# Chapter 2

# Angular Momentum, Hydrogen Atom, and Helium Atom

# Contents

2.1	Angular momenta and their addition	24
2.2	Hydrogenlike atoms	38
2.3	Pauli principle, Hund's rules, and periodical table	42
<b>2.4</b>	Ground state of helium atom: 1st approximation	48

## **Basic Questions**

A. What are the eigenvalues of angular momentum operator?

- **B.** What are the quantum numbers of a state of the single electron in hydrogen atom?
- **C.** What is total electron spin of ground-state helium atom, and the spin eigenstate?

# 2.1 Angular momentum and addition of two angular momenta

#### 2.1.1 Schrödinger Equation in 3D

Consider the Hamiltonian of a particle of mass m in a central potential V(r)

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(r) \ .$$

Since V(r) depends on r only, it is natural to express  $\nabla^2$  in terms of spherical coordinates  $(r, \theta, \varphi)$  as

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \,.$$

#### **Operators in Spherical Coordinates**

A. Laplacian operator

By coordinate transformation between Cartesian (x,y,z) and spherical coordinates  $(r,\theta,\varphi)$ 

$$\begin{array}{rcl} x & = & r\sin\theta\cos\varphi, & r = \sqrt{x^2 + y^2 + z^2} \\ y & = & r\sin\theta\sin\varphi, & \tan^2\theta = \frac{x^2 + y^2}{z^2} \\ z & = & r\cos\theta, & \tan\varphi = \frac{y}{x} \end{array}$$

we have

$$\frac{\partial r}{\partial x} = \sin \theta \cos \varphi, \quad \frac{\partial r}{\partial y} = \sin \theta \sin \varphi, \quad \frac{\partial r}{\partial z} = \cos \theta$$

$$\frac{\partial \theta}{\partial x} = \frac{1}{r} \cos \theta \cos \varphi, \quad \frac{\partial \theta}{\partial y} = \frac{1}{r} \cos \theta \sin \varphi, \quad \frac{\partial \theta}{\partial z} = -\frac{1}{r} \sin \theta$$

$$\frac{\partial \varphi}{\partial x} = -\frac{1}{r} \frac{\sin \varphi}{\sin \theta}, \quad \frac{\partial \varphi}{\partial y} = -\frac{1}{r} \frac{\cos \varphi}{\sin \theta}, \quad \frac{\partial \varphi}{\partial z} = 0.$$

Using the derivative rule

$$\frac{\partial}{\partial x} = \frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial x}\frac{\partial}{\partial \theta} + \frac{\partial \varphi}{\partial x}\frac{\partial}{\partial \varphi}$$

$$= \sin \theta \cos \varphi \frac{\partial}{\partial r} + \frac{1}{r} \cos \theta \cos \varphi \frac{\partial}{\partial \theta} - \frac{1}{r} \frac{\sin \varphi}{\sin \theta} \frac{\partial}{\partial \varphi}$$
$$\frac{\partial}{\partial y} = \sin \theta \sin \varphi \frac{\partial}{\partial r} + \frac{1}{r} \cos \theta \sin \varphi \frac{\partial}{\partial \theta} - \frac{1}{r} \frac{\cos \varphi}{\sin \theta} \frac{\partial}{\partial \varphi}$$
$$\frac{\partial}{\partial z} = \cos \theta \frac{\partial}{\partial r} - \frac{1}{r} \sin \theta \frac{\partial}{\partial \theta}$$

Therefore

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \left(\sin\theta\cos\varphi\frac{\partial}{\partial r} + \frac{1}{r}\cos\theta\cos\varphi\frac{\partial}{\partial\theta} - \frac{1}{r}\frac{\sin\varphi}{\sin\theta}\frac{\partial}{\partial\varphi}\right) \\ \times \left(\sin\theta\cos\varphi\frac{\partial}{\partial r} + \frac{1}{r}\cos\theta\cos\varphi\frac{\partial}{\partial\theta} - \frac{1}{r}\frac{\sin\varphi}{\sin\theta}\frac{\partial}{\partial\varphi}\right) \\ + \left(\sin\theta\sin\varphi\frac{\partial}{\partial r} + \frac{1}{r}\cos\theta\sin\varphi\frac{\partial}{\partial\theta} - \frac{1}{r}\frac{\cos\varphi}{\sin\theta}\frac{\partial}{\partial\varphi}\right) \\ \times \left(\sin\theta\sin\varphi\frac{\partial}{\partial r} + \frac{1}{r}\cos\theta\sin\varphi\frac{\partial}{\partial\theta} - \frac{1}{r}\frac{\cos\varphi}{\sin\theta}\frac{\partial}{\partial\varphi}\right) \\ + \left(\cos\theta\frac{\partial}{\partial r} - \frac{1}{r}\sin\theta\frac{\partial}{\partial\theta}\right) \times \left(\cos\theta\frac{\partial}{\partial r} - \frac{1}{r}\sin\theta\frac{\partial}{\partial\theta}\right)$$

and this is equal to, after some considerable algebra

$$\nabla^{2} = \frac{\partial^{2}}{\partial r^{2}} + \frac{1}{r^{2}} \frac{\partial^{2}}{\partial \theta^{2}} + \frac{1}{r^{2} \sin^{2} \theta} \frac{\partial^{2}}{\partial \varphi^{2}} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{\cot \theta}{r^{2}} \frac{\partial}{\partial \theta}$$
$$= \frac{1}{r^{2}} \frac{\partial}{\partial r} \left( r^{2} \frac{\partial}{\partial r} \right) + \frac{1}{r^{2} \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^{2} \sin^{2} \theta} \frac{\partial^{2}}{\partial \varphi^{2}}$$
$$= \frac{1}{r^{2}} \frac{\partial}{\partial r} \left( r^{2} \frac{\partial}{\partial r} \right) + \frac{1}{r^{2}} \hat{A} \left( \theta, \varphi \right)$$

with definition

$$\hat{A}(\theta,\varphi) \equiv \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\varphi^2} \,.$$

B. Angular momentum operators Consider first the z-component, using the above formulas for  $\frac{\partial}{\partial x}$  and  $\frac{\partial}{\partial y}$ 

$$\hat{L}_{z} = -i\hbar \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$$
$$= (-i\hbar) r \sin \theta \cos \varphi \left( \sin \theta \sin \varphi \frac{\partial}{\partial r} + \frac{1}{r} \cos \theta \sin \varphi \frac{\partial}{\partial \theta} - \frac{1}{r} \frac{\cos \varphi}{\sin \theta} \frac{\partial}{\partial \varphi} \right)$$

$$-(-i\hbar)r\sin\theta\sin\varphi\left(\sin\theta\cos\varphi\frac{\partial}{\partial r} + \frac{1}{r}\cos\theta\cos\varphi\frac{\partial}{\partial\theta} - \frac{1}{r}\frac{\sin\varphi}{\sin\theta}\frac{\partial}{\partial\varphi}\right)$$
$$= -i\hbar\frac{\partial}{\partial\varphi}$$

similarly we can derive the x- and y-components as

$$\hat{L}_x = -i\hbar \left( -\sin\varphi \frac{\partial}{\partial\theta} - \cot\theta \cos\varphi \frac{\partial}{\partial\varphi} \right)$$
$$\hat{L}_y = -i\hbar \left( +\cos\varphi \frac{\partial}{\partial\theta} - \cot\theta \sin\varphi \frac{\partial}{\partial\varphi} \right)$$

¿From the definition of the raising and lowering operators

$$\hat{L}^{\pm} \equiv \hat{L}_x \pm i\hat{L}_y$$

it is straightforward to obtain

$$\hat{L}^{\pm} = -i\hbar e^{\pm i\varphi} \left( \pm i\frac{\partial}{\partial\theta} - \cot\theta \frac{\partial}{\partial\varphi} \right) \,.$$

