

Chapter 4 Quantum Mechanics in Three Dimensions

- the four quantum numbers

4.1 Time-independent Schrödinger equation in spherical coordinates

➤ Laplacian

(i) One-dimension : $\hat{p} = -i\hbar \frac{\partial}{\partial x}$

Three-dimensions : $\mathbf{\hat{p}} = p_x \hat{i} + p_y \hat{j} + p_z \hat{k}$, p_x, p_y, p_z is component of $\mathbf{p}$

$$p_x \rightarrow -i\hbar \frac{\partial}{\partial x} , p_y \rightarrow -i\hbar \frac{\partial}{\partial y} , p_z \rightarrow -i\hbar \frac{\partial}{\partial z}$$

$$\mathbf{p} \rightarrow -i\hbar \nabla , \quad \nabla \equiv \frac{\partial}{\partial x} \hat{i} + \frac{\partial}{\partial y} \hat{j} + \frac{\partial}{\partial z} \hat{k}$$

(ii) from $\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V$

➡ $\hat{H} = \mathbf{p}^2/2m + V = -\frac{\hbar^2}{2m} \nabla^2 + V$

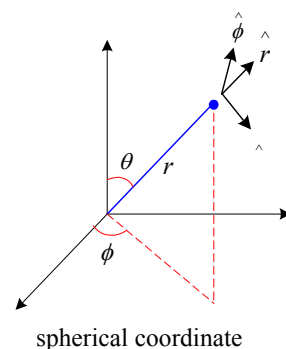
$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \text{ is Laplacian for Cartesian coordinates}$$

(iii) **Laplacian** for spherical coordinates

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \left(\frac{\partial^2}{\partial \phi^2} \right) \dots\dots\dots(4.1)$$

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V \Psi \quad V=V(\mathbf{r}, t) \quad \Psi = \Psi(\mathbf{r}, t)$$

normalization : $\int |\Psi|^2 d\mathbf{r} = 1$



➤ Time-independent Schrödinger equation

Let potential V is independent of time

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi \quad \dots\dots\dots(4.2)$$

$$\Psi_n(\mathbf{r}, t) = \psi_n(\mathbf{r}) e^{\frac{iE_n t}{\hbar}}, \quad \Psi(\mathbf{r}, t) = \sum c_n \psi_n(\mathbf{r}) e^{\frac{iE_n t}{\hbar}}$$

from equation (4.1),(4.2)

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2\psi}{\partial\phi^2}\right)\right] + V\psi = E\psi \quad \dots\dots\dots(4.3)$$

separation of variables :

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

$Y(\theta, \phi)$ is the spherically symmetric potentials, $V=V(r)$

potential only affects the $R(r)$

then equation (4.3)

$$\rightarrow -\frac{\hbar^2}{2m}\left[\frac{Y}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{R}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{R}{r^2\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right] + VRY = ERY$$

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

$$\rightarrow \left\{\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}[V(r) - E] = l(l+1) \quad \dots\dots\dots(4.4)\right.$$

$$\left.\frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right] = -l(l+1) \quad \dots\dots\dots(4.5)\right\}$$

➤ The angular equation

equation (4.5) is called angular equation

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

$$\rightarrow \sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{\partial^2 Y}{\partial \phi^2} = -l(l+1)Y \sin^2 \theta \quad \dots\dots\dots(4.6)$$

try **separation of variables** again :

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

$\Phi(\phi)$: azimuthal function

equation (4.6)

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

$$\rightarrow \left[\frac{1}{\Theta} \sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + l(l+1) \sin^2 \theta \right] + \frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = 0$$

$$\rightarrow \begin{cases} \frac{1}{\Theta} \sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + l(l+1) \sin^2 \theta = m^2 & \dots\dots\dots(4.7) \\ \frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = -m^2 & \dots\dots\dots(4.8) \end{cases}$$

(i) from equation (4.8) : $\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = -m^2 \quad \rightarrow \quad \Phi(\phi) = e^{im\phi}$

and $\Phi(\phi) = \Phi(\phi + 2\pi) \quad \rightarrow \quad e^{im\phi} = e^{im(\phi+2\pi)}$

$$\rightarrow \cos(m\phi)[\cos(2\pi m) - 1] - \sin(m\phi)\sin(2\pi m) + i\{\sin(m\phi)[\cos(2\pi m) - 1] + \cos(m\phi)\sin(2\pi m)\} = 0$$

$$\rightarrow \begin{cases} \cos(m\phi)[\cos(2\pi m) - 1] - \sin(m\phi)\sin(2\pi m) = 0 \\ \sin(m\phi)[\cos(2\pi m) - 1] + \cos(m\phi)\sin(2\pi m) = 0 \end{cases}$$

$$\rightarrow \cos(2\pi m) = 1, \quad \sin(2\pi m) = 0$$

$$\rightarrow m = 0, \pm 1, \pm 2, \dots\dots\dots$$

(ii) then equation (4.7)

$$\frac{1}{\Theta} \sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + l(l+1) \sin^2 \theta = m^2$$

$$\rightarrow \sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + [l(l+1) \sin^2 \theta - m^2] \Theta = 0 \quad \dots\dots\dots(4.9)$$

$$\rightarrow \Theta(\theta) = AP_l^m(\cos \theta)$$

$$\text{where } P_l^m(\cos \theta) = (1 - \cos^2 \theta)^{\frac{|m|}{2}} \left(\frac{d}{d(\cos \theta)} \right)^{|m|} P_l(\cos \theta)$$

$$\text{and } P_l(\cos \theta) = \frac{1}{2^l l!} \left(\frac{d}{d(\cos \theta)} \right)^l (\cos^2 \theta - 1)^l \quad \dots\dots\dots(4.10)$$

P_l^m is **associated Legendre function**
 P_l is **l th Legendre polynomial**

discussion:

