Quantum Mechanics

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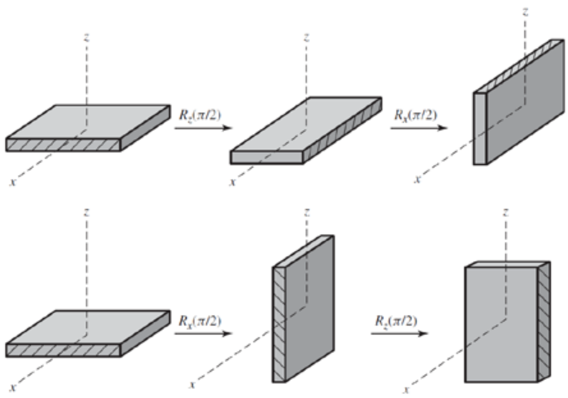
IV. Theory of Angular Momentum

4.1 Rotations and Angular Momentum

4.1.1 Classical Rotations

In classical mechanics, rotation about the same axis commute, whereas rotations about different axes do not.



If we define a 3×3 orthogonal matrix R to perform the rotation from the original vector $\mathbf{V}$ to the final vector $\mathbf{V}'$:

$$\begin{pmatrix} V_x' \\ V_y' \\ V_z' \end{pmatrix} = R \begin{pmatrix} V_x \\ V_y \\ V_z \end{pmatrix}, \tag{4.1}$$

the matrix should satisfy the normalization condition

$$RR^T = R^T R = 1\,. \tag{4.2}$$

For a rotation around the z-axis with an angle ϕ (define counterclockwise to be positive), the rotation matrix is

$$R_z(\phi) = \begin{pmatrix} \cos\phi & -\sin\phi & 0 \\ \sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{pmatrix}. \tag{4.3}$$

For an infinitesimal rotation $\varepsilon = \sin\phi$, the matrix neglecting higher orders of ε becomes

$$R_z(\varepsilon) = \begin{pmatrix} 1-\frac{\varepsilon^2}{2} & -\varepsilon & 0 \\ \varepsilon & 1-\frac{\varepsilon^2}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}. \quad (4.4)$$

Likewise, we have

$$R_x(\varepsilon) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1-\frac{\varepsilon^2}{2} & -\varepsilon \\ 0 & \varepsilon & 1-\frac{\varepsilon^2}{2} \end{pmatrix}, \quad (4.5)$$

and

$$R_y(\varepsilon) = \begin{pmatrix} 1-\frac{\varepsilon^2}{2} & 0 & \varepsilon \\ 0 & 1 & 0 \\ -\varepsilon & 0 & 1-\frac{\varepsilon^2}{2} \end{pmatrix}. \quad (4.6)$$

Comparing the two subsequent rotations around *x*- and *y*-axes

$$R_x(\varepsilon)R_y(\varepsilon) = \begin{pmatrix} 1-\frac{\varepsilon^2}{2} & 0 & \varepsilon \\ \varepsilon^2 & 1-\frac{\varepsilon^2}{2} & -\varepsilon \\ -\varepsilon & \varepsilon & 1-\varepsilon^2 \end{pmatrix} \quad (4.7)$$

and

$$R_y(\varepsilon)R_x(\varepsilon) = \begin{pmatrix} 1-\frac{\varepsilon^2}{2} & \varepsilon^2 & \varepsilon \\ 0 & 1-\frac{\varepsilon^2}{2} & -\varepsilon \\ -\varepsilon & \varepsilon & 1-\varepsilon^2 \end{pmatrix}, \quad (4.8)$$

we may conclude that: (1) Infinitesimal rotations about different axes commute with ε^2 and higher orders ignored; (2) If terms of order ε^2 are kept, we have

$$R_x(\varepsilon)R_y(\varepsilon) - R_y(\varepsilon)R_x(\varepsilon) = \begin{pmatrix} 0 & -\varepsilon^2 & 0 \\ \varepsilon^2 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} = R_z(\varepsilon^2) - 1. \quad (4.9)$$

Because $R_{\text{any}}(0) = 1$, where *any* stands for any rotation axis, we finally have

$$R_x(\varepsilon)R_y(\varepsilon) - R_y(\varepsilon)R_x(\varepsilon) = R_z(\varepsilon^2) - R_{\text{any}}(0). \quad (4.10)$$

4.1.2 Infinitesimal Rotations in Quantum Mechanics

Define the rotation operator $\mathscr{D}(R)$:

$$|\alpha\rangle_R = \mathscr{D}(R)|\alpha\rangle , \tag{4.11}$$

where $|\alpha\rangle_R$ and $|\alpha\rangle$ stand for the kets of the rotated and original system, respectively. The infinitesimal operator can be postulated as

$$U_\varepsilon = 1 - iG\varepsilon , \tag{4.12}$$

with a Hermitian operator *G*. We previously have seen that for an infinitesimal translation,

$$G \to \frac{p_x}{\hbar}, \quad \varepsilon \to \mathrm{d}x , \tag{4.13}$$

while for an infinitesimal time evolution,

$$G \to \frac{H}{\hbar}, \quad \varepsilon \to \mathrm{d}t . \tag{4.14}$$

Analogously, for an infinitesimal rotation around the *k*th axis by angle $\mathrm{d}\phi$, if we define J_k to be the corresponding angular-momentum operator, then

$$G \to \frac{J_k}{\hbar}, \quad \varepsilon \to \mathrm{d}\phi . \tag{4.15}$$

Therefore, the rotation operator

$$\mathscr{D}(\hat{\mathbf{n}}, \mathrm{d}\phi) = 1 - \left(\frac{\mathbf{J}\cdot\hat{\mathbf{n}}}{\hbar}\right)\mathrm{d}\phi , \tag{4.16}$$

where $\hat{\mathbf{n}}$ is the direction of the rotation axis. A finite rotation can be obtained by compounding successively infinitesimal rotations about the same axis. For instance, a finite rotation about the *z*-axis by angle ϕ has the operator

$$\mathscr{D}_z(\phi) = \lim_{N\to\infty}\left[1 - i\left(\frac{J_z}{\hbar}\right)\left(\frac{\phi}{N}\right)\right]^N = \exp\left(-i\frac{J_z\phi}{\hbar}\right) = 1 - i\frac{J_z\phi}{\hbar} - \frac{J_z^2\phi^2}{2\hbar^2} + \cdots . \tag{4.17}$$

We further *postulate* that $\mathscr{D}(R)$ has the same group properties as *R*:

(1) Identity:

$$\mathscr{D}(R)\cdot 1 = \mathscr{D}(R) ; \tag{4.18}$$

(2) Closure:

$$\mathscr{D}(R_1)\mathscr{D}(R_2) = \mathscr{D}(R_3) ; \tag{4.19}$$

(3) Inverse:

$$\begin{aligned} \mathscr{D}(R)\mathscr{D}^{-1}(R) &= 1 \\ \mathscr{D}^{-1}(R)\mathscr{D}(R) &= 1 \end{aligned} ; \tag{4.20}$$

(4) Associativity:

$$\begin{aligned} \mathscr{D}(R_1)\left[\mathscr{D}(R_2)\mathscr{D}(R_3)\right] &= \left[\mathscr{D}(R_1)\mathscr{D}(R_2)\right]\mathscr{D}(R_3) \\ &= \mathscr{D}(R_1)\mathscr{D}(R_2)\mathscr{D}(R_3) \end{aligned} . \tag{4.21}$$

Then by using the truncated Eq. (4.17), the quantum correspondence to Eq. (4.10) is

$$\begin{aligned}&\left(1-i\frac{J_x\varepsilon}{\hbar}-\frac{J_x^2\varepsilon^2}{2\hbar^2}\right)\left(1-i\frac{J_y\varepsilon}{\hbar}-\frac{J_y^2\varepsilon^2}{2\hbar^2}\right)-\left(1-i\frac{J_y\varepsilon}{\hbar}-\frac{J_y^2\varepsilon^2}{2\hbar^2}\right)\left(1-i\frac{J_x\varepsilon}{\hbar}-\frac{J_x^2\varepsilon^2}{2\hbar^2}\right)\\&=1-i\frac{J_z\varepsilon^2}{\hbar}-1\end{aligned}, \tag{4.22}$$

whose terms of order ε automatically drop out, and equating terms of order ε^2 leads to

$$\left[J_x, J_y\right]=i\hbar J_z . \tag{4.23}$$

Generalizing the above equation, we obtain the **fundamental commutation relations of angular momentum**:

$$\left[J_i, J_j\right]=i\hbar\varepsilon_{ijk}J_k , \tag{4.24}$$

where ε_{ijk} is the Levi-Civita symbol with

$$\begin{aligned}\varepsilon_{xyz}&=\varepsilon_{yzx}=\varepsilon_{zxy}=1\\\varepsilon_{yxz}&=\varepsilon_{xzy}=\varepsilon_{zyx}=-1\end{aligned} \tag{4.25}$$

and 0 otherwise.