C. Angular momentum square

In order to obtain the square of angular momentum operator in the spherical coordinates, consider  $\left(\hat{L}_x\right)^2$ 

$$\begin{aligned} \frac{\left(\hat{L}_x\right)^2}{-\hbar^2} &= \left(\sin\varphi\frac{\partial}{\partial\theta} + \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\right)^2 \\ &= \sin\varphi\frac{\partial}{\partial\theta}\sin\varphi\frac{\partial}{\partial\theta} + \sin\varphi\frac{\partial}{\partial\theta}\cot\theta\cos\varphi\frac{\partial}{\partial\varphi} + \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\sin\varphi\frac{\partial}{\partial\theta} \\ &+ \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\cot\theta\cos\varphi\frac{\partial}{\partial\varphi} \\ &= \sin^2\varphi\frac{\partial^2}{\partial\theta^2} + \sin\varphi\cos\varphi\frac{\partial}{\partial\theta}\cot\theta\frac{\partial}{\partial\varphi} + \cot\theta\cos^2\varphi\frac{\partial}{\partial\theta} \\ &+ \cot\theta\cos\varphi\sin\varphi\frac{\partial^2}{\partial\varphi\partial\theta} - \cot^2\theta\cos\varphi\sin\varphi\frac{\partial}{\partial\varphi} + \cot^2\theta\cos^2\varphi\frac{\partial^2}{\partial\varphi^2} \\ &\frac{\left(\hat{L}_y\right)^2}{-\hbar^2} &= \left(\cos\varphi\frac{\partial}{\partial\theta} - \cot\theta\sin\varphi\frac{\partial}{\partial\varphi}\right)^2 \\ &= \cos^2\varphi\frac{\partial^2}{\partial\theta^2} - \sin\varphi\cos\varphi\frac{\partial}{\partial\theta}\cot\theta\frac{\partial}{\partial\varphi} + \cot\theta\sin^2\varphi\frac{\partial}{\partial\theta} \\ &- \cot\theta\cos\varphi\sin\varphi\frac{\partial^2}{\partial\varphi\partial\theta} + \cot^2\theta\sin\varphi\cos\varphi\frac{\partial}{\partial\varphi} + \cot^2\theta\sin^2\varphi\frac{\partial^2}{\partial\theta} \end{aligned}$$

now

$$\begin{aligned} \frac{\hat{L}^2}{-\hbar^2} &= \frac{\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2}{-\hbar^2} = \frac{\partial^2}{\partial\theta^2} + \cot\theta \frac{\partial}{\partial\theta} + \left(\cot^2\theta + 1\right) \frac{\partial^2}{\partial\varphi^2} \\ &= \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\varphi^2} = \hat{A}\left(\theta,\varphi\right) \\ &= \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} - \frac{1}{\sin^2\theta} \frac{\hat{L}_z^2}{\hbar^2} \end{aligned}$$

where  $\hat{A}\left(\theta,\phi\right)$  is as defined before in the Laplacian  $\nabla^{2}$ .

The Schrödinger eq. becomes

$$\begin{cases} -\frac{\hbar^2}{2m} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right] + V(r) \end{cases} \Psi(r, \theta, \varphi) \\ = E \Psi(r, \theta, \varphi)$$

or

$$\left\{ \left[ -\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + V(r) \right] + \frac{\hat{L}^2}{2mr^2} \right\} \Psi(r,\theta,\varphi) = E \Psi(r,\theta,\varphi) \,.$$

This eq. is separable. Let

$$\Psi\left(r,\theta,\varphi\right) = R\left(r\right)Y\left(\theta,\varphi\right)$$

where  $Y(\theta, \varphi)$  is assumed to be the eigenstate of  $\hat{L}^2$  with eigenvalue  $\lambda$ 

$$\hat{L}^{2}Y\left(\theta,\varphi\right) = \lambda Y\left(\theta,\varphi\right)$$

we have the equation for the radial part of wavefunction

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

The solution of this equation depends on the given potential V(r). But the solution for the angular part of wavefunction  $Y(\theta, \varphi)$  is universal and can be discussed in general.

#### 2.1.2 Operators and their algebra

Classically, angular momentum is defined as

$$\mathbf{L} = \mathbf{r} \times \mathbf{p}$$

or in component form

$$L_x = yp_z - zp_y, \quad L_y = zp_x - xp_z, \quad L_z = xp_y - yp_x$$

in QM, they all become operator

$$\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \quad \hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z, \quad \hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x.$$

Their commutation relations are given by

$$\begin{split} \begin{bmatrix} \hat{L}_x, \ \hat{L}_y \end{bmatrix} &= \ [\hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \ \hat{z}\hat{p}_x - \hat{x}\hat{p}_z] \\ &= \ [\hat{y}\hat{p}_z, \ \hat{z}\hat{p}_x] + [\hat{z}\hat{p}_y, \ \hat{x}\hat{p}_z] \\ &= \ \hat{y} \left[\hat{p}_z, \ \hat{z}\right]\hat{p}_x + [\hat{z}, \ \hat{p}_z]\hat{p}_y \hat{x} \\ &= \ -i\hbar\hat{y}\hat{p}_x + i\hbar\hat{p}_y \hat{x} \\ &= \ i\hbar\hat{L}_z \\ \begin{bmatrix} \hat{L}_y, \ \hat{L}_z \end{bmatrix} = \ i\hbar\hat{L}_x \\ \begin{bmatrix} \hat{L}_z, \ \hat{L}_x \end{bmatrix} = \ i\hbar\hat{L}_y \end{split}$$

we can memorize these relations by

$$\mathbf{\hat{L}} imes \mathbf{\hat{L}} = i\hbar \mathbf{\hat{L}}$$
 .

In spherical coordinates, these operators are expressed as

$$\hat{L}_{x} = -i\hbar \left( -\sin\varphi \frac{\partial}{\partial\theta} - \cot\theta \cos\varphi \frac{\partial}{\partial\varphi} \right)$$
$$\hat{L}_{y} = -i\hbar \left( +\cos\varphi \frac{\partial}{\partial\theta} - \cot\theta \sin\varphi \frac{\partial}{\partial\varphi} \right)$$
$$\hat{L}_{z} = -i\hbar \frac{\partial}{\partial\varphi}$$

and

$$\hat{L}^2 = -\hbar^2 \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right) \,.$$

Hence the Laplacian operator  $\nabla^2$  and Hamiltonian take the following simple form

$$\begin{aligned} \nabla^2 &= \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{\hat{L}^2}{\hbar^2 r^2} \\ \hat{H} &= -\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + V(r) + \frac{1}{2m} \frac{\hat{L}^2}{r^2} \end{aligned}$$

It is easy to see  $\hat{L}_z$  commutes with  $\hat{L}^2$ 

$$\left[\hat{L}_z,\ \hat{L}^2\right] = 0$$

and  $\hat{L}^2$  commute with operators  $\hat{H}$  ,

$$\left[\hat{L}^2,\ \hat{H}\right] = 0 \ .$$

(note: we also have  $[\hat{L}_x, \hat{L}^2] = [\hat{L}_y, \hat{L}^2] = 0$ ) Therefore we can find a wavefunction which is eigenfunctions to both  $\hat{H}, \hat{L}^2$ , and  $\hat{L}_z$ . Furthermore, since they are separable, the eigenfunction of  $\hat{H}$  can be written in general as

$$\Psi_{n,l,m}(r,\theta,\varphi) = R_{nl}(r)\,\Theta_l(\theta)\,\Phi_m(\varphi) = R_{nl}(r)\,Y_{l,m}(\theta,\varphi)$$

with

$$\begin{aligned} \hat{L}_{z}\Phi_{m}\left(\varphi\right) &= \lambda_{m}\Phi_{m}\left(\varphi\right) \rightarrow -i\frac{\partial}{\partial\varphi}\Phi_{m}\left(\varphi\right) = \lambda_{m}\Phi_{m}\left(\varphi\right) \\ \hat{L}^{2}Y_{l,m}\left(\theta,\varphi\right) &= \lambda_{l,m}Y_{l,m}\left(\theta,\varphi\right) \rightarrow \left(-\frac{\hbar^{2}}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{\lambda_{m}^{2}}{\sin^{2}\theta}\right)\Theta_{l}\left(\theta\right) = \lambda_{l,m}\Theta_{l}\left(\theta\right) \\ \hat{H}\Psi_{n,l,m}\left(r,\theta,\varphi\right) &= \lambda_{n,l,m}\Psi_{n,l,m}\left(r,\theta,\varphi\right) \\ \rightarrow \left(-\frac{\hbar^{2}}{2\mu}\frac{1}{r^{2}}\frac{\partial}{\partial r}r^{2}\frac{\partial}{\partial r} + V\left(r\right) + \frac{1}{2\mu}\frac{\lambda_{l,m}}{r^{2}}\right)R_{nl}\left(r\right) = \lambda_{n,l,m}R_{nl}\left(r\right) \end{aligned}$$

In Dirac notation

$$\begin{array}{rcl} \Phi_m\left(\varphi\right) & \to & |m\rangle \\ Y_{l,m}\left(\theta,\varphi\right) & \to & |l,m\rangle \\ \Psi_{n,l,m}\left(r,\theta,\varphi\right) & \to & |n,l,m\rangle \ . \end{array}$$