(a) $P_l^m = P_l^{-m}$, $Y_l^{-m} = (-1)^m Y_l^m$

(b) from equation (4.10) , l must be a positive integer

(c) if $|m| > l$, $P_l^m = 0$

so given l , m has $(2l+1)$ possible value

$$m = -l, -l+1, \dots, -1, 0, 1, \dots, l-1, l$$

(d) spherical harmonics are orthonormal

$$\int_0^{2\pi} \int_0^\pi [Y_l^m]^* [Y_l^{m'}] \sin \theta d\theta d\phi = \delta_{ll'} \delta_{mm'}$$

➤ The radial equation

From equation (4.4)

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

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

let $u(r) = rR(r)$

$$\rightarrow \boxed{-\frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + \left[V + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \right] u = Eu} \dots\dots(4.11)$$

equation (4.11) is **radial equation**

discussion :

(a) normalize

$$\int_0^\infty |u|^2 dr = 1$$

(b) given a specific potential V , and solve (4.11)

example

the infinite spherical well $V(r) = \begin{cases} 0, & \text{if } r < a \\ \infty, & \text{if } r \geq a \end{cases}$

boundary conditions : $u(0) = u(a) = 0$

so inside the well : $\frac{d^2 u}{dr^2} = \left[\frac{l(l+1)}{r^2} - \frac{2mE}{\hbar^2} \right] u$

the easy situation $l = 0 \rightarrow \frac{d^2 u}{dr^2} = -k^2 u$, $k = \frac{\sqrt{2mE}}{\hbar}$

$$\rightarrow u(r) = A \sin(kr) + B \cos(kr)$$

$$\rightarrow R(r) = A \frac{1}{r} \sin(kr) + B \frac{1}{r} \cos(kr)$$

when $r \rightarrow 0$, $\frac{\cos(kr)}{r} \rightarrow \infty$ so $B = 0$

$$\rightarrow R(r) = A \frac{1}{r} \sin(kr)$$

for boundary condition $u(a) = 0$

$$\rightarrow \sin(ka) = 0 \rightarrow k = \frac{n\pi}{a}, n = 1, 2, 3, \dots$$

$$\text{energy } E_{nl} = E_{n0} = \frac{k^2 \hbar^2}{2m} = \frac{n^2 \pi^2 \hbar^2}{2ma^2}, n = 1, 2, 3, \dots$$

normalize :

$$\int_0^\infty |u(r)|^2 dr = \int_0^a |A \sin(n\pi/a)|^2 dr = 1$$

$$\longrightarrow A = \sqrt{\frac{2}{a}}$$

stationary state $\psi_{nlm} = \psi_{n00} = R(r)Y_0^0(\theta, \phi) = \sqrt{\frac{2}{a}} \frac{1}{r} \sin\left(\frac{n\pi}{a}r\right) \sqrt{\frac{1}{4\pi}}$

$$= \frac{1}{\sqrt{2a\pi}} \frac{1}{r} \sin\left(\frac{n\pi}{a}r\right)$$

summary

(a) energy depends only on n, l

there are $(2l+1)$ different wave function have same energy level

(b) normalize

$$\int |\psi|^2 d\mathbf{r} = \iiint |\psi|^2 r^2 \sin\theta dr d\theta d\phi = \int |R|^2 r^2 dr \int |Y|^2 \sin\theta d\theta d\phi = 1$$

normalize R, Y

$$\int_0^\infty |R|^2 r^2 dr = 1, \quad \int_0^{2\pi} \int_0^\pi |Y|^2 \sin\theta d\theta d\phi = 1$$

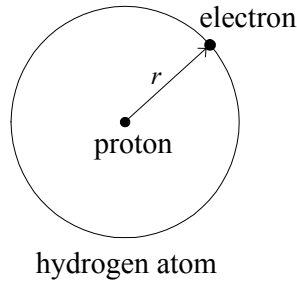
normalized Y function is **spherical harmonics**

and is $Y_l^m(\theta, \phi) = (-1)^m \sqrt{\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!}} e^{im\phi} P_l^m(\cos\theta)$

(c) stationary states are labeled by three **quantum numbers** (n, l, m)

4.2 Hydrogen atom

the Coulomb potential $V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}$, $Z = 1$ for hydrogen atom



➤ The radial wave function

$$\text{radial equation : } -\frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + \left[-\frac{e^2}{4\pi\epsilon_0 r} + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \right] u = Eu$$

for bound state $E < 0$, let $k = \frac{\sqrt{-2mE}}{\hbar}$ is real

$$\rightarrow \frac{1}{k^2} \frac{d^2 u}{dr^2} = \left[1 - \frac{me^2}{2\pi\epsilon_0 \hbar^2 k^2 r} + \frac{l(l+1)}{(kr)^2} \right] u$$

$$\text{let } \rho = kr, \quad \rho_0 = \frac{me^2}{2\pi\epsilon_0 \hbar^2 k}$$

$$\rightarrow \frac{d^2 u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2} \right] u \dots\dots\dots(4.12)$$

solve equation (4.12) as below

(i) see $\rho \rightarrow \infty$, it approximate

$$\frac{d^2 u}{d\rho^2} = u$$

$$\rightarrow u(\rho) = Ae^{-\rho} + Be^{\rho}$$

for large ρ , $B = 0$, $u(\rho) \approx Ae^{-\rho}$

(ii) see $\rho \rightarrow 0$, it approximate

$$\frac{d^2 u}{d\rho^2} = \frac{l(l+1)}{\rho^2} u$$

$$\rightarrow u(\rho) = C\rho^{l+1} + D\rho^{-1}$$

$$\text{for small } \rho, D=0, \quad u(\rho) \approx C\rho^{l+1}$$

(iii) now let $u(\rho) = \rho^{l+1} e^{-\rho} v(\rho)$

then equation (4.12) is :

$$\rho \frac{d^2 v}{d\rho^2} + 2(l+1-\rho) \frac{dv}{d\rho} + [\rho_0 - 2(l+1)]v = 0$$

