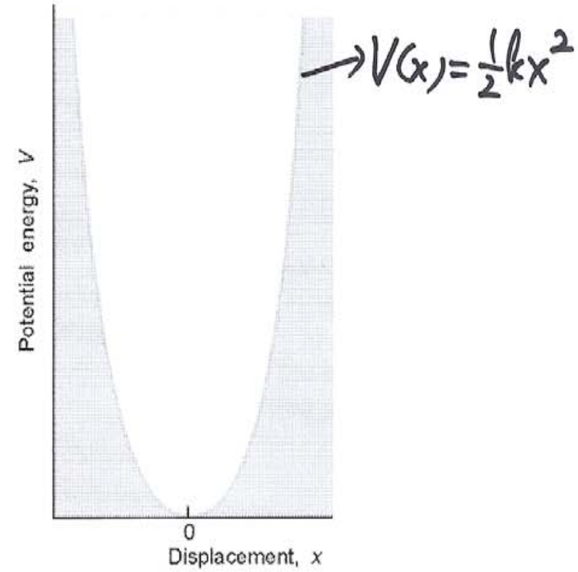
Vibrational motion

Harmonic oscillator

e.g., diatomic molecule: N_2

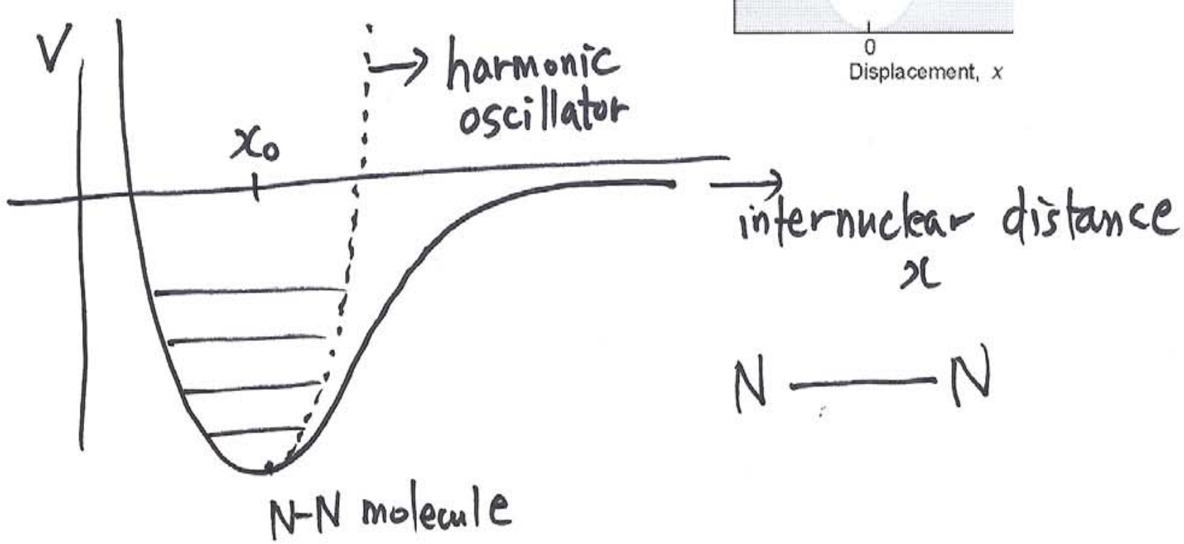
Force, F = -kx, k: force constant

$F = -dV/dx \Rightarrow V = 1/2kx^2$



internuclear potential energy

N_2



Schrödinger equation

$$-(\hbar^2/2m)(d^2\Psi/dx^2) + 1/2kx^2\,\Psi = E\Psi$$

Solution of this equation:

$$\psi'' + \frac{2m}{\hbar^2}\left(E - \frac{1}{2}kx^2\right)\psi = 0, \quad \frac{2mE}{\hbar^2} = \alpha, \quad \frac{mk}{\hbar^2} = \beta^2$$

$$\psi'' + (\alpha - \beta^2 x^2)\psi = 0, \quad \sqrt{\beta}\cdot x = \xi\ (\mathrm{Xi}), \quad dx = \frac{d\xi}{\sqrt{\beta}}, \quad d\xi = \sqrt{\beta}\cdot dx$$

$$\beta\frac{d^2\psi}{d\xi^2} + (\alpha - \beta\xi^2)\psi = 0$$

$$\psi'' + \left(\frac{\alpha}{\beta} - \xi^2\right)\psi = 0$$

For large values, $\xi \to \pm\infty$ (asymptotic region)

$$\psi'' - \xi\psi = 0 \Rightarrow \psi(\xi) \simeq e^{\pm\frac{1}{2}\xi^2}$$

$$\rightarrow \psi' = \pm\xi e^{\pm\frac{1}{2}\xi^2}, \quad \psi'' = \pm\left(e^{\pm\frac{1}{2}\xi^2} \pm \xi^2 e^{\pm\frac{1}{2}\xi^2}\right) = e^{\pm\frac{1}{2}\xi^2}(\xi^2 \pm 1) \simeq \xi^2 e^{\pm\frac{1}{2}\xi^2}$$

+ exponential : not acceptable since $e^{+\bigcirc} \Rightarrow \psi \to \infty$ (X)