Instead of dealing with  $\hat{L}_x$ ,  $\hat{L}_y$ , and  $\hat{L}_z$ , one can define angular raising and lowering operators  $\hat{L}^+$  and  $\hat{L}^-$  as,

$$\hat{L}^{\pm} \equiv \hat{L}_x \pm i\hat{L}_y = -i\hbar e^{\pm i\varphi} \left(\pm i\frac{\partial}{\partial\theta} - \cot\theta\frac{\partial}{\partial\varphi}\right)$$

and we have the equivalent set  $\hat{L}_x, \hat{L}_y$ , and  $\hat{L}_z$  or  $\hat{L}^-, \hat{L}^+$  and  $\hat{L}_z$ . The algebra for this 2nd set is more convenient. It is easy to show the commutations between three operators  $L_z, L^{\pm}$  are given by

$$\left[\hat{L}_z, \ \hat{L}^{\pm}\right] = \pm \hbar \hat{L}^{\pm}, \quad \left[\hat{L}^+, \ \hat{L}^-\right] = 2\hbar \hat{L}_z .$$

Note: Compare this algebra with harmonic oscillator  $[\hat{a}, \hat{a}^{\dagger}] = 1$ . These algebra will determine the eigenfunctions and eigenvalues of  $\hat{L}^2$ . It is also easy to derive

$$\hat{L}^{+}\hat{L}^{-} = \hat{L}^{2} - \hat{L}_{z}^{2} + \hbar\hat{L}_{z}, \hat{L}^{-}\hat{L}^{+} = \hat{L}^{2} - \hat{L}_{z}^{2} - \hbar\hat{L}_{z},$$

and

$$\hat{L}^2 = \hat{L}_z^2 + \hbar \hat{L}_z + \hat{L}^- \hat{L}^+ = \hat{L}_z^2 - \hbar \hat{L}_z + \hat{L}^+ \hat{L}^- = \hat{L}_z^2 + \frac{1}{2} \left( \hat{L}^+ \hat{L}^- + \hat{L}^- \hat{L}^+ \right)$$

Note: compare this with harmonic oscillator  $\hat{H} = \hbar \omega \left( \hat{a}^{\dagger} \hat{a} + \frac{1}{2} \right)$ .

#### 2.1.3 Eigenvalues and eigenfunctions

(i) Solution for  $\Phi_m(\varphi)$  is simple

$$-i\hbar \frac{\partial}{\partial \varphi} \Phi_m(\varphi) = \lambda_m \Phi_m(\varphi)$$
$$\Phi_m(\varphi) = \frac{1}{\sqrt{2\pi}} e^{i\lambda_m \varphi/\hbar}$$

and using spherical symmetry of the system, we must have

$$\Phi_m(\varphi + 2\pi) = \Phi_m(\varphi) \rightarrow \frac{\lambda_m}{\hbar} = m = 0, \pm 1, \pm 2, \cdots$$

therefore

$$\hat{L}_z |m\rangle = m\hbar |m\rangle, \quad m = 0, \pm 1, \pm 2, \cdots.$$

(ii) Consider the eigenequations

$$\hat{L}^2 \left| l, m \right\rangle = \lambda_{l,m} \left| l, m \right\rangle$$

it is obvious  $|l, m\rangle$  is also eigenfunction of  $\hat{L}_z$ 

$$\hat{L}_{z}\left|l,m\right\rangle = \hbar m\left|l,m\right\rangle$$

we next examine the effect of  $\hat{L}^+$  and  $\hat{L}^-$  when acting on  $|l, m\rangle$ . We divide the whole process by following steps.

(a) Using the commutation relationship  $\left[\hat{L}_z, \ \hat{L}^{\pm}\right] = \pm \hbar \hat{L}^{\pm}$ , we have

$$\hat{L}_{z}\hat{L}^{\pm}\left|l,m\right\rangle = \left(\hat{L}^{\pm}\hat{L}_{z}\pm\hat{L}^{\pm}\right)\left|l,m\right\rangle = \left(\hbar m\hat{L}^{\pm}\pm\hbar\hat{L}^{\pm}\right)\left|l,m\right\rangle = \hbar\left(m\pm1\right)\hat{L}^{\pm}\left|l,m\right\rangle$$

therefore,  $\hat{L}^+$  effectively increases m by a unity and  $\hat{L}^-$  effectively decreases m by a unity, hence we write

$$\hat{L}^{\pm}\left|l,m\right\rangle = C_{\pm}\left(l,m\right)\left|l,m\pm1\right\rangle$$

where  $C_{\pm}(l,m)$  are constants. Therefore, the states  $|l,m\rangle$  with  $m = 0, \pm 1, \pm 2, \cdots$  can be related by raising or lowering operator  $\hat{L}^{\pm}$ .

(b)  $\hat{L}^2$  degeneracy. The eigenvalue of  $\hat{L}^2$  is independent of m,  $\lambda_{l,m} = \lambda_l$ 

$$\hat{L}^2 |l, m\rangle = \lambda_l |l, m\rangle$$

Proof: using  $\left[\hat{L}^2, \ \hat{L}^{\pm}\right] = 0$ , we have

$$\hat{L}^{2} \hat{L}^{\pm} |l, m\rangle = C_{\pm} \hat{L}^{2} |l, m \pm 1\rangle = \lambda_{l, m \pm 1} C_{\pm} |l, m \pm 1\rangle = \lambda_{l, m \pm 1} \hat{L}^{\pm} |l, m\rangle$$

$$= \hat{L}^{\pm} \hat{L}^{2} |l, m\rangle = \lambda_{l, m} \hat{L}^{\pm} |l, m\rangle$$

hence

$$\lambda_{l,m\pm 1} = \lambda_{l,m} \quad \to \lambda_l$$

(c) For a given  $\lambda_l$  (or l), the values of m must be bounded. Because  $\left\langle \left(\hat{L}_x^2 + \hat{L}_y^2\right) \right\rangle > 0$ ,  $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \rightarrow \hat{L}_x^2 + \hat{L}_y^2 + \hbar^2 m^2$ . Let this maximum value of |m| be  $M_l \equiv l$ , remember l is only an index for labeling. Hence

$$|l,m\rangle$$
,  $m=0,\pm 1,\pm 2,\cdot\cdot\cdot,\pm l$ 

Altogether, there are (2l+1) values of m.

(d) Consider state  $|l, l\rangle$ . Since its *m* is at maximum, cannot increase any more, we must have

$$\hat{L}^+ |l, l\rangle = 0$$

hence

$$\hat{L}^2 |l,l\rangle = \left( \hat{L}_z^2 + \hbar \hat{L}_z + \hat{L}^- \hat{L}^+ \right) |l,l\rangle = \hbar^2 \left( l^2 + l \right) |l,l\rangle$$

$$= \hbar^2 l \left( l+1 \right) |l,l\rangle .$$

Using the degeneracy of  $\hat{L}^2$ , we have

$$\hat{L}^2 |l, m\rangle = \hbar^2 l (l+1) |l, m\rangle, \quad m = 0, \pm 1, \pm 2, \cdots, \pm l$$

(e) We can now determine the coefficients  $C_{\pm}(l,m)$ 

$$\hat{L}^{\pm} \left| l, m \right\rangle = C_{\pm} \left( l, m \right) \left| l, m \pm 1 \right\rangle$$
.

Using the fact that  $(\hat{L}^{-})^{\dagger} = \hat{L}^{+}$ , assuming  $|l, m\rangle$  and  $|l, m \pm 1\rangle$  have already been normalized, we have

$$\hat{L}^{+} |l, m\rangle = C_{+} (l, m) |l, m + 1\rangle C_{+}^{2} (l, m) = \left(\langle l, m | \hat{L}^{-} \right) \left( \hat{L}^{+} | l, m \rangle \right) = \langle l, m | \hat{L}^{-} \hat{L}^{+} | l, m \rangle = \langle l, m | \left( \hat{L}^{2} - \hat{L}_{z}^{2} - \hbar \hat{L}_{z} \right) | l, m \rangle = \hbar^{2} \left[ l (l + 1) - m (m + 1) \right]$$

or

$$C_{+}(l,m) = \hbar \sqrt{l(l+1) - m(m+1)}$$

similarly

$$C_{-}(l,m) = \hbar \sqrt{l(l+1) - m(m-1)}$$
.

(f) From the definition of  $\hat{L}^+$  in spherical coordinate

$$\hat{L}^{+} = -i\hbar e^{i\varphi} \left( i\frac{\partial}{\partial\theta} - \cot\theta \frac{\partial}{\partial\varphi} \right)$$

and using the fact that

$$\hat{L}^{+}\left|l,l\right\rangle=0$$

we derive the equation for the highest-order spherical harmonic function,  $|l,l\rangle = Y_{ll}(\theta,\phi)$ 

$$\left(\frac{\partial}{\partial\theta} - l\cot\theta\right)Y_{ll} = 0, \quad Y_{ll} = c\,e^{il\phi}\sin^l\theta, \quad c = \frac{(-1)^l}{\sqrt{4\pi}}\sqrt{\frac{(2l+1)!!}{(2l)!!}}$$

where c is the normalization constant, determined by

$$2\pi \int_0^\pi \sin^{2l+1} \theta d\theta = 2\pi \left( \int_0^{\pi/2} + \int_{\pi/2}^\pi \right) \sin^{2l+1} \theta d\theta = 2\pi \left( \int_0^{\pi/2} \sin^{2l+1} \theta d\theta + \int_0^{\pi/2} \cos^{2l+1} \theta d\theta \right)$$
$$= 4\pi \int_0^{\pi/2} \sin^{2l+1} \theta d\theta = 4\pi \frac{(2l)!!}{(2l+1)!!} .$$

By applying  $L^-$  repeatedly, we obtain the general spherical harmonic,  $Y_{lm}(\theta, \varphi)$ .

