~~Timely~~ ~~Solutions~~ Copy

AFRESH001 PHY 401

e.g. $R|j\rangle = r|j\rangle$

$S|j\rangle = s|j\rangle$

$R|\psi_j\rangle = r|\psi_j\rangle$

$S|\psi_j\rangle = s|\psi_j\rangle$

$R|\psi_j\rangle = r_j|\psi_j\rangle$

$S_j|\psi_j\rangle = s_j|\psi_j\rangle$

Theorem IV (necessary): shows that two observables are compatible i.e. they commute.

Proof

Let's consider two operators R and S with their corresponding eigen values r & s having the same eigen function ψ_j

$SR|j\rangle = s_j|j\rangle = r_j s_j|j\rangle$

$RS|j\rangle = R s_j|j\rangle = s_j R|j\rangle = r_j s_j|j\rangle$

Since

$r_j s_j = s_j r_j$

$SR|j\rangle = RS|j\rangle$

i.e. $[S, R]|j\rangle = (SR - RS)|j\rangle$

but $|j\rangle \neq 0$

then $[S, R] = 0$

$(SR - RS) = 0$ ✓

$SR = RS$ proved

Hence since S and R commute then they are compatible.

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Theorem V : (Sufficient) 9/10/24

If R and S commute and either R or S has "non degenerate" eigen values, then the eigen function of the operator S are the eigen function of the operator R and vice versa.

Proof

Let the operators R and S commute and let their eigen function be ψ with their corresponding eigen values r and s

$$R\psi = r\psi \quad \text{---} (1)$$

$$S\psi = s\psi \quad \text{---} (2)$$

operating S on (2) and R on (2) we have

vice-versa proof

$$SR\psi = sr\psi \quad \text{---} (3)$$

$$RS\psi = rs\psi \quad \text{---} (4)$$

subtracting eqn (3) from (4)

$$(RS - SR)\psi = (rs - sr)\psi \quad \text{---} (5)$$

$R \neq S$

$(RS - SR)\psi \neq 0$

since $\psi \neq 0$

$$\therefore rs - sr = 0 \quad \text{---} (6)$$

$$\Rightarrow (RS - SR)\psi = 0$$

$$[R, S] = 0$$

Proofed

Afreshool copy — Linear combination ... using the inner product definition ... Samuel

Theorem III: If the operators A and B are Hermitian, then $AB + BA$ is also Hermitian

Proof

(ii) An operator is said to be Hermitian if the operator is equal to its complex conjugate
i.e. $A = A^* = A^+$
equal to it's transpose conjugate

i.e. $A = A^* = A^+$

$B = B^* = B^+$

$AB = B^* A^*$

$BA = A^* B^*$

$\langle m | AB + BA | n \rangle = \langle m | AB | n \rangle + \langle m | BA | n \rangle$

$= \langle B^* m | A | n \rangle + \langle A^* m | B | n \rangle$

(iii) $= \langle B^* A^* m | n \rangle + \langle A^* B^* m | n \rangle$

$\langle m | AB + BA | n \rangle = \langle (B^* A^* + A^* B^*) m | n \rangle$

$\langle m | AB + BA | n \rangle = \langle (AB + BA) m | n \rangle$

Since operator addition is commutative hence $AB + BA$ are Hermitian

Proved

NOTE NOTE NOTE

Kronecker delta function

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Theorem VII: If the operators A and B are Hermitian then $i(AB - BA)$ is also Hermitian.

Proof

$i(AB - BA) = iAB - iBA$

but $AB = B^* A^*$

$BA = A^* B^*$

$iAB = (iAB)^* = -iB^* A^*$

$iBA = (iBA)^* = -iA^* B^*$

$\langle m | i(AB - BA) | n \rangle = \langle m | iAB | n \rangle - \langle m | iBA | n \rangle$

$= \langle (-iB^* A^*) m | n \rangle -$

$\langle (-iA^* B^*) m | n \rangle$

$\langle m | i(AB - BA) | n \rangle = \langle -iB^* A^* m | n \rangle + \langle iA^* B^* m | n \rangle$

$= \langle i(A^* B^* - B^* A^*) m | n \rangle$

$= \langle i(BA - AB) m | n \rangle$

Proved.

since operator subtraction is commutative.

Theorem VIII: If A and B are Hermitian operators then show that $(A + iB)^\dagger$ is Hermitian equal to $(A - iB)$

Proof

$(A + iB)^\dagger = (A - iB)$

$(A + iB)^\dagger = A^\dagger + (iB)^\dagger$

Since A & B are Hermitian

$A^\dagger = A$

$B = B^\dagger$

$(iB)^\dagger = -iB^\dagger$

operator subtraction is commutative

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$$\langle m|(A+iB)^{+}|n\rangle = \langle m|A|n\rangle + \langle m|iB|n\rangle$$

$$= \langle A^{+} m|n\rangle + \langle -iB^{+} m|n\rangle$$

$$= \langle (A^{+} - iB^{+}) m|n\rangle$$

$$= \langle (A - iB)^{+} m|n\rangle$$

Proved

Q. No (3a)

Theorem $\boxed{X}$: If A and B are Hermitian operators show that

$$(\Delta B)^2 \cdot (\Delta A)^2 \geq \frac{(C)^2}{4}$$

Proof

According to Heisenberg uncertainty principle

$$\Delta x \cdot \Delta P_x \geq \hbar/2 \quad \text{---- (a)}$$

$$\Delta y \cdot \Delta P_y \geq \hbar/2 \quad \text{---- (b)}$$

$$\Delta z \cdot \Delta P_z = \hbar/2 \quad \text{---- (c)}$$

$$\Delta E \cdot \Delta t = \hbar \quad \text{---- (d)}$$

from (a)

$$\Delta x \cdot \Delta P_x \geq \frac{\hbar}{2}$$

Squaring both sides of (a) yields

$$(\Delta x)^2 \cdot (\Delta P_x)^2 = \frac{\hbar^2}{4} \quad \text{---- (i)}$$

from (i) let $\Delta x = A$

$\Delta P_x = B$

putting A & B for Δx & ΔP_x in eqn (i) respectively

$$(\Delta A)^2 \cdot (\Delta B)^2 \geq \frac{\hbar^2}{4} \quad \text{---- (2)}$$

or

$$(\Delta B)^2 \cdot (\Delta A)^2 \geq \frac{\hbar^2}{4} \quad \text{---- (4)}$$

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let $iC = [A,B]\psi$

$$= (AB - BA)\psi \quad \text{——} (4)$$

but

$$x = A \ \& \ p_x = B$$

then $iC = (xp_x - p_x x)\psi$ —— (5)

Now the operators of the momentum is

$$p_{op} = \hat{p} = -i\hbar\nabla$$

$$\nabla = \hat{i}\frac{\partial}{\partial x} + \hat{j}\frac{\partial}{\partial y} + \hat{k}\frac{\partial}{\partial z}$$

$$p_{x\,op} = \hat{p}_x = -i\hbar\frac{\partial}{\partial x}$$

$$x_{op} = \hat{x} = x$$

RHS of (5)

$$(xp_x - p_x x)\psi$$

$$= \left\{x\left(-i\hbar\frac{\partial}{\partial x}\right) - \left(-i\hbar\frac{\partial}{\partial x}\right)x\right\}\psi$$

$$= -i\hbar x\frac{\partial}{\partial x}\psi + i\hbar\frac{\partial}{\partial x}(x\psi)$$

$$= \cancel{-i\hbar x\frac{\partial}{\partial x}\psi} + \cancel{i\hbar x\frac{\partial}{\partial x}\psi} + i\hbar\psi\cancel{\frac{\partial x}{\partial x}}$$

$$= i\hbar\psi$$

$$(xp_x - p_x x)\psi = i\hbar\psi$$

$$(xp_x - p_x x) = i\hbar \quad \text{——} (6)$$

putting (6) into (5) yields

$$iC = i\hbar$$

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$\Rightarrow \quad C = \hbar$ —— (7)

substituting (7) in (8)
yields

$$(\Delta B)^2 (\Delta A)^2 = \frac{C^2}{4} \quad \text{—— (8)}$$

But $A = A^* = A$
$B = B^* = B$
$C = C^{*} = C$ } —— (9)
Hermitian operator

putting (9) into (8) yields

$$(\Delta B)^2 (\Delta A)^2 = \frac{(C)^2}{4}$$

Proofed

Equation Of Motion In Matrix Form

Time rate of change of ψ:

$$i\hbar \frac{\partial}{\partial t} \psi(r,t) = H\psi(r,t) \quad \text{—— (1)}$$

where $H = \frac{-\hbar^2}{2m} \nabla^2 (r,t) + V(r,t)$

Hamiltonian notation

Time rate of change of typical matrix energy is given by

$$\int \psi^* F \psi \, d\tau = \iint \psi^*(r,t) F(r, r', t) \psi(r', t) \, d\tau \, d\tau'$$

—— (2)

F is a general operator which may depend on time explicitly.

By differentiating w.r.t time and simplifying and making use of certain [illegible] identity eqn (2) can be written as

$$\frac{dF}{dt} = \frac{\partial F}{\partial t} + \frac{1}{i\hbar}[F, H]$$

$$= \frac{\partial F}{\partial t} + \frac{1}{i\hbar}(FH - HF) \quad \text{--- (3)}$$

eqn (3) is Heisenberg form of equation of motion of a dynamical variable which can also be written as

$$\frac{dF}{dt} = \frac{\partial F}{\partial t} - \frac{i}{\hbar}(FH - HF)$$

$L = T + V$ $\quad L - T$

$H = 2T - V$

$T - (L - T)$

$H = 2T - L$

Classical Lagrangian of Hamilton's Equation of Motion

$$\frac{dL}{dq_i} - \frac{d}{dt}\left(\frac{dL}{d\dot{q}_i}\right) = 0 \quad \text{--- (2)}$$

$i = 0, 1, 2, 3 \ldots$

$$\left.\begin{aligned} p_i &= \frac{\partial H}{\partial q_i} \\ \dot{q}_i &= \frac{\partial H}{\partial p_i} \end{aligned}\right\} \text{Hamiltonian equ} \quad \text{--- (1.)}$$

$L = T + V$

$H = T - V = 2T - L$

The time dependency of any function of the coordinate momentia and the time calculated along a moving phase point is

$$\left.\begin{aligned} p_i &= \frac{\partial H}{\partial q_i} \\ \dot{q}_i &= -\frac{\partial H}{\partial p_i} \end{aligned}\right\}$$

$$\frac{dF}{dt}(q_1 \dots q_n, p_1 \dots p_n, t) = \frac{\partial F}{\partial t} + \sum_{i=1}^{n}\left(\frac{\partial F}{\partial q_i}\dot{q}_i + \frac{\partial F}{\partial p_i}\dot{p}_i\right) \quad \text{— (2)}$$

substituting eqn (1a) into (2) yields

$$\frac{dF}{dt}(q_1 \dots q_n, p_1 \dots p_n, t) = \frac{\partial F}{\partial t} + \sum_{i=1}^{n}\left(\frac{\partial F}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial H}{\partial q_i}\frac{\partial F}{\partial p_i}\right) \quad \text{— (3)}$$

The poisson bracket of any given function is given by

$$\{A, B\} = \sum_{i=1}^{N}\left(\frac{\partial A}{\partial q_i}\frac{\partial B}{\partial p_i} - \frac{\partial B}{\partial q_i}\frac{\partial A}{\partial p_i}\right) \quad \text{— (4)}$$

$$\{F, H\} = \sum_{i=1}^{N}\left(\frac{\partial F}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial H}{\partial q_i}\frac{\partial F}{\partial p_i}\right) \quad \text{— (5)}$$

Comparing eqn ~~(5) and~~ eqn (3) yield

$$\frac{dF}{dt}(q_1 \dots q_n, p_1 \dots p_n, t) = \frac{\partial F}{\partial t} + \{F, H\} \quad \text{— (6)}$$

$$\boxed{\{F, H\} = \frac{1}{i\hbar}[F, H] = \frac{1}{i\hbar}(FH - HF)}$$

relationship b/w Poisson bracket & commutators.

eqn (6) is the eqn of motions in matrix form.