— exponential : physically acceptable

For all ξ, $\psi(\xi) = H(\xi) e^{-\frac{1}{2}\xi^2}$

$$\psi'(\xi) = H' e^{-\frac{1}{2}\xi^2} - \xi e^{-\frac{1}{2}\xi^2} \cdot H$$

$$\psi'' = H'' e^{-\frac{1}{2}\xi^2} - \xi e^{-\frac{1}{2}\xi^2} \cdot H' - e^{-\frac{1}{2}\xi^2} \cdot H + \xi^2 e^{-\frac{1}{2}\xi^2} H - \xi e^{-\frac{1}{2}\xi^2} \cdot H'$$

$$= -e^{-\frac{1}{2}\xi^2}\left(H'' - 2\xi H' - H + H\xi^2\right)$$

Put these to Schrödinger equation $\left(\psi'' + \left(\frac{\alpha}{\beta} - \xi^2\right)\psi = 0\right)$

$$\cancel{e^{-\frac{1}{2}\xi^2}}\left(H'' - 2\xi H' - H + \cancel{H\xi^2}\right) + \left(\frac{\alpha}{\beta} - \cancel{\xi^2}\right) H \cancel{e^{-\frac{1}{2}\xi^2}} = 0$$

$$H'' - 2\xi H' + \left(\frac{\alpha}{\beta} - 1\right) H = 0$$, Hermite equation

To solve this equation, expand $H(\xi)$ in a power series in ξ

$$H(\xi) = \sum_{k=1}^{\infty} a_k \cdot \xi^k$$

(i) even state

$$\psi(-\xi) = \psi(\xi)$$

$$H(\xi) = \sum_{k=0}^{\infty} C_k \cdot \xi^{2k} \quad (C_0 \neq 0)$$

put to the Hermite equation

$$\sum_{k=0}^{\infty} \left[2k(2k-1) C_k \xi^{2(k-1)} + \left(\frac{\alpha}{\beta} - 1 - 4k\right) C_k \cdot \xi^{2k} \right] = 0$$

$\psi(k)$ should not be diverged, $\therefore \frac{\alpha}{\beta} = 4N + 1$, $N = 0, 1, 2 \cdots$

(ii) odd state

$$H(\xi) = \sum_{k=0}^{\infty} d_k \xi^{2k+1}, \quad d_0 \neq 0. \quad \frac{\alpha}{\beta} = 4N+3, \; N = 0, 1, 2 \cdots$$

$\Rightarrow N = 1, 3, 5, 7 \cdots$

$$\therefore \frac{\alpha}{\beta} - 1 = 2n, \quad n = 0, 1, 2 \cdots$$

$$\frac{2mE}{\hbar^2} = \alpha, \quad \frac{mk}{\hbar^2} = \beta^2 \Rightarrow E = \frac{\hbar^2}{2m}\alpha = \frac{\hbar^2}{2m}(2n+1)\beta = \frac{\hbar^2}{2m}(2n+1)\frac{\sqrt{mk}}{\hbar}$$

$$= \hbar\sqrt{\frac{k}{m}}\left(n + \frac{1}{2}\right), \quad \omega = \sqrt{\frac{k}{m}} = 2\pi\nu_0$$

$\therefore E = (h/2\pi)(2\pi\nu_0)(v + ½) = h\nu_0(n + ½) = \hbar\omega\ (v + ½)$, $v = 0,1,2\ldots.$

$\Delta E = E_{v+1} - E_v = \hbar\omega$ (same ΔE)

if $m\uparrow \Rightarrow \omega \rightarrow 0 \Rightarrow \Delta E \rightarrow 0$: classical mechanics

- zero point energy

$$E_0 = \frac{1}{2}\hbar\omega$$

$\Rightarrow$ ~ 3×10^{-20} J, 0.2 eV, 15 kJ/mol

$\Rightarrow$ uncertainty of position, momentum $\rightarrow$ kinetic energy

c.f. C.M.: particle can be perfectly still

- particle in a box *vs.* harmonic oscillator

Wavefunction for harmonic oscillator

$\Psi(x) = N \text{ x (polynomial in x) x (Gaussian function)}$
$\Psi_v(x) = N_v H_v(y) e^{-y^2/2}$, $y = x/\alpha$, $\alpha = (\hbar^2/mk)^{1/4}$

N_v: normalization constant
$H_v(y)$: Hermite polynomial
Gaussian function: $e^{-y^2/2}$

Hermite polynomials, $H_v(y)$

v	$H_v(y)$
0	1
1	$2y$
2	$4y^2-2$
3	$8y^3-12y$
…..	

$\therefore v = 0$ (wavefunction for ground state)

$\Rightarrow \Psi_0(x) = N_0 H_0(y) e^{-y2/2} = N_0 e^{-x2/2\alpha 2}$

$\Psi_0^{\,2}(x) = N_0^{\,2} e^{-x2/\alpha 2}$

largest at zero displacement ($x = 0$)

- $v = 1$ (1^{st} excited state)

$\Rightarrow \Psi_1(x) = N_1 2y\, e^{-y2/2} = (2N_1/\alpha)xe^{-x2/2\alpha2}$

node at $x = 0$

maximum probability at $x = \pm\alpha$ ($y = \pm 1$)