(iii) For a general angular momentum  $\hat{\mathbf{L}}$ , all above derivations are still valid, except that we do not have the representation  $\hat{L}_z = -i\hbar\partial/\partial\varphi$ , etc. And the corresponding rotational invariance  $\Phi(\varphi + 2\pi) = \Phi(\varphi) \rightarrow m = 0, \pm 1, \pm 2, \cdots$  are hence not necessarily true. Hence we derive the following general **angular momentum theorem**,

$$\hat{\mathbf{L}}^2 |l, m\rangle = \hbar^2 l (l+1) |l, m\rangle \hat{L}_z |l, m\rangle = \hbar m |l, m\rangle m = -l, -l+1, \cdots, l-1, l$$

with (2l+1) values of m. As 2l+1 must be an integer, l must be an integer or half-odd-integer.

**Example: Electron spin**. An electron has an intrinsic angular momentum, called spin, denoted as  $\hat{S}$ , with quantum number S. Experimentally, it was found S = 1/2. The corresponding z-component quantum number is therefore given by m = -1/2, 1/2. Therefore, applying the above universal algebra to the spin angular momentum, we have

$$\begin{split} \hat{S}^2 \left| S, m \right\rangle &= \hbar^2 S \left( S + 1 \right) \left| S, m \right\rangle \\ &= \hbar^2 \frac{1}{2} \left( \frac{1}{2} + 1 \right) \left| S, m \right\rangle \\ &= \frac{3}{4} \hbar^2 \left| S, m \right\rangle, \quad m = -\frac{1}{2}, \frac{1}{2} \\ \hat{S}_z \left| S, m \right\rangle &= \hbar m \left| S, m \right\rangle. \end{split}$$

Since for an electron, S = 1/2 is fixed and well-know,  $\hat{S}^2 = \frac{3}{4}\hbar^2$  is a constant. We denote  $m = -\frac{1}{2}$  as spin-up state, and  $m = -\frac{1}{2}$  as spin-down state, we write

$$\left|S,m=\frac{1}{2}\right\rangle = \left|\uparrow\right\rangle \to \chi_{\uparrow}, \quad \left|S,m=-\frac{1}{2}\right\rangle = \left|\downarrow\right\rangle \to \chi_{\downarrow}$$

and

$$\hat{S}_{z}\left|\uparrow\right\rangle = \frac{\hbar}{2}\left|\uparrow\right\rangle, \quad \hat{S}_{z}\left|\downarrow\right\rangle = -\frac{\hbar}{2}\left|\downarrow\right\rangle \ .$$

#### 2.1.4 Addition of Angular Momenta

We know that the eigenstates of a general angular momentum  $\hat{\mathbf{L}}$  has two quantum numbers (qn): l - angular momentum qn and m - magnetic qn, the corresponding eigen eqs. are

$$\hat{L}^2 |l,m\rangle = \hbar^2 l (l+1) |l,m\rangle \hat{L}_z |l,m\rangle = \hbar m |l,m\rangle, \quad m = -l, -l+1, \cdots, l-1, l$$

The reason is simply that these two operators commute with one another  $[\hat{L}^2, \hat{L}_z] = 0$ . People usually refer these proper qn's as **good quantum numbers**.

Now we consider addition of two angular momenta

$$\begin{aligned} \hat{\mathbf{L}} &= \hat{\mathbf{L}}_1 + \hat{\mathbf{L}}_2 \\ \hat{L}^2 &= \hat{L}_1^2 + \hat{L}_2^2 + 2\hat{\mathbf{L}}_1 \cdot \hat{\mathbf{L}}_2 \\ \hat{\mathbf{L}}_1 \cdot \hat{\mathbf{L}}_2 &= \hat{L}_{x1}\hat{L}_{x2} + \hat{L}_{y1}\hat{L}_{y2} + \hat{L}_{z1}\hat{L}_{z2} \ . \end{aligned}$$

Physical examples are the total angular momentum of two separate particles, or the total momentum of the orbital and spin angular momenta of a single particle, etc. The eigen states of  $\hat{L}_1^2$  and  $\hat{L}_2^2$  are known separately as

$$\hat{L}_{i}^{2} |l_{i}, m_{i}\rangle = \hbar^{2} l_{i} (l_{i} + 1) |l_{i}, m_{i}\rangle, \quad i = 1, 2 \hat{L}_{zi} |l_{i}, m_{i}\rangle = \hbar m_{i} |l_{i}, m_{i}\rangle, \quad m_{i} = -l_{i}, -l_{i} + 1, \cdots, l_{i} - 1, l_{i}.$$

We want to know what are the good qn's for the eigenstates of total  $\hat{\mathbf{L}}$ , and what are the eigenvalues.

The algebra for total  $\hat{\mathbf{L}}$  is the same as before. It is easy to prove

$$\begin{bmatrix} \hat{L}^2, \ \hat{L}_1^2 \end{bmatrix} = \begin{bmatrix} \hat{L}^2, \ \hat{L}_2^2 \end{bmatrix} = \begin{bmatrix} \hat{L}^2, \ \hat{L}_z \end{bmatrix} = 0$$
$$\hat{L}_z = \hat{L}_{z1} + \hat{L}_{z2}$$

but

$$\begin{bmatrix} \hat{L}^2, \ \hat{L}_{z1} \end{bmatrix} = 2 \begin{bmatrix} \hat{L}_{x1} \hat{L}_{x2} + \hat{L}_{y1} \hat{L}_{y2}, \ \hat{L}_{z1} \end{bmatrix}$$

$$= 2i\hbar \left( -\hat{L}_{y1} \hat{L}_{x2} + \hat{L}_{x1} \hat{L}_{y2} \right) \neq 0$$

$$\begin{bmatrix} \hat{L}^2, \ \hat{L}_{z2} \end{bmatrix} = 2 \begin{bmatrix} \hat{L}_{x1} \hat{L}_{x2} + \hat{L}_{y1} \hat{L}_{y2}, \ \hat{L}_{z2} \end{bmatrix}$$

$$= 2i\hbar \left( -\hat{L}_{x1} \hat{L}_{y2} + \hat{L}_{y1} \hat{L}_{x2} \right) \neq 0 .$$

Therefore, we can find a common eigen state to  $\hat{L}_1^2$ ,  $\hat{L}_2^2$ ,  $\hat{L}^2$ ,  $\hat{L}_z$  and denote as  $|l_1, l_2, l, m\rangle$ , these are **good quantum numbers**. ( $m_1$  and  $m_2$  are not good quantum numbers). The eigen eqs. are

$$\begin{split} \hat{L}_{1}^{2} \left| l_{1}, l_{2}, l, m \right\rangle &= \hbar^{2} l_{1} \left( l_{1} + 1 \right) \left| l_{1}, l_{2}, l, m \right\rangle \\ \hat{L}_{1}^{2} \left| l_{1}, l_{2}, l, m \right\rangle &= \hbar^{2} l_{2} \left( l_{2} + 1 \right) \left| l_{1}, l_{2}, l, m \right\rangle \\ \hat{L}^{2} \left| l_{1}, l_{2}, l, m \right\rangle &= \hbar^{2} l \left( l + 1 \right) \left| l_{1}, l_{2}, l, m \right\rangle \\ \hat{L}_{2} \left| l_{1}, l_{2}, l, m \right\rangle &= \hbar m \left| l_{1}, l_{2}, l, m \right\rangle, \quad m = -l, -l + 1, \cdots, l - 1, l \end{split}$$

etc.