4.1.3 Spin ½ Systems and Finite Rotations

The spin 1/2 systems have the lowest number of dimensions $N=2$, whose spin operators are defined by

$$\begin{aligned}S_x&=\left(\frac{\hbar}{2}\right)\{|+\rangle\langle-|+|-\rangle(+]\}\\S_y&=\left(\frac{i\hbar}{2}\right)\{-|+\rangle\langle-|+|-\rangle(+]\},\\S_z&=\left(\frac{\hbar}{2}\right)\{|+\rangle\langle+|-|-\rangle(-]\}\end{aligned} \tag{4.26}$$

which satisfy the commutation relations Eq. (4.24). A finite rotation by a finite angle ϕ about the z-axis can be described by

$$|\alpha\rangle_R=\mathscr{D}_z(\phi)|\alpha\rangle \tag{4.27}$$

with

$$\mathscr{D}_z(\phi)=\exp\left(-i\frac{S_z\phi}{\hbar}\right). \tag{4.28}$$

Under this rotation, the expectation value of S_x changes as

$$\langle S_x\rangle\to_R\langle\alpha|S_x|\alpha\rangle_R=\langle\alpha|\mathscr{D}_z^\dagger(\phi)S_x\mathscr{D}_z(\phi)|\alpha\rangle . \tag{4.29}$$

Because

$$
\begin{aligned}
&\left(\frac{\hbar}{2}\right)\exp\left(i\frac{S_z\phi}{\hbar}\right)\{|+\rangle\langle-|+|-\rangle\langle+|\}\exp\left(-i\frac{S_z\phi}{\hbar}\right)\\
&=\left(\frac{\hbar}{2}\right)\left(\exp\left(i\frac{\phi}{2}\right)|+\rangle\langle-|\exp\left(i\frac{\phi}{2}\right)+\exp\left(-i\frac{\phi}{2}\right)|-\rangle\langle+|\exp\left(-i\frac{\phi}{2}\right)\right),\\
&=\frac{\hbar}{2}\left[(|+\rangle\langle-|+|-\rangle\langle+|)\cos\phi+i(|+\rangle\langle-|-|-\rangle\langle+|)\sin\phi\right]\\
&=S_x\cos\phi-S_y\sin\phi
\end{aligned}
\tag{4.30}
$$

we have

$$
\langle S_x\rangle\rightarrow_R\langle\alpha|S_x|\alpha\rangle_R=\langle S_x\rangle\cos\phi-\langle S_y\rangle\sin\phi\,. \tag{4.31}
$$

Similarly,

$$
\langle S_y\rangle\rightarrow\langle S_y\rangle\cos\phi+\langle S_x\rangle\sin\phi \tag{4.32}
$$

Because S_z commutes with $\mathscr{D}_z(\phi)$, we have

$$
\langle S_z\rangle\rightarrow\langle S_z\rangle\,. \tag{4.33}
$$

The above can be generalized to be

$$
\langle J_k\rangle\rightarrow\sum_l R_{kl}\langle J_l\rangle \tag{4.34}
$$

with R_{kl} the elements of the 3×3 orthogonal rotation matrix R exactly the same as in classical mechanics.

When apply the rotation operator Eq. (4.28) to a general ket, we obtain

$$
\begin{aligned}
\exp\left(-i\frac{S_z\phi}{\hbar}\right)|\alpha\rangle&=\exp\left(-i\frac{S_z\phi}{\hbar}\right)(|+\rangle\langle+|\alpha\rangle+|-\rangle\langle-|\alpha\rangle)\\
&=\exp\left(-i\frac{\phi}{2}\right)|+\rangle\langle+|\alpha\rangle+\exp\left(i\frac{\phi}{2}\right)|-\rangle\langle-|\alpha\rangle
\end{aligned}\,. \tag{4.35}
$$

We then have

$$
|\alpha\rangle_{R_z(2\pi)}\rightarrow-|\alpha\rangle \tag{4.36}
$$

and

$$
|\alpha\rangle_{R_z(4\pi)}\rightarrow|\alpha\rangle\,. \tag{4.37}
$$

4.1.4 Spin Precession

The Hamiltonian for spin precession is

$$
H=-\left(\frac{e}{m_ec}\right)\mathbf{S}\cdot\mathbf{B}=\omega S_z\,, \tag{4.38}
$$

where

$$
\omega\equiv\frac{|e|B}{m_ec}\,. \tag{4.39}
$$

The corresponding time-evolution operator is

$$\mathscr{U}(t,0) = \exp\left(-i\frac{Ht}{\hbar}\right) = \exp\left(-i\frac{S_z \omega t}{\hbar}\right), \tag{4.40}$$

which is exactly the same as Eq. (4.28) by setting $\phi = \omega t$. Eqs. (4.31), (4.32) and (4.33) becomes

$$\begin{aligned} \langle S_x \rangle_t &= \langle S_x \rangle_0 \cos(\omega t) - \langle S_y \rangle_0 \sin(\omega t) \\ \langle S_y \rangle_t &= \langle S_y \rangle_0 \cos(\omega t) + \langle S_x \rangle_0 \sin(\omega t). \\ \langle S_z \rangle_t &= \langle S_z \rangle_0 \end{aligned} \tag{4.41}$$

After $t = \frac{2\pi}{\omega}$, the spin returns to its original direction. According to Eq. (4.35), the time-evolution of the state ket is

$$|\alpha, t_0 = 0; t\rangle = \exp\left(-i\frac{\omega t}{2}\right)|+\rangle\langle+|\alpha\rangle + \exp\left(i\frac{\omega t}{2}\right)|-\rangle\langle-|\alpha\rangle. \tag{4.42}$$

4.1.5 Pauli Two-Component Formalism

The two-component spinor formalism introduced by W. Pauli in 1926 defines the base kets in the matrix form

$$\chi_+ \equiv |+\rangle \doteq \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \chi_- \equiv |-\rangle \doteq \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \tag{4.43}$$

An arbitrary state ket in the matrix form

$$|\alpha\rangle = |+\rangle\langle+|\alpha\rangle + |-\rangle\langle-|\alpha\rangle \doteq \begin{pmatrix} \langle+|\alpha\rangle \\ \langle-|\alpha\rangle \end{pmatrix} \tag{4.44}$$

can be written as a **two-component spinor**

$$\chi = \begin{pmatrix} \langle+|\alpha\rangle \\ \langle-|\alpha\rangle \end{pmatrix} \equiv \begin{pmatrix} c_+ \\ c_- \end{pmatrix} = c_+\chi_+ + c_-\chi_-. \tag{4.45}$$

Define the **Pauli matrices**

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \tag{4.46}$$

then the expectation value

$$\langle S_k \rangle = \langle \alpha | S_k | \alpha \rangle = \sum_{a'=+,-} \sum_{a''=+,-} \langle \alpha | a' \rangle \langle a' | S_k | a'' \rangle \langle a'' | \alpha \rangle = \left(\frac{\hbar}{2}\right) \chi^\dagger \sigma_k \chi. \tag{4.47}$$

The two relations of the Pauli matrix:

$$\sigma_i^2 = 1 \tag{4.48}$$

and

$$\sigma_i \sigma_j + \sigma_j \sigma_i = 0, \quad i \neq j \tag{4.49}$$

are equal to the anti-commutation relation

$$\{\sigma_i, \sigma_j\} = 2\delta_{ij}. \tag{4.50}$$

Along with the commutation relations

$$\left[\sigma_i,\sigma_j\right]=2i\varepsilon_{ijk}\sigma_k\,, \tag{4.51}$$

we obtain

$$\sigma_i\sigma_j=-\sigma_j\sigma_i=i\sigma_k\,,\quad i\neq j\neq k\,. \tag{4.52}$$

Other properties include

$$\begin{aligned}&\sigma_i^\dagger=\sigma_i\\&\det\left(\sigma_i\right)=1\,.\\&\mathrm{Tr}\left(\sigma_i\right)=0\end{aligned} \tag{4.53}$$

If $\mathbf{a}$ is a vector in three dimensions, then

$$\boldsymbol{\sigma}\cdot\mathbf{a}\equiv\sum_k a_k\sigma_k=\begin{pmatrix}a_3 & a_1-ia_2\\ a_1+ia_2 & -a_3\end{pmatrix}. \tag{4.54}$$

For two three-dimensional vectors $\mathbf{a}$ and $\mathbf{b}$, we have

$$\begin{aligned}&\left(\boldsymbol{\sigma}\cdot\mathbf{a}\right)\left(\boldsymbol{\sigma}\cdot\mathbf{b}\right)=\sum_j\sigma_j a_j\sum_k\sigma_k b_k\\&=\sum_j\sum_k\left(\frac{1}{2}\left\{\sigma_j,\sigma_k\right\}+\frac{1}{2}\left[\sigma_j,\sigma_k\right]\right)a_jb_k=\sum_j\sum_k\left(\delta_{jk}+i\varepsilon_{ikl}\sigma_l\right)a_jb_k\,.\\&=\mathbf{a}\cdot\mathbf{b}+i\boldsymbol{\sigma}\cdot\left(\mathbf{a}\times\mathbf{b}\right)\end{aligned} \tag{4.55}$$

Specifically, if the components of **a** are all real, we have

$$\left(\boldsymbol{\sigma}\cdot\mathbf{a}\right)^2=\left|\mathbf{a}\right|^2. \tag{4.56}$$

In the two-component formalism, the rotation operator

$$\mathscr{D}\left(\hat{\mathbf{n}},\phi\right)=\exp\left(-i\frac{\mathbf{S}\cdot\hat{\mathbf{n}}\phi}{\hbar}\right)\doteq\exp\left(-i\frac{\boldsymbol{\sigma}\cdot\hat{\mathbf{n}}\phi}{2}\right). \tag{4.57}$$