Ψ Ψ^2

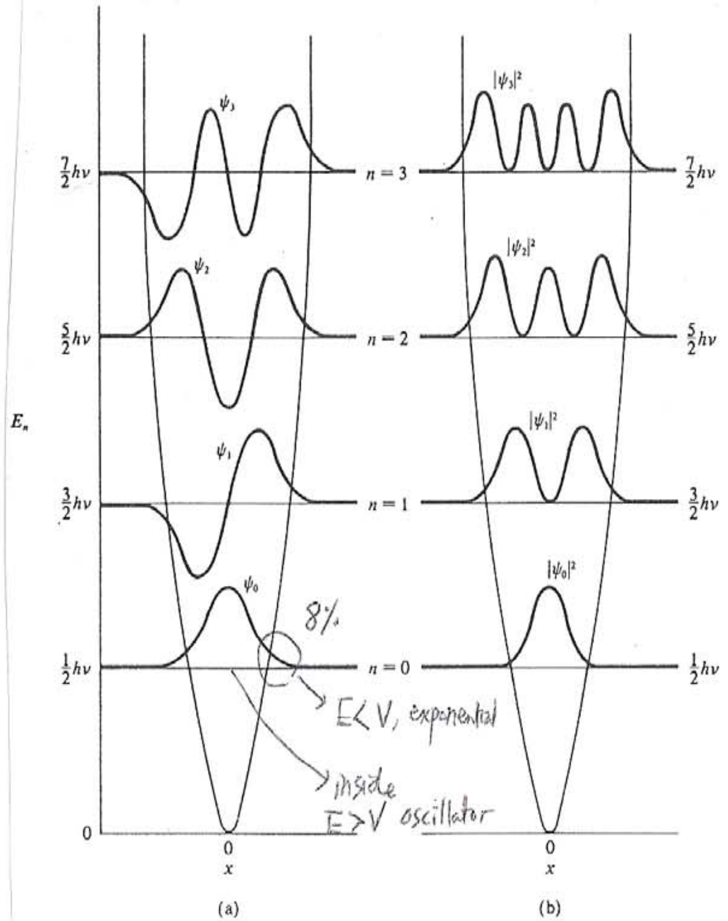
⋮

odd

even

odd → anti-sym

even → symmetric



$$N_v = \frac{1}{(\alpha \pi^{1/2} 2^v v!)^{1/2}}$$ (example)

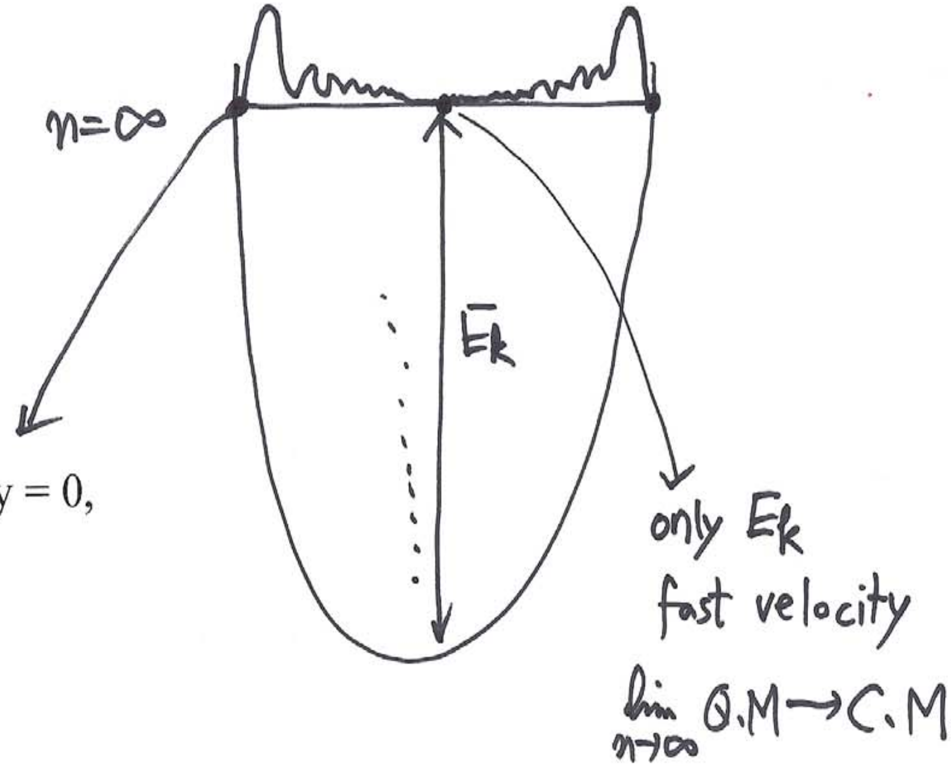
$f(x) = f(-x)$: even
$f(x) = -f(-x)$: odd

- oscillator may be found at extensions with V>E that are forbidden by classical mechanics (negative kinetic energy)

$\Rightarrow$ Lowest energy: 8% in classical forbidden region
"tunnel effect" : independent of k, m

$\Rightarrow$v (quantum number) $\uparrow \Rightarrow$ probability $\downarrow$
$v \to \infty \Rightarrow$ probability $\to 0$

- V = ∞



E_k = 0 at turning point, velocity = 0,
probability: highest

largest amplitudes near the turning points of the classical motion
(at V = E, kinetic energy = 0)