The question is: for a given  $l_1$  and  $l_2$ , what are the possible values for l. For this purpose, we consider the following few steps:

(a) Total dimensionality (no. of independent states) is  $(2l_1 + 1) \times (2l_2 + 1)$ . This will restrict the number of possible l

$$\sum_{l} (2l+1) = (2l_1+1) \times (2l_2+1) \; .$$

(b) Starting with the state

$$|l_1, m_1 = l_1 \rangle |l_2, m_2 = l_2 \rangle$$

it is eigenstate of  $\hat{L}_z$ 

$$\hat{L}_{z}\left(\left|l_{1}, m_{1}=l_{1}\right\rangle\left|l_{2}, m_{2}=l_{2}\right\rangle\right)=\hbar\left(l_{1}+l_{1}\right)\left(\left|l_{1}, m_{1}=l_{1}\right\rangle\left|l_{2}, m_{2}=l_{2}\right\rangle\right)$$

and since  $m = l_1 + l_1$  is the largest possible value for  $m, l = l_1 + l_1$  is the largest possible value for l. This is the only one. Hence

$$|l_1, l_2, l_1 + l_1, l_1 + l_1\rangle = |l_1, l_1\rangle |l_2, l_2\rangle$$

(c) Next, consider state with  $m = l_1 + l_1 - 1$ . There are two possible l, with  $l = l_1 + l_1$  and  $l = l_1 + l_1 - 1$ , hence denoted as

$$|l_1, l_2, l_1 + l_1, l_1 + l_1 - 1\rangle$$
,  $|l_1, l_2, l_1 + l_1 - 1, m = l_1 + l_1 - 1\rangle$ 

In terms of  $|l_1, m_1\rangle |l_2, m_2\rangle$  representation, these are a linear combination of two possible states, as seen in the following table

(d) Continue this process, the possible value of l decreases by one, and number of states increases by one. Therefore,

$$l = l_1 + l_2, l_1 + l_2 - 1, l_1 + l_2 - 2, \cdots, |l_1 - l_2|$$

the minimum value is  $|l_1 - l_2|$  since l must be a positive number.

(e) And we have identity

$$\sum_{l=|l_1-l_2|}^{l_1+l_2} (2l+1) = (2l_1+1) \times (2l_2+1)$$
  
= 2 (l\_1 - l\_2 + 0) + 1, let l\_1 > l\_2  
+2 (l\_1 - l\_2 + 1) + 1

$$+2 (l_1 - l_2 + 2) + 1$$
  
...  
$$+2 (l_1 - l_2 + 2l_2) + 1$$
  
$$= 2l_1 (2l_2 + 1) - 2l_2 (2l_2 + 1) + 2 \times \frac{1}{2} 2l_2 (2l_2 + 1) + (2l_2 + 1)$$
  
$$= (2l_1 + 1) \times (2l_2 + 1)$$

where we have used

$$1 + 2 + 3 + \dots + n = \frac{1}{2}n(n+1)$$
.

Angular momentum addition theorem: Total angular momentum  $\hat{\mathbf{L}} = \hat{\mathbf{L}}_1 + \hat{\mathbf{L}}_2$  eigenstates are denoted by good quantum numbers  $|l_1, l_2, l, m\rangle$ , and eigenvalues are given by

$$\hat{\mathbf{L}}^2|l_1, l_2, l, m\rangle = \hbar^2 l(l+1)|l_1, l_2, l, m\rangle, \quad \hat{L}_z|l_1, l_2, l, m\rangle = \hbar m|l_1, l_2, l, m\rangle$$

with m = -l, -l + 1, ..., l - 1, l, and  $l = l_1 + l_2, l_1 + l_2 - 1, ..., |l_1 - l_2|$ .

**Example**. An electron is in a state with orbital angular momentum l = 5. Its total angular momentum

$$\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$$

has possible quantum numbers as

$$J = \frac{11}{2}, \frac{9}{2}$$

and the total number of states

$$\left(2 \times \frac{11}{2} + 1\right) + \left(2 \times \frac{9}{2} + 1\right) = (2 \times 5 + 1)\left(2 \times \frac{1}{2} + 1\right) = 22$$

**Example**. Eigenvalues of operator  $\hat{H} = \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$ . Write this operator as

$$\hat{H} = \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = \frac{1}{2} \left( \hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2 \right)$$

and its eigenstates are characterized by the good quantum numbers  $|l, s, j, m_i\rangle$ . So

$$\hat{H} |l, s, j, m_j \rangle = \frac{1}{2} \left( \hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2 \right) |l, s, j, m_j \rangle$$

$$= \frac{\hbar^2}{2} \left[ j \left( j + 1 \right) - l \left( l + 1 \right) - s \left( s + 1 \right) \right] |l, s, j, m_j \rangle$$

$$= \frac{\hbar^2}{2} \left[ j \left( j + 1 \right) - l \left( l + 1 \right) - \frac{3}{4} \right] |l, s, j, m_j \rangle, \quad j = l \pm \frac{1}{2} .$$

Two spin-1/2 systems. Two interacting spins have the following Heisenberg Hamiltonian

$$\hat{H} = \alpha \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2$$

where  $\alpha$  is the coupling constant. Determines its eigenvalues and eigenstates. Write the Hamiltonian as

$$\hat{H} = \alpha \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 = \frac{\alpha}{2} \left[ \hat{\mathbf{S}}^2 - \hat{\mathbf{S}}_1^2 - \hat{\mathbf{S}}_2^2 \right], \quad \hat{\mathbf{S}} = \hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2$$

hence its eigenvalues are, using  $s_1 = s_2 = 1/2$ 

$$E_{s} = \frac{\alpha \hbar^{2}}{2} \left[ s \left( s + 1 \right) - s_{1} \left( s_{1} + 1 \right) - s_{2} \left( s_{2} + 1 \right) \right]$$
$$= \frac{\alpha \hbar^{2}}{2} \left[ s \left( s + 1 \right) - \frac{3}{2} \right].$$

By the angular momentum addition theorem, there are only two possible values for s: 0, 1. So the eigenvalues are

$$E_0 = -\frac{3\alpha\hbar^2}{4}, \quad E_1 = \frac{\alpha\hbar^2}{4}.$$

In order to determine the corresponding eigenstates  $|s, m\rangle$ , we first observe that, considering the quantum number m for  $\hat{S}_z$ , there is only one state for  $E_0$  with m = 0, denoted as  $|0, 0\rangle$  with eigenequation

$$\hat{H} \left| 0, 0 \right\rangle = E_0 \left| 0, 0 \right\rangle \;;$$

there are three states for  $E_1$  since there three possible *m* values  $m = 0, \pm 1$ , denoted as  $|1, 0\rangle$  and  $|1, \pm 1\rangle$  with eigen equations

$$\hat{H} |1,0\rangle = E_1 |1,0\rangle, \quad \hat{H} |1,\pm 1\rangle = E_1 |1,\pm 1\rangle.$$

Note that these later three states are degenerate. All these four states are obtained from the following four basis states  $|\uparrow\rangle_1 |\uparrow\rangle_2$ ,  $|\downarrow\rangle_1 |\uparrow\rangle_2$ ,  $|\uparrow\rangle_1 |\downarrow\rangle_2$ ,  $|\downarrow\rangle_1 |\downarrow\rangle_2$ . It is easy to see that only one basis state  $|\uparrow\rangle_1 |\uparrow\rangle_2$  gives m = 1, hence

$$|1,+1\rangle = |\uparrow\rangle_1 |\uparrow\rangle_2$$
;

similarly there is only one state with m = -1, hence

$$|1,-1\rangle = |\downarrow\rangle_1 |\downarrow\rangle_2$$
;

and the other two basis state,  $|\downarrow\rangle_1|\uparrow\rangle_2$  and  $|\uparrow\rangle_1|\downarrow\rangle_2$ , clearly have m = 0. Their combinations will give  $|0,0\rangle$  and  $|1,0\rangle$ . The only two possible independent combinations are

$$\frac{1}{\sqrt{2}}\left(\left|\downarrow\right\rangle_{1}\left|\uparrow\right\rangle_{2}\pm\left|\uparrow\right\rangle_{1}\left|\downarrow\right\rangle_{2}\right)$$

with the normalization factor  $1/\sqrt{2}$ . By directly applying the Hamiltonian  $\hat{H}$  to these two states (see Exercise 2, Question 4), it is easy to show that

$$|0,0\rangle = \frac{1}{\sqrt{2}} \left(|\downarrow\rangle_1 |\uparrow\rangle_2 - |\uparrow\rangle_1 |\downarrow\rangle_2\right)$$

and

$$|1,0\rangle = \frac{1}{\sqrt{2}} \left( |\downarrow\rangle_1 |\uparrow\rangle_2 + |\uparrow\rangle_1 |\downarrow\rangle_2 \right) \,.$$

Conclusion: the two-spin Hamiltonian  $\hat{H} = \alpha \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2$  has two levels, a singlet level with energy  $E_0 = -\frac{3\alpha\hbar^2}{4}$  and state  $\frac{1}{\sqrt{2}} (|\downarrow\rangle_1 |\uparrow\rangle_2 - |\uparrow\rangle_1 |\downarrow\rangle_2)$  and a triplet level with energy  $E_1 = \frac{\alpha\hbar^2}{4}$  and three states  $|\uparrow\rangle_1 |\uparrow\rangle_2, \frac{1}{\sqrt{2}} (|\downarrow\rangle_1 |\uparrow\rangle_2 + |\uparrow\rangle_1 |\downarrow\rangle_2)$  and  $|\downarrow\rangle_1 |\downarrow\rangle_2$ .