From Eq. (4.56), we know

$$\left(\boldsymbol{\sigma}\cdot\hat{\mathbf{n}}\right)^n=\begin{cases}1 & n\text{ is even}\\ \boldsymbol{\sigma}\cdot\hat{\mathbf{n}} & n\text{ is odd}\end{cases}, \tag{4.58}$$

so Eq. (4.57) becomes

$$\begin{aligned}&\exp\left(-i\frac{\boldsymbol{\sigma}\cdot\hat{\mathbf{n}}\phi}{2}\right)=\left[1-\frac{\left(\boldsymbol{\sigma}\cdot\hat{\mathbf{n}}\right)^2}{2!}\left(\frac{\phi}{2}\right)^2+\frac{\left(\boldsymbol{\sigma}\cdot\hat{\mathbf{n}}\right)^4}{4!}\left(\frac{\phi}{2}\right)^4-\cdots\right]\\&-i\left[\left(\boldsymbol{\sigma}\cdot\hat{\mathbf{n}}\right)\frac{\phi}{2}-\frac{\left(\boldsymbol{\sigma}\cdot\hat{\mathbf{n}}\right)^3}{3!}\left(\frac{\phi}{2}\right)^3+\cdots\right]\\&=\mathbf{I}\cos\left(\frac{\phi}{2}\right)-i\boldsymbol{\sigma}\cdot\hat{\mathbf{n}}\sin\left(\frac{\phi}{2}\right)\\&=\begin{pmatrix}\cos\left(\frac{\phi}{2}\right)-in_z\sin\left(\frac{\phi}{2}\right) & \left(-in_x-n_y\right)\sin\left(\frac{\phi}{2}\right)\\ \left(-in_x+n_y\right)\sin\left(\frac{\phi}{2}\right) & \cos\left(\frac{\phi}{2}\right)+in_z\sin\left(\frac{\phi}{2}\right)\end{pmatrix}\end{aligned}\,. \tag{4.59}$$

Under rotations,

$$\chi \to \exp\left(-i\frac{\boldsymbol{\sigma}\cdot\hat{\mathbf{n}}\phi}{2}\right)\chi \,, \tag{4.60}$$

and it is $\chi^\dagger \boldsymbol{\sigma} \chi$ rather than $\boldsymbol{\sigma}$ itself to be regarded as a vector:

$$\chi^\dagger \sigma_k \chi \to \sum_l R_{kl} \chi^\dagger \sigma_l \chi \,, \tag{4.61}$$

which can be explicitly proved by using

$$\exp\left(i\frac{\sigma_3 \phi}{2}\right)\sigma_1 \exp\left(-i\frac{\sigma_3\phi}{2}\right) = \sigma_1 \cos\phi - \sigma_2 \sin\phi \tag{4.62}$$

and so on.

4.1.6 SO(3), SU(2), and Euler Rotations

The set of all multiplication operations with orthogonal matrices R forms a SO(3) group:

(1) The product of any two orthogonal matrices is another orthogonal matrix.

$$\left(R_1 R_2\right)\left(R_1 R_2\right)^T = R_1 R_2 R_2^T R_1^T = 1 \,. \tag{4.63}$$

(2) The associative law holds.

$$R_1\left(R_2 R_3\right) = \left(R_1 R_2\right) R_3 \,. \tag{4.64}$$

(3) The identity matrix 1 is a member of the class of all orthogonal matrices.

$$R \cdot 1 = 1 \cdot R = R \,. \tag{4.65}$$

(4) The inverse matrix R^{-1} is also a member.

$$RR^{-1} = R^{-1} R = 1 \tag{4.66}$$

The name SO(3) has S standing for special (no inversion operation), O for orthogonal, and 3 for three dimensions.

A **unitary unimodular matrix** is defined as

$$U\left(a,b\right) = \begin{pmatrix} a & b \\ -b^* & a^* \end{pmatrix}, \tag{4.67}$$

where a and b (known as the **Cayley-Klein parameters**) are complex numbers satisfying the unimodular condition

$$|a|^2 + |b|^2 = 1 \,. \tag{4.68}$$

The unitary property is

$$U\left(a,b\right)^\dagger U\left(a,b\right) = \begin{pmatrix} a^* & -b \\ b^* & a \end{pmatrix}\begin{pmatrix} a & b \\ -b^* & a^* \end{pmatrix} = 1 \,. \tag{4.69}$$

The rotation of a spin 1/2 system Eq. (4.59) can be written as $U\left(a,b\right)$ by letting

$$\begin{aligned} \mathrm{Re}\left(a\right) &= \cos\left(\frac{\phi}{2}\right), \quad \mathrm{Im}\left(a\right) = -n_z \sin\left(\frac{\phi}{2}\right) \\ \mathrm{Re}\left(b\right) &= -n_y \sin\left(\frac{\phi}{2}\right), \quad \mathrm{Im}\left(b\right) = -n_x \sin\left(\frac{\phi}{2}\right) \end{aligned} . \tag{4.70}$$

Because

$$U\left(a_1,b_1\right)U\left(a_2,b_2\right)=U\left(a_1a_2-b_1b_2^*,a_1b_2+a_2^*b_1\right) \tag{4.71}$$

with the unimodular condition

$$\left|a_1a_2-b_1b_2^*\right|^2+\left|a_1b_2+a_2^*b_1\right|^2=1 \tag{4.72}$$

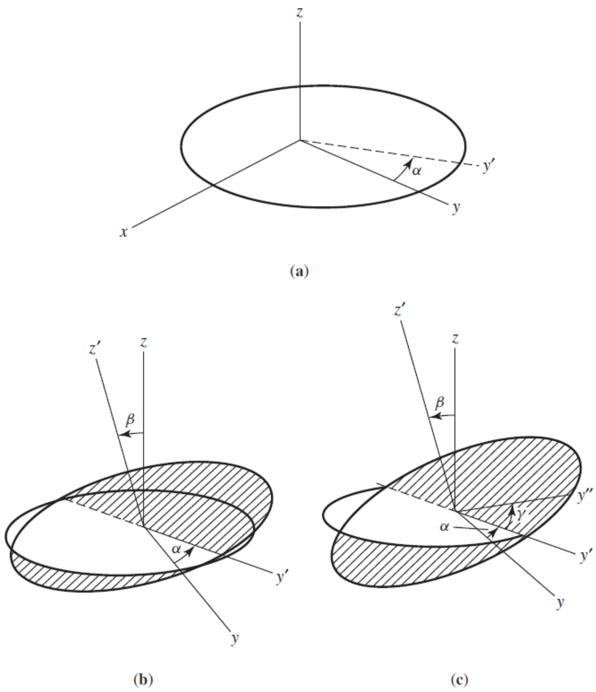
and

$$U^{-1}\left(a,b\right)=U\left(a^*,-b\right), \tag{4.73}$$

it belongs to the SU(2) group, where S stands for special (constrained to be unimolecular), U for unitary, and 2 for dimensionality 2.

Euler rotations by three angles α,β,γ turn out to rotate about fixed axes:

$$R\left(\alpha,\beta,\gamma\right)=R_z\left(\alpha\right)R_y\left(\beta\right)R_z\left(\gamma\right). \tag{4.74}$$



Applying this set of operations to spin ½ systems in quantum mechanics. By using Eq. (4.59), we have the rotation operation of the unitary unimodular form

$$\mathscr{D}\left(\alpha,\beta,\gamma\right)=\mathscr{D}_z\left(\alpha\right)\mathscr{D}_y\left(\beta\right)\mathscr{D}_z\left(\gamma\right), \tag{4.75}$$

which for spin ½ system is

$$\mathscr{D}(\alpha,\beta,\gamma)=\exp\left(-i\frac{\sigma_3\alpha}{2}\right)\exp\left(-i\frac{\sigma_2\beta}{2}\right)\exp\left(-i\frac{\sigma_3\gamma}{2}\right)$$
$$=\begin{pmatrix}\exp\left(-i\frac{\alpha}{2}\right) & 0\\ 0 & \exp\left(i\frac{\alpha}{2}\right)\end{pmatrix}\begin{pmatrix}\cos\left(\frac{\beta}{2}\right) & -\sin\left(\frac{\beta}{2}\right)\\ \sin\left(\frac{\beta}{2}\right) & \cos\left(\frac{\beta}{2}\right)\end{pmatrix}\begin{pmatrix}\exp\left(-i\frac{\gamma}{2}\right) & 0\\ 0 & \exp\left(i\frac{\gamma}{2}\right)\end{pmatrix}. \quad (4.76)$$
$$=\begin{pmatrix}\exp\left(-i\frac{\alpha+\gamma}{2}\right)\cos\left(\frac{\beta}{2}\right) & -\exp\left(-i\frac{\alpha-\gamma}{2}\right)\sin\left(\frac{\beta}{2}\right)\\ \exp\left(i\frac{\alpha-\gamma}{2}\right)\sin\left(\frac{\beta}{2}\right) & \exp\left(i\frac{\alpha+\gamma}{2}\right)\cos\left(\frac{\beta}{2}\right)\end{pmatrix}$$

This 2×2 matrix is called the $j=\frac{1}{2}$ irreducible representation of the rotation operation $\mathscr{D}(\alpha,\beta,\gamma)$. Its matrix elements in terms of the angular-momentum operators are

$$\mathscr{D}^{(1/2)}_{m'm}(\alpha,\beta,\gamma)=\left\langle j=\frac{1}{2},m'\right|\exp\left(-i\frac{J_z\alpha}{\hbar}\right)\exp\left(-i\frac{J_y\beta}{\hbar}\right)\exp\left(-i\frac{J_z\gamma}{\hbar}\right)\left|j=\frac{1}{2},m\right\rangle. \quad (4.77)$$

4.2 Density Operators and Pure Versus Mixed Ensembles

4.2.1 Ensemble Averages and Density Operator

A **mixed ensemble** is a mixture of pure ensembles (single quantum states), whose fractional populations satisfy the normalization condition

$$\sum_i w_i=1. \quad (4.78)$$

The **ensemble average** of an observable *A* in a mixed ensemble is defined by

$$[A]\equiv\sum_i w_i\left\langle\alpha^{(i)}\right|A\left|\alpha^{(i)}\right\rangle=\sum_i\sum_{a'}w_i\left|\left\langle a'\middle|\alpha^{(i)}\right\rangle\right|^2 a', \quad (4.79)$$

where $|a'\rangle$ is an eigenket of *A*. The probabilistic concepts enter twice: (1) quantum probability $\left|\left\langle a'\middle|\alpha^{(i)}\right\rangle\right|^2$ for finding *A* in eigenstate $|a'\rangle$; (2) statistical probability of finding *A* in the ensemble of a quantum-mechanical state $\left|\alpha^{(i)}\right\rangle$.