use power series

$$v(\rho) = \sum_{j=0}^{\infty} a_j \rho^j$$

$$\rightarrow \sum_{j=0}^{\infty} j(j-1)a_j \rho^{j-1} + \sum_{j=0}^{\infty} 2(l+1)ja_j \rho^{j-1} - 2 \sum_{j=0}^{\infty} ja_j \rho^j + \sum_{j=0}^{\infty} [\rho_0 - 2(l+1)]a_j \rho^j = 0$$

$$\rightarrow \sum_{j=0}^{\infty} j(j+1)a_{j+1} \rho^j + \sum_{j=0}^{\infty} 2(l+1)(j+1)a_{j+1} \rho^j - 2 \sum_{j=0}^{\infty} ja_j \rho^j + [\rho_0 - 2(l+1)] \sum_{j=0}^{\infty} a_j \rho^j = 0$$

$$\rightarrow a_{j+1} = \frac{2(j+l+1) - \rho_0}{(j+1)(j+2l+2)} a_j \dots\dots\dots(4.13)$$

for large ρ corresponding to large j

$$\text{then } a_{j+1} \cong \frac{2j}{j(j+1)} a_j = \frac{2}{j+1} a_j$$

$$\rightarrow a_j \cong a_0 \frac{2^j}{j!} = A \frac{2^j}{j!}, j = 0, 1, 2, \dots$$

$$\rightarrow v(\rho) = A \sum_{j=0}^{\infty} \frac{2^j}{j!} \rho^j = A e^{2\rho}$$

→ $u(\rho) = A\rho^{l+1}e^\rho$, but when $\rho \rightarrow \infty$, $u(\rho)$ is infinity

so must be a $j_{\max}$ such that $a_{j_{\max}+1} = 0$

then equation (4.13) $2(j_{\max} + l + 1) - \rho_0 = 0$

define $n = j_{\max} + l + 1$ (4.14)

→ $\rho_0 = 2n$

result

$v(\rho)$ is a polynomial of degree $j_{\max}$

and
$$E = -\frac{\hbar^2 k^2}{2m} = -\frac{me^4}{8\pi^2 \epsilon_0^2 \hbar^2 \rho_0^2}$$

→ **Bohr formula :**

$$E_n = -\left[\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi \epsilon_0} \right)^2 \right] \frac{1}{n^2} = E_1 \frac{1}{n^2} \quad n = 1, 2, 3, \dots$$

ground state : $E_1 = -\left[\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi \epsilon_0} \right)^2 \right] = -13.6 \text{ eV}$ is **binding energy**

hen $k = \frac{me^2}{4\pi \epsilon_0 \hbar^2} \frac{1}{n} = \frac{1}{an}$, $\rho = \frac{r}{an}$

$$a = \frac{4\pi \epsilon_0 \hbar^2}{me^2} = 0.529 \times 10^{-10} \text{ m} \quad \text{is **Bohr radius**}$$

from equation (4.14) can see $j_{\max} \geq 0$ then $l_{\max} = n - 1$

n	l	j_{max}	$v(\rho)$	$R_{nl}(r)$
1	0	0	a_0	$R_{10} = \frac{a_0}{a} e^{-\frac{r}{a}}$
2	0	1	$a_0(1-\rho)$	$R_{20} = \frac{a_0}{2a} (1 - \frac{r}{2a}) e^{-\frac{r}{2a}}$
2	1	0	a_0	$R_{21} = \frac{a_0}{4a^2} r e^{-\frac{r}{2a}}$
3	0	2	$a_0(1-2\rho + \frac{2}{3}\rho^2)$	$R_{30} = \frac{a_0}{3a} (1 - \frac{2r}{3a} + \frac{2}{27} \frac{r^2}{a^2}) e^{-\frac{r}{3a}}$
3	1	1	$a_0(1 - \frac{1}{2}\rho)$	$R_{31} = \frac{a_0}{9a^2} r (1 - \frac{r}{6a}) e^{-\frac{r}{3a}}$
3	2	0	a_0	$R_{32} = \frac{a_0}{27a^3} r^2 e^{-\frac{r}{3a}}$
	$\vdots$		$\vdots$	$\vdots$
	$\vdots$		$\vdots$	$\vdots$

(iv) another representation of $v(\rho)$

$$v(\rho) = L_{n-l-1}^{2l+1}(2\rho)$$

$$\text{where } L_{n-l-1}^{2l+1}(2\rho) = (-1)^{2l+1} \left(\frac{d}{d(2\rho)} \right)^{2l+1} L_{n+l}(2\rho)$$

$$\text{and } L_{n+l}(2\rho) = e^{2\rho} \left(\frac{d}{d(2\rho)} \right)^{n+l} [e^{-2\rho} (2\rho)^{n+l}]$$

normalization of ψ is

$$\psi_{nlm} = \sqrt{\left(\frac{2}{na} \right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} e^{-\frac{r}{na}} \left(\frac{2r}{na} \right)^l L_{n-l-1}^{2l+1}(2r/na) Y_l^m(\theta, \phi)$$

➤ Spectrum of hydrogen

From Bohr formula

$$E_\gamma = E_i - E_f = -\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi \epsilon_0} \right)^2 \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \text{ eV}$$

$$E_\gamma = h\nu = 2\pi\hbar\nu = 2\pi\hbar \frac{c}{\lambda}$$

$$\rightarrow \frac{1}{\lambda} = \frac{m}{4\pi\hbar^3 c} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \dots\dots\dots(4.15)$$

$$R = \frac{m}{4\pi\hbar^3 c} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 = 1.09677.581 \text{ cm}^{-1}$$