# 2.2 Hydrogen-like Atom

The system of a Hydrogen-like atom consists of an electron and a nucleus containing Z protons, interacting with attractive Coulomb potential. The Hamiltonian for the relative motion is given by

$$\begin{split} \hat{H} &= -\frac{\hbar^2}{2\mu} \nabla^2 + V\left(r\right), \quad V\left(r\right) = -\frac{e^2}{4\pi\epsilon_0} \frac{Z}{r} \\ &= -\frac{\hbar^2}{2\mu} \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + V\left(r\right) + \frac{1}{2\mu} \frac{\hat{L}^2}{r^2} \end{split}$$

with reduced mass  $\mu = m_e m_n / (m_e + m_n)$  where  $m_n$  is the nuclear mass. The Schrödinger eq.

$$\hat{H}|n,l,m\rangle = \lambda_{n,l,m}|n,l,m\rangle, \quad \hat{H}\Psi_{n,l,m}(r,\theta,\varphi) = \lambda_{n,l,m}\Psi_{n,l,m}(r,\theta,\varphi)$$

with

$$\begin{split} \Psi_{n,l,m}\left(r,\theta,\varphi\right) &= R_{n,l,m}\left(r\right)Y_{l,m}\left(\theta,\varphi\right) \to |n,l,m\rangle\\ Y_{l,m}\left(l,m\right) &= \Theta_{l,m}\left(\theta\right)\Phi_{m}\left(\varphi\right) \to |l,m\rangle\\ \Phi_{m}\left(\varphi\right) &\to |m\rangle, \quad m=0,\pm 1,\pm 2,\cdots,\pm l \end{split}$$

and

$$\hat{L}^{2} |l,m\rangle = \hbar^{2} l (l+1) |l,m\rangle, \quad \hat{L}_{z} |l,m\rangle = \hbar m |l,m\rangle$$

Therefore, eigen problem for  $\hat{H}$  becomes,  $R_{n,l,m}(r) \to R_{n,l}(r), \lambda_{n,l,m} \to \lambda_{n,l}$ 

$$\left(-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}+V\left(r\right)+\frac{\hbar^2l\left(l+1\right)}{2\mu}\frac{1}{r^2}\right)R_{n,l}\left(r\right)=\lambda_{n,l}R_{n,l}\left(r\right)$$

Solution of this eigenequation is not universal, depending on the given V(r). For the Coulomb potential  $V(r) = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$ , we have

$$l = 0, 1, 2, \cdots, (n-1)$$

for the condition existing solution,

$$\lambda_{n,l} = \lambda_n = -\frac{e^2}{8\pi\epsilon_0 a_0} \frac{Z^2}{n^2} \approx -13.6 \frac{1}{n^2} \text{ (eV)}, \quad a_0 = \frac{4\pi\epsilon_0 \hbar^2}{\mu e^2} \approx 0.53 \times 10^{-10} \text{ (m)}$$

for the eigenvalues, and

$$R_{n,l}(r) = e^{-Zr/na_0} r^l \left( C_0 + C_1 r + C_2 r^2 + \dots + C_{n-l-1} r^{n-l-1} \right)$$

for the eigenfunctions, where  $C_i$  are real constants. We plot the first few radial probability distributions in Fig. 2. In Fig. 3, we plot the angular parts probability distributions. (Figures are copied from Gasiorowicz's Quantum Physics)



Fig. 2 Radial probability distributions  $r^2 R_{nl}^2(r)$ . The horizontal axis is r in units of  $a_0$ .



Fig. 3 Angular probability distributions  $|Y_{lm}(\theta, \phi)|^2$ . The sketches represent sections of the distributions made in the *z*-*x* plane. It should be understood that the three-dimensional distributions are obtained by rotating the figures about the *z*-axis.

### Summary of Hydrogen Atom QM

QM of Hydrogen (or Hydrogen-like atoms)

$$\hat{H} |n, l, m, m_s \rangle = E_n |n, l, m, m_s \rangle, \quad E_n = -13.6 \frac{Z^2}{n^2} \text{ (eV)},$$

$$|n, l, m, m_s \rangle \rightarrow R_{n,l} (r) Y_{l,m} (\theta, \varphi) \chi_{m_s}$$

$$\hat{H} = -\frac{\hbar^2}{2\mu} \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r} + \frac{1}{2\mu} \frac{\hat{L}^2}{r^2}$$

with reduced mass  $\mu$  and electron spin  $m_s = \pm 1/2$ . The degeneracy for each given n is

$$D_n = \sum_{l=0}^{n-1} (2l+1) = n^2$$
.

 $Y_{l,m}\left(\theta,\varphi\right)$  is the eigenstate of angular momentum  $\hat{L}^{2}$ 

$$\hat{L}^{2} |l,m\rangle = \hbar^{2} l (l+1) |l,m\rangle, \quad |l,m\rangle \to Y_{l,m} (\theta,\varphi) = \Theta_{l,m} (\theta) \Phi_{m} (\varphi)$$

$$\hat{L}^{2} = -\hbar^{2} \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} - \frac{1}{\sin^{2} \theta} \frac{\hat{L}_{z}^{2}}{\hbar^{2}} \right)$$

with degeneracy for each given l

$$\sum_{m=-l}^{l} 1 = 2l+1$$

where  $\Phi_{m}(\varphi)$  is the eigenstate of  $\hat{L}_{z}$ 

$$\hat{L}_{z} |m\rangle = \hbar m |m\rangle, \quad |m\rangle \to \Phi_{m} (\varphi), \quad m = 0, \pm 1, \pm 2, \cdots, \pm l$$

$$\hat{L}_{z} = -i\hbar \frac{\partial}{\partial \varphi}, \quad \Phi_{m} (\varphi) = \frac{1}{\sqrt{2\pi}} e^{im\varphi}.$$

### 2.3 Pauli exclusion principle and periodic table

In this section, we introduce some important concepts of quantum many-body theory as atoms and molecules are many-body systems. We will mainly ignore the interactions between electrons and only consider their Coulomb repulsion by empirical rules.

Consider two identical particle system (e.g., two electrons in a Helium atom). Suppose their wavefunction is  $\psi(x_1, x_2)$ , where  $x_i$  is the coordinate of the *i*th particle, e.g.,  $x = (\mathbf{r}, \sigma)$  with r the spatial position and  $\sigma = \uparrow, \downarrow$  the spin of the particle, etc.

Consider the exchange operation  $\hat{P}$ : exchanging the coordinates of the two particles,

$$\hat{P}_{1\leftrightarrow 2}\psi\left(x_{1},x_{2}\right)=\psi\left(x_{2},x_{1}\right)$$

If we choose  $\psi(x_1, x_2)$  as an eigenstate of  $\hat{P}_{1\leftrightarrow 2}$  with eigenvalue p, then the eigenequation is

$$\hat{P}_{1\leftrightarrow 2}\psi\left(x_{1},x_{2}\right)=p\psi\left(x_{1},x_{2}\right).$$

Acting  $\hat{P}_{1\leftrightarrow 2}$  second time we get back to the original state,

$$p^{2}\psi(x_{1}, x_{2}) = \psi(x_{1}, x_{2}), \text{ or } p^{2} = 1$$

Therefore, p can only has two values

$$p = \pm 1.$$

The quantum particles with p = 1 are referred to as Boson particles, or simply Bosons; The quantum particles with p = -1 are referred to as Fermion particles, or simply Fermions. A more general analysis shows that with integer spin are always Bosons, and particles with half-odd-integer spins are always Fermions. For example, electrons and protons are Fermions, and photons (light quanta) are Bosons; Helium-4 is Boson because its spin is zero, but Helium-3 atom is Fermion with spin 1/2.

For a general quantum many-body wavefunction, the exchange operation is

$$P_{n \leftrightarrow m} \psi \left( \cdots, x_n, \cdots, x_m, \cdots \right) = \pm \psi \left( \cdots, x_m, \cdots, x_n, \cdots \right) ,$$

where + corresponds to Boson system, and - to Fermion system. This is a exact property of a quantum many-body system.