- expectation values

$$\langle \Omega \rangle = \int_{-\infty}^{\infty} \psi_v^* \hat{\Omega} \psi_v \, dx = \langle v' | \hat{\Omega} | v \rangle$$

Dirac bracket notation

mean displacement

$$\langle x \rangle = 0 \quad , \quad \langle x^2 \rangle = \left(v + \frac{1}{2}\right) \frac{\hbar}{(mk)^{1/2}}$$

(e.g.)

$$\langle V \rangle = \langle \tfrac{1}{2} k x^2 \rangle = \tfrac{1}{2} k \langle x^2 \rangle = \tfrac{1}{2} \left(v + \tfrac{1}{2}\right) \hbar\omega = \tfrac{1}{2} E_v$$

$\langle E_K \rangle = \frac{1}{2} E_v$ mean potential E = mean kinetic E

-

$$\omega = \sqrt{\frac{k}{m}} \Rightarrow E = \hbar\omega_0 \left(v + \frac{1}{2}\right)$$

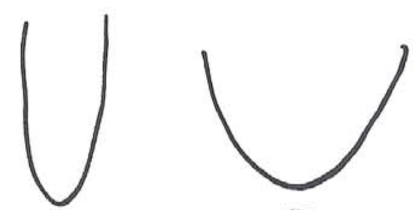
$k \uparrow$ $\omega \uparrow$ $E \uparrow$

$$\Delta E = h\nu_0 = h\sqrt{\frac{k}{m}}$$

N≡N

H–H

I–I



H_2

I_2

$k \downarrow$ potential $E \downarrow$

예: The potential energy curve for H_2 is close to a harmonic oscillator. The first vibrational transition is at 4000 cm^{-1}.

(a) Calculate the force constant *k* of the hydrogen molecule.

(b) Calculate the vibrational transition energy for D_2 (in cm^{-1}) assume same force constant with H_2.

(c) Calculate the zero point energy of this H_2.

Application to rotational motion

Schrödinger equations for three basic types of motion: translation, vibration, **rotation** $\rightarrow$ "quantization"

3. **Rotational motion**

(1) Rotation in 2-D

(2) Rotation in 3-D

(3) Spin

(1) Rotation in 2-D (a particle on a ring)

Mass m, radius r (in xy plane)

Total energy = kinetic energy (V=0)

$E = p^2/2m$

Angular momentum L_z (or J_z, z-direction)
(perpendicular to xy plane)

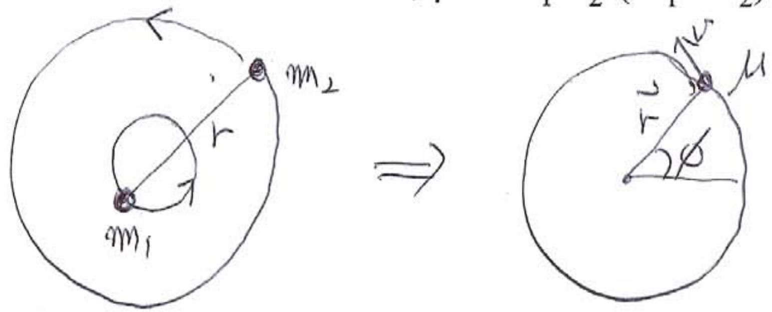
$L_z = J_z = \pm pr$

$\Rightarrow$ $E = J_z^2/2mr^2 = J_z^2/2I$ ($I = mr^2$, moment of inertia)

Q.M. angular momentum, rotational energy $\Rightarrow$ "quantized"

$|r|$: fixed $\Rightarrow$ "rigid rotor"

Diatomic: reduced mass, $\mu = m_1m_2/(m_1+m_2)$



Schrödinger equation

$$-(\hbar^2/2m)(\partial^2/\partial x^2 + \partial^2/\partial y^2)\Psi(x,y) + V(x,y)\Psi(x,y) = E\Psi(x,y)$$

$$H\psi = E\psi$$

$x,y \rightarrow r, \phi$ change of variables

$\partial f/\partial x = (\partial r/\partial x)\partial f/\partial r + (\partial\phi/\partial x)\partial f/\partial\phi$

$f(x,y) \rightarrow f(r,\phi)$

✓$\partial/\partial x = (\partial r/\partial x)\partial/\partial r + (\partial\phi/\partial x)\partial/\partial\phi$

$r = \sqrt{}(x^2 + y^2)$, $\phi = \tan^{-1}(y/x)$, $x = r\cos\phi$, $y = r\sin\phi$

$\partial r/\partial x = ½(x^2 + y^2)^{-1/2}\cdot 2x = 2x/2\sqrt{}(x^2 + y^2) = x/r = \cos\phi$

$\partial\phi/\partial x = (-y/x^2)/[1 + (y/x)^2] = -y/(x^2 + y^2) = -r\sin\phi/r^2 = -\sin\phi/r$

✓$\partial/\partial y = (\partial r/\partial y)\partial/\partial r + (\partial\phi/\partial y)\partial/\partial\phi$

$\partial r/\partial y = 2y/2\sqrt{}(x^2 + y^2) = r\sin\phi/r = \sin\phi$

$\partial\phi/\partial y = (1/x)/[1 + (y/x)^2] = x/(x^2 + y^2) = r\cos\phi/r^2 = \cos\phi/r$