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where $\frac{dF}{dt}$ implies total time derivative of F along a moving, ~~instance~~ phase point

F is a dynamical variable

$\frac{\partial F}{\partial t}$ implies explicite time dependent of F and

$\{F, H\}$ implies change in F due to the motion of the moving phase point at which F is evaluated.

x

Relationship Between Poisson Bracket & Commutator Bracket.

Let's consider two operators A and B then the poisson bracket ~~and~~ their commutator bracket can be written as

$$\{A, B\} = \frac{1}{i\hbar}[A, B] = -\frac{i}{\hbar}[A, B]$$

$$= -\frac{i}{\hbar}(AB - BA)$$

Assignment

Using the uncertainty principle to show that

$$\Delta x \, \Delta\lambda \geq \frac{\lambda^2}{2\pi}$$

that use De broglie hypothesis

$$\lambda = \frac{h}{p_x} \Rightarrow p_x = \frac{h}{\lambda} \Rightarrow \Delta p_x = -h\lambda^{-2}\Delta\lambda$$

substitute and simplify from Heisenberg

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Angular Momentum, L

$[L_x L_y] = i\hbar L_z \quad [J_x J_y] = i\hbar J_z$
$[L_z, L_x] = i\hbar L_y \quad [J_z, J_x] = i\hbar J_y$
$[L_y, L_z] = i\hbar L_x \quad [J_y, J_z] = i\hbar J_x$

1. ~~Angular momentum~~ Space is isotropic
2. Lagrangian is invariant

$\Rightarrow$ Hamiltonian is invariant and hence poisson bracket commute

$H = 2T - L$

$\{H, L\} = 0$

The orbital angular momentum of a system is in constant motion under

(a) space is isotropic
(b) Lagrangian of the system is invariant under rotation

Essentially therefore, it means that the classical Hamiltonian will be invariant under rotation since Hamiltonian $H = 2T - L$

This simplicity indicates that the physical system was rotationally invariant or symmetric. The implication of this is that the poisson bracket of the Hamiltonian and the angular momentum vanished i.e commute.

i.e $\{H, L\} = 0$

$$\{H, L\} = \frac{1}{i\hbar}[H, L]$$
$$= \frac{1}{i\hbar}[HL - LH]$$
$$= 0$$

Similarly their commutator bracket also commute.

Difference Between The Classical & Quantum Angular Momentum

In the quantum situation we are concerned with infinite dimensional space i.e the

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$L = L_x \hat{i} + L_y \hat{j} + L_z \hat{k}$

We may thus have commutation between the Hamiltonian and all the three angular momentum component but there cannot be commutation between any pair of operator corresponding to a pair of component. Hence no more than one component operator can be a constant of motion.

i.e

$[H, L_x] = 0$

$[H, L_y] = 0$

$[H, L_z] = 0$

2. In the classical situation we are concerned only with orbital angular momentum or at least with such angular momenta as are associated with the space-time description

$$\vec{L} = \vec{r} \times \vec{P}$$

$$\vec{r} = x\hat{i} + y\hat{j} + z\hat{k}$$

$$\vec{P} = P_x\hat{i} + P_y\hat{j} + P_z\hat{k}$$

$$\vec{L} = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ x & y & z \\ P_x & P_y & P_z \end{vmatrix}$$

$$= \hat{i}\begin{vmatrix} y & z \\ P_y & P_z \end{vmatrix} - \hat{j}\begin{vmatrix} x & z \\ P_x & P_z \end{vmatrix} + \hat{k}\begin{vmatrix} x & y \\ P_x & P_y \end{vmatrix}$$

$$= \hat{i}(yP_z - zP_y) - \hat{j}(xP_z - zP_x) + \hat{k}(xP_y - yP_x)$$

$$= \hat{i}(yP_z - zP_y) + \hat{j}(zP_x - xP_z) + \hat{k}(xP_y - yP_x) \quad (1)$$

$$\text{but } \vec{L} = \vec{L}_x \hat{i} + \vec{L}_y \hat{j} + \vec{L}_z \hat{k} \quad (2)$$

Comparing eqn (1) and (2)

implies

$$\left.\begin{aligned} \vec{L}_x &= yP_z - zP_y \\ \vec{L}_y &= zP_x - xP_z \\ \vec{L}_z &= xP_y - yP_x \end{aligned}\right\} \quad \text{--- (3)}$$

but $P_{op} = -i\hbar\nabla$

$$\nabla = \hat{i}\frac{\partial}{\partial x} + \hat{j}\frac{\partial}{\partial y} + \hat{k}\frac{\partial}{\partial z}$$

$$\therefore P_{op} = -i\hbar\frac{\partial}{\partial x} - i\hbar\frac{\partial}{\partial y} - i\hbar\frac{\partial}{\partial z} \quad \text{--- (4)}$$

$$P_{op} = \hat{P} = \hat{i}P_x + \hat{j}P_y + \hat{k}P_z \quad \text{--- (5)}$$

Comparing (4) and (5) we have

$$\left.\begin{aligned} P_x &= -i\hbar\,\partial/\partial x \\ P_y &= -i\hbar\,\partial/\partial y \\ P_z &= -i\hbar\frac{\partial}{\partial z} \end{aligned}\right\} \quad \text{--- (6)}$$

Using eqn (6) in (3) yields

$$\begin{aligned} \vec{L}_x &= yP_z - zP_y \\ &= y\left(-i\hbar\frac{\partial}{\partial z}\right) - z\left(-i\hbar\,\partial/\partial y\right) \\ &= -i\hbar\left(y\,\partial/\partial z - z\,\partial/\partial y\right) \quad \text{--- (7)} \end{aligned}$$

$$\begin{aligned} \vec{L}_y &= zP_x - xP_z \\ &= z\left(-i\hbar\frac{\partial}{\partial x}\right) - x\left(-i\hbar\,\partial/\partial z\right) \\ &= -i\hbar\left(z\,\partial/\partial x - x\,\partial/\partial z\right) \quad \text{--- (8)} \end{aligned}$$

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$$L_z = x\left(-i\hbar\frac{\partial}{\partial y}\right) - y\left(-i\hbar\frac{\partial}{\partial x}\right)$$

$$= -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \quad (9)$$

To Proof the Commutator

$$[\vec{L}_x, \vec{L}_y] = i\hbar L_z$$

$$[\vec{L}_y, L_z] = i\hbar \vec{L}_x$$

$$[\vec{L}_z, \vec{L}_x] = -i\hbar \vec{L}_y$$

$$[\vec{L}_y, \vec{L}_x] = -i\hbar L_z$$

$$[\vec{L}_z, \vec{L}_y] = -i\hbar L_x$$

$$[\vec{L}_x, \vec{L}_z] = -i\hbar L_y$$

$$[\vec{L}_y, \vec{L}_z] = (L_y L_z - L_z L_y)$$

$$= \left[(-i\hbar)\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\right]\left[(-i\hbar)\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\right]$$

$$- \left[(-i\hbar)\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\right]\left[(-i\hbar)\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\right]$$

$$= (-i\hbar)^2\left[z\frac{\partial}{\partial x}\left(x\frac{\partial}{\partial y}\right) - z\frac{\partial}{\partial x}\left(y\frac{\partial}{\partial x}\right) - x\frac{\partial}{\partial x}\left(x\frac{\partial}{\partial y}\right) + x\frac{\partial}{\partial x}\left(y\frac{\partial}{\partial x}\right)\right]$$

$$- (i\hbar)^2\left[x\frac{\partial}{\partial y}\left(z\frac{\partial}{\partial x}\right) - x\frac{\partial}{\partial y}\left(x\frac{\partial}{\partial z}\right) - y\frac{\partial}{\partial x}\left(z\frac{\partial}{\partial x}\right) + y\frac{\partial}{\partial x}\left(x\frac{\partial}{\partial z}\right)\right]$$

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Separation of the Wave Equation

The wave equation (1) can be written in spherical polar coordinate as

$$-\frac{\hbar^2}{2m}\left[\nabla^2 + V(\vec{r})\right]\psi(\vec{r}) = E\,\psi(\vec{r}) \quad (1)$$

Now in spherical coordinate

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right]$$

$$+ V\psi(r) = E\psi \quad (2)$$

Solving for the radial and the angular part of (2) by substituting

$$\psi(r,\theta,\phi) = R(r)\,Y(\theta,\phi) \quad (3)$$

Now substituting eqn (3) into (2) yields

$$-\frac{\hbar^2}{2m}\left\{\frac{Y}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{R}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{R}{r^2\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right\}$$

$$+ (V-E)RY = 0$$

$$-\frac{\hbar^2}{2mr^2}\left\{Y\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{R}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{R}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right\} + (E-V)RY = 0 \quad (4)$$

Dividing both sides of eqn (4) by eqn (3) we obtain

$$-\frac{\hbar^2}{2mr^2}\left\{\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{1}{Y\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{Y\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right\} + (E-V) = 0$$

Start here (18)

$$[L_z, \vec{L}^2] = [L_y, \vec{L}^2] = [L_x, \vec{L}^2] =$$

$$\vec{L}^2 = \vec{L}_x^2 + \vec{L}_y^2 + \vec{L}_z^2$$

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

$$\therefore [\vec{L}, \vec{L}^2] = 0 \quad \text{———} \; *$$

Eqn * tells us that $\vec{L}^2$ and $\vec{L}_z$ has common eigen functions

$$[\vec{L}_z, \vec{L}^2] = (\vec{L}_z \vec{L}^2 - \vec{L}^2 \vec{L}_z)\psi$$

Let the eigen function be ψ_{lm}. The integral indices l, m are related to the eigen values of $\vec{L}^2$ and $\vec{L}_z$ as shown in the eigen function equation

$$\vec{L}^2 \psi_{lm} = \hbar^2 l(l+1)\psi_{lm} \quad \text{———} \; (*')$$

$$l = 0, 1, 2 \ldots$$

$$\vec{L}_z \psi_{lm} = \hbar m \psi_{lm} \quad \text{———} \; (*'')$$

The form of eqn *'' indicates that the eigen values of $\vec{L}^2$ are $(2l+1)$ fold degenerate where

ψ_{lm} is the wave function

$\hbar m$ is the eigen value of $\vec{L}_z$

$\hbar^2 l(l+1)$ is the eigen value of $\vec{L}^2$

l is the orbital angular momentum quantum number

m is the magnetic quantum number.