Now let us consider its consequence. A general Hamiltonian of N-particle system is

$$\hat{H} = \sum_{i=1}^{N} \hat{H}_i + \hat{V}$$

where  $\hat{V}$  is the interaction potential and usually given by

$$\hat{V} = \frac{1}{2} \sum_{i \neq j}^{N} V\left(\mathbf{r}_{ij}\right) \; .$$

For example

$$\hat{V} = \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{12}}$$

for helium atom and

$$\hat{V} = \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}}\right)$$

for lithium. Now consider the simplest approximation by ignoring  $\hat{V}$ , (the corresponding wavefunction is the zero-order approximation to the true eigenstate), the Hamiltonian becomes separate

$$\hat{H} \approx \sum_{i=1}^{N} \hat{H}_i$$

and the wavefunction becomes a product of single particle states. In general, we refer to such approximation as **the independent-particle approximation**. The essence of this approximation is to keep the quantum nature of particles but ignoring their dynamic interactions (later, we will include some corrections due to Coulomb repulsion by empirical Hund's rule). Assume that we have solved the single-particle Schrödinger eq.

$$\hat{H}_{1}\Phi_{k}\left(x_{1}\right)=E_{k}\Phi_{k}\left(x_{1}\right)$$

the total wavefunction may be written as

$$\Psi(x_1, x_2, \cdots, x_N) \propto \Phi_{k1}(x_1) \Phi_{k2}(x_2) \cdots \Phi_{kN}(x_N)$$

not taking the exchange symmetry into account. In order to include this important quantum symmetry, consider first a 2-particle system, N = 2,

$$\psi_B(x_1, x_2) = \frac{1}{\sqrt{2}} \left[ \varphi_{n_1}(x_1) \varphi_{n_2}(x_2) + \varphi_{n_1}(x_2) \varphi_{n_2}(x_1) \right] \quad \text{for Bosons}$$

[or  $\varphi_{n1}(x_1)\varphi_{n1}(x_2)$  etc.] and

$$\psi_F(x_1, x_2) = \frac{1}{\sqrt{2}} \left[ \varphi_{n_1}(x_1) \varphi_{n_2}(x_2) - \varphi_{n_1}(x_2) \varphi_{n_2}(x_1) \right]$$
 for Fermions

so that  $\psi_B(x_1, x_2) = \psi_B(x_2, x_1)$  for Bosons and  $\psi_F(x_1, x_2) = -\psi_F(x_2, x_1)$  for Fermions. One can also construct a symmetric wavefunction for two Bosons by a single wavefunction as  $\psi_B(x_1, x_2) = \varphi_{n_1}(x_1)\varphi_{n_1}(x_2)$ , or  $\varphi_{n_2}(x_1)\varphi_{n_2}(x_2)$ . Extending t o N-particle system, for the Fermions, we can write the wavefunction as a determinant, **Slater determinant**,

$$\psi(x_1, \cdots, x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_{n_1}(x_1) & \varphi_{n_1}(x_2) & \cdots & \varphi_{n_1}(x_N) \\ \varphi_{n_2}(x_1) & \varphi_{n_2}(x_2) & \cdots & \varphi_{n_2}(x_N) \\ \cdots & & & \\ \varphi_{n_N}(x_1) & \varphi_{n_N}(x_2) & \cdots & \varphi_{n_N}(x_N) \end{vmatrix}$$

Notice that if  $k_1 = k_2$ ,  $\psi_F(x_1, x_2) = 0$ , but not  $\psi_B(x_1, x_2)$ . This indicates that two Fermions cannot occupy the same state, but it two bosons are allowed to occupy the same state. It can be extended to a more general statement:

A state can only be occupied by at most a single Fermion; But it can be occupied by any number of Bosons.

The first above statement is **Pauli exclusion principle**. The second statement is the property that leads to the so-called Bose-Einstein condensation of bosons at low temperature. As active ingredients in atoms and molecules are electrons which are fermions, we will mainly use Pauli principle. It is obvious that in the independent-particle approximation (e.g., ignoring particle interactions), the ground state of an N-electron system is given by the Slater determinant constructed from the lowest N single particle states. For atoms, these single particles states are naturally the eigenstates of hydrogenlike atoms as we discussed previously. For molecules, these single particle states are constructed by a linear combinations of atomic states at different nuclear configurations. We will discuss QM of molecules in the last chapter. Sometimes it is convenient to separate total wavefunction as discussed above into product of spatial and spin parts of wavefunctions, namely

$$\Psi(x_1,\cdots,x_N)=\psi(\mathbf{r_1},\cdots,\mathbf{r_N})\chi(\sigma_1,\cdots,\sigma_N).$$

Hence, if spin wavefunction  $\chi$  is antisymmetric, the spatial wavefunction  $\psi$  must be symmetric in order for the total wavefunction  $\Psi$  to be antisymmetric, vice versa.

Now we apply this simple analysis to atoms, the elements on the periodical table, where the identical fermions are electrons with spin-1/2. We will qualitatively discuss the ground states of the atoms. In the next section, we will attempt to calculate the ground-state energy value of the two electron system, helium atom. By solving the Schrödinger equation of hydrogenlike atoms in the previous section, we know the electron's states in an atom can be characterized by four quantum numbers  $(n, l, m, m_s)$ : n - principle quantum number specified main energy levels (shells), l - (orbital) angular momentum quantum number, and m - (orbital) magnetic quantum number and  $m_s$  - spin magnetic quantum number. We extend this to many-electron's state ignoring the interactions, spin-orbit couplings, etc., by using the independent-particle approximation. Using notation

$$l = 0 \rightarrow s$$
 state,  $1 \rightarrow p$  state,  $2 \rightarrow d$  state  $\cdots$ 

and noticing m and  $m_s$  are degenerate quantum numbers, we conclude that s shell can take up to two electrons (single orbital with m = 0 but one electron with spin up  $m_s = 1/2$ , the other electron with spin down  $m_s = -1/2$ ); p shell can take up to 6 electrons (three states specified by m = 1, 0, -1, each can take one electron with spin up and one electron with spin down); d shell can take up to 10 electrons (5 states with m = 2, 1, 0, -1, -2, each can take two electrons), etc. These energy levels are ordered as,

orbitals (shells) :	1s	2s	2p	3s	3p	4s	3d	4p	5s	
electron no. :	2	4	10	12	18	20	30	36	38	• • •

In the above table, we also list total possible maximal number of electrons.

In this independent-particle picture, the way each electron of an atom occupies a particular hydrogen state is called **electron configuration**. As we are mainly interested in the ground state, the electron configuration of an atom is given by filling these hydrogen orbitals from the lowest, in the ordered series as

$$(1s)(2s)(2p)(3s)(3p)(4s)(3d)(4p)(5s)\cdots$$

We notice that a given electron configuration will not uniquely determine some basic properties (such as total angular momentum, spins etc.) of the corresponding atom. More information can be specified by using the so called atomic spectral term (or atomic term) to represent states of an atoms. Some correction to independent-particle approximation for the ground-state atomic term due to Coulomb repulsion will be considered by the empirical rules.

Atomic spectral terms. We use notation  ${}^{(2S+1)}L_J$  to denote a particular atomic state where S is its total spin, L its total orbital angular momentum and J the total angular momentum (spins and orbitals). We use capital Latin letters for each value of orbital quantum number as

For example,  ${}^{2}P_{3/2}$  denotes levels with L = 1, S = 1/2 and J = 3/2. The difference in energy between atomic levels having different L and S but the same electron configuration is due repulsive Coulomb interaction between electrons. These energy differences are small. We have the following empirical **Hund's rules** (F.Hund, 1925) concerning relative position of levels with the same configuration but different L and S:

- (i) For a given shell (configuration), the term with greatest possible value of S gives the lowest energy;
- (ii) The greatest possible value of L (for this S) has the lowest energy;
- (iii) For half or less than half filling shell, J = |L S| gives lowest energy; For more than half-filling shell, J = L + S gives lowest energy.

The origin of the first rule is obvious: the largest total spin corresponds to symmetric (parallel) spin wavefunction and antisymmetric orbital wavefunction, the later reduces electron-electron repulsive interaction energy.

**Example.** Helium (Z = 2) has a simple configuration  $(1s)^2$ . Hence S = 0 and L = 0. The ground state term is  ${}^1S_0$  with J = 0. We will use this term to construct an approximate wavefunction to calculate its ground-state energy in the next section.

**Example.** Carbon (Z = 6) has electron configuration as  $(1s)^2(2s)^2(2p)^2$ . There are three p orbitals with m = 1, 0, -1 as l = 1. Two electrons with both spin equal to 1/2 (corresponding to total largest spin S = 1) are in orbital m = 1, 0 with total maximal M = 1 + 0 = 1, corresponding to L = 1. Hence the ground state term is  ${}^{3}P_{0}$ . It is less than half-filling, J = |L - S| = 0. The other two possible terms are  ${}^{1}S$  and  ${}^{1}D$ . They correspond to higher energies. Do you know how to obtain these terms? Hint: Use symmetry argument.

**Example.** Nitrogen (Z = 7): He $(2s)^2(2p)^3$ . Three electrons with total spin S = 3/2 are in states m = 1, 0, -1 with total maximal M = 0 corresponding to L = 0. Ground state term is therefore  ${}^4S_{3/2}$ . Other terms are  ${}^2P$  and  ${}^2D$ .