R is **Rydberg constant**

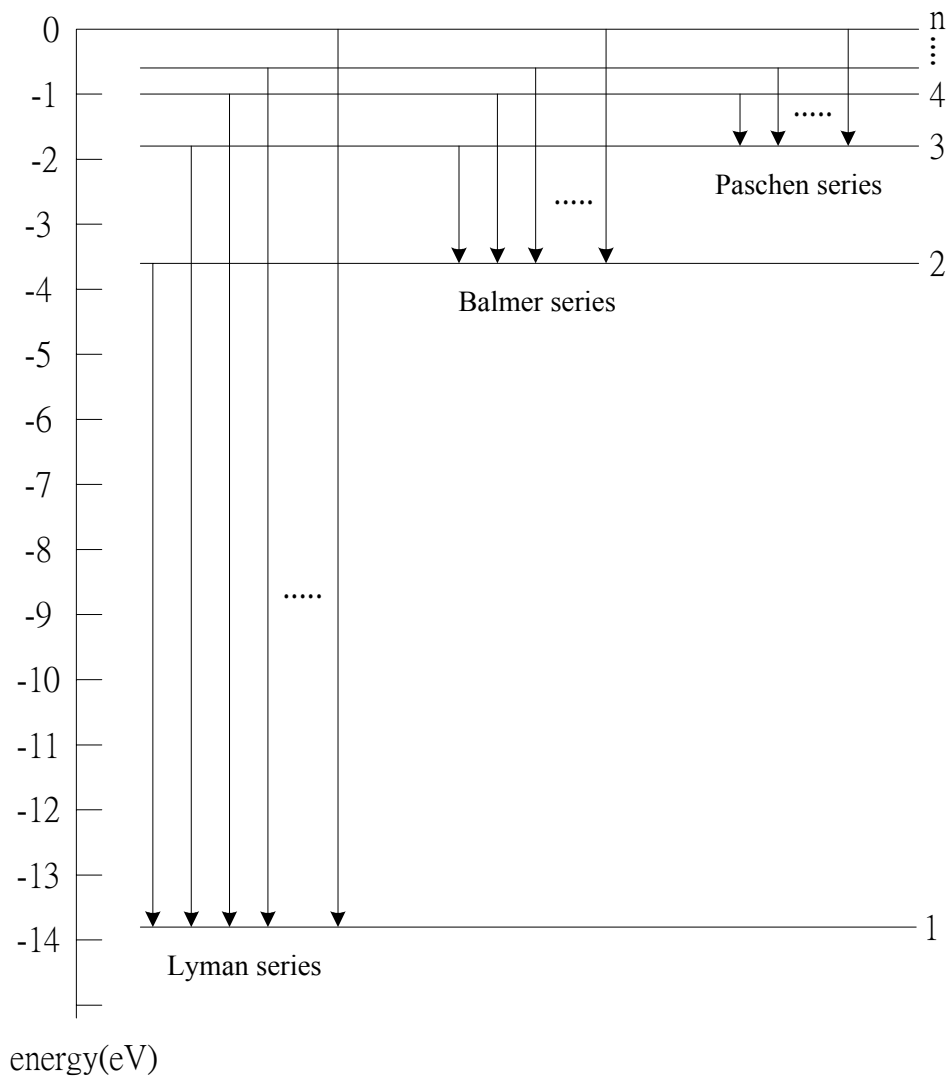
Equation (4.15) is **Rydberg formula** for spectrum of hydrogen

the spectrum of hydrogen :

$n_f = 1 \rightarrow$ ultraviolet region , the **Lyman series**

$n_f = 2 \rightarrow$ visible region , the **Balmer series**

$n_f = 3 \rightarrow$ infrared region , the **Paschen series**



transitions in the spectrum of hydrogen

4.3 Angular momentum

classical mechanics operator : $\mathbf{L} = \mathbf{r} \times \mathbf{p}$

quantum mechanics operator : $\mathbf{L} = \mathbf{r} \times \mathbf{p} = (x\hat{i} + y\hat{j} + z\hat{k}) \times (-i\hbar\nabla)$

$$\begin{aligned}
 &= -i\hbar \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ x & y & z \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \end{vmatrix} \\
 &= (yP_z - zP_y)\hat{i} + (zP_x - xP_z)\hat{j} + (xP_y - yP_x)\hat{k} \\
 &\equiv L_x\hat{i} + L_y\hat{j} + L_z\hat{k}
 \end{aligned}$$

➤ **Commutation relation**

$$\begin{aligned}
 \text{see } [L_x, L_y]f &= (yP_z - zP_y)(zP_x - xP_z)f - (zP_x - xP_z)(yP_z - zP_y)f \\
 &= -\hbar^2 \left[y \frac{\partial}{\partial z} \left(z \frac{\partial f}{\partial x} \right) - yx \frac{\partial^2 f}{\partial z^2} - z^2 \frac{\partial^2 f}{\partial y \partial x} + zx \frac{\partial^2 f}{\partial y \partial z} \right] \\
 &\quad + \hbar^2 \left[zy \frac{\partial^2 f}{\partial x \partial z} - z^2 \frac{\partial^2 f}{\partial x \partial y} - xy \frac{\partial^2 f}{\partial z^2} + x \frac{\partial}{\partial z} \left(z \frac{\partial f}{\partial y} \right) \right] \\
 &= \hbar^2 \left(x \frac{\partial f}{\partial y} - y \frac{\partial f}{\partial x} \right) \\
 &= i\hbar L_z f
 \end{aligned}$$