Spherically Symmetry Potential in Three Dimension

It is generally impossible to obtain analytical solution of the Bridgman 3-dimensional Schrodinger's equation

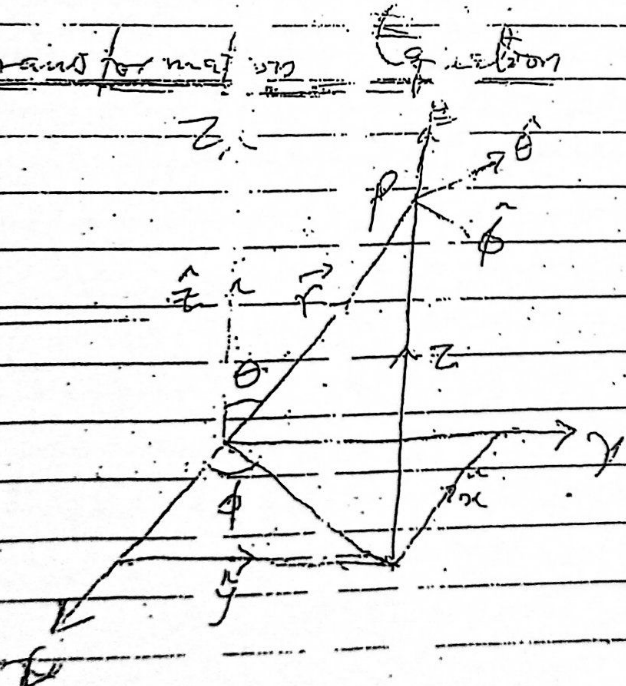
$$\left\{-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right\}\psi(\vec{r}) = E\psi(\vec{r})$$

One of the most important practical coordinate system is about the free particle equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) = E\,\psi(\vec{r}) \quad \text{--- (2)}$$

This equation can be separated in the spherical polar coordinate form.

Transformation Equation



Examples

$$x = r\sin\theta\cos\phi$$
$$y = r\sin\theta\sin\phi$$
$$z = r\cos\theta$$

Remark

(1) If the potential energy is spherically symmetric so that $V(\vec{r}) = V(r)$ is a function only of the magnitude of r of $\vec{r}$ measured from same origin, the wave equation can ~~always~~ only be separated in spherical coordinate.

(2) Many problem of physical interest can be represented exactly or approximately in terms of spherically symmetric potential of various shapes

$x = r\sin\theta\cos\phi$

$y = r\sin\theta\sin\phi$

$z = r\cos\theta$

$$= (-i\hbar)^2 \Big[\cancel{zx\frac{\partial^2}{\partial x \partial y}} + \cancel{z\frac{\partial}{\partial}\left(\frac{\partial x}{\partial x}\right)} - \cancel{zy\frac{\partial^2}{\partial x^2}}$$

$$\cancel{z\frac{\partial}{\partial x}\left(\frac{\partial y}{\partial x}\right)} - \cancel{x^2\frac{\partial^2}{\partial z \partial y}} - \cancel{x\frac{\partial}{\partial y}\left(\frac{\partial x}{\partial z}\right)}$$

$$+ \cancel{xy\frac{\partial^2}{\partial z \partial x}} + \cancel{x\frac{\partial}{\partial x}\left(\frac{\partial y}{\partial z}\right)} - \cancel{xz\frac{\partial^2}{\partial y \partial x}}$$

$$- \cancel{x\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial y}\right)} + \cancel{x^2\frac{\partial^2}{\partial y \partial z}} + \cancel{x\frac{\partial}{\partial y}\left(\frac{\partial x}{\partial y}\right)}$$

$$+ \cancel{yz\frac{\partial^2}{\partial x^2}} + \cancel{\frac{y}{x}\left(\frac{\partial z}{\partial x}\right)} - \cancel{yx\frac{\partial^2}{\partial x \partial z}}$$

$$- \cancel{y\frac{\partial}{\partial z}\left(\frac{\partial x}{\partial x}\right)} \Big]$$

$$= (-i\hbar)^2 \left[z\frac{\partial}{\partial y} - y\frac{\partial}{\partial z} \right]$$

$$= i^2\hbar^2 \left[z\frac{\partial}{\partial y} - y\frac{\partial}{\partial z} \right]$$

$$[L_y, L_z] = -\hbar^2 \left[z\frac{\partial}{\partial y} - y\frac{\partial}{\partial z} \right] \quad \text{— (i)}$$

but $\vec{L}_x = -i\hbar\left(z\frac{\partial}{\partial y} - y\frac{\partial}{\partial z}\right)$

$$\Rightarrow \left(z\frac{\partial}{\partial y} - y\frac{\partial}{\partial z} \right) = \frac{\vec{L}_x}{-i\hbar} \quad \text{— (ii)}$$

substituting (ii) into (i) yields

hence

$$[\vec{L}_y, \vec{L}_z] = -\hbar^2 \cdot \frac{\vec{L}_x}{i\hbar}$$

$$[\vec{L}_y, \vec{L}_z] = \frac{-\hbar \vec{L}_x}{i}$$

but $\frac{1}{i} = -i$

$$[\vec{L}_y, \vec{L}_z] = -(-i)\hbar L_x$$

$$[\vec{L}_y, \vec{L}_z] = i\hbar L_x$$

Proved.

$$\frac{\hbar^2}{2mr^2}\left\{\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right]\right\}$$

$$+(E-V)=0 \quad \text{——— (5)}$$

Dividing both sides of (5) by $\frac{\hbar^2}{2mr^2}$

we have

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right]$$

$$+\frac{2mr^2}{\hbar^2}(E-V)=0$$

——— (6)

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2mr^2}{\hbar^2}(E-V)=$$

$$-\frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right]$$

——— (7)

* Since LHS depends only on r and the RHS depends only on θ, ϕ, both sides must be equal to a constant. Let the constant be λ. Then the radial part of eqn (7) is given by

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2mr^2}{\hbar^2}\left[E-V\right]=\lambda$$

——— (8)

And the angular part is given by

$$-\frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right]=\lambda$$

——— (9)

From eqn (8) divide both side by r^2 we obtain

$$\frac{1}{Rr^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2m}{\hbar^2}(E-V)=\frac{\lambda}{r^2}$$

$$\frac{1}{Rr^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2m}{\hbar^2}(E-V)-\frac{\lambda}{r^2}=0$$

——— (10)

multiplying eqn (10) through by R yields

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\left[\frac{2m}{\hbar^2}(E-V)-\frac{\lambda}{r^2}\right]R=0$$

——— (11)

From eqn (9) we have

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}-\lambda Y=0 \longrightarrow (12)$$

Further separating eqn (12) by letting

$$Y(\theta,\phi)=\Theta(\theta)\Phi(\phi) \longrightarrow (13)$$

substituting (13) into (12) we obtain

$$\frac{\Phi}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{\Theta}{\sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2}+\lambda\Theta\Phi=0 \longrightarrow (14)$$

Dividing eqn (14) by eqn (13) we obtain

$$\frac{1}{\Theta\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{1}{\Phi\sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2}+\lambda=0 \longrightarrow (15)$$

multiplying eqn (15) through by $\sin^2\theta$ yields

$$\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}+\lambda\sin^2\theta=0$$

separating the variables, we have

$$\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\lambda\sin^2\theta=-\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2} \longrightarrow (17)$$

Since the LHS of eqn (17) depends only on θ and the RHS depends only on ϕ, both sides must be equal to a constant.

Let the constant be r then we have

$$-\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}=r$$

$$\frac{\partial^2\Phi}{\partial\phi^2}=-r\Phi$$

$$\frac{\partial^2\Phi}{\partial\phi^2}+r\Phi=0 \longrightarrow (18)$$

similarly

$$\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\lambda\sin^2\theta=r \longrightarrow (19)$$

$$\cancel{\frac{d}{dw}\left[(1-w^2)\frac{dP}{dw}\right]} +$$

Dividing both sides of 19 by $\sin^2\theta$ yields

$$\frac{1}{\Theta \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \lambda = \frac{\nu}{\sin^2\theta}$$

multiply through by Θ

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \left(\lambda - \frac{\nu}{\sin^2\theta}\right)\Theta = 0 \quad (20)$$

From (20) the auxiliary eqn is given by

$$m^2 + r = 0$$

$$m = \pm\sqrt{-r} = \pm i r^{1/2}$$

let $r = \nu^{1/2}$

$$\therefore m = \pm i\nu$$

General solution

$$\Phi(\phi) = e^{\pm i\nu^{1/2}\phi}$$

$(2\pi)^{-1/2} e^{\pm m\phi}$ if $(\nu = m^2)$

$\frac{\partial\phi}{\partial\phi}$ must be continuous throughout the domain $0 \le \Phi \le 2\pi$

$\Phi(\phi) = (2\pi)^{-1/2} e^{\pm m\phi}$ if $\nu = m^2$

$$\Phi(\phi) = Ae^{i\nu^{1/2}\phi} + Be^{-i\nu^{1/2}\phi} \qquad \nu \neq 0 \quad (21)$$

$$\Phi(\phi) = A + B\phi \qquad \nu = 0 \quad (22)$$

where $\Phi \in [0, 2\pi)$

$$\Rightarrow 0 \le \Phi < 2\pi$$

Remarks

(1) $\Phi(\phi)$ and $\partial\Phi/\partial\phi$ must be continuous throughout the domain i.e. $0 \le \phi < 2\pi$

(2) This demands that ν be chosen equals to the square of an integer

eqn (21) & (22) thus becomes

$$\Phi(\phi) = (2\pi)^{-1/2} e^{\pm m\phi} \quad (\text{if } \nu = m^2) \quad (23)$$

All physically meaningful solutions are included if m is allowed to be

$$\Phi(\phi) = Ae^{m\phi i} + Be^{m i\phi} \qquad (21)$$

positive or negative integer or zero

(3) $(2\pi)^{-1/2}$ are chosen as multiplying constant in order that Φ be normalized to unity under the range of ϕ

Rigid Rotator

This is used in the studies of molecular vibration

Wave Equation for Rigid Rotator

The three dimensional wave eqn for rigid rotator in spherical coordinate for schrodinger's equation is given by

$$-\frac{\hbar}{2m}\nabla^2\psi + V(r)\psi = E\psi$$

In spherical coordinate

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{2m}{\hbar^2}(E-V)\psi = 0 \quad \text{--- (1)}$$

Let the mass m be replaced by the moment of inertia I and r be unity. For a free particle we V = 0 eqn 1 becomes

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{2I}{\hbar^2}E\psi = 0 \quad \text{--- (2)}$$

Eqn (2) represent the precessional motion of the free axis and the rotation of the system respectively. Since it involve two independent variables are θ & ϕ, we make use of separation of variables methods

$$\text{Let } \psi(\theta,\phi) = Y(\theta)\,Z(\phi) \quad \text{--- (3)}$$

Substituting eqn (3) into (2) yields

$$\frac{Z}{\sin\theta}\left(\sin\theta\frac{\partial}{\partial\theta}Y\right) + \frac{Y}{\sin^2\theta}\frac{\partial^2 Z}{\partial\phi^2} + \frac{2I}{\hbar^2}EYZ = 0 \quad \text{--- (4)}$$

$\Phi(\phi) = e^{m i \phi}$

multiplying eqn (4) through by

$\frac{\sin^2\theta}{YZ}$ yields

$$\frac{\sin\theta}{Y}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{Z}\frac{\partial^2 Z}{\partial\phi^2} + \frac{2IE}{\hbar^2}\sin^2\theta = 0 \quad (5)$$

Separating the variables we have

$$\frac{\sin\theta}{Y}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{2IE\sin^2\theta}{\hbar^2} = -\frac{1}{Z}\frac{\partial^2 Z}{\partial\phi^2} \quad (6)$$

Let $\beta = \frac{2IE}{\hbar^2}$ eqn (6) becomes

$$\frac{\sin\theta}{Y}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \beta\sin^2\theta = -\frac{1}{Z}\frac{\partial^2 Z}{\partial\phi^2} \quad (7)$$

Since LHS of eqn (7) depend only on θ and the RHS depend only on ϕ, then both sides must be equals to a constant.