Using a more general basis set $\{|b'\rangle\}$, we can rewrite the above ensemble average to be

$$\begin{aligned}[A]&=\sum_i w_i\sum_{b'}\sum_{b''}\left\langle\alpha^{(i)}\middle|b'\right\rangle\langle b'|A|b''\rangle\left\langle b''\middle|\alpha^{(i)}\right\rangle\\ &=\sum_{b'}\sum_{b''}\left(\sum_i w_i\left\langle b''\middle|\alpha^{(i)}\right\rangle\left\langle\alpha^{(i)}\middle|b'\right\rangle\right)\langle b'|A|b''\rangle\end{aligned}. \quad (4.80)$$

Define the **density operator**

$$\rho\equiv\sum_i w_i\left|\alpha^{(i)}\right\rangle\left\langle\alpha^{(i)}\right|. \quad (4.81)$$

The elements of the corresponding **density matrix** are

$$\langle b''|\rho|b'\rangle = \sum_i w_i \langle b''|\alpha^{(i)}\rangle\langle\alpha^{(i)}|b'\rangle . \tag{4.82}$$

The ensemble average Eq. (4.80) can then be rewritten with the density operator as

$$[A] = \sum_{b'}\sum_{b''}\langle b''|\rho|b'\rangle\langle b'|A|b''\rangle = \mathrm{tr}(\rho A) . \tag{4.83}$$

The density operator has the following properties:

(1) It is Hermitian, as evidenced by Eq. (4.81).

(2) It satisfies the normalization condition $\mathrm{tr}(\rho) = 1$.

(3) A pure ensemble can be represented by $\rho = |\alpha^{(n)}\rangle\langle\alpha^{(n)}|$.

(4) $\rho^2 \le \rho$ and "=" only for a pure ensemble.

(5) $\mathrm{tr}(\rho^2) \le 1$ and "=" only for a pure ensemble.

If the basis set is continuous, for instance, the position eigenkets $\{|\mathbf{x}'\rangle\}$, Eq. (4.83) becomes

$$[A] = \int \mathrm{d}^3x' \int \mathrm{d}^3x'' \langle\mathbf{x}''|\rho|\mathbf{x}'\rangle\langle\mathbf{x}'|A|\mathbf{x}''\rangle , \tag{4.84}$$

and the density matrix becomes

$$\langle\mathbf{x}''|\rho|\mathbf{x}'\rangle = \langle\mathbf{x}''|\left(\sum_i w_i |\alpha^{(i)}\rangle\langle\alpha^{(i)}|\right)|\mathbf{x}'\rangle = \sum_i w_i \psi_i(\mathbf{x}'')\psi_i^*(\mathbf{x}') , \tag{4.85}$$

where ψ_i is the wave function corresponding to the state ket $|\alpha^{(i)}\rangle$.

4.2.2 Time Evolution of Ensembles

If w_i does not change, the change in $\rho(t_0) = \sum_i w_i |\alpha^{(i)}\rangle\langle\alpha^{(i)}|$ is solely governed by the time evolution of $|\alpha_i\rangle$. Because the time volution of $|\alpha_i\rangle$ satisfies the Schrödinger equation, we obtain

$$i\hbar\frac{\partial\rho}{\partial t} = \sum_i w_i \left(H|\alpha^{(i)},t_0;t\rangle\langle\alpha^{(i)},t_0;t| - |\alpha^{(i)},t_0;t\rangle\langle\alpha^{(i)},t_0;t|H\right) = -[\rho, H] . \tag{4.86}$$

It can be regarded as the quantum-mechanical analogue of Liouville's theorem in classical statistical mechanics,

$$\frac{\partial\rho_{\text{classical}}}{\partial t} = -[\rho_{\text{classical}}, H]_{\text{classical}} , \tag{4.87}$$

where $\rho_{\text{classical}}$ stands for the density of representative points in phase space.

4.2.3 Quantum Statistical Mechanics

If we define

$$\sigma = -\mathrm{tr}(\rho\ln\rho) = -\sum_k \rho_{kk}\ln\rho_{kk} , \tag{4.88}$$

for a completely random ensemble

$$\rho \doteq \frac{1}{N}\begin{pmatrix} 1 & & & & & & 0 \\ & 1 & & & & & \\ & & 1 & & & & \\ & & & \ddots & & & \\ & & & & 1 & & \\ & & & & & 1 & \\ 0 & & & & & & 1 \end{pmatrix}, \tag{4.89}$$

we have

$$\sigma = -\sum_{k=1}^{N} \frac{1}{N} \ln\left(\frac{1}{N}\right) = \ln N \ . \tag{4.90}$$

For a pure ensemble

$$\rho \doteq \frac{1}{N}\begin{pmatrix} 0 & & & & & & 0 \\ & 0 & & & & & \\ & & 1 & & & & \\ & & & \ddots & & & \\ & & & & 0 & & \\ & & & & & 0 & \\ 0 & & & & & & 0 \end{pmatrix}, \tag{4.91}$$

we have $\sigma = 0$.

The system **entropy** is defined as

$$S = k_{\mathrm{B}}\sigma \tag{4.92}$$

where k_{B} is the Boltzmann constant.

When thermal equilibrium is established, we have

$$\frac{\partial \rho}{\partial t} = 0 \ . \tag{4.93}$$

According to Eq. (4.86), ρ and H can be simultaneously diagonalized, so the kets used in writing Eq. (4.88) may be taken to be energy eigenkets. Then ρ_{kk} stands for the fractional population for an energy eigenstate with energy eigenvalue E_k .

In the canonical ensemble, we may derive from the principles of statistical mechanics to obtain

$$\rho_{kk} = \frac{\exp(-\beta E_k)}{\sum_{l}^{N} \exp(-\beta E_l)} = \frac{\exp(-\beta E_k)}{Z}, \tag{4.94}$$

where $\beta = \dfrac{1}{k_{\mathrm{B}} T}$ with T the temperature, and the **partition function**

$$Z = \sum_{l}^{N} \exp(-\beta E_l) = \mathrm{tr}\left[\exp(-\beta H)\right]. \tag{4.95}$$

The density operator in the canonical ensemble can then be written as

$$\rho = \frac{\exp(-\beta H)}{Z}. \tag{4.96}$$

Then we have

$$[A] = \frac{\mathrm{tr}\big(\exp(-\beta H)A\big)}{Z} = \frac{\sum_{k}^{N} \langle A \rangle_k \exp(-\beta E_k)}{\sum_{k}^{N} \exp(-\beta E_k)} \ . \tag{4.97}$$

In particular, the internal energy

$$U=\frac{\sum_k^N E_k\exp\left(-\beta E_k\right)}{\sum_k^N\exp\left(-\beta E_k\right)}=-\frac{\partial}{\partial\beta}\ln Z\ . \tag{4.98}$$

For a spin ½ system in the canonical ensemble, with a magnetic moment $\frac{e\hbar}{2m_e c}$ subject to a uniform magnetic field in the *z*-direction, the Hamiltonian is given by Eq. (4.38). Because *H* and S_z commute, in the S_z basis, we have

$$\rho\doteq\begin{pmatrix}\exp\left(-\frac{\beta\hbar\omega}{2}\right) & 0\\ 0 & \exp\left(\frac{\beta\hbar\omega}{2}\right)\end{pmatrix}/Z\ , \tag{4.99}$$

where the partition function is

$$Z=\exp\left(-\frac{\beta\hbar\omega}{2}\right)+\exp\left(\frac{\beta\hbar\omega}{2}\right). \tag{4.100}$$

We can then compute

$$\left[S_x\right]=\left[S_y\right]=0,\quad \left[S_z\right]=-\left(\frac{\hbar}{2}\right)\tanh\left(\frac{\beta\hbar\omega}{2}\right). \tag{4.101}$$

The paramagnetic susceptibility may be computed as

$$\chi=\left(\frac{e}{m_e c}\right)\left[S_z\right]/B=\frac{-e\hbar}{2m_e cB}\tanh\left(\frac{\beta\hbar\omega}{2}\right), \tag{4.102}$$

which is called the **Brillouin's formula**.

4.3 Orbital Angular Momentum

4.3.1 Eigenvalues and Eigenstates of Angular Momentum

We define a new operator

$$\mathbf{J}^2\equiv J_xJ_x+J_yJ_y+J_zJ_z\ , \tag{4.103}$$

which commutes with any J_k :

$$\left[\mathbf{J}^2,J_k\right]=0,\quad k=1,2,3\ . \tag{4.104}$$

The above can be proved for the case of $k=3$ as

$$\begin{aligned}[J_xJ_x+J_yJ_y+J_zJ_z,J_z]&=J_x\left[J_x,J_z\right]+\left[J_x,J_z\right]J_x+J_y\left[J_y,J_z\right]+\left[J_y,J_z\right]J_y\\&=J_x\left(-i\hbar J_y\right)+\left(-i\hbar J_y\right)J_x+J_y\left(i\hbar J_x\right)+\left(i\hbar J_x\right)J_y\\&=0\end{aligned}\ . \tag{4.105}$$

The cases of $k=1,2$ can be proved in the same way. Because J_x, J_y and J_z do not commute with each other, we choose J_z only to be diagonalized simultaneously with $\mathbf{J}^2$.