➡ $[L_x, L_y] = i\hbar L_z$

similarly $[L_y, L_z] = i\hbar L_x$, $[L_z, L_x] = i\hbar L_y$

L_x, L_y, L_z do not commute

Generalized uncertainty principle :

$$\sigma_x^2 \sigma_y^2 \geq \left(\frac{1}{2i} \langle i\hbar L_z \rangle \right)^2 = \frac{\hbar^2}{4} \langle L_z \rangle^2 \quad \text{➡} \quad \sigma_x \sigma_y \geq \frac{\hbar}{2} |\langle L_z \rangle|$$

square of total angular momentum : $L^2 = L_x^2 + L_y^2 + L_z^2$

can find $[L^2, L_x] = 0$, $[L^2, L_y] = 0$, $[L^2, L_z] = 0$

or $[L^2, \mathbf{L}] = 0$ ($\mathbf{L} \equiv L_x + L_y + L_z$) ➡ L^2 and $\mathbf{L}$ commute

so $L^2 f = \lambda f$ $L_z f = \mu f$ have same eigenstates f

define $L_{\pm} = L_x \pm iL_y$ thus $\begin{cases} [L_z, L_+] = \hbar(L_x + iL_y) = \hbar L_+ \\ [L_z, L_-] = -\hbar(L_x - iL_y) = -\hbar L_- \\ [L^2, L_{\pm}] = 0 \end{cases}$

$$\begin{cases} L_+ L_- = L_x^2 + L_y^2 - i(L_x L_y - L_y L_x) = L^2 - L_z^2 + \hbar L_z \\ L_- L_+ = L_x^2 + L_y^2 + i(L_x L_y - L_y L_x) = L^2 - L_z^2 - \hbar L_z \end{cases}$$

➡ $\begin{cases} L^2 = L_+ L_- + L_z^2 - \hbar L_z & \dots\dots(4.16) \\ L^2 = L_- L_+ + L_z^2 + \hbar L_z & \dots\dots(4.17) \end{cases}$

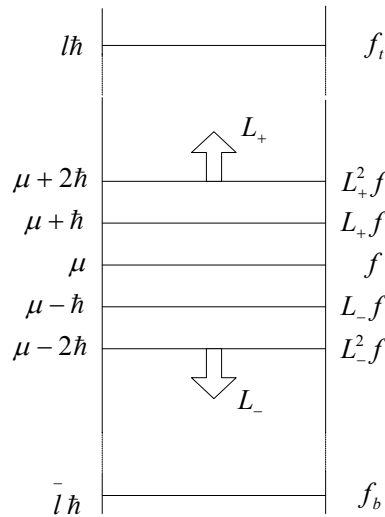
➤ **Eigenvalues for algebraic theory**

from $L^2 f = \lambda f$ $L_z f = \mu f$ have same eigenstates f

then (i) $L^2(L_{\pm} f) = L_{\pm}(L^2 f) = L_{\pm}(\lambda f) = \lambda(L_{\pm} f)$

$$\begin{aligned} L_z(L_{\pm} f) &= (L_z L_{\pm} - L_{\pm} L_z) f + L_{\pm} L_z f = \pm \hbar L_{\pm} f + L_{\pm} \mu f \\ &= (\mu \pm \hbar)(L_{\pm} f) \end{aligned}$$

$$\begin{aligned} \text{(ii)} \quad L_z(L_{\pm}^2 f) &= (L_{\pm} L_z \pm \hbar L_{\pm}) L_{\pm} f = L_{\pm} (L_z L_{\pm} \pm \hbar L_{\pm}) f \\ &= L_{\pm} (L_{\pm} L_z \pm 2\hbar L_{\pm}) f = L_{\pm}^2 (L_z \pm 2\hbar) f \\ &= (\mu \pm 2\hbar)(L_{\pm}^2 f) \end{aligned}$$



the ladder of angular momentum states and
corresponding eigenvalue in z-direction

$$L_+ f_t = 0$$

from $L_z f_t = l\hbar f_t$, $L^2 f_t = \lambda f_t$ and equation (4.16)

$$\begin{aligned} \Rightarrow L^2 f_t &= (L_- L_+ + L_z^2 + \hbar L_z) f_t = (0 + l^2 \hbar^2 + l\hbar^2) f_t \\ &= \hbar^2 l(l+1) f_t \end{aligned}$$

$$\Rightarrow \lambda = \hbar^2 l(l+1)$$

similarly , $L_- f_b = 0$, $L_z f_b = \bar{l}\hbar f_b$

from equation (4.17)

$$L^2 f_b = (L_+ L_- + L_z^2 - \hbar L_z) f_b = \hbar^2 \bar{l}(\bar{l}-1) f_b = \lambda f_b$$

$$\rightarrow \lambda = \hbar^2 \bar{l}(\bar{l}-1)$$

$$\hbar^2 l(l+1) = \hbar^2 \bar{l}(\bar{l}-1) \rightarrow \bar{l} = -l$$

from $-l$ to l must integer steps, so l must be integer or *half-integer*

$$l = 0, 1/2, 1, 3/2, \dots \quad m \text{ (or } m_l) = -l, -l+1, \dots, l-1, l$$

compare the angular equation at former section, we find l is $0, 1, 2, \dots$

The angular equation is used the *analytic* method, in this section we use *algebraic* method for the angular momentum.

But it is not contradiction. For general angular momentum, in quantum mechanics we need to consider not only **orbital angular momentum** but **spin angular momentum**.

The angular momentum is the sum of orbital and spin angular momentum.

The effect of *half-integer* is the behavior of spin evidently, and it will introduce in the later section (4.4)

➤ Eigenfunctions of angular momentum

(i) angular momentum represent in spherical coordinates

$$\nabla = \hat{r} \frac{\partial}{\partial r} + \hat{\theta} \frac{1}{r} \frac{\partial}{\partial \theta} + \hat{\phi} \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi}, \quad \mathbf{r} = r \hat{r}$$

$$\begin{aligned} \rightarrow \mathbf{L} = \mathbf{r} \times \mathbf{p} &= -i\hbar \left[r(\hat{r} \times \hat{r}) \frac{\partial}{\partial r} + (\hat{r} \times \hat{\theta}) \frac{\partial}{\partial \theta} + \frac{1}{\sin \theta} (\hat{r} \times \hat{\phi}) \frac{\partial}{\partial \phi} \right] \\ &= -i\hbar \left(\hat{\phi} \frac{\partial}{\partial \theta} - \hat{\theta} \frac{1}{\sin \theta} \frac{\partial}{\partial \phi} \right) \end{aligned}$$

$$\begin{aligned} \text{where } \hat{\theta} &= \cos \theta \cos \phi \hat{i} + \cos \theta \sin \phi \hat{j} - \sin \theta \hat{k} \\ \hat{\phi} &= -\sin \phi \hat{i} + \cos \phi \hat{j} \end{aligned}$$