Let the constant be n^2

Hence

$$\frac{\sin\theta}{Y}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \beta\sin^2\theta = n^2 \quad (8)$$

$$\frac{1}{Z}\frac{\partial^2 Z}{\partial\phi^2} = n^2 \quad (9)$$

Energy Levels Of Rigid Rotators

From eqn (9)

$$\frac{1}{Z}\frac{\partial^2 Z}{\partial\phi^2} = n^2$$

$$\frac{d^2 Z}{d\phi^2} + n^2 Z = 0 \quad (10)$$

The auxiliary eqn is given by

$m^2 + n^2 = 0$

$m = \pm\sqrt{-n^2} = \pm in$

The general solution is given by

$$Z(\phi) = N_\phi\, e^{\pm in\phi} \qquad (11)$$

where N_ϕ is called the normalization constant.

For Z to be single-valued, it must have the same value for $\phi = 0$ and $\phi = 2\pi$

i.e. $Z(0) = Z(2\pi)$

or

$$N_\phi = N_\phi\, e^{\pm 2\pi i n}$$

apply the Euler's equation

$$N_\phi = N_\phi\left(\cos 2\pi n + i \sin 2\pi n\right)$$

Normalization constant

$$\cos 2\pi n + i \sin 2\pi n = 1$$

If $n = 0$ or an integer

$$\therefore Z(\phi) = N_\phi\, e^{in\phi} \qquad (12)$$

$$(n = 0, \pm 1, \pm 2, \ldots)$$

For normalization we have

$$\int_0^{2\pi} Z Z^* d\phi = 1$$

$$\int_0^{2\pi} N_\phi e^{in\phi} \cdot N_\phi e^{-in\phi}\, d\phi = 1$$

$$\int_0^{2\pi} N_\phi^2\, e^{in(\phi-\phi)}\, d\phi = 1$$

$$N_\phi^2 \int_0^{2\pi} e^{0}\, d\phi = 1$$

$$N_\phi^2 \int_0^{2\pi} d\phi = 1$$

$$\Rightarrow N_\phi^2 \left[\phi\right]_0^{2\pi} = 1$$

$$N_\phi^2 \left(2\pi - 0\right] = 1$$

$$N_\phi^2 (2\pi) = 1$$

$$N_\phi^2 = \frac{1}{2\pi}$$

$$N_\phi = \frac{1}{\sqrt{2\pi}}$$

$$N_\phi = (2\pi)^{-1/2}$$

$$\therefore Z_\phi = N_\phi e^{in\phi}$$

$$= (2\pi)^{-1/2} e^{in\phi} \quad \text{——} \quad (1.3)$$

This functions are orthogonal because

$$\int_0^{2\pi} Z_{n'}^* Z_n \, d\phi = \int_0^{2\pi} \frac{1}{\sqrt{2\pi}} \left(e^{in'\phi}\right)^* \frac{1}{\sqrt{2\pi}} e^{in\phi} \, d\phi$$

$$= \frac{1}{2\pi} \int_0^{2\pi} e^{i(n'-n)\phi} \, d\phi = 0$$

if $n' \neq n$

—— (1.4)

Using the nomenclature, let

$$x = \cos\theta$$

$$\frac{dx}{d\theta} = -\sin\theta$$

$$\frac{d}{d\theta} = \frac{d}{dx} \frac{dx}{d\theta} = -\sin\theta \frac{d}{dx}$$

—— (1.5)

now putting eqn (15) into (14) we have

~~from eqn (8)~~

$$\frac{\sin\theta}{Y}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\beta\sin^2\theta=n^2$$

Dividing through by $\frac{\sin^2\theta}{Y}$

$$\frac{1}{Y\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\left(\beta-\frac{n^2}{\sin^2\theta}\right)Y=0 \quad (16)$$

$$\frac{1}{\cancel{\sin\theta}}\left[-\cancel{\sin\theta}\frac{\partial}{\partial x}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)\right]+\left(\beta-\frac{n^2}{\sin^2\theta}\right)Y=0$$

$$-\frac{d}{dx}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\left(\beta-\frac{n^2}{\sin^2\theta}\right)Y=0$$

$$-\frac{d}{dx}\left[\sin\theta\left(-\sin\theta\frac{dY}{dx}\right)\right]+\left(\beta-\frac{n^2}{\sin^2\theta}\right)Y=0$$

$$\frac{d}{dx}\left(\sin^2\theta\frac{dY}{dx}\right)+\left(\beta-\frac{n^2}{\sin^2\theta}\right)Y=0 \quad (17)$$

Using ~~trigonometry~~ identity

$$\sin^2\theta=1-\cos^2\theta$$

but $\cos^2\theta=x^2$

since $x=\cos\theta$

$$\therefore \sin^2\theta=1-x^2 \quad (*)$$

putting (*) into (17) yields

$$\frac{d}{dx}\left[(1-x^2)\frac{dY}{dx}\right]+\left[\beta-\frac{n^2}{(1-x^2)}\right]Y=0 \quad (18)$$

$-1\le x\le 1$

We therefore identify $Y(\theta)$ as the associated Legendre polynomial $P_l^n(x)$ of degree l which satisfies the condition of finiteness) provided we restricted β to each value.

$$\beta = 2IE/\hbar^2 = l(l+1)$$

$; l = 0, 1, 2 \ldots n$

$$\frac{2IE}{\hbar^2} = l(l+1)$$

$$E_l = \frac{\hbar^2 l(l+1)}{2I} \quad ; l = 0, 1, 2 \ldots n \qquad \text{—— (29)}$$

E_l are the allowed energy eigen value for the rigid rotator with free axis

$$E_0 = \frac{\hbar^2}{2I} 0(0+1) = 0$$

$$E_1 = \frac{\hbar^2}{2I} 1(1+1) = \frac{2\hbar^2}{2I} = \frac{\hbar^2}{I}$$

Since $x = \cos\theta$ eqn (11) has a solution

$$Y_{ln}(\theta) = N_\theta P_l^n(\theta) = N_\theta P_l^n(\cos\theta) \qquad \text{—— (20)}$$

where N_θ is the normalization constant. From eqn (20) we have for normalization

$$\int_0^\pi |Y_{l,n}(\theta)|^2 \sin\theta \, d\theta = N_\theta^2 \int_{-1}^{1} |P_l^n(x)|^2 dx$$

$$\int_0^\pi |Y_{ln}(\theta)|^2 \sin\theta \, d\theta = N_\theta^2 \frac{(l+n)!}{(l-n)!} \frac{2\pi}{(2l+1)} = 1 \qquad \text{—— (21)}$$

$$N_\theta^2 \frac{(l+n)!}{(l-n)!} \frac{2\pi}{(2l+1)} = 1$$

$$N_\theta^2 = \frac{(l-n)!}{(l+n)!} \frac{(2l+1)}{2\pi}$$

$$N_\theta = \sqrt{\frac{(l-n)!}{(l+n)!} \frac{(2l+1)}{2\pi}} \qquad \text{—— (22)}$$

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Substituting eqn 22 into eqn 20 yield

$$\psi_{l,n}(\theta) = \left[\frac{(l-n)!}{(l+n)!}\,\frac{(2l+1)}{2\pi}\right]^{1/2} P_l^n(\cos\theta)$$ —— (23)

Eigen Function for Rigid Rotator & Degeneracy State

From eqn (3), (11) and 23

$$\psi(\theta,\phi) = Y(\theta)\,Z(\phi)$$ —— (3)

$$Z(\phi) = N_\phi\, e^{\pm i n\phi}$$ —— (4)

$$\psi_{l,n}(\theta,\phi) = Y_{l,n}(\theta)\,Z(\phi) = \left[\frac{(2l+1)}{4\pi}\cdot\frac{(l-n)!}{(l+n)!}\right]^{1/2} P_l^n(\cos\theta)\, e^{in\phi}$$

where $l = 0, 1, 2, 3 \ldots$

$n = 0, \pm 1, \pm 2, \pm 3 \ldots \pm l$

Clearly $\psi^*_{l,n}(\theta,\phi) = (-1)^n \psi_{l,-n}$ —— (25)

The first five spherical harmonics are:

$$\psi_{0,0} = \left[\frac{(2(0)+1)}{4\pi}\cdot\frac{(0-0)!}{(0+0)!}\right]^{1/2} P_0^0(\cos\theta)\, e^{i(0)\phi}$$

$$= \left(\frac{1}{4\pi}\cdot\frac{0!}{0!}\right)^{1/2} P_0^0 \cos\theta\ (1)$$

$$= \left(\frac{1}{4\pi}\right)^{1/2} P_0^0 \cos\theta$$

but $P_0^0(\cos\theta) = 1$

$$\therefore \quad \psi_{0,0} = \left(\frac{1}{1}\right)^{1/2} \left(\frac{1}{4\pi}\right)^{1/2}$$

$$\psi_{0,0} = \left(\frac{1}{4\pi}\right)^{1/2}$$

$$\psi_{1,1} = \left[\left(\frac{2(1)+1}{4\pi}\right) \cdot \frac{(1-1)!}{(1+1)!}\right]^{1/2} P_1^1(\cos\theta)\, e^{i\phi}$$

$$= \left(\frac{3}{4\pi} \cdot \frac{0!}{2!}\right)^{1/2} P_1^1(\cos\theta)\, e^{i\phi}$$

$$= \left(\frac{3}{8\pi}\right)^{1/2} P_1^1(\cos\theta)\, e^{i\phi}$$

but $P_1^1(\cos\theta) = \sin\theta$

$$\psi_{1,1} = \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta\, e^{i\phi}$$

$$\psi_{1,0} = \left[\frac{2(1)+1}{4\pi} \cdot \frac{(1-0)!}{(1+0)!}\right] P_0^1(\cos\theta)\, e^{i(0)\phi}$$

$$= \left(\frac{3}{4\pi} \cdot \frac{1!}{1!}\right)^{1/2} P_0^1(\cos\theta)\,(1)$$

$$= \left(\frac{3}{4\pi}\right)^{1/2} P_0^1(\cos\theta)$$

but $P_0^1(\cos\theta) = \cos\theta$

$$\psi_{1,0} = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$$

$$\psi_{1,-1} = \left[\frac{2(1)+1}{4\pi} \cdot \frac{[1-(-1)]!}{(1-1)!}\right]^{1/2} P_{-1}^1(\cos\theta)\, e^{-i\phi}$$

$$= \left(\frac{3}{4\pi} \cdot \frac{2!}{0!}\right)^{1/2} P_{-1}^1(\cos\theta)\, e^{-i\phi}$$

$$= \left(\frac{3}{2\pi}\right)^{1/2} P_{-1}^1(\cos\theta)\, e^{-i\phi}$$

but $P_{-1}^{1}(\cos\theta) = \sin\theta$

$$\psi_{1,-1} = \left(\frac{3}{2\pi}\right)^{1/2} \sin\theta \, e^{-i\phi}$$

Assignment

Find $\psi_{0,2}$, $\psi_{1,-2}$, $\psi_{1,-3}$, $\psi_{2,2}$, $\psi_{3,-2}$, $\psi_{0,3}$, $\psi_{2,-3}$, $\psi_{0,4}$.

$$\psi_{1,2} = \left(\frac{2(1)+1}{4\pi} \cdot \frac{(1-2)!}{(1+2)!}\right)^{1/2} P_2^{1}(\cos\theta)\, e^{2i\phi}$$

$$= \left(\frac{3}{4\pi} \cdot \frac{-1!}{3!}\right)^{1/2} P_2^{1}(\cos\theta)\, e^{2i\phi}$$

$$= \left(\frac{3}{4\pi} \cdot \frac{1}{3\times 2\times 1}\right)^{1/2} P_2^{1}(\cos\theta)\, e^{2i\phi}$$

$$= \left(\frac{1}{8\pi}\right)^{1/2} P_2^{1}(\cos\theta)\, e^{2i\phi}$$

but $P_1^{2}(\cos\theta) = \cos^2\theta$

$$\psi_{1,2} = \left(\frac{1}{8\pi}\right)^{1/2} \cos^2\theta \, e^{i2\phi}$$

The eigen function $\psi_{l,n}$ are eigen functions with the eigen values E_l as given as equation (24) which depends on l. Since

$Z_n \phi$ is orthogonal, it follows that

$$\int_{-1}^{1} P_l^{n}(x) P_k^{n}(x)\, dx = \int_0^{\pi} P_l^{n}(\cos\theta) P_k^{n}(\cos\theta) \sin\theta \, d\theta = 0 \quad l \neq k$$

Remark

The energy is determined by l alone and for each l $(l > 0)$ there are $(2l+1)$ values of

($m = 0, \pm 1, \pm 2 \ldots \pm l$) possible. This simply means that $(2l+1)$ eigen function are observable or possible for each energy state.