By denoting the eigenvalues of $\mathbf{J}^2$ and J_z by *a* and *b*, respectively, we have

$$\mathbf{J}^2 |a,b\rangle = a|a,b\rangle$$
$$J_z |a,b\rangle = b|a,b\rangle \tag{4.106}$$

To determine the allowed values for *a* and *b*, we then define the non-Hermitian **ladder operators**

$$J_{\pm} = J_x \pm iJ_y . \tag{4.107}$$

According to Eq. (4.24), they satisfy the commutation relation

$$[J_+, J_-] = 2\hbar J_z \tag{4.108}$$

and

$$[J_z, J_{\pm}] = \pm\hbar J_{\pm} . \tag{4.109}$$

Furthermore, it is obvious that

$$[\mathbf{J}^2, J_{\pm}] = 0 \tag{4.110}$$

Because

$$J_z (J_{\pm}|a,b\rangle) = ([J_z, J_{\pm}] + J_{\pm}J_z)|a,b\rangle = (b \pm \hbar)(J_{\pm}|a,b\rangle) , \tag{4.111}$$

J_+ (J_-) applying to the eigenket of J_z results in an increase (decrease) of the eigenvalue by one unit of $\hbar$. However, it does not change the eigenvalue of $\mathbf{J}^2$:

$$\mathbf{J}^2 (J_{\pm}|a,b\rangle) = J_{\pm}\mathbf{J}^2|a,b\rangle = a(J_{\pm}|a,b\rangle) . \tag{4.112}$$

Therefore, $J_{\pm}|a,b\rangle$ are simultaneous eigenkets of $\mathbf{J}^2$ and J_z with eigenvalues *a* and $b \pm \hbar$.

Since

$$\mathbf{J}^2 - J_z^2 = \frac{1}{2}(J_+J_- + J_-J_+) = \frac{1}{2}(J_+J_+^+ + J_+^+J_+) , \tag{4.113}$$

along with the fact that $J_+J_+^\dagger$ and $J_+^\dagger J_+$ must have non-negative expectation values because

$$J_+^\dagger|a,b\rangle \xleftrightarrow{\text{DC}} \langle a,b|J_+ , \quad J_+|a,b\rangle \xleftrightarrow{\text{DC}} \langle a,b|J_+^+ , \tag{4.114}$$

we have

$$\langle a,b|(\mathbf{J}^2 - J_z^2)|a,b\rangle \geq 0 , \tag{4.115}$$

which implies that

$$a \geq b^2 . \tag{4.116}$$

It therefore follows that there must have a $b_{\max}$ such that

$$J_+|a,b_{\max}\rangle = 0 , \tag{4.117}$$

which also implies

$$J_-J_+|a,b_{\max}\rangle = 0 . \tag{4.118}$$

On the other hand,

$$J_-J_+ = J_x^2 + J_y^2 - i(J_yJ_x - J_xJ_y) = \mathbf{J}^2 - J_z^2 - \hbar J_z , \tag{4.119}$$

so

$$\left(\mathbf{J}^2 - J_z^2 - \hbar J_z\right)\left|a, b_{\max}\right\rangle = 0\,. \tag{4.120}$$

This is satisfied only if

$$a - b_{\max}^2 - b_{\max}\hbar = 0 \Rightarrow a = b_{\max}\left(b_{\max} + \hbar\right). \tag{4.121}$$

Similarly, from Eq. (4.116), there must also exist a $b_{\min}$ such that

$$J_-\left|a, b_{\min}\right\rangle = 0\,. \tag{4.122}$$

By writing that

$$J_+ J_- = \mathbf{J}^2 - J_z^2 + \hbar J_z \tag{4.123}$$

in analogy with Eq. (4.119), we conclude that

$$a = b_{\min}\left(b_{\min} - \hbar\right). \tag{4.124}$$

Comparing with Eq. (4.121), we infer that

$$b_{\min} = -b_{\max}\,. \tag{4.125}$$

Therefore, the allowed values of *b* lies within $\left[-b_{\max,} b_{\max}\right]$.

Because we have to apply J_+ successively to $\left|a, b_{\min}\right\rangle$ to reach $\left|a, b_{\max}\right\rangle$, we must have

$$b_{\max} = b_{\min} + n\hbar\,, \tag{4.126}$$

where *n* is some integer. As a result, we get

$$b_{\max} = \frac{n\hbar}{2}\,. \tag{4.127}$$

Define $j \equiv \dfrac{b_{\max}}{\hbar}$, we have

$$j = \frac{n}{2}\,. \tag{4.128}$$

The maximal eigenvalue of J_z is $j\hbar$, where *j* is an integer or a half-integer. According to Eq. (4.121), the eigenvalue of $\mathbf{J}^2$ is given by

$$a = \hbar^2 j\left(j+1\right). \tag{4.129}$$

Also define $m \equiv \dfrac{b}{\hbar}$, the allowed values are

$$m = -j, -j+1, \cdots j-1, j\,, \tag{4.130}$$

totally $2j+1$ states. Instead of $\left|a, b\right\rangle$, the simultaneous eigenket of $\mathbf{J}^2$ and J_z can now be denoted by $\left|j, m\right\rangle$. The basic eigenvalue equations now read

$$\mathbf{j}^2\left|j, m\right\rangle = j\left(j+1\right)\hbar^2\left|j, m\right\rangle \tag{4.131}$$

and

$$J_z\left|j, m\right\rangle = m\hbar\left|j, m\right\rangle. \tag{4.132}$$

Note that the quantization of angular momentum is obtained by using only the commutation relations $\left[J_i, J_j\right] = i\hbar\varepsilon_{ijk}J_k$, which is a consequence of the properties of rotations along with the definition of J_k as the generator of rotation.

The matrix elements of the angular-momentum operators can be worked out as follows. From Eqs. (4.131) and (4.132), we have

$$\left\langle j', m' \right| \mathbf{J}^2 \left| j, m \right\rangle = j\left(j+1\right)\hbar^2 \delta_{j'j}\delta_{m'm} \tag{4.133}$$

and

$$\left\langle j', m' \right| J_z \left| j, m \right\rangle = m\hbar \delta_{j'j}\delta_{m'm} . \tag{4.134}$$

To obtain the matrix elements of $J_{\pm}$, we first consider

$$\left\langle j, m \right| J_+^\dagger J_+ \left| j, m \right\rangle = \left\langle j, m \right| \left(\mathbf{J}^2 - J_z^2 - \hbar J_z \right) \left| j, m \right\rangle = \hbar^2 \left[j\left(j+1\right) - m^2 - m \right] . \tag{4.135}$$

On the other hand, we have

$$J_+ \left| j, m \right\rangle = c_{jm}^+ \left| j, m+1 \right\rangle , \tag{4.136}$$

where c_{jm}^+ is a multiplicative constant subject to the normalization requirement. Comparing the above two equations, we obtain

$$\left| c_{jm}^+ \right|^2 = \hbar^2 \left[j\left(j+1\right) - m\left(m+1\right) \right] = \hbar^2 \left(j-m\right)\left(j+m+1\right) . \tag{4.137}$$

Choosing c_{jm}^+ to be real and positive, we get

$$J_+ \left| j, m \right\rangle = \hbar \sqrt{\left(j-m\right)\left(j+m+1\right)} \left| j, m+1 \right\rangle . \tag{4.138}$$

Similarly, we can get

$$J_- \left| j, m \right\rangle = \hbar \sqrt{\left(j+m\right)\left(j-m+1\right)} \left| j, m-1 \right\rangle . \tag{4.139}$$

Therefore, the matrix elements of $J_{\pm}$ is

$$\left\langle j', m' \right| J_{\pm} \left| j, m \right\rangle = \hbar \sqrt{\left(j \mp m\right)\left(j \pm m+1\right)} \delta_{j'j}\delta_{m', m\pm 1} . \tag{4.140}$$

The matrix elements of a rotation R specified by $\hat{\mathbf{n}}$ and ϕ is

$$\mathscr{D}_{m'm}^{(j)}\left(R\right) = \left\langle j, m' \right| \exp\left(-i\frac{\mathbf{J}\cdot\hat{\mathbf{n}}\phi}{\hbar} \right) \left| j, m \right\rangle . \tag{4.141}$$

Note that the same j-value appears in the ket and bra because those with different j-values vanish, so rotations cannot change the j-value.

The rotation matrices characterized by definite j form a group because: (1) the identity is a member, (2) the inverse is also a member, (3) the product of any two members is also a member

$$\sum_{m'} \mathscr{D}_{m''m'}^{(j)}\left(R_1\right) \mathscr{D}_{m'm}^{(j)}\left(R_2\right) = \mathscr{D}_{m''m}^{(j)}\left(R_1 R_2\right) , \tag{4.142}$$

and (4) the corresponding rotation operator is unitary

$$\mathscr{D}_{m'm}\left(R^{-1}\right) = \mathscr{D}_{mm'}^{*}\left(R\right) . \tag{4.143}$$

Because

$$\mathscr{D}(R)|j,m\rangle = \sum_{m'} |j,m'\rangle\langle j,m'|\mathscr{D}(R)|j,m\rangle = \sum_{m'} |j,m'\rangle \mathscr{D}^{(j)}_{m'm}(R), \tag{4.144}$$

the matrix element $\mathscr{D}^{(j)}_{m'm}(R)$ is just the amplitude for the rotated state to be found in $|j,m'\rangle$ when the original state is $|j,m\rangle$.