$$\rightarrow \mathbf{L} = -i\hbar \left[(-\sin \phi \hat{i} + \cos \phi \hat{j}) \frac{\partial}{\partial \theta} - (\cos \theta \cos \phi \hat{i} + \cos \theta \sin \phi \hat{j} - \sin \theta \hat{k}) \frac{1}{\sin \theta} \frac{\partial}{\partial \phi} \right]$$

$$\begin{aligned}
\rightarrow L_x &= -i\hbar \left(-\sin\phi \frac{\partial}{\partial\theta} - \cos\phi \cot\theta \frac{\partial}{\partial\phi} \right) \\
L_y &= -i\hbar \left(\cos\phi \frac{\partial}{\partial\theta} - \sin\phi \cot\theta \frac{\partial}{\partial\phi} \right) \\
L_z &= -i\hbar \frac{\partial}{\partial\phi} \\
L_+ &= \hbar e^{i\phi} \left(\frac{\partial}{\partial\theta} + i \cot\theta \frac{\partial}{\partial\phi} \right) \quad , \quad L_- = -\hbar e^{-i\phi} \left(\frac{\partial}{\partial\theta} - i \cot\theta \frac{\partial}{\partial\phi} \right)
\end{aligned}$$

(ii) for eigenfunction $f_l^m(\theta, \phi)$

$$L_z f = -i\hbar \frac{\partial f}{\partial\phi} = m\hbar f \quad \rightarrow \quad f = g(\theta)e^{im\phi}$$

f is also eigenfunction of L^2 , and from equation (4.16)

$$\begin{aligned}
\text{then } L^2 f &= (L_+ L_- + L_z^2 - \hbar L_z) f \\
&= \hbar e^{i\phi} \left(\frac{\partial}{\partial\theta} + i \cot\theta \frac{\partial}{\partial\phi} \right) (-\hbar e^{-i\phi}) \left(\frac{\partial f}{\partial\theta} - i \cot\theta \frac{\partial f}{\partial\phi} \right) - \hbar^2 \frac{\partial^2 f}{\partial\phi^2} + i\hbar^2 \frac{\partial f}{\partial\phi} \\
&= \hbar^2 l(l+1) f
\end{aligned}$$

$$\rightarrow \sin\theta \frac{d}{d\theta} \left(\sin\theta \frac{dg}{d\theta} \right) + [l(l+1)\sin^2\theta - m^2]g = 0 \quad \dots\dots\dots(4.17)$$

compare equation (4.17) and (4.9)

$$g(\theta) \equiv \Theta(\theta) \quad , \quad \text{so} \quad f_l^m(\theta, \phi) = g(\theta)e^{im\phi} \equiv Y_l^m(\theta, \phi)$$

the spherical harmonics are the eigenfunctions of L^2 and L_z

4.4 Spin of algebraic theory

spin angular momentum operator $\mathbf{S}$

$$[S_x, S_y] = i\hbar S_z \quad , \quad [S_y, S_z] = i\hbar S_x \quad , \quad [S_z, S_x] = i\hbar S_y$$

$$[S^2, S_x] = [S^2, S_y] = [S^2, S_z] = 0$$

$$S_{\pm} = (S_x \pm iS_y) \quad \begin{cases} [S_z, S_+] = \hbar(S_x + iS_y) = \hbar S_+ \\ [S_z, S_-] = -\hbar(S_x - iS_y) = -\hbar S_- \\ [S^2, S_{\pm}] = 0 \end{cases}$$

$$S^2 |sm_s\rangle = \hbar^2 s(s+1) |sm_s\rangle, \quad S_z |sm_s\rangle = \hbar m_s |sm_s\rangle \quad \dots\dots\dots(4.18)$$

$$\begin{aligned} S_z S_+ |sm_s\rangle &= S_+ S_z |sm_s\rangle + \hbar S_+ |sm_s\rangle = m_s \hbar S_+ |sm_s\rangle + \hbar S_+ |sm_s\rangle \\ &= (m_s + 1) \hbar S_+ |sm_s\rangle \end{aligned}$$

$$\text{and } S_z |s(m_s + 1)\rangle = (m_s + 1) \hbar |s(m_s + 1)\rangle$$

$$\longrightarrow S_+ |sm_s\rangle = c_+ |s(m_s + 1)\rangle, \quad c_+ \text{ is constant}$$

$$\langle sm_s | S_- S_+ |sm_s\rangle = c_+ \langle sm_s | S_- |s(m_s + 1)\rangle = c_+ \langle S_+ sm_s | s(m_s + 1)\rangle$$

$$\text{where } \langle S_+ sm_s | = (\langle S_+ sm_s \rangle)^* = (S_+ |sm_s\rangle)^* = [c_+ |s(m_s + 1)\rangle]^* = c_+^* \langle s(m_s + 1) |$$

$$\text{so } \langle sm_s | S_- S_+ |sm_s\rangle = c_+ c_+^* \langle s(m_s + 1) | s(m_s + 1)\rangle$$

$$\longrightarrow |c_+|^2 = \langle sm_s | S^2 - S_z - \hbar S_z |sm_s\rangle = [s(s+1) - m_s^2 - m_s] \hbar^2$$

$$c_+ = \sqrt{[s(s+1) - m_s^2 - m_s] \hbar^2}$$

$$\longrightarrow S_+ |sm_s\rangle = \hbar \sqrt{s(s+1) - m_s^2 - m_s} |s(m_s + 1)\rangle \quad \dots\dots\dots(4.19)$$

$$\text{similarly } S_- |sm_s\rangle = \hbar \sqrt{s(s+1) - m_s^2 + m_s} |s(m_s - 1)\rangle \quad \dots\dots\dots(4.20)$$

$$s = 0, \frac{1}{2}, 1, \frac{3}{2}, \dots\dots\dots, \quad m_s : -s, -s+1, \dots\dots\dots, s-1, s$$