Thus the degeneracy is $(2l+1)$ fold.

Legendre Polynomial

$$\frac{d}{dw}\left[(1-w^2)\frac{dP}{dw}\right] + \left(\lambda - \frac{m^2}{(1-w^2)}\right)P = 0$$

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] + (V-E)\psi = 0$$

$$\frac{1}{r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right] + \frac{2m}{\hbar^2}(E-V) = 0 \quad \text{— (1)}$$

Solving for the radial and the angular part. Let

$$\psi(r,\theta,\phi) = R(r)\,Y(\theta,\phi) \quad \text{— (2)}$$

substituting eqn (2) into (1) yields

$$\frac{1}{r^2}\left[Y\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{R}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{R}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right] + \frac{2m}{\hbar^2}(E-V) = 0 \quad \text{— (3)}$$

Dividing both sides of (3) by (2) yields

$$\frac{1}{r^2}\left[\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{1}{Y\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{Y\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right] + \frac{2m}{\hbar^2}(E-V) = 0 \quad \text{— (4)}$$

multiply through by r^2 yields

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{1}{Y\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{dY}{d\theta}\right) + \frac{1}{Y\sin^2\theta}\frac{d^2Y}{d\phi^2} + \frac{2mr^2}{\hbar^2}(E-V) = 0 \quad \text{— (5)}$$

Now separating the variables we have

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2mr^2}{\hbar^2}(E-V)=$$

$$=-\frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right] \quad (5)$$

Since the RHS of (5) depends only on θ and the LHS depends only on θ & ϕ ~~then~~ both sides must be equal ~~to~~ constant. Let ~~the constant~~ be λ thus the radial part of (5) is given by

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2mr^2}{\hbar^2}(E-V)=\lambda$$

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left[\frac{2mr^2}{\hbar^2}(E-V)-\lambda\right]R=0 \quad (7)$$

The angular part of (5) is given by

$$-\frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{dY}{d\theta}\right)+\frac{1}{\sin^2\theta}\frac{d^2Y}{d\phi^2}\right]=\lambda$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}+\lambda Y=0 \quad (8)$$

Now let $Y(\theta,\phi)=\Theta(\theta)\,\Phi(\phi)$ — (9)

Now putting eqn (9) into (8) yields

$$\frac{\Phi}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{\Theta}{\sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2}+\lambda\Theta\Phi=0 \quad (10)$$

Dividing (10) through by Y yields

$$\frac{1}{\Theta\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{d\Theta}{\partial\theta}\right)+\frac{1}{\Phi\sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2}+\lambda=0 \quad (11)$$

Now separating the variables yields

$$\frac{1}{\Theta\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\lambda=-\frac{1}{\Phi\sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2} \quad (12)$$

multiplying ~~both sides of (32)~~ by $\sin\theta$ yields

$$\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \lambda\sin^2\theta = -\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}$$

(33)

Since the LHS of (33) depends only on θ ~~and the RHS~~ only on ϕ, thus both sides must be equal to a constant, then let the constant be ν, thus (33) becomes

$$-\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = \nu$$

$w = \cos\theta$

$d/d\theta$

$$\frac{d^2\Phi}{d\phi^2} = -\nu\Phi$$

$$\frac{d^2\Phi}{d\phi^2} + \nu\Phi = 0 \quad (34)$$

$$\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \lambda\sin^2\theta = \nu$$

$$\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \left[\lambda\sin^2\theta - \nu\right]\Theta = 0$$

$$\frac{d}{d\theta} = -\sin\theta\frac{d}{dw} \quad (35)$$

let $w = \cos\theta$ $\quad \frac{d}{d\theta} = \frac{d}{dw}\frac{dw}{d\theta} = -\sin\theta\frac{d}{dw}$

$w = \cos\theta$ $\quad \frac{d}{d\theta} = \frac{d}{dw}\frac{dw}{d\theta}$ $\quad \frac{d}{d\theta} = -\sin\theta\frac{d}{dw}$

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \left[\lambda - \frac{\nu}{\sin^2\theta}\right]\Theta = 0$$

$$\frac{-\sin\theta}{\sin\theta}\frac{d}{dw}\left[\sin\theta\left(-\sin\theta\frac{d}{dw}\right)\Theta\right] + \left[\lambda - \frac{\nu}{\sin^2\theta}\right]\Theta = 0$$

$$\frac{d}{dw}\left(\sin^2\theta\frac{d\Theta}{dw}\right) + \left(\lambda - \frac{\nu}{\sin^2\theta}\right) = 0$$

let $\sin^2\theta = 1 - \cos^2\theta = 1 - w^2$

$$\frac{d}{dw}\left[(1-w^2)\frac{d\Theta}{dw}\right] + \left[\lambda - \frac{\nu}{(1-w^2)}\right]\Theta = 0$$

$\Theta \rightarrow P$

$$\frac{d}{dw}\left[(1-w^2)\frac{dP}{dw}\right] + \left[\lambda - \frac{\nu}{(1-w^2)}\right]P = 0$$

* $\Theta = P$

$B = \lambda$.

WAVE EQN FOR HYDROGEN ATOM

P. Sam

The P.E for H-atom

$$V(r) = \frac{-ze^2}{r} \quad (1)$$

eqn (1) represents the attractive columb interaction between the nucleus of $+ze$ and e^-.

Regarding the hydrogen atom as system of two charge particle of masses m_1 and m_2 between which Columbic forces are operative, the hamiltonian for the total system can be written as

$$H\psi = E\psi$$

$$H = \frac{\hbar^2}{2m}\nabla^2\psi + V\psi$$

for two masses m_1 & m_2

$$H = \frac{-\hbar^2}{2}\left[\frac{\nabla_1^2}{m_1} + \frac{\nabla_2^2}{m_2}\right]\psi + V\psi$$

$$H = -\frac{\hbar^2}{2}\left[\frac{\nabla_1^2}{m_1} + \frac{\nabla_2^2}{m_2}\right] + V(x_1, y_1, z_1, x_2, y_2, z_2) \quad (2)$$

but

$$H_T\psi_T = E_T\psi_T$$

substituting eqn (2) into the above and defining ∇_1^2 & ∇_2^2 yields

$$-\frac{\hbar^2}{2m_1}\left[\frac{\partial^2\psi_T}{\partial x_1^2} + \frac{\partial^2\psi_T}{\partial y_1^2} + \frac{\partial^2\psi_T}{\partial z_1^2}\right] - \frac{\hbar^2}{2m_2}\left[\frac{\partial^2\psi_T}{\partial x_2^2} + \frac{\partial^2\psi_T}{\partial y_2^2} + \frac{\partial^2\psi_T}{\partial z_2^2}\right]$$

$$+\left[V(x_1, y_1, z_1, x_2, y_2, z_2) - E_T\right]\psi_T = 0 \quad (3)$$

where ψ_T is the wave function for the total system. eqn (3) is called the six dimensional hydrogen atom

Remark

(i) The potential energy depends only on relative coordinate i.e $V(r)$

$V = V(x_1 - x_2, y_1 - y_2, z_1 - z_2)$ since the force exerted by the proton and the electron on each other are directed

$$H_T = \left[\frac{-\hbar^2}{2m_1}\left(\frac{\partial^2\psi}{\partial x_1^2} + \frac{\partial^2\psi}{\partial y_1^2} + \frac{\partial^2\psi}{\partial z_1^2}\right) + \frac{\hbar^2}{2m_2}\left(\frac{\partial^2\psi}{\partial x_2^2}\right.\right.$$

p. sam

(2) The six coordinate of the electron and the proton are replaced by the three relative coordinate x, y, z and the three coordinate X, Y, Z of the centre of mass defined by along a straight line joining them

$$\left.\begin{aligned} x &= x_1 - x_2 \\ y &= y_1 - y_2 \\ z &= z_1 - z_2 \end{aligned}\right\} \quad \text{——} (4)$$

$$\left.\begin{aligned} X &= \frac{m_1 x_1 + x_2 m_2}{M} \\ Y &= \frac{m_1 y_1 + m_2 y_2}{M} \\ Z &= \frac{m_1 z_1 + m_2 z_2}{M} \end{aligned}\right\} \quad \text{——} (5)$$

Using (3), (4) and (5) we have

$$\frac{\partial \psi_T}{\partial x_1} = \frac{\partial \psi_T}{\partial X}\frac{\partial X}{\partial x_1} + \frac{\partial \psi_T}{\partial x}\frac{\partial x}{\partial x_1} \quad \text{——} (6)$$

From (4) & (5)

$$\left.\begin{aligned} \frac{\partial X}{\partial x_1} &= \frac{m_1}{M} \\ \frac{\partial x}{\partial x_1} &= 1 \end{aligned}\right\} \quad (6a)$$

substituting (6a) into (6) yields

$$\frac{\partial \psi_T}{\partial x_1} = \left[\frac{\partial}{\partial X}\left(\frac{m_1}{M}\right) + \frac{\partial}{\partial x}(1)\right]\psi_T$$

$$= \left(\frac{m_1}{M}\frac{\partial}{\partial X} + \frac{\partial}{\partial x}\right)\psi_T \quad \text{——} (7)$$

$$\frac{\partial^2 \psi_T}{\partial x_1^2} = \left(\frac{m_1^2}{M^2}\frac{\partial^2}{\partial X^2} + \frac{2m_1}{M}\frac{\partial^2}{\partial x \partial X} + \frac{\partial^2}{\partial x^2}\right)\psi_T \quad \text{——} (7a)$$

(35)

$|V - \omega^2 T| = 0$

$|A - \lambda x| = 0$

p. 5

also

$$\frac{\partial \psi_T}{\partial x_2} = \frac{\partial \psi_T}{\partial X}\frac{\partial X}{\partial x_2} + \frac{\partial \psi_T}{\partial x}\frac{\partial x}{\partial x_2} \qquad \text{— 7(b)}$$

$$\frac{\partial \psi_T}{\partial x_2} = \left(\frac{m_2}{M}\frac{\partial}{\partial X} - \frac{\partial}{\partial x}\right)\psi_T$$

$$\frac{\partial^2 \psi_T}{\partial x^2} = \left[\frac{m_2^2}{M^2}\frac{\partial^2}{\partial X^2} - \frac{2m_2}{M}\frac{\partial^2}{\partial x\,\partial X} + \frac{\partial^2}{\partial x^2}\right]\psi_T \qquad \text{— (8)}$$