The general rotation characterized by Euler angles described in Eq. (4.75) (not limited to spin ½ system) can have the matrix realization as

$$\begin{aligned}\mathscr{D}^{(j)}_{m'm}(\alpha,\beta,\gamma) &= \langle j,m'|\exp\left(-i\frac{J_z\alpha}{\hbar}\right)\exp\left(-i\frac{J_y\beta}{\hbar}\right)\exp\left(-i\frac{J_z\gamma}{\hbar}\right)|j,m\rangle \\ &= \exp\left[-i\left(m'\alpha+m\gamma\right)\right]d^{(j)}_{m'm}(\beta)\end{aligned}, \tag{4.145}$$

where

$$d^{(j)}_{m'm}(\beta) \equiv \langle j,m'|\exp\left(-i\frac{J_y\beta}{\hbar}\right)|j,m\rangle \tag{4.146}$$

are the matrix elements of a new matrix $d^{(j)}(\beta)$.

For the $j=\frac{1}{2}$ case,

$$d^{1/2}(\beta) = \begin{pmatrix} \cos(\beta/2) & -\sin(\beta/2) \\ \sin(\beta/2) & \cos(\beta/2) \end{pmatrix}. \tag{4.147}$$

For the $j=1$ case, because

$$J_y = \frac{J_+ - J_-}{2i}, \tag{4.148}$$

we can use Eq. (4.140) to obtain

$$J_y^{(j=1)} = \frac{\hbar}{2}\begin{pmatrix} 0 & -\sqrt{2}i & 0 \\ \sqrt{2}i & 0 & -\sqrt{2}i \\ 0 & \sqrt{2}i & 0 \end{pmatrix}. \tag{4.149}$$

Moreover, because for $j=1$ only, it can be verified that

$$\exp\left(-i\frac{J_y\beta}{\hbar}\right) = 1-\left(\frac{J_y}{\hbar}\right)^2(1-\cos\beta) - i\left(\frac{J_y}{\hbar}\right)\sin\beta. \tag{4.150}$$

Therefore, we obtain

$$d^{(1)}(\beta) = \begin{pmatrix} \frac{1}{2}(1+\cos\beta) & -\frac{1}{\sqrt{2}}\sin\beta & \frac{1}{2}(1-\cos\beta) \\ \frac{1}{\sqrt{2}}\sin\beta & \cos\beta & -\frac{1}{\sqrt{2}}\sin\beta \\ \frac{1}{2}(1-\cos\beta) & \frac{1}{\sqrt{2}}\sin\beta & \frac{1}{2}(1+\cos\beta) \end{pmatrix}. \tag{4.151}$$

4.3.2 Orbital Angular Momentum as Rotation Generator

An orbital angular momentum is defined as

$$\mathbf{L} = \mathbf{x} \times \mathbf{p} \,, \tag{4.152}$$

which satisfies the angular-momentum commutation relations

$$\left[L_i, L_j\right] = i\varepsilon_{ijk}\hbar L_k \,. \tag{4.153}$$

These commutation relations are consistent with the commutation relations of **x** and **p**:

$$\begin{aligned}\left[L_x, L_y\right] &= \left[yp_z - zp_y, zp_x - xp_z\right] = \left[yp_z, zp_x\right] + \left[zp_y, xp_z\right] \\ &= yp_x\left[p_z, z\right] + p_y x\left[z, p_z\right] = i\hbar\left(xp_y - yp_x\right) \\ &= i\hbar L_z\end{aligned} \,, \tag{4.154}$$

and vice versa.

Considering the property of the translation operator, the fact that L_z generates an infinitesimal rotation about the *z*-axis can be verified by

$$\begin{aligned}\left[1 - i\left(\frac{\delta\phi}{\hbar}\right)L_z\right]\left|x', y', z'\right\rangle &= \left[1 - i\frac{p_y}{\hbar}\left(\delta\phi x'\right) + i\frac{p_x}{\hbar}\left(\delta\phi y'\right)\right]\left|x', y', z'\right\rangle \\ &= \left|x' - y'\delta\phi, y' + x'\delta\phi, z'\right\rangle\end{aligned} \,. \tag{4.155}$$

Therefore, the wave function for the rotated state

$$\left\langle x', y', z'\right|\left[1 - i\left(\frac{\delta\phi}{\hbar}\right)L_z\right]\left|\alpha\right\rangle = \left\langle x' + y'\delta\phi, y' - x'\delta\phi, z'\middle|\alpha\right\rangle \,. \tag{4.156}$$

In spherical coordinates, the above becomes

$$\begin{aligned}\left\langle r,\theta,\phi\right|\left[1 - i\left(\frac{\delta\phi}{\hbar}\right)L_z\right]\left|\alpha\right\rangle &= \left\langle r,\theta,\phi - \delta\phi\middle|\alpha\right\rangle \\ &= \left\langle r,\theta,\phi\middle|\alpha\right\rangle - \delta\phi\frac{\partial}{\partial\phi}\left\langle r,\theta,\phi\middle|\alpha\right\rangle\end{aligned} \,. \tag{4.157}$$

Because $\left\langle r,\theta,\phi\right|$ is an arbitrary state, we can identify

$$\left\langle \mathbf{x}'\right|L_z\left|\alpha\right\rangle = -i\hbar\frac{\partial}{\partial\phi}\left\langle \mathbf{x}'\middle|\alpha\right\rangle \,, \tag{4.158}$$

Analogous to Eq. (4.156), the rotation about the *x*-axis by angle $\delta\phi_x$ has

$$\left\langle x', y', z'\right|\left[1 - i\left(\frac{\delta\phi_x}{\hbar}\right)L_x\right]\left|\alpha\right\rangle = \left\langle x', y' + z'\delta\phi_x, z' - y'\delta\phi_x\middle|\alpha\right\rangle \,. \tag{4.159}$$

In spherical coordinates, the above equation becomes

$$\left\langle \mathbf{x}'\right|L_x\left|\alpha\right\rangle = -i\hbar\left(-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)\left\langle \mathbf{x}'\middle|\alpha\right\rangle \,. \tag{4.160}$$

Likewise,

$$\left\langle \mathbf{x}'\right|L_y\left|\alpha\right\rangle = -i\hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)\left\langle \mathbf{x}'\middle|\alpha\right\rangle \,. \tag{4.161}$$

According to the above two equations, we have

$$\left\langle \mathbf{x}'\right|L_\pm\left|\alpha\right\rangle = -i\hbar\exp\left(\pm i\phi\right)\left(\pm i\frac{\partial}{\partial\theta} - \cot\theta\frac{\partial}{\partial\phi}\right)\left\langle \mathbf{x}'\middle|\alpha\right\rangle \,. \tag{4.162}$$

Because

$$L^2 = L_z^2 + \frac{1}{2}\left(L_+L_- + L_-L_+\right), \tag{4.163}$$

we have

$$\langle \mathbf{x}'|\mathbf{L}^2|\alpha\rangle = -\hbar^2\left(\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\right)\langle \mathbf{x}'|\alpha\rangle . \tag{4.164}$$

Below we connect $\mathbf{L}^2$ to the angular part of the Laplacian. First, we have

$$\begin{aligned}
\mathbf{L}^2 &= \sum_{ijlmk}\varepsilon_{ijk}x_i p_j \varepsilon_{lmk}x_l p_m = \sum_{ijlm}\left(\delta_{il}\delta_{jm} - \delta_{im}\delta_{jl}\right)x_i p_j x_l p_m \\
&= \sum_{ijlm}\left[\delta_{il}\delta_{jm}x_i\left(x_l p_j - i\hbar\delta_{jl}\right)p_m - \delta_{im}\delta_{jl}x_i p_j\left(p_m x_l + i\hbar\delta_{lm}\right)\right] \\
&= \mathbf{x}^2\mathbf{p}^2 - i\hbar\mathbf{x}\cdot\mathbf{p} - \sum_{ijlm}\delta_{im}\delta_{jl}\left[x_i p_m\left(x_l p_j - i\hbar\delta_{jl}\right) + i\hbar\delta_{lm}x_i p_j\right] \\
&= \mathbf{x}^2\mathbf{p}^2 - \left(\mathbf{x}\cdot\mathbf{p}\right)^2 + i\hbar\mathbf{x}\cdot\mathbf{p}
\end{aligned} . \tag{4.165}$$

Because

$$\langle \mathbf{x}'|\mathbf{x}\cdot\mathbf{p}|\alpha\rangle = \mathbf{x}'\cdot\left(-i\hbar\nabla'\langle \mathbf{x}'|\alpha\rangle\right) = -i\hbar r\frac{\partial}{\partial r}\langle \mathbf{x}'|\alpha\rangle , \tag{4.166}$$

and likewise,

$$\langle \mathbf{x}'|\left(\mathbf{x}\cdot\mathbf{p}\right)^2|\alpha\rangle = -\hbar^2 r\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\langle \mathbf{x}'|\alpha\rangle\right) = -\hbar^2\left(r^2\frac{\partial^2}{\partial r^2}\langle \mathbf{x}'|\alpha\rangle + r\frac{\partial}{\partial r}\langle \mathbf{x}'|\alpha\rangle\right), \tag{4.167}$$

we finally get

$$\langle \mathbf{x}'|\mathbf{L}^2|\alpha\rangle = r^2\langle \mathbf{x}'|\mathbf{p}^2|\alpha\rangle + \hbar^2\left(r^2\frac{\partial^2}{2r^2}\langle \mathbf{x}'|\alpha\rangle + 2r\frac{\partial}{\partial r}\langle \mathbf{x}'|\alpha\rangle\right). \tag{4.168}$$

In terms of the kinetic energy, we have

$$\begin{aligned}
\frac{1}{2m}\langle \mathbf{x}'|\mathbf{p}^2|\alpha\rangle &= -\frac{\hbar^2}{2m}\nabla'^2\langle \mathbf{x}'|\alpha\rangle \\
&= -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{2r^2}\langle \mathbf{x}'|\alpha\rangle + \frac{2}{r}\frac{\partial}{\partial r}\langle \mathbf{x}'|\alpha\rangle - \frac{1}{\hbar^2 r^2}\langle \mathbf{x}'|\mathbf{L}^2|\alpha\rangle\right)
\end{aligned} . \tag{4.169}$$

Because the first two terms in the last line are just the radial part of the Laplacian acting on $\langle \mathbf{x}'|\alpha\rangle$, the last term must be the angular part of the Laplaican acting on $\langle \mathbf{x}'|\alpha\rangle$, in agreement with Eq. (4.164).