✓ $\partial^2/\partial x^2 = (\partial/\partial x)(\partial/\partial x) = [\cos\phi(\partial/\partial r) - (-\sin\phi/r)(\partial/\partial\phi)]^2$, r is fixed $\rightarrow \partial/\partial r = 0$

$= (1/r^2)\sin\phi\, [(\partial/\partial\phi)\sin\phi(\partial/\partial\phi)] = (\sin\phi/r^2)[\cos\phi(\partial/\partial\phi) + \sin\phi(\partial^2/\partial\phi^2)]$

✓ $\partial^2/\partial y^2 = [(\cos\phi/r)(\partial/\partial\phi)]^2 = (\cos\phi/r^2)(\partial/\partial\phi)[\cos\phi(\partial/\partial\phi)]$

$= (\cos\phi/r^2)[-\sin\phi(\partial/\partial\phi) + \cos\phi(\partial^2/\partial\phi^2)]$

$\therefore (\partial^2/\partial x^2 + \partial^2/\partial y^2) = (1/r^2)(\partial^2/\partial\phi^2)$, $V(x,y) = 0$ (no external force)

$\Rightarrow$ $-(\hbar^2/2m)(\partial^2/\partial x^2 + \partial^2/\partial y^2)\Psi(x,y) + V(x,y)\Psi(x,y) = E\Psi(x,y)$

$\Rightarrow$ $-(\hbar^2/2m)(1/r^2)(d^2/d\phi^2)\Psi(\phi) = E\Psi(\phi)$

$mr^2 = I$ (moment of inertia), $\Psi''(\phi) + (2IE/\hbar^2)\Psi(\phi) = 0$

let $2IE/\hbar^2 = m_l^2$

$\Psi(\phi) = A\exp(im_l\phi)$, $m_l = \pm\sqrt{(2IE)}/\hbar$

Normalization,

$\therefore\ \Psi(\phi) = \exp(im_l\phi)/\sqrt{(2\pi)}$

Cyclic boundary condition: Ψ should be single-valued

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

$\Psi(\phi + 2\pi) = \exp[im_l(\phi + 2\pi)]/\sqrt{(2\pi)}$

$= [\exp(im_l\phi)\exp(im_l 2\pi)]/\sqrt{(2\pi)}$

$= \exp(im_l\phi)/\sqrt{(2\pi)} = \Psi(\phi)$

$\therefore \exp(im_l 2\pi) = 1 \Rightarrow m_l = 0, \pm1, \pm2, \pm3, \ldots.$

$(\cos(m_l 2\pi) + i\sin(m_l 2\pi) = 1)$

$2IE/\hbar^2 = m_l^2 \Rightarrow$ $\mathbf{E_{m\mathit{l}} = (m_{\mathit{l}}\hbar)^2/2I}$, $m_l = 0, \pm1, \pm2, \pm3, \ldots.$

cf. Classical Mechanics

$E = p^2/2m = (L/r)^2/2m = L^2/2I$, $L = rp$

$J_z = \mathbf{L = m_{\mathit{l}}\hbar}$, $m_l = 0, \pm1, \pm2, \pm3, \ldots.$

- de Broglie relation

$$\lambda = h/p = h/(J_z/r) = h/(m_l\hbar/r) = h/(m_l h/2\pi r) = 2\pi r/m_l$$

$$m_l\lambda = 2\pi r$$

- angular momentum (J_z) is quantized: $m_l\hbar$

- Energy is quantized, $E_{ml} = (m_l\hbar)^2/2I$, $m_l = 0, \pm1, \pm2, \pm3, \ldots.$

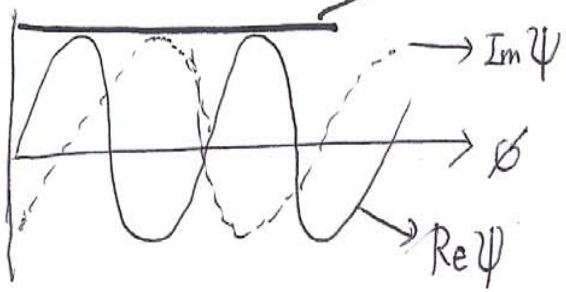
$|m_l|$: doubly degenerate except $m_l = 0$

- Wavefunction,

$$\Psi_{ml}(\phi) = \exp(im_l\phi)/\sqrt{(2\pi)}$$
$$= 1/\sqrt{(2\pi)}[\cos(m_l\phi) + i\sin(m_l\phi)]$$

real part of Ψ

-Probability, $\Psi_{ml}{}^{*}\,\Psi_{ml} = 1/(2\pi)$



$|\psi|^2$: independent of ϕ

Equal probability of finding the particle anywhere on the ring
⇒Uncertainty principle: angle & angular momentum → inability to specify them

cf. orbital angular momentum

	C.M	Q.M operator
orbital angular momentum l_z	$l_z = xp_y - yp_x$	$\hat{l}_z = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$ $\left(\because \hat{p}_x = \frac{\hbar}{i}\frac{\partial}{\partial x}\right)$

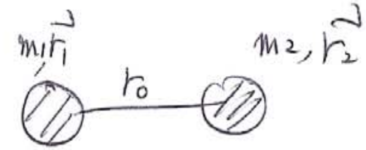
r, ϕ $\hat{l}_z = \frac{\hbar}{i}\frac{\partial}{\partial \phi}$