Similarly,

$$\frac{\partial^2 \psi_T}{\partial y_1^2} = \left[\frac{M_2^2}{M^2}\frac{\partial^2}{\partial Y^2} + \frac{2m_1}{M}\frac{\partial^2}{\partial y\,\partial Y} + \frac{\partial^2}{\partial y^2}\right]\psi_T \qquad \text{— (9)}$$

$$\frac{\partial^2 \psi_T}{\partial y_2^2} = \left[\frac{m_2^2}{M^2}\frac{\partial^2}{\partial Y^2} - \frac{2m_1}{M}\frac{\partial^2}{\partial y\,\partial Y} + \frac{\partial^2}{\partial y^2}\right]\psi_T \qquad \text{— (10)}$$

also

$$\frac{\partial^2 \psi_T}{\partial z_1^2} = \left[\frac{m_1^2}{M^2}\frac{\partial^2}{\partial Z^2} + \frac{2m_1}{M}\frac{\partial^2}{\partial z\,\partial Z} + \frac{\partial^2}{\partial z^2}\right]\psi_T \qquad \text{— (11)}$$

$$\frac{\partial^2 \psi_T}{\partial z_2^2} = \left[\frac{m_1^2}{M^2}\frac{\partial^2}{\partial Z^2} - \frac{2m_1}{M}\frac{\partial^2}{\partial z\,\partial Z} + \frac{\partial^2}{\partial z^2}\right]\psi_T \qquad \text{— (12)}$$

Multiplying both sides of 7(a) by M/m_1 and 8 by M/m_2 we get

$$\frac{M}{m_1}\frac{\partial^2 \psi_T}{\partial x_1^2} = \frac{M}{m_1}\left[\frac{m_1^2}{M^2}\frac{\partial^2}{\partial X^2} + \frac{2m_1}{M}\frac{\partial^2}{\partial x\,\partial X} + \frac{\partial^2}{\partial x^2}\right]\psi_T$$

$$= \left[\frac{m_1}{M}\frac{\partial^2}{\partial X^2} + \frac{2\,\partial^2}{\partial x\,\partial X} + \frac{M}{m_1}\frac{\partial^2}{\partial x^2}\right]\psi_T \qquad \text{— (13)}$$

and

$$\frac{M}{m_2}\frac{\partial^2 \psi_T}{\partial x_2^2} = \left[\frac{m_2}{M}\frac{\partial^2}{\partial X^2} - \frac{2\,\partial^2}{\partial x\,\partial X} + \frac{M}{m_2}\frac{\partial^2}{\partial x^2}\right]\psi_T \qquad \text{— (14)}$$

Now adding eqn (13) and (14)

p.saw

$$M\left(\frac{1}{m_1}\frac{\partial^2\psi_T}{\partial x_1^2}+\frac{1}{m_2}\frac{\partial^2\psi_T}{\partial x_2^2}\right) = \frac{m_1}{M}\frac{\partial^2\psi_T}{\partial X^2} + \cancel{2\frac{\partial^2\psi_T}{\partial x\,\partial X}}$$

$$+\frac{M}{m_1}\frac{\partial^2\psi_T}{\partial x^2}+\frac{m_2}{M}\frac{\partial^2\psi_T}{\partial X^2} - \cancel{2\frac{\partial^2\psi_T}{\partial x\,\partial X}}$$

$$+\frac{M}{m_2}\frac{\partial^2\psi_T}{\partial x^2}$$

$$=\frac{m_1}{M}\frac{\partial^2\psi_T}{\partial X^2}+\frac{M}{m_1}\frac{\partial^2\psi_T}{\partial x^2}+\frac{m_2}{M}\frac{\partial^2\psi_T}{\partial X^2}+\frac{M}{m_2}\frac{\partial^2\psi_T}{\partial x^2}$$

$$=\frac{1}{M}\left(m_1\frac{\partial^2\psi_T}{\partial X^2}+m_2\frac{\partial^2\psi_T}{\partial X^2}\right)+$$

$$M\left(\frac{1}{m_1}\frac{\partial^2\psi_T}{\partial x^2}+\frac{1}{m_2}\frac{\partial^2\psi_T}{\partial x^2}\right)$$

$$=\frac{1}{M}(m_1+m_2)\frac{\partial^2\psi_T}{\partial X^2}+M\left(\frac{1}{m_1}+\frac{1}{m_2}\right)\frac{\partial^2\psi_T}{\partial x^2}$$

$$=\frac{1}{M}(m_1+m_2)\frac{\partial^2\psi_T}{\partial X^2}+M\left(\frac{m_1+m_2}{m_1 m_2}\right)\frac{\partial^2\psi_T}{\partial x^2} \qquad (15)$$

where $M=\sum m_i = m_1+m_2$

$$\frac{1}{\mu}=\frac{m_1+m_2}{m_1 m_2}$$

Then eqn (15) becomes

$$M\left[\frac{1}{m_1}\frac{\partial^2\psi_T}{\partial x_1^2}+\frac{1}{m_2}\frac{\partial^2\psi_T}{\partial x_2^2}\right]=\cancel{\frac{M}{M}}\frac{\partial^2\psi_T}{\partial X^2}+\frac{M}{\mu}\frac{\partial^2\psi_T}{\partial x^2}$$

$$M\left[\frac{1}{m_1}\frac{\partial^2\psi_T}{\partial x_1^2}+\frac{1}{m_2}\frac{\partial^2\psi_T}{\partial x_2^2}\right]=\frac{\partial^2\psi_T}{\partial X^2}+\frac{M}{\mu}\frac{\partial^2\psi_T}{\partial x^2}$$

dividing through by M yields

$$\frac{1}{m_1}\frac{\partial^2\psi_T}{\partial x_1^2}+\frac{1}{m_2}\frac{\partial^2\psi_T}{\partial x_2^2}=\frac{1}{M}\frac{\partial^2\psi_T}{\partial X^2}+\frac{1}{\mu}\frac{\partial^2\psi_T}{\partial x^2} \qquad (16)$$

p. 5a

Similarly

$$\frac{1}{m_1}\frac{\partial^2\psi_T}{\partial y_1^2}+\frac{1}{m_2}\frac{\partial^2\psi_T}{\partial y_2^2}=\frac{1}{M}\frac{\partial^2\psi_T}{\partial Y^2}+\frac{1}{\mu}\frac{\partial^2\psi_T}{\partial y^2} \quad (17)$$

Also

$$\frac{1}{m_1}\frac{\partial^2\psi_T}{\partial z_1^2}+\frac{1}{m_2}\frac{\partial^2\psi_T}{\partial z_2^2}=\frac{1}{M}\frac{\partial^2\psi_T}{\partial Z^2}+\frac{1}{\mu}\frac{\partial^2\psi_T}{\partial z^2} \quad (18)$$

Putting eqn (16) (17) & (18) into (3) we get

$$\left(-\frac{\hbar^2}{2\mu}\nabla^2_{xyz}-\frac{\hbar^2}{2M}\nabla^2_{XYZ}\right)\psi_T + \left(V(x,y,z)-E_T\right)\psi_T=0 \quad (19)$$

Using the separation of variable method

let $\psi_T=\psi(x,y,z)\phi(X,Y,Z)$ (20)

Substituting (20) into (19) yields

$$\left(-\frac{\hbar^2}{2\mu}\phi\nabla^2_{xyz}\psi-\frac{\hbar^2}{2M}\psi\nabla^2_{XYZ}\phi\right) + \left(V(x,y,z)-E_T\right)\psi\phi=0 \quad (21)$$

Dividing both sides of (21) by (20) yields

$$-\frac{\hbar^2}{2\mu}\frac{1}{\psi}\nabla^2_{xyz}\psi-\frac{\hbar^2}{2M}\frac{1}{\phi}\nabla^2_{XYZ}\phi + \left(V_{x,y,z}-E_T\right)=0 \quad (22)$$

Now separating the variables yields

$$\Phi\left[-\frac{\hbar^2}{2\mu}\nabla^2_{x,y,z}+V_{xyz}\right]\psi=-\frac{1}{\Phi}\left[-\frac{\hbar^2}{2M}\nabla^2_{XYZ}-E_T\right]\Phi$$

(23)

Since ψ the LHS depends only on ψ and the RHS depends only on Φ, let both sides be constant, let the constant be E

$$\frac{1}{\psi}\left[-\frac{\hbar^2}{2\mu}\nabla^2_{x,y,z}+V_{x,y,z}\right]\psi=E$$

(24)

and

$$-\frac{1}{\Phi}\left[-\frac{\hbar^2}{2M}\nabla^2_{XYZ}-E_T\right]\Phi=E$$

(25)

from (24)

$$\left[-\frac{\hbar^2}{2\mu}\nabla^2_{x,y}+V_{x,y,z}\right]\psi=E\psi$$

from (25)

$$\left[-\frac{\hbar^2}{2M}\nabla^2_{XYZ}-E_T\right]\Phi=-E\Phi$$

(27)

from (26)

$$-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right)+\left(V_{(x,y,z)}-E\right)\psi=0$$

(28)

from (27)

$$-\frac{\hbar^2}{2M}\left(\frac{\partial^2\Phi}{\partial X^2}+\frac{\partial^2\Phi}{\partial Y^2}+\frac{\partial^2\Phi}{\partial Z^2}\right)+(E-E_T)\Phi=0$$

(29)

Equation (28) and (29) are the two 3-dimensional separate equations of the hydrogen atom.

Comment / Remark

(1) Eqn 29 tells us that the centre of mass of the system moves like a free particle of mass M and translational $(E_T - E)$, so that E is the internal energy.

(2) The particle is in a central potential i.e. the potential depends only upon r of the particle from the centre of force and not upon the direction of the vector $\vec{r}$.

(3) Since the Hamiltonian has spherical symmetry we can apply the spherical polar coordinate - Eqn (28) becomes

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi$$

$$+ (V_{(r)} - E)\psi = 0$$

$$\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi$$

$$+ [E - V_{(r)}] = 0 \quad \text{—— (30)}$$

Let $\psi(r,\theta,\phi) = R(r)\,X(\theta,\phi)$ —— (31)

putting 31 into 30

$$\frac{\hbar^2}{2\mu r^2}\left[X\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{R}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial X}{\partial\theta}\right) + \frac{R}{\sin^2\theta}\frac{\partial^2 X}{\partial\phi^2}\right]$$

$$+ [E - V(r)]RX = 0$$

—— (32)

dividing eqn 32 by 31 yields

$$\frac{\hbar^2}{2\mu r^2}\left\{\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial X}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 X}{\partial\phi^2}\right]\frac{1}{X}\right\}$$

$$+ (E - V(r)) = 0 \quad \text{—— (33)}$$

Multiplying (33) by $2\mu r^2/\hbar^2$

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{1}{X}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial X}{\partial\theta}\right] + \frac{1}{\sin^2\theta}\frac{\partial^2 X}{\partial\phi^2}\right)$$

$$+ \frac{2\mu r^2}{\hbar^2}\left[E - V(r)\right] = 0$$

Separating the variables yields

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2\mu r^2}{\hbar^2}\left(E-V(r)\right)=$$

$$-\frac{1}{Y}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right) \quad (35)$$

Since the LHS of (35) depends only on r & RHS on θ & ϕ, each must be equal to constant (β)

Hence

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2\mu r^2}{\hbar^2}\left(E-V(r)\right)=\beta$$

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\left[\frac{2\mu r^2}{\hbar^2}\left(E-V(r)\right)-\beta\right]R=0$$

dividing through by r^2 yields

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\left(\frac{2\mu}{\hbar^2}\left(E-V(r)\right)-\frac{\beta}{r^2}\right)R=0 \quad (36)$$

also

$$\frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right]=-\beta$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}+\beta Y=0 \quad (37)$$

from (36)

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\left[\frac{2\mu}{\hbar^2}\left(E-V(r)\right)-\frac{\beta}{r^2}\right]R=0$$

let $\beta = l(l+1)$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\left[\frac{2\mu}{\hbar^2}\left(E-V(r)\right)-\frac{l(l+1)}{r^2}\right]R=0 \quad (38)$$

Putting eqn (1) into (38) yields

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\left[\frac{2\mu}{\hbar^2}E+\frac{2Ze^2\mu}{\hbar^2 r}-\frac{l(l+1)}{r^2}\right]R=0$$

Since only E correspond to bound and introducing a new parameter n and a new variable ρ i.e.