**Example.** Oxygen (Z = 8): He $(2s)^2(2p)^4$ . Equivalent to two holes (two missing electrons for filled shell) in 2p orbitals. Its ground state term is therefore same as carbon,  ${}^3P$ . However, as it is more than half-filling, J = L + S = 2. So we have  ${}^3P_2$  for its ground state.

**Example.** Boron (Z = 5) and fluorine (Z = 9) have similar term but different J values, due to electron-hole symmetry. Can you write down their electron configurations and figure out their ground state terms?

Notice the particle-hole symmetry discussed in the last two examples. A hole is equivalent to an electron in its quantum nature; it is defined as the missing electron(s) for the otherwise filled shell.

Z	• Element	Configuration	Term*	Ionization Potential e
1	H	(1 <i>s</i> )	${}^{2}S_{1/2}$	13.6
2	He	$(1s)^2$	<sup>1</sup> S <sub>0</sub>	24.6
3	Li	(He)(2s)	${}^{2}S_{1/2}$	5.4
4	Be	$(He)(2s)^2$	${}^{1}S_{0}$	9.3
5	В	$(\text{He})(2s)^2(2p)$	${}^{2}P_{1/2}$	8.3
6	С	$(\text{He})(2s)^2(2p)^2$	$^{3}P_{0}$	11.3
7	N	$(\text{He})(2s)^2(2p)^3$	${}^{4}S_{3/2}$	14.5
8	0	$(\text{He})(2s)^2(2p)^4$	${}^{3}P_{2}$	13.6
9	F	$(\text{He})(2s)^2(2p)^5$	${}^{2}P_{3/2}$	17.4
10	Ne	$(\text{He})(2s)^2(2p)^6$	${}^{1}S_{0}$	21.6
11 .	Na	(Ne)(3s)	${}^{2}S_{1/2}$	5.1
12	Mg	$(Ne)(3s)^2$	${}^{1}S_{0}$	7.6
13	Al	$(Ne)(3s)^2(3p)$	${}^{2}P_{1/2}$	6.0
14	Si	$(Ne)(3s)^2(3p)^2$	${}^{3}P_{0}$	8.1
15	Р	$(Ne)(3s)^2(3p)^3$	<sup>4</sup> S <sub>3/2</sub>	11.0
16	S	$(Ne)(3s)^2(3p)^4$	${}^{3}P_{2}$	10.4
17	<b>C</b> 1	$(Ne)(3s)^2(3p)^5$	<sup>2</sup> P <sub>3/2</sub>	13.0
18	Ar	$(Ne)(3s)^2(3p)^6$	${}^{1}S_{0}$	15.8

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# 2.4 Ground state of helium atom

There two electrons in a helium atom and we are dealing with two identical particles. Consider in general helium-like ions with the following Hamiltonian describing two electrons interacting each other and with a nucleus containing Z protons

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{Ze^2}{4\pi\epsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{4\pi\epsilon_0}\frac{1}{r_{12}}$$

As a first approximation, we want to estimate the ground state energy of this Helium atom by applying approximate two-body state of Slater determinant discussed earlier,

$$\Psi_0 = \frac{1}{\sqrt{2}} \left[ \psi_1(x_1) \psi_2(x_2) - \psi_2(x_1) \psi_1(x_2) \right],$$

using the knowledge from hydrogen-like ions. Note x includes position and spin, i.e.  $x = (\mathbf{r}, \sigma)$  with spin  $\sigma = \uparrow, \downarrow$  and the single body wavefunction  $\psi(x)$  is a product of spatial and spin parts  $\psi(x) = \phi(\mathbf{r})\chi(\sigma)$ .

For the spatial wavefunction, we use the eigenstates  $\phi_{nlm}(\mathbf{r})$  for a single electron  $\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r}$  are

$$\phi_{1s}(\mathbf{r}) = R_{10}(r) Y_{00}(\theta, \phi) = \sqrt{\frac{Z^3}{\pi a_0^3}} e^{-Zr/a_0}$$
  
$$\phi_{2s}(\mathbf{r}) = R_{20}(r) Y_{00}(\theta, \phi) = \sqrt{\frac{Z^3}{8\pi a_0^3}} \left(1 - \frac{Zr}{2a_0}\right) e^{-Zr/a_0}$$
  
...

with  $\phi_{1s}(\mathbf{r})$  as the ground state, and eigenvalues

$$E_{nl} = E_n = -\frac{e^2}{8\pi\epsilon_0 a_0} \frac{Z^2}{n^2}, \quad n = 1, 2, \cdots$$

For the ground state of Helium atom, we want both electrons in the lowest energy state  $\phi_{1s}(\mathbf{r})$ , and antisymmetry requirement can be realized in the spin part of wave-function, constructed from two spin states  $|\uparrow\rangle$  or  $|\downarrow\rangle$ ,

$$\Psi_0(1,2) = \phi_{1s}(\mathbf{r}_1) \phi_{1s}(\mathbf{r}_2) \chi(\sigma_1,\sigma_2), \quad \chi(\sigma_1,\sigma_2) = \frac{1}{\sqrt{2}} \left( |\uparrow\rangle_1 |\downarrow\rangle_2 - |\downarrow\rangle_1 |\uparrow\rangle_2 \right)$$

hence  $\Psi(1,2) = -\Psi(2,1)$ . This is a spin-singlet state. Another possible trial state is the spin-triplet,

$$\Psi_{0}'(1,2) = \frac{1}{\sqrt{2}} \left[ \phi_{1s}(\mathbf{r}_{1}) \phi_{2s}(\mathbf{r}_{2}) - \phi_{2s}(\mathbf{r}_{1}) \phi_{1s}(\mathbf{r}_{2}) \right] \tau(\sigma_{1},\sigma_{2}),$$
  
$$\tau(\sigma_{1},\sigma_{2}) = |\uparrow\rangle_{1} |\uparrow\rangle_{2}, \quad \frac{1}{\sqrt{2}} \left( |\uparrow\rangle_{1} |\downarrow\rangle_{2} + |\downarrow\rangle_{1} |\uparrow\rangle_{2} \right), \quad |\downarrow\rangle_{1} |\downarrow\rangle_{2}$$

but this will give higher energy due to the present of the higher level state  $\phi_{2s}(\mathbf{r}_1)$ . (It is quite easy to test experimentally if the ground state Helium is singlet or triplet.) Using the singlet state  $\Psi_t(1, 2)$ , we evaluate the energy expectation value

$$\left\langle \hat{H} \right\rangle = 2 \cdot \left\langle \left( \frac{\hbar^2}{2m} \nabla_1^2 - \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r_1} \right) \right\rangle + \frac{e^2}{4\pi\epsilon_0} \left\langle \frac{1}{r_{12}} \right\rangle$$

$$= 2 \cdot \left( -\frac{Z^2 e^2}{8\pi\epsilon_0 a_0} \right) + \frac{5}{4} \frac{Ze^2}{8\pi\epsilon_0 a_0}$$

$$= \left( -2Z^2 + \frac{5}{4}Z \right) \text{ Ry}, \quad \text{Ry} = \frac{e^2}{8\pi\epsilon_0 a_0}$$

$$= -5.50 \text{ Ry}, \quad Z = 2$$

which is only 6% above the experimental result of -5.81 Ry. In the first line of the above equation, evaluation of  $< 1/r_{12} >$  is nontrivial. See the following math note.

**Math Note**: Evaluation of  $\left< \frac{1}{r_{12}} \right>$ 

In this note, we evaluate the following integral from Helium problem,

$$\left\langle \frac{1}{r_{12}} \right\rangle = \frac{1}{\pi^2} \left( \frac{Z}{a_0} \right)^6 \int d^3 r_1 d^3 r_1 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} e^{-2Z(r_1 + r_2)/a_0}$$

•

First we use the expression (Fourier transformation)

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \int \frac{d^3k}{(2\pi)^3} e^{i\mathbf{k}\cdot(\mathbf{r}_1 - \mathbf{r}_2)} \frac{4\pi}{k^2}$$

hence

$$\left\langle \frac{1}{r_{12}} \right\rangle = \frac{1}{\pi^2} \left( \frac{Z}{a_0} \right)^6 \int \frac{d^3k}{(2\pi)^3} \frac{4\pi}{k^2} \left| \int d^3r_1 e^{i\mathbf{k}\cdot\mathbf{r}_1 - 2Zr_1/a_0} \right|^2$$

now

$$\int d^3 r_1 e^{i\mathbf{k}\cdot\mathbf{r}_1 - 2Zr_1/a_0} = \frac{16\pi Z/a_0}{\left[k^2 + (2Z/a_0)^2\right]^2}$$

and finally

$$\left\langle \frac{1}{r_{12}} \right\rangle = \frac{4Z}{\pi a_0} \int_0^\infty \frac{dx}{\left(x^2 + 1\right)^4} = \frac{5}{8} \frac{Z}{a_0} \; .$$