summary

- (a) l is orbital angular momentum quantum number;
 s is the **spin** of particular species in particles.
- (b) l can take on any **integer** value ; when system is perturbed ,
 l will change from a value to another.
 s is fixed.; for any given particles , it has specific of s (table 4.1)

table(4.1)

particles	spin s
π mesons	0
electrons	1/2
photons	1
deltas	3/2
gravitons	2

➤ **The operator of the spin 1/2 state**

$|\frac{1}{2} \frac{1}{2}\rangle$ is **spin up** $|\frac{1}{2} -\frac{1}{2}\rangle$ is **spin down**

spinor (spin state)

$$\chi = \begin{bmatrix} a \\ b \end{bmatrix} = a\chi_+ + b\chi_-$$

where spin eigenstate

$$\chi_+ = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \quad \text{or} \quad \alpha = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \quad \text{for spin up, corresponding to eigenvalue } \frac{\hbar}{2}$$

$$\chi_- = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \quad \text{or} \quad \beta = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \quad \text{for spin down, corresponding to eigenvalue } -\frac{\hbar}{2}$$

$|a|^2$ represent the probability of spin up

$|b|^2$ represent the probability of spin down

$$|a|^2 + |b|^2 = 1$$

The matrix form of S_x , S_y , S_z :

from equation (4.18), we can find

$$S^2\chi_+ = \frac{3}{4}\hbar^2\chi_+, \quad S^2\chi_- = \frac{3}{4}\hbar^2\chi_-, \quad S_z\chi_+ = \frac{1}{2}\hbar\chi_+, \quad S_z\chi_- = -\frac{1}{2}\hbar\chi_-$$

and equation (4.19), (4.20) now become to

$$S_+\chi_- = \hbar\chi_+, \quad S_-\chi_+ = \hbar\chi_-, \quad S_+\chi_+ = S_-\chi_- = 0$$

$$S_x = \frac{1}{2}(S_+ + S_-) \quad , \quad S_y = \frac{1}{2i}(S_+ - S_-)$$

$$\rightarrow S_x \chi_+ = \frac{\hbar}{2} \chi_- , S_x \chi_- = \frac{\hbar}{2} \chi_+ , S_y \chi_+ = -\frac{\hbar}{2i} \chi_- , S_y \chi_- = \frac{\hbar}{2i} \chi_+ ,$$

$$\text{let } S_x = \begin{bmatrix} a & c \\ b & d \end{bmatrix} \rightarrow \begin{cases} \begin{bmatrix} a & c \\ b & d \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} = \frac{\hbar}{2} \begin{bmatrix} 0 \\ 1 \end{bmatrix} \\ \begin{bmatrix} a & c \\ b & d \end{bmatrix} \begin{bmatrix} 0 \\ 1 \end{bmatrix} = \frac{\hbar}{2} \begin{bmatrix} 1 \\ 0 \end{bmatrix} \end{cases} \rightarrow \begin{cases} a = 0 , b = \frac{\hbar}{2} \\ c = \frac{\hbar}{2} , d = 0 \end{cases}$$

$$\text{so } S_x = \frac{\hbar}{2} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$

$$\text{similarly } S_y = \frac{\hbar}{2} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} , S_z = \frac{\hbar}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

Pauli spin matrices:

$$\mathbf{S} = (S_x + S_y + S_z) = \frac{\hbar}{2} \boldsymbol{\sigma} = \frac{\hbar}{2} (\sigma_x + \sigma_y + \sigma_z)$$

$$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} , \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} , \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

We call $\boldsymbol{\sigma}$ the Pauli operator

$$\boldsymbol{\sigma} = \begin{bmatrix} 1 & 1-i \\ 1+i & -1 \end{bmatrix}$$

➤ Addition of spin angular momenta

Suppose two spin 1/2 particles

The spin angular momentum corresponding to these two particles are $S^{(1)}$, $S^{(2)}$

The total angular momentum of the composite state
(such as two electron of helium atom) is :

$$S = S^{(1)} + S^{(2)} \quad , \quad S^2 = S_x^2 + S_y^2 + S_z^2$$

each particle can have spin up or spin down

so spin eigenstate of $S_z^{(1)} : \alpha(1), \beta(1)$

spin eigenstate of $S_z^{(2)} : \alpha(2), \beta(2)$

there are four possibilities of the composite state :

$$\alpha(1)\alpha(2), \beta(1)\beta(2), \alpha(1)\beta(2), \alpha(2)\beta(1)$$

(i)

$$\begin{aligned} S_z \chi_1 \chi_2 &= (S_z^{(1)} \chi_1) \chi_2 + \chi_1 (S_z^{(2)} \chi_2) \\ &= (\hbar m_{s1} \chi_1) \chi_2 + \chi_1 (\hbar m_{s2} \chi_2) \\ &= (m_{s1} + m_{s2}) \hbar \chi_1 \chi_2 \end{aligned}$$

it represent that composite state $\chi_1 \chi_2$ have eigenvalues $(m_{s1} + m_{s2})$ in z-component

spin eigenstates of S_z	eigenvalue m_s
$\alpha(1)\alpha(2)$	1
$\alpha(1)\beta(2)$	0
$\alpha(2)\beta(1)$	0
$\beta(1)\beta(2)$	-1

so for $m_s = 1, -1 \rightarrow s = 1$; [$\alpha(1)\alpha(2); \alpha(2)\beta(2)$]

$m_s = 0 \rightarrow s = 0 \text{ or } 1$ [$\alpha(1)\beta(2); \alpha(2)\beta(1)$]

$\alpha(1)\beta(2)$, $\alpha(2)\beta(1)$ have the same eigenvalue $m_s = 0$

Now rearrange the eigenstate χ by selecting a suitable value of c_1, c_2 in the superposition form

$$\chi = c_1 \alpha(1)\beta(2) + c_2 \alpha(2)\beta(1)$$

(ii)