4.3.3 Spherical Harmonics

A spinless particle subjected to a spherical symmetrical potential is separable in spherical coordinates, and the eigenfunctions can be written as

$$\langle \mathbf{x}'|n,l,m\rangle = R_{nl}\left(r\right)Y_l^m\left(\theta,\phi\right), \tag{4.170}$$

where n is some quantum number other than l and m. When the Hamiltonian is spherically symmetrical, H commutes with $\mathbf{L}^2$ and L_z, and thus the energy eigenkets are also the eigenkets of $\mathbf{L}^2$ and L_z. Due to the commutation relations of L_k, $k=1,2,3$, the eigenvalues of $\mathbf{L}^2$ and

L_z are expected to be $l(l+1)\hbar$ and $m\hbar$, $m=-l,-l+1,\cdots,l-1,l$.

Define a **direction eigenket** $|\hat{\mathbf{n}}\rangle$,

$$Y_l^m(\theta,\phi)=Y_l^m(\hat{\mathbf{n}})=\langle\hat{\mathbf{n}}|l,m\rangle\,, \tag{4.171}$$

which is the amplitude for a state characterized by *l*, *m* to be found in the direction $\hat{\mathbf{n}}$ specified by (θ,ϕ).

Knowing relations involving orbital angular-momentum eigenkets, we can immediately write the corresponding relations involving the spherical harmonics. For example, taking

$$L_z|l,m\rangle=m\hbar|l,m\rangle \tag{4.172}$$

and multiplying $\langle\hat{\mathbf{n}}|$ on the left, by using Eq. (4.158), we obtain

$$-i\hbar\frac{\partial}{\partial\phi}\langle\hat{\mathbf{n}}|l,m\rangle=m\hbar\langle\hat{\mathbf{n}}|l,m\rangle\,, \tag{4.173}$$

which is just

$$-i\hbar\frac{\partial}{\partial\phi}Y_l^m(\theta,\phi)=m\hbar Y_l^m(\theta,\phi)\,, \tag{4.174}$$

implying that ϕ-dependence of $Y_l^m(\theta,\phi)$ must behave like $\exp(im\phi)$. Likewise, according to Eq. (4.164) and

$$\mathbf{L}^2|l,m\rangle=l(l+1)\hbar^2|l,m\rangle\,, \tag{4.175}$$

we have

$$\left[\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+l(l+1)\right]Y_l^m=0\,. \tag{4.176}$$

By using the completeness relation for the direction eigenkets

$$\int \mathrm{d}\Omega_{\hat{\mathbf{n}}}|\hat{\mathbf{n}}\rangle\langle\hat{\mathbf{n}}|=1\,, \tag{4.177}$$

the orthogonality relation

$$\langle l',m'|l,m\rangle=\delta_{ll'}\delta_{mm'} \tag{4.178}$$

leads to

$$\int_0^{2\pi}\mathrm{d}\phi\int_{-1}^{1}\mathrm{d}(\cos\theta)Y_{l'}^{m'*}(\theta,\phi)Y_l^m(\theta,\phi)=\delta_{ll'}\delta_{mm'}\,. \tag{4.179}$$

For the case of $m=l$,

$$L_+|l,l\rangle=0\,, \tag{4.180}$$

which, because of Eq. (4.162), leads to

$$-i\hbar\exp(i\phi)\left(i\frac{\partial}{\partial\theta}-\cot\theta\frac{\partial}{\partial\phi}\right)\langle\hat{\mathbf{n}}|l,l\rangle=0\,. \tag{4.181}$$

Because the Φ-dependence must behave like $\exp(il\phi)$, the above equation is satisfied by

$$\langle \hat{\mathbf{n}} | l, l \rangle = Y_l^l(\theta, \phi) = c_l \exp(il\phi) \sin^l \theta \,, \tag{4.182}$$

where

$$c_l = \frac{(-1)^l}{2^l l!} \sqrt{\frac{(2l+1)(2l)!}{4\pi}} \tag{4.183}$$

to meet the normalization requirement given by Eq. (4.179).

Starting from Eq. (4.182), by applying

$$\begin{aligned} \langle \hat{\mathbf{n}} | l, m-1 \rangle &= \frac{\langle \hat{\mathbf{n}} | L_- | l, m \rangle}{\hbar \sqrt{(l+m)(l-m+1)}} \\ &= \frac{\exp(-i\phi)}{\sqrt{(l+m)(l-m+1)}} \left(-\frac{\partial}{\partial \theta} + i \cot\theta \frac{\partial}{\partial \phi} \right) \langle \hat{\mathbf{n}} | l, m \rangle \end{aligned} \tag{4.184}$$

successively, we can obtain all Y_l^m with *l* fixed. The result for $m \geq 0$ is

$$Y_l^m(\theta, \phi) = \frac{(-1)^l}{2^l l!} \sqrt{\frac{(2l+1)}{4\pi} \frac{(l+m)!}{(l-m)!}} \frac{\exp(im\phi)}{\sin^m \theta} \frac{\mathrm{d}^{l-m}}{\mathrm{d}(\cos\theta)^{l-m}} (\sin\theta)^{2l} \,, \tag{4.185}$$

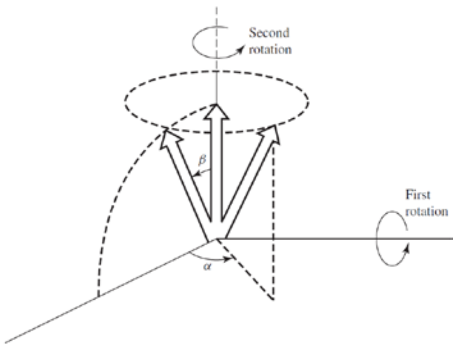
and

$$Y_l^{-m}(\theta, \phi) = (-1)^m \left[Y_l^m(\theta, \phi) \right]^* . \tag{4.186}$$

For $m = 0$,

$$Y_l^0(\theta, \phi) = \sqrt{\frac{2l+1}{4\pi}} P_l(\cos\theta) . \tag{4.187}$$

The *l* values can only be an integer and not a half-integer.



The spherical harmonics can be connected with the approach of the rotation matrices. The general direction eigenket $|\hat{\mathbf{n}}\rangle$ can be expressed by applying an appropriate rotation operator $\mathscr{D}(R) = \mathscr{D}(\alpha = \phi, \beta = \theta, \gamma = 0)$ to the positive *z*-axis direction eigenket $|\hat{\mathbf{z}}\rangle$, such that

$$|\hat{\mathbf{n}}\rangle = \mathscr{D}(R) |\hat{\mathbf{z}}\rangle . \tag{4.188}$$

By applying the completeness relation, the above equation can be rewritten as

$$|\hat{\mathbf{n}}\rangle = \sum_l \sum_m \mathscr{D}(R) |l, m\rangle \langle l, m | \hat{\mathbf{z}} \rangle \,, \tag{4.189}$$

which, multiplied by $\langle l, m'|$ on the left, becomes

$$\langle l, m'|\hat{\mathbf{n}}\rangle = \sum_m \mathscr{D}^{(l)}_{m'm}\left(\alpha = \phi, \beta = \theta, \gamma = 0\right)\langle l, m|\hat{\mathbf{z}}\rangle . \tag{4.190}$$

Because

$$\langle l, m|\hat{\mathbf{z}}\rangle = Y_l^{m*}\left(\theta = 0, \phi\right)\delta_{m0} = \sqrt{\frac{2l+1}{4\pi}}\, P_l\left(\cos\theta\right)\Big|_{\cos\theta=1}\delta_{m0} = \sqrt{\frac{2l+1}{4\pi}}\delta_{m0} , \tag{4.191}$$

Eq. (4.190) becomes

$$Y_l^{m'*}\left(\theta, \phi\right) = \langle l, m'|\hat{\mathbf{n}}\rangle = \sqrt{\frac{2l+1}{4\pi}} D^{(l)}_{m'0}\left(\alpha = \phi, \beta = \theta, \gamma = 0\right) \tag{4.192}$$

or

$$D^{(l)}_{m0}\left(\alpha, \beta, \gamma = 0\right) = \sqrt{\frac{4\pi}{2l+1}}\, Y_l^{m*}\left(\theta, \phi\right)\Big|_{\theta=\beta, \phi=\alpha} . \tag{4.193}$$

Of particular importance is the $m = 0$ case:

$$d^{(l)}_{00}\left(\beta\right)\Big|_{\beta=\theta} = P_l\left(\cos\theta\right) . \tag{4.194}$$

4.4 Schrödinger's Equation for Central Potentials

The spherically symmetrical Hamiltonian system has the form

$$H = \frac{\mathbf{p}^2}{2m} + V\left(r\right). \tag{4.195}$$

Because

$$\left[\mathbf{L}, \mathbf{p}^2\right] = \left[\mathbf{L}, \mathbf{x}^2\right] = 0 , \tag{4.196}$$

we have

$$\left[\mathbf{L}, H\right] = \left[\mathbf{L}^2, H\right] = 0 , \tag{4.197}$$

which means that the angular momentum is conserved.