(41)

$$n = \frac{Ze^2}{\hbar}\left(\frac{\mu}{2|E|}\right)^{\frac{1}{2}}$$

$$\rho = \left(\frac{8\mu|E|}{\hbar}\right)^{\frac{1}{2}} r \quad \text{— (40)}$$

Hence

$$r = \frac{\rho}{\left(8\mu|E|/\hbar^2\right)^{\frac{1}{2}}}$$

3i Con cas the case $E < 0$

differentiating eqn (39)

$$\frac{1}{r^2}\left[r^2\frac{\partial^2 R}{\partial r^2} + 2r\frac{\partial R}{\partial r}\right] + \left[\frac{2\mu E}{\hbar^2} + \frac{2Ze^2\mu}{\hbar^2 r} - \frac{l(l+1)}{r^2}\right]R = 0$$

$$\frac{\partial^2 R}{\partial r^2} + \frac{2}{r}\frac{\partial R}{\partial r} + \left[\frac{2\mu E}{\hbar^2} + \frac{2Ze^2\mu}{\hbar^2 r} - \frac{l(l+1)}{r^2}\right]R = 0 \quad \text{— (41)}$$

putting eqn (40) into (41) yields

$$\frac{\partial^2 R}{\partial \rho^2} + \frac{2}{\rho}\frac{\partial R}{\partial \rho} + \left[\frac{2\mu E}{\hbar^2} + \frac{2Ze^2\mu}{\hbar^2 \rho}\left(\frac{8\mu|E|}{\hbar^2}\right)^{\frac{1}{2}} - \frac{l(l+1)}{r^2}\right]R = 0 \quad \text{— (42)}$$

$$\frac{\partial^2 R}{\partial \rho^2} + \frac{2}{\rho}\frac{\partial R}{\partial \rho} + \left[-\frac{1}{4} + \frac{n}{\rho} - \frac{l(l+1)}{\rho^2}\right]R = 0 \quad \text{— (43)}$$

where ρ range from 0 to ∞

Energy Level Asymptotic Solutions Of The Hydrogen Atom

The behaviours of $R(\rho)$ in the Asymptotic region $\rho \to \infty$ is determined by

$$\frac{d^2 R}{d\rho^2} - \frac{1}{4} R = 0$$

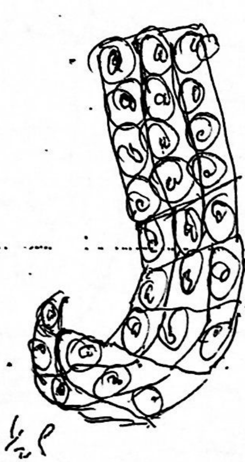
$$\frac{d^2 R}{d\rho^2} - \frac{1}{4} R = 0 \quad \text{--- (44)}$$

$$m^2 - 1/4 = 0$$

$$m^2 = \frac{1}{4} \quad m = \pm\frac{1}{2}$$

$$R(\rho) = A e^{\pm\frac{1}{2}\rho}$$

$$R(\rho) = A e^{\frac{1}{2}\rho} + B e^{-\frac{1}{2}\rho} \quad \text{--- (45)}$$



Thus for (44) we seek a finite solution of the form

$$A(\rho)\, e^{-\frac{\rho}{2}}$$

where $A(\rho)$ is a polynomial of finite order in ρ. Hence the general solution of $A(\rho)$ is

$$A(\rho) = \rho^k (b_0 + b_1\rho + b_2\rho^2 + b_3\rho^3 + \cdots)$$

$$= \rho^k F(\rho) \qquad b_0 \neq 0$$

where $F(\rho) = b_0 + b_1\rho + b_2\rho^2 + b_3\rho^3 + \cdots$

k is not negative in order that $R(\rho)$ will not divert at $\rho = 0$

Let's try a solution of the form

$$R(\rho) = e^{-\frac{\rho}{2}} \rho^l F(\rho) = S F(\rho) \quad \text{--- (46)}$$

where $S = e^{-\frac{\rho}{2}} \rho^l$

so that $R' = SF' + \left(-\frac{1}{2} + \frac{l}{\rho}\right) SF$

55

P. Sam

$$R' = SF'' + 2\left(-\tfrac{1}{2} + \tfrac{l}{\rho}\right)SF' + \left(\tfrac{1}{4} - \tfrac{1}{\rho} + \tfrac{l^2}{\rho^2} - \tfrac{l}{\rho^2}\right)SF$$

Putting (48) into (43) gives

$$\rho F'' + \left[(2l+1) + 1 - \rho\right]F' + (n-l-1)F = 0 \quad (48)$$

Comparing eq with associated Legendre equation

$$x\frac{d^2}{dx^2}L_n^m(x) + (m+1-x)\frac{d}{dx}L_n^m(x) + (n-m)L_n^m(x) = 0 \quad (50)$$

Suggest that $F(\rho)$ may be identify with $L_k^p(\rho)$ provided $p = (2l+1)$

$$k = \rho + n - l - 1 = n + l \quad (51)$$

$$F(\rho) = L_{n+l}^{2l+1}(\rho) \quad (52)$$

Both p and k must be equal to zero or integer or $2l+1$ and $n+l$. Thus the associated Legendre polynomial is

$$L_n^m(x) = \frac{d^m}{dx^m}L_n(x) = \frac{d^m}{dx^m}\left[e^x\frac{d^n}{dx^n}(x^n e^{-x})\right]$$

Therefore for $L_{n+l}^{2l+1}(\rho)$ not to vanish we should have $2l+1 \le n+l$ or $n \ge 1$

The lowest value of n follows that $n = 1, 2, 3 \ldots$

eq (52) satisfied the condition function

(44)

Energy Levels of Hydrogen Atom

From (40) we have

$$E_n = -\frac{\mu e^4 Z^2}{2n^2\hbar^2} \; ; \; n = 1, 2, 3 \ldots$$

Since

$$n = \frac{Ze^2}{\hbar}\left[\frac{\mu}{2|E|}\right]^{1/2}$$

$$\rho = \left[\frac{8\mu|E|}{\hbar^2}\right]^{1/2} r$$

then

$$n^2 = \frac{Z^2e^4}{\hbar^2}\,\frac{\mu}{2|E|}$$

using $|E|$ the subject

$$|E| = \frac{Z^2e^4\mu}{2\hbar^2n^2}$$

$$E_n = -\frac{Z^2e^4\mu}{2\hbar^2n^2}$$

$$\rho = \left[\frac{8\mu\left(\frac{Z^2e^4\mu}{2\hbar^2n^2}\right)}{\hbar^2}\right]^{1/2} r$$

$$= \left[\frac{4Z^2\mu^2e^4}{\hbar^4n^2}\right]^{1/2} r$$

$$= \frac{2Z\mu e^2}{\hbar^2 n}\, r$$

p. Sam

$$\rho = \frac{2Z}{n a_0} r$$

where $a_0 = \frac{\hbar^2}{\mu e^2}$

$$E_n = -\frac{m e^4}{8 \varepsilon_0 h^2} \cdot \frac{1}{n^2}$$ — (55)

(54) thus becomes

$$E_n = \frac{-\mu e^4 Z^2}{2n^2 \hbar^2} = \frac{-Z^2 e^2}{2n^2}\left(\frac{\mu e^2}{\hbar^2}\right)$$

$$= -\frac{Z^2 e^2}{2n^2} \cdot \frac{1}{a_0}$$

$$\therefore E_n = -\frac{Z^2 e^2}{2 a_0} \cdot \frac{1}{n^2}$$ — (56)

where $a_0 = \frac{4\pi \varepsilon_0 \hbar^2}{m e^2}$

the first Bohr radius

Hydrogen-like Eigen functions study

From 47 and (52) the radial function can be written as

$$R_{n,l}(r) = N_r \, e^{-\rho/2} \rho^l L^{2l+1}_{n+l}(\rho)$$ — (57)

And the normalized R is

$$R_{n,l}(r) = \left\{\left(\frac{2Z}{n a_0}\right)^3 \frac{n-l-1}{2n[(n+l)!]^3}\right\}^{1/2} e^{-\rho/2} \rho^l L^{2l+1}_{n+l}(\rho)$$ — (58)

where $N_r = \left\{\left(\frac{2Z}{n a_0}\right)^3 \frac{n-l-1}{2n[(n+l)!]^3}\right\}^{1/2}$

but from (58)

$$\rho = \frac{2Zr}{na_0}$$

$$\therefore a_0 = \frac{\hbar^2}{\mu e^2} = 0.53\times10^{-8}\text{ cm}$$

The first few radial functions are

$$R_{1,0}(r) = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$$

$$R_{20}(r) = \frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0}$$

$$R_{21}(r) = \frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0}\, e^{-Zr/2a_0}$$

The complete eigen functions

$$\psi_{n,l,m}(r,\theta,\phi) = R_{nl}(r)\, Y_{lm}(\theta)\, Z_m(\phi)$$

$$= C_{nlm}\, e^{-\rho/2} \rho^{l} L^{2l+1}_{n+l}(\rho)\, P^m_l(\cos\theta)\, e^{im\phi} \quad (59)$$

where

$$C_{nlm} = N_r N_\theta N_\phi$$

The ground eigen function is given by

$$\psi_{1,0,0} = C_{100}\, e^{-Zr/a_0}$$

$$= \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0} \quad (60)$$

Remarks / Comments

(1) Since ψ_{100} does not depends on θ and ϕ, the ground state of the hydrogen atom is spherical

symmetric
~~obtained~~
twice

C_{100} can also be directly obtained on integrating by parts

$$C_{100}^2\, 4\pi \int_0^\infty \left| e^{-Zr/a_0} \right|^2 r^2\, dr$$

$$= C_{100}^2\, \pi \left(\frac{a_0}{Z} \right)^3 = 1$$

(2) The states of hydrogen atom are refers to as s, p, d, f states according to the values 0, 1, 2, 3 of quantum number l

(3) The probability of finding the electron at a distance between r and $r + dr$ from the origin is

$$|\psi_{100}|^2\, 4\pi r^2\, dr$$

(4) The function $|\psi_{100}|^2 r^2 dr$ has a maximum at ~~ao~~ $r = a_0$ the Bohr radius of the first orbit. Therefore in the hydrogen atom, the electron is most likely to be found at a distance a_0 from the proton.

Degeneracy in H_2 Atom

From (54) and (55) we note the following

(1) ~~Eqn~~ Eqn (54) which is the wave function describing the electron in the hydrogen atom depends on three quantum numbers n, m, l

n and ... depends ~~...~~ only on l so ... w.r.t ... both are degenerate states with ... l and m different ... same n but l are degenerate and ... otherwise ... as accidental refers to
And thus accidental degeneracy is peculiar to Coulomb's field.