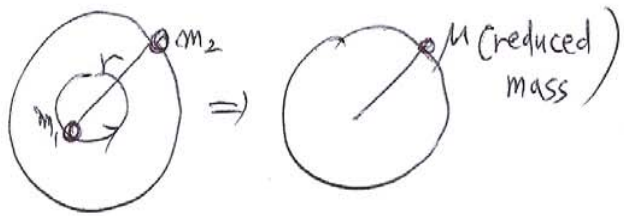
$$\Rightarrow \hat{l}_z \psi_{m_l} = \frac{\hbar}{i}\frac{\partial \psi_{m_l}}{d\phi} = i m_l \frac{\hbar}{i} e^{i m_l \phi} = m_l \hbar \psi_{m_l}$$

(2) Rotation in 3-D (a particle on a sphere)

Electrons in atoms, rotating molecules: free to move anywhere on the surface of a sphere of radius r

e.g., diatomic molecule (rotating molecules)





Schrödinger equation

$$H\Psi = E\Psi$$

$$H = -(\hbar^2/2m)(\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2) + V(x,y,z)$$
$$= -(\hbar^2/2m)\nabla^2 + V$$

In polar coordinates (r: fixed)

$\nabla^2 = \partial^2/\partial r^2 + (2/r)\partial/\partial r + (1/r^2)\Lambda^2$ Λ^2 : legendrian

$\Lambda^2 = (1/\sin^2\theta)(\partial^2/\partial\phi^2) + (1/\sin\theta)(\partial/\partial\theta)\sin\theta(\partial/\partial\theta)$

R is const $\Rightarrow \partial/\partial r = 0$, $\partial^2/\partial r^2 = 0$

Free to move $\Rightarrow V = 0$

$\nabla^2 = (1/r^2)[(\partial^2/\partial\theta^2) + (\cos\theta/\sin\theta)(\partial/\partial\theta) + (1/\sin^2\theta)(\partial^2/\partial\phi^2)]$

$-(\hbar^2/2m)\nabla^2\Psi = E\Psi$

$-(\hbar^2/2m\, r^2)[(\partial^2/\partial\theta^2) + (\cos\theta/\sin\theta)(\partial/\partial\theta) + (1/\sin^2\theta)(\partial^2/\partial\phi^2)]\Psi(\theta, \phi) = E\Psi(\theta, \phi)$

$\Psi(\theta, \phi) = \Theta(\theta)\,\Phi(\phi)$: separation of variables

$\Phi(\partial^2/\partial\theta^2)\Theta + (\cos\theta/\sin\theta)\Phi(\partial/\partial\theta)\Theta + (\Theta/\sin^2\theta)(\partial^2/\partial\phi^2)\Phi = -(2IE/\hbar^2)\Theta\Phi$

$(1/\Theta)(\partial^2/\partial\theta^2)\Theta + (1/\Theta)(\cos\theta/\sin\theta)(\partial/\partial\theta)\Theta + (1/\Phi)(1/\sin^2\theta)(\partial^2/\partial\phi^2)\Phi = -(2IE/\hbar^2)$

Put $(1/\Phi)(\partial^2/\partial\phi^2)\Phi = -m_l^2$, m_l: separation constant

$\Rightarrow$ (i) $d^2/d\phi^2)\Phi + m_l^2\Phi = 0$

(ii) $(d^2/d\theta^2)\Theta + (\cos\theta/\sin\theta)(d/d\theta)\Theta + [(2IE/\hbar^2) - (m_l^2/\sin^2\theta)]\Theta = 0$

$\Rightarrow$ (i) $\Phi = \exp(im_l\phi)/\sqrt{(2\pi)}$, $m_l = 0, \pm1, \pm2, \pm3, \ldots.$

(ii) $s = \cos\theta$, $\beta = 2IE/\hbar^2$

$G(s) = \Theta(\cos\theta)$, $d\Theta/d\theta = -\sin\theta(dG/ds)$,

$d^2\Theta/d\theta^2 = \sin^2\theta(d^2G/ds^2) - \cos\theta(dG/ds)$,

$\therefore\ (1-s^2)(d^2G/ds^2) - 2s(dG/ds) + [\beta - (m_l^2/1-s^2)] = 0$

$$G_l^{|m_l|}(s) = \frac{1}{2^l \cdot l!}(1-s^2)^{|m_l/2|} \cdot \frac{d^{l+|m_l|}}{ds^{l+|m_l|}}(1-s^2)^l$$

$$\Theta_{l,m_l}(\theta) = \left[\frac{(2l+1)(l-|m_l|)!}{2(l+|m_l|)!}\right]^{1/2} \cdot P_l^{|m_l|}(\cos\theta)$$

$\Downarrow$

associated Legendre functions

$\beta = 2IE/\hbar^2$

$\beta = l(l+1)$, $l = 0,1,2,3\ldots$ (quantum number)

$-l \leq m_l \leq l$, $m_l = -l, -l+1, \ldots 0, 1, 2, \ldots l$

$$\Psi(\theta, \phi) = \Theta(\theta)\,\Phi(\phi) = \left[\frac{(2l+1)(l-|m_l|)!}{2(l+|m_l|)!}\right]^{1/2} \cdot P_l^{|m_l|}(\cos\theta) \cdot \frac{1}{\sqrt{2\pi}} \cdot e^{im_l\phi}$$