S^2, S_z have the same eigenstates

$\alpha(1)\alpha(2)$, $\beta(1)\beta(2)$ and χ must also be eigenstates of S^2

proof

$$\text{from } S^2 = [S^{(1)} + S^{(2)}]^2 = [S^{(1)2} + S^{(2)2} + 2S^{(1)}S^{(2)}]$$

$$\text{where } S^{(1)}S^{(2)} = S_x^{(1)}S_x^{(2)} + S_y^{(1)}S_y^{(2)} + S_z^{(1)}S_z^{(2)}$$

1.

$$\begin{aligned} S^2 \alpha(1)\alpha(2) &= [S^{(1)2} + S^{(2)2} + 2S^{(1)}S^{(2)}] \alpha(1)\alpha(2) \\ &= S^{(1)2} \alpha(1)\alpha(2) + \alpha(1)S^{(2)2} \alpha(2) + 2S^{(1)}S^{(2)} \alpha(1)\alpha(2) \\ &\quad + \frac{3}{4}\hbar^2 \alpha(1)\alpha(2) + \frac{3}{4}\hbar^2 \alpha(1)\alpha(2) \\ &\quad + 2[S_x^{(1)}\alpha(1)S_x^{(2)}\alpha(2) + S_y^{(1)}\alpha(1)S_y^{(2)}\alpha(2) + S_z^{(1)}\alpha(1)S_z^{(2)}\alpha(2)] \\ &= \frac{3}{2}\hbar^2 \alpha(1)\alpha(2) \\ &\quad + 2\left[\left(\frac{\hbar}{2}\right)^2 \beta(1)\beta(2) + \left(-\frac{\hbar}{2i}\right)^2 \beta(1)\beta(2) + \left(\frac{\hbar}{2}\right)^2 \alpha(1)\alpha(2)\right] \\ &= 2\hbar^2 \alpha(1)\alpha(2) \end{aligned}$$

from equation (4.18)

$\alpha(1)\alpha(2)$ is the eigenstates of S^2

and the corresponding eigenvalue is $2\hbar^2 = s(s+1)\hbar^2$

$$\Rightarrow s = 1$$

2.

similarly, we also can get $S^2 \beta(1)\beta(2) = 2\hbar^2 \beta(1)\beta(2)$

$$\Rightarrow s = 1$$

3.

$$\begin{aligned} S^2 \chi &= [S^{(1)2} + S^{(2)2} + 2S^{(1)}S^{(2)}][c_1\alpha(1)\beta(2) + c_2\beta(1)\alpha(2)] \\ &= \frac{3}{2}\hbar^2 c_1\alpha(1)\beta(2) + \hbar^2 c_1\beta(1)\alpha(2) - \frac{\hbar^2}{2} c_1\alpha(1)\beta(2) \\ &\quad + \frac{3}{2}\hbar^2 c_2\beta(1)\alpha(2) + \hbar^2 c_2\alpha(1)\beta(2) - \frac{\hbar^2}{2} c_2\beta(1)\alpha(2) \\ &= c_1\hbar^2[\alpha(1)\beta(2) + \beta(1)\alpha(2)] + c_2\hbar^2[\alpha(1)\beta(2) + \beta(1)\alpha(2)] \\ &= (c_1 + c_2)\hbar^2[\alpha(1)\beta(2) + \beta(1)\alpha(2)] \\ &= s(s+1)\hbar^2[c_1\alpha(1)\beta(2) + c_2\beta(1)\alpha(2)] \end{aligned}$$

$$\begin{aligned} &\rightarrow (c_1 + c_2)\hbar^2[\alpha(1)\beta(2) + \beta(1)\alpha(2)] \\ &= s(s+1)\hbar^2[c_1\alpha(1)\beta(2) + c_2\beta(1)\alpha(2)] \end{aligned}$$

$$\rightarrow \begin{cases} c_2 = (s^2 + s - 1)c_1 \\ c_1 = (s^2 + s - 1)c_2 \end{cases}$$

c_1, c_2 have non-trivial solution

$$\rightarrow \begin{vmatrix} s^2 + s - 1 & -1 \\ -1 & s^2 + s - 1 \end{vmatrix} = 0 \rightarrow (s^2 + s)(s^2 + s - 2) = 0$$

$$\rightarrow s = 0, 1$$

$$s = 0, \quad c_1 = -c_2 \quad \text{normalize eigenstate : } \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

$$s = 1, \quad c_1 = c_2 \quad \text{normalize eigenstate : } \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)]$$

spin eigenstate of S^2, S_z	s	m_s	
$\alpha(1)\alpha(2)$	1	1	} triplet state
$\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)]$	1	0	
$\beta(1)\beta(2)$	1	-1	
$\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$	0	0	singlet state

summary

If we combine spin s_1 with spin s_2 ; the total spin :

$$s = (s_1 + s_2), (s_1 + s_2 - 1), (s_1 + s_2 - 2), \dots, |s_1 - s_2|$$

the highest s occurs when they are aligned parallel

the lowest s occurs when they are antiparallel

example

1.
combine a particle of spin $3/2$ with another of spin 2

total spin could get $7/2, 5/2, 3/2, 1/2$;
2.
A hydrogen atom , the angular momentum of electron is $l + 1/2$
or $l - 1/2$ (orbital + spin) .

if the electron combine with the proton ,
the atom's total angular momentum quantum number is

 $l + 1, l, l - 1$

Conclusion

the four quantum number determine a state of a particle

- (i) *principal quantum number* n

$$n = 1, 2, 3, \dots;$$

- (ii) *azimuthal quantum number* l

$$l = 0, 1, \dots, n-1 \quad ; l \text{ determine the shape of orbit}$$

l	0	1	2	3	4	5	6
orbit sign	s	p	d	f	g	h	i

- (iii) *magnetic quantum number* m_l

$$m_l = -l, -l+1, \dots, l-1, l \quad ; m_l \text{ determine the orientation of orbit}$$

- (iv) *spin quantum number* m_s