~~Concept of Parity~~
~~Rep ... for Parity~~
~~Operators~~

Using bracket notation to evaluate the integral

$B_n \ (n = 0, 1, 2)$ for $\psi = 1 - x^2$

$$\psi_0(\xi) = \left(\frac{1}{\pi^{1/2}}\right)^{1/2} e^{\xi/2} \quad (1)$$

$$\psi_0(\xi) = \left(\frac{1}{\pi}\right)^{1/4} e^{\xi/2}$$

But $\xi = \alpha^{1/2} x = \sqrt{\alpha}\, x$

$$\psi_0(x) = \left(\frac{1}{\pi}\right)^{1/4} e^{\alpha^{1/2} x/2}$$

Heisenberg favours classical mechanics because it present quantitative approach in which dynamic variables such as the coordinate momentum component and energy of a particle appears in the equation of motion

$$\psi_n(\xi) = \left(\frac{1}{\pi^{1/2} 2^n n!}\right)^{1/2} e^{\xi/2} H_n(\xi)$$

$$\psi_1(\xi) = \left(\frac{1}{\pi^{1/2} 2^1 1!}\right)^{1/2} e^{\xi/2} H_1(\xi)$$

$$\psi_n(\xi) = \left(\frac{1}{\pi^{1/2} 2^n n!}\right)^{1/2} e^{1/2} H_n(\xi)$$

$$\psi_1(x) = \left(\frac{1}{2\pi^{1/2}}\right)^{1/2} e^{\alpha^{1/2} x/2} \quad 2\alpha^{1/2} x$$

$$\psi_2(\xi) = \left(\frac{1}{\pi^{1/2} 2^n 2!}\right)^{1/2} e^{\xi/2} H_2(\xi)$$

$$\psi_1(x) = \left(\frac{1}{2\pi^{1/2}}\right)^{1/2} e^{\alpha^{1/2} x/2} \alpha^{1/2} x$$

$$\psi_2(\xi) = \left(\frac{1}{\pi^{1/2} 8}\right)^{1/2} e^{\xi/2} (2 - 4\alpha^{1/2} x)$$

$$\psi_1(x) = \left(\frac{1}{4\pi}\right)^{1/4} 2x\, \alpha^{1/2} e^{\alpha^{1/2} x}$$

$$\psi_2(\xi) = \left(\frac{1}{64\pi}\right)^{1/4} e^{\alpha x/2} 2 - \left(\frac{1}{64\pi}\right)^{1/4} e^{\alpha x/2} 4x\alpha^{1/2}$$

$$\psi_1(x) = \left(\frac{2^4}{4\pi}\right)^{1/4} x\, \alpha^{1/2} e^{\alpha^{1/2} x} \qquad \rho = \sqrt{\frac{8\mu|E|}{\hbar^2}}$$

$$\psi_2(x) = \left(\frac{16}{64\pi}\right)^{1/4} e^{\alpha^{1/2} x/2} - \left(\frac{256}{64\pi}\right)^{1/4} e^{\alpha^{1/2} x/2} \alpha^{1/2} x$$

$$\psi_1(x) = \left(\frac{16}{4\pi}\right)^{1/4} x\, \alpha^{1/2} e^{\alpha^{1/2} x}$$

$$\psi_1(x) = \left(\frac{4}{\pi}\right)^{1/4} x\, \alpha^{1/2} e^{\alpha^{1/2} x} \qquad \rho = \sqrt{\frac{8\mu|E|}{\hbar^2}} \qquad \psi_2(x) = \left(\frac{1}{4\pi}\right)^{1/4} e^{\alpha^{1/2} x/2} - \left(\frac{4}{\pi}\right)^{1/4} x\, \alpha^{1/2} e^{\alpha^{1/2} x/2}$$

$$B_0 = \int_{-\infty}^{\infty} \psi_{0(x)} \psi^*_{2(x)}\, dx$$

$$= \int_{-\infty}^{\infty} \left(\frac{1}{\pi}\right)^{1/4} e^{\frac{\alpha^{1/2} x}{2}} (1 - x^2)\, dx$$

$$= \int_{-\infty}^{\infty} \left(\frac{1}{\pi}\right)^{1/4} e^{\frac{\alpha^{1/2} x}{2}} dx - \int x^2 \left(\frac{1}{\pi}\right)^{1/4} e^{\frac{\alpha^{1/2} x}{2}} dx$$

$$= \left(\frac{1}{\pi}\right)^{1/4} \int_{-\infty}^{\infty} e^{\frac{\alpha^{1/2} x}{2}} dx - \left(\frac{1}{\pi}\right)^{1/4} \int_{-\infty}^{\infty} x^2 e^{\frac{\alpha^{1/2} x}{2}} dx$$

$B_1 = ?$

$B_2 = ?$

Unitary Transformations

This is a linear homogeneous transformation which preserves length and angles. These ~~is~~ scalar (inner) product are invariant. It ~~involve~~ the connection between two basis ψ_n and ψ_m.

$\Longrightarrow$ Geometrical Interpretation.

$$\text{if} \quad f = \sum_n f_n \psi_n \qquad (1)$$

$$f_m = (\psi_n, f) \qquad (2)$$

$$(\psi_n, f) = \langle \psi_n | f \rangle$$

The geometrical interpretation is a rotation in the space spanned by the basic vector ψ_n as given by the equation above.

Eqn (2) can also be written as

$$f_n = (\varphi_n, F) = \langle \varphi_n | F \rangle = \int_{-\infty}^{\infty} \varphi_n^*(x) F(x)$$

or

$$f_n = \int_{-\infty}^{\infty} \varphi_n^* F \, d\tau$$

where $d\tau$ is volume element

Using unitary transformation

let $\Omega|\omega\rangle = \omega|\omega\rangle$ —— (1)

where Ω is an hermitian operator and $|\omega\rangle$ is an eigen state with eigen value ω.

Taking the inner product of eqn (1) with the bra $\langle\omega|$ yields

$$\langle\omega|\Omega|\omega\rangle = \langle\omega|\omega|\omega\rangle \quad \text{—— (2)}$$

Taking the adjoint of (2) yields

$$\langle\omega|\Omega^+|\omega\rangle = \omega^* \langle\omega|\omega\rangle \quad \text{—— (3)}$$

but Ω is hermitian operator

then $\Omega^+ = \Omega = \Omega^*$

$$\langle\omega|\Omega|\omega\rangle = \omega^* \langle\omega|\omega\rangle \quad \text{—— (4)}$$

equating (2) and (4) yields

$$\omega\langle\omega|\omega\rangle = \omega^* \langle\omega|\omega\rangle$$

$$\omega\langle\omega|\omega\rangle - \omega^* \langle\omega|\omega\rangle = 0$$

$$(\omega - \omega^*)\langle\omega|\omega\rangle = 0$$

$$\langle\omega|\omega\rangle \neq 0$$

$$\therefore \omega - \omega^* = 0$$

$$\omega = \omega^*$$

therefore ω is hermitian and real.

$\bar{\Phi}(r,\theta) = f(r,\theta)\, e^{\pm 2\pi i c}$

Using Euler formula

$\Phi(r,\theta) = f(r,\theta)\left[\cos 2\pi c \pm i \sin 2\pi c\right]$

$\Phi(\phi) = f(r,\theta)\, e^{ic\phi}$

$\Phi(\phi) = f(r,\theta)\, e^{ic\phi}$

$$\frac{\sin\theta}{\Phi}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Phi}{\partial\theta}\right) + \beta\sin^2\theta = c^2$$

$$\frac{1}{Z}\frac{d^2 Z}{d\phi^2} = -c^2$$

$$\frac{d^2 Z}{d\phi^2} + c^2 Z = 0$$

$$Z(\phi) = f(r,\theta)\, e^{\pm i c\phi}$$

for Z to be a single value it must have the same value for $\phi = 0$ & $\phi = 2\pi$.

$$Z(0) = Z(2\pi)$$

$$H = \tfrac{1}{2} m \dot{x}^2 + V(x)$$

(a) $[H, x]$ (b) $[x, [x, H]]$

(a) $H = \frac{1}{2} m \dot{x}^2 + V(x)$

$$= \frac{(m\dot{x})^2}{2m} + V(x)$$

$$= \frac{p^2}{2m} + V(x)$$

$$P_{op} = i\hbar \frac{\partial}{\partial x}$$

$$H_{op} = \frac{\left(-i\hbar \partial/\partial x\right)^2}{2m} + V(x)$$

$$H_{op} = \frac{i^2\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)$$

$$H_{op} = \frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)$$

(a) $[H, x]\psi = (Hx - xH)\psi$

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

$$= \frac{-\hbar^2}{2m}\frac{\partial^2(x\psi)}{\partial x^2} + \cancel{Vx\psi} + \frac{\hbar^2 x}{2m}\frac{\partial^2\psi}{\partial x^2} - \cancel{V(x)\psi}$$

$$= \cancel{-\frac{\hbar^2}{2m} x \frac{\partial^2\psi}{\partial x^2}} - \frac{\hbar^2}{2m}\psi\frac{\partial^2 x}{\partial x^2} + \cancel{\frac{\hbar^2}{2m}\frac{\partial\psi}{\partial x}}$$

$$= \frac{-\hbar^2}{2m}\psi\frac{\partial^2 x}{\partial x^2}$$

$$[H, x]\psi = \frac{-\hbar^2}{2m}\psi$$

$$[H, x] = -\frac{\hbar^2}{2m}$$

$$A_{m+1} = \left\{ J(J+1) - m^2 - m \right\}^{1/2} \hbar e^{i\delta}$$

where δ is phase shift.

Soln

$$J_\pm = J_x \pm i J_y \qquad (1)$$

Taking the norm of $J_+ |jm\rangle$ of eqn (1)

$$\| J_+ |jm\rangle \|^2 = \left(J_+ |jm\rangle^\dagger \right)\left(J_+ |jm\rangle \right)$$

$$= \langle jm | (J_+^\dagger J_+) | jm \rangle$$

$$= \langle jm | J_- J_+ | jm \rangle \qquad (2)$$

but $J_- J_+ = J^2 - J_z^2 - \hbar J_z \qquad (3)$

since $J^2 = J_x^2 + J_y^2 + J_z^2$

substituting eqn (3) into (2) yields

$$\| J_+ |jm\rangle \|^2 = \langle jm | J^2 - J_z^2 - \hbar J_z | jm \rangle \qquad (4)$$

but
$$\left.\begin{aligned} J^2 &= \hbar^2 j(j+1) \\ J_z &= \hbar m \end{aligned}\right\} \qquad (5)$$

Substituting (5) into (4) yields

$$\| J_+ |jm\rangle \|^2 = \hbar^2 j(j+1) - \hbar^2 m^2 - \hbar^2 m$$

$$\| J_+ |jm\rangle \| = \hbar \left[j(j+1) - m(m+1) \right]^{1/2} \qquad (6)$$

but $J_+ |jm\rangle$ is proportional to $|j, m+1\rangle$

Thus $J_+ |jm\rangle = |j, m+1\rangle \qquad (7)$

Hence eqn (6) becomes

$$[x,[x,H]] = [x[x,H] - [x,H]x]$$

$$= [x[x H_{op} - H_{op} x] - [xH_{op} - H_{op} x]x]$$

$$= \left(x, -\frac{\hbar^2}{2m}\right) - \left(-\frac{\hbar^2}{2m} x\right)$$

$$= \frac{-\hbar^2 x}{2m} + \frac{\hbar^2 x}{2m}$$

$$= 0$$

Proof that $[J_z, J_\pm] = \pm\hbar J_\pm$

$$[J_z, J_+] = \hbar J_+$$

$$[J_z, J_-] = -\hbar J_-$$

Proof

Recall $J_+ = J_x + iJ_y$

$$J_- = J_x - iJ_y$$

$$J_\pm = J_x \pm iJ_y$$

$$[J_x, J_y] = i\hbar J_z$$

$$[J_z, J_x] = i\hbar J_y$$

$$[J_y, J_z] = i\hbar J_x$$

Similarly $[J_y, J_x] = -i\hbar J_z$

$$[J_x, J_z] = -i\hbar J_y$$

$$[J_z, J_y] = -i J_x$$