Normalized wavefunction, $Y_{l,m_l}(\theta, \phi) = \Theta_{l,m_l}(\theta)\,\Phi_{l,m_l}(\phi)$ (spherical harmonics) e.g., Table 9.3 (구판 12.3)

Table 9.3 The spherical harmonics

l	m_l	$Y_{l,m_l}(\theta,\varphi)$
0	0	$\left(\frac{1}{4\pi}\right)^{1/2}$
1	0	$\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$
	±1	$\mp\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta\, e^{\pm i\phi}$
2	0	$\left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta-1)$
	±1	$\mp\left(\frac{15}{8\pi}\right)^{1/2}\cos\theta\sin\theta\, e^{\pm i\phi}$
	±2	$\left(\frac{15}{32\pi}\right)^{1/2}\sin^2\theta\, e^{\pm 2i\phi}$
3	0	$\left(\frac{7}{16\pi}\right)^{1/2}(5\cos^3\theta-3\cos\theta)$
	±1	$\mp\left(\frac{21}{64\pi}\right)^{1/2}(5\cos^2\theta-1)\sin\theta\, e^{\pm i\phi}$
	±2	$\left(\frac{105}{32\pi}\right)^{1/2}\sin^2\theta\cos\theta\, e^{\pm 2i\phi}$
	±3	$\mp\left(\frac{35}{64\pi}\right)^{1/2}\sin^3\theta\, e^{\pm 3i\phi}$

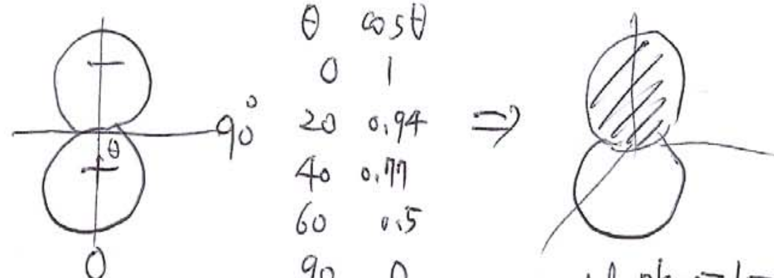
- wavefunction

Y_{l,m_l}

$l=0$	$m_l=0$	Y_{l,m_l} $\left(\frac{1}{4\pi}\right)^{1/2}$
$l=0$	$m_l=0$	$\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$
$l=2$	$m_l=0$	$\left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta-1)$
$l=1$	$m_l=1$	$-\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta\cdot e^{+i\phi}$

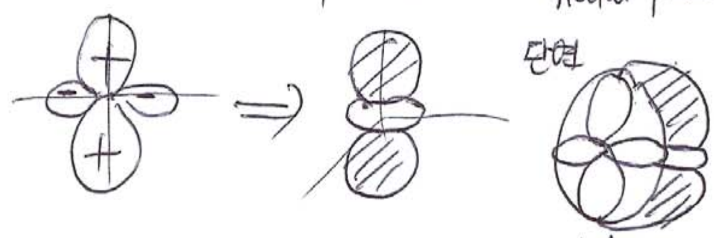
$e^{+i\phi} \Downarrow \cos\phi + i\sin\phi \Downarrow$ real

nodal plane = 0 = l



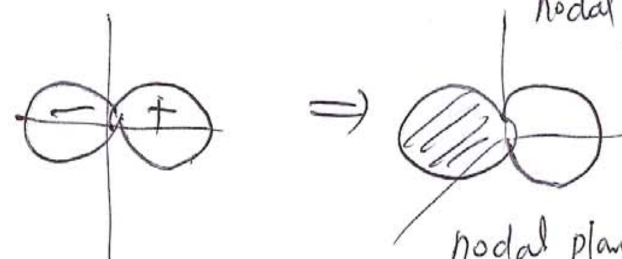
θ	$\cos\theta$
0	1
20	0.94
40	0.77
60	0.5
90	0

nodal plane = 1 = l



단면

nodal plane = 2 = l

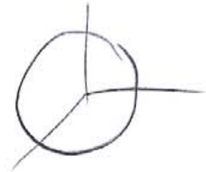


nodal plane = 1 = l

$Y_{l,ml}(\theta, \phi)$

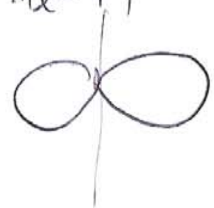
- Probability, $Y_{l,ml}{}^2(\theta, \phi)$

$l=0$ $m_l=0$

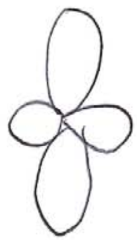


$l=1$ $m_l=0$

$m_l=+1$

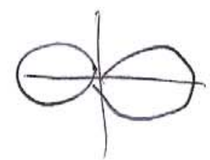


$l=2$ $m_l=0$

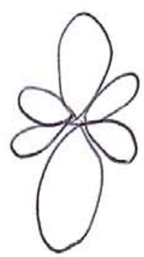


$m_l=+1$

$m_l=+2$



$l=3$ $m_l=0$



- $E = l(l+1)(\hbar^2/2I)$, $l = 0,1,2,3\ldots$
  energy is quantized, independent of m_l
  same energy $\Rightarrow$ $(2l+1)$ different wavefunctions
  $\Rightarrow$ quantum number l is $(2l+1)$-fold degenerate

- angular momentum (L, L_z)

  classical mechanics: angular momentum L, $E = L^2/2I$ (L = J in the textbook)

  $\Rightarrow$ magnitude of angular momentum (L) $= [l(l+1)]^{1/2}\hbar$, $l = 0,1,2,3\ldots$
  z-component of angular momentum (L_z) $= m_l\hbar$, $m_l = -l, -l+1, \ldots 0,1,2,\ldots l$

  c.f.) $\hat{L}_z = \frac{\hbar}{i}\frac{\partial}{\partial\phi}$, $\hat{L}_z\psi(\theta,\phi) = \frac{\hbar}{i}\frac{\partial}{\partial\phi}\Theta(\theta)\Phi(\phi)$

$$= \Theta(\theta)\cdot m_l\hbar\,\Phi(\phi) \qquad \left(\because \Phi = \frac{1}{\sqrt{2\pi}}e^{im_l\phi}\right)$$

$$= \underline{\underline{m_l\hbar}}\cdot\Theta(\theta)\Phi(\phi)$$

- space quantization

$L = [l(l + 1)]^{1/2}\hbar$, $l = 0,1,2,3\ldots$

$L_z = m_l\hbar$, $m_l = -l, -l+1,\ldots 0,1,2,\ldots l$

Q. M.: a rotating body may not take up
an arbitrary orientation

1921. Stern & Gerlach

$\Rightarrow$ Angular momentum is quantized

- Uncertainty principle

if L_z is known, impossible to know the other two components (L_x, L_y)

z component 와 x, y component가 동시에 정확히 define 안된다

$\hat{A}, \hat{B}$, $[\hat{A},\hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$ if $=0$, A, B → commute

if $\neq 0$, do not commute ⇒ uncertainty principle

e.g.) $\hat{A} = \hat{L}^2$, $\hat{B} = \hat{L}_z$

$\hat{L}^2 \hat{L}_z Y_{l,m_l} = \hat{L}^2 (m_l \hbar Y_{l,m_l}) = l(l+1)\hbar^2 m_l \hbar Y_{l,m_l}$

$\hat{L}_z \hat{L}^2 Y_{l,m_l} = \hat{L}_z \{ l(l+1)\hbar^2 Y_{l,m_l} \} = m_l \hbar\, l(l+1)\hbar^2 Y_{l,m_l}$

⇒ $[\hat{L}_z, \hat{L}^2] = 0$ allow simultaneous, exact specification possible

e.g.) $\hat{x}, \hat{p}_x$, $[\hat{x}, \hat{p}_x] = (\hat{x}\hat{p}_x - \hat{p}_x \hat{x}] = x\frac{\hbar}{i}\frac{\partial}{\partial x} - \frac{\hbar}{i}\frac{\partial}{\partial x} x = -\frac{\hbar}{i} \neq 0$ do not commute ⇒ forbid!

e.g.) $\hat{x}, \hat{p}_y$, $[\hat{x}, \hat{p}_y] = \frac{\hbar}{i}[x\frac{\partial}{\partial y} - x\frac{\partial}{\partial y}) = 0$, allowed

Y_{l,m_l}

$$\left.\begin{aligned} [\hat{L}_x, \hat{L}_y] &= i\hbar \hat{L}_z \\ [\hat{L}_y, \hat{L}_z] &= i\hbar \hat{L}_x \\ [\hat{L}_z, \hat{L}_x] &= i\hbar \hat{L}_y \end{aligned}\right\} \Rightarrow$$

forbid simultaneous, exact specification (uncertainty principle)

⇓

if L_z is known → impossible of specifying L_x, L_y

$[\hat{L}^2, \hat{L}_z] = 0$, $[\hat{L}^2, \hat{L}_x] = 0$, $[\hat{L}^2, \hat{L}_y] = 0$

(3) Spin

- Stern-Gelach observed 2 bands of Ag atoms:
  angular momentum $l \rightarrow 2l + 1$ orientations
  $\Rightarrow$ to get 2 orientations $\rightarrow$ $l = ½$??, l must be integer

$\Rightarrow$suggestion: not due to orbital angular momentum (motion of electron around atomic nucleus), but motion of electron about its own axis **"spin"**

Ag: [Kr]$4d^{10}\underline{5s^1}$
Magnitude of spin angular momentum = $[s(s + 1)]^{1/2}\hbar$, s = 0,1,2,3…
z-axis: $m_s\hbar$, $m_s = s$, s-1,….,-s

Electron: only one value of s is allowed, s = ½
angular momentum $1/2\sqrt{3}\hbar = 1/2\sqrt{3}\hbar$

$\Rightarrow$ Intrinsic property of the electron

$2s + 1$ = different orientations

$m_s = +1/2$, $\alpha \uparrow$
$m_s = -1/2$, $\beta \downarrow$

- proton, neutron ($s = ½$) $\Rightarrow$ angular momentum, $(3/4)^{1/2}\hbar$: ½ spin "fermions" (constitute matter)
- mesons, photon, $s = 1 \Rightarrow$ angular momentum, $(2)^{1/2}\hbar$: integer spin (including 0) "boson" (responsible for the forces that bind fermions together)

c.f. l(angular momentum quantum number), m_l(orbital magnetic q. #), s(spin angular q. #), m_s(spin magnetic q. #)