4.4.1 The Radial Equation

According to Eq. (4.197), we should search for energy eigenstates $|\alpha\rangle = |Elm\rangle$ where

$$\begin{aligned} H|Elm\rangle &= E|Elm\rangle \\ \mathbf{L}^2|Elm\rangle &= l\left(l+1\right)\hbar^2|Elm\rangle . \\ L_z|Elm\rangle &= m\hbar|Elm\rangle \end{aligned} \tag{4.198}$$

Combining with Eqs. (4.169) and (4.170), we arrive at the **radial equation**

$$\left[-\frac{\hbar^2}{2mr^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}}{\mathrm{d}r}\right) + \frac{l\left(l+1\right)\hbar^2}{2mr^2} + V\left(r\right)\right] R_{El}\left(r\right) = ER_{El}\left(r\right) . \tag{4.199}$$

By replacing

$$R_{El}\left(r\right) = \frac{u_{El}\left(r\right)}{r} , \tag{4.200}$$

Eq. (4.199) reduces to

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2u_{El}}{\mathrm{d}r^2}+\left[\frac{l(l+1)\hbar^2}{2mr^2}+V(r)\right]u_{El}(r)=Eu_{El}(r). \tag{4.201}$$

The normalization condition is

$$\int r^2\mathrm{d}rR_{El}^*(r)R_{El}(r)=\int\mathrm{d}ru_{El}^*(r)u_{El}(r)=1. \tag{4.202}$$

The physical interpretation of $u_{El}(r)$ is a one-dimensional wave function for a particle moving in an effective potential

$$V_{\text{eff}}(r)=V(r)+\frac{l(l+1)\hbar^2}{2mr^2}, \tag{4.203}$$

which demonstrates the existence of an "angular momentum barrier" if $l\neq 0$, which keeps the amplitude for locating the particle near the origin is small except for *s*-states.

For small values of r, Eq. (4.201) becomes

$$\frac{\mathrm{d}^2u_{El}}{\mathrm{d}r^2}=\frac{l(l+1)}{r^2}u_{El}(r),\quad r\to 0, \tag{4.204}$$

which has the general solution

$$u_{El}(r)=Ar^{l+1}+\frac{B}{r^l}. \tag{4.205}$$

It is required that $B=0$ to allow the wave function normalizable. So we are left with

$$R_{El}(r)\to r^l,\quad r\to 0. \tag{4.206}$$

For bound states $E<0$ when $r\to\infty$, Eq. (4.201) becomes

$$\frac{\mathrm{d}^2u_E}{\mathrm{d}r^2}=\kappa^2u, \tag{4.207}$$

where $\kappa^2\equiv -2mE/\hbar^2>0$, whose solution is simply

$$u_E(r)\propto\exp(-\kappa r). \tag{4.208}$$

Defining dimensionless variable $\rho\equiv\kappa r$, and removing both the short-distance and the long-distance behavior, the wave function can be written as

$$u_{El}(\rho)=\rho^{l+1}\exp(-\rho)w(\rho), \tag{4.209}$$

where $w(\rho)$ is "well-behaved" and satisfies

$$\frac{\mathrm{d}^2w}{\mathrm{d}\rho^2}+2\left(\frac{l+1}{\rho}-1\right)\frac{\mathrm{d}w}{\mathrm{d}\rho}+\left[\frac{V}{E}-\frac{2(l+1)}{\rho}\right]w=0. \tag{4.210}$$

4.4.2 The Free Particle and the Infinite Spherical Well

For a free particle, define

$$k\equiv\frac{\sqrt{2mE}}{\hbar},\quad \rho\equiv kr, \tag{4.211}$$

Eq. (4.199) becomes

$$\frac{\mathrm{d}^2 R}{\mathrm{d}\rho^2}+\frac{2}{\rho}\frac{\mathrm{d}R}{\mathrm{d}\rho}+\left[1-\frac{l(l+1)}{\rho^2}\right]R=0\,. \tag{4.212}$$

The solutions of this differential equation are *spherical Bessel functions*:

$$\begin{aligned} j_l(\rho) &= (-\rho)^l\left(\frac{1}{\rho}\frac{d}{d\rho}\right)^l\left(\frac{\sin\rho}{\rho}\right) \\ n_l(\rho) &= -(-\rho)^l\left(\frac{1}{\rho}\frac{d}{d\rho}\right)^l\left(\frac{\cos\rho}{\rho}\right) \end{aligned}\,. \tag{4.213}$$

Since when $\rho\to 0$, $j_l(\rho)\to\rho^l$ corresponds to Eq. (4.206) but $n_l(\rho)\to\rho^{-l-1}$ does not, $j_l(\rho)$ is the only set of solutions. It can be shown that, on the complex plane,

$$j_l(z)=\frac{1}{2i^l}\int_{-1}^{1}\mathrm{d}s\exp(izs)P_l(s)\,. \tag{4.214}$$

The first few spherical Bessel functions are

$$\begin{aligned} j_0(\rho) &= \frac{\sin\rho}{\rho} \\ j_1(\rho) &= \frac{\sin\rho}{\rho^2}-\frac{\cos\rho}{\rho} \\ j_2(\rho) &= \left(\frac{3}{\rho^3}-\frac{1}{\rho}\right)\sin\rho-\frac{3\cos\rho}{\rho^2} \end{aligned}\,. \tag{4.215}$$

For a particle confined to an infinite spherical well

$$V(r)=\begin{cases}0, & r<a\\ \infty, & r\ge a\end{cases}, \tag{4.216}$$

the wave function is constrained to be zero at $r=a$, which leads to the “quantization condition” $j_l(ka)=0$. The energy levels can then be computed as

$$\begin{aligned} E_{l=0} &= \frac{\hbar^2}{2ma^2}\left[\pi^2,(2\pi)^2,(3\pi)^2,\cdots\right] \\ E_{l=1} &= \frac{\hbar^2}{2ma^2}\left[4.49^2,7.73^2,10.90^2,\cdots\right] \\ E_{l=2} &= \frac{\hbar^2}{2ma^2}\left[5.84^2,8.96^2,12.25^2,\cdots\right] \end{aligned}\,. \tag{4.217}$$

Note that this series of energy levels shows no degeneracies in *l*.

4.4.3 The Isotropic Harmonic Oscillator

An isotropic harmonic oscillator has the Hamiltonian

$$H=\frac{\mathbf{p}^2}{2m}+\frac{1}{2}m\omega^2 r^2\,. \tag{4.218}$$

Introducing dimensionless energy λ and radial coordinate ρ through

$$E=\frac{1}{2}\hbar\omega\lambda,\quad r=\left(\frac{\hbar}{m\omega}\right)^{1/2}\rho\,, \tag{4.219}$$

Eq. (4.201) becomes

$$\frac{\mathrm{d}^2u}{\mathrm{d}\rho^2}-\frac{l(l+1)}{\rho^2}u(\rho)+(\lambda-\rho^2)u(\rho)=0\,. \tag{4.220}$$

To remove the behavior for large and small ρ values, we write

$$u(\rho)=\rho^{l+1}\exp(-\rho^2/2)f(\rho)\,. \tag{4.221}$$

The differential equation for $f(\rho)$ is thus

$$\rho\frac{\mathrm{d}^2 f}{\mathrm{d}\rho^2}+2\left[(l+1)-\rho^2\right]\frac{\mathrm{d}f}{\mathrm{d}\rho}+\left[\lambda-(2l+3)\right]\rho f(\rho)=0\,. \tag{4.222}$$

By writing $f(\rho)$ in the form of an infinite series, namely

$$f(\rho)=\sum_{n=0}^{\infty}a_n\rho^n\,, \tag{4.223}$$

and insert it into Eq. (4.222), we obtain $a_1=0$ and

$$\sum_{n=2}^{\infty}\left\{(n+2)(n+1)a_{n+2}+2(l+1)(n+2)a_{n+2}-2na_n+\left[\lambda-(2l+3)\right]a_n\right\}\rho^{n+1}=0\,. \tag{4.224}$$

The above leads to the recursion relation

$$a_{n+2}=\frac{2n+2l+3-\lambda}{(n+2)(n+2l+3)}a_n\,, \tag{4.225}$$

indicating that $a_n=0$ for odd *n*, and

$$\frac{a_{n+2}}{a_n}\to\frac{1}{q}\,, \tag{4.226}$$

where $q\equiv\frac{n}{2}$. Therefore, for large values of ρ, Eq. (4.223) becomes

$$f(\rho)\to c\sum_q\frac{1}{q!}(\rho^2)^q\propto\exp(\rho^2)\,, \tag{4.227}$$

where *c* is a constant. Therefore, the series has to terminate to meet the normalization condition, which requires in Eq. (4.225),

$$2n+2l+3-\lambda=0 \tag{4.228}$$

For some even value of $n=2q$, the energy eigenvalues are

$$E_{ql}=\left(2q+l+\frac{3}{2}\right)\hbar\omega\equiv\left(N+\frac{3}{2}\right)\hbar\omega \tag{4.229}$$

for $q=0,1,2,\cdots$, $l=0,1,2,\cdots$, and $N\equiv 2q+l$, which is referred to as the "principle" quantum number. It can be shown that *q* counts the number of nodes in the radial function.

We may also write the Hamiltonian Eq. (4.218) as

$$H=H_x+H_y+H_z\,, \tag{4.230}$$

where $H_i=a_i^{\dagger}a_i+\frac{1}{2}$ for $i=x,y,z$. The energy eigenstates can then be labeled as $\left|n_x,n_y,n_z\right\rangle$ instead of $\left|Nlm\right\rangle$, and the energy eigenvalues are

$$E=\left(n_x+\frac{1}{2}+n_y+\frac{1}{2}+n_z+\frac{1}{2}\right)\hbar\omega=\left(N+\frac{3}{2}\right)\hbar\omega\,, \tag{4.231}$$

where $N=n_x+n_y+n_z$.

4.4.4 The Columb Potential

The Column potential is given by

$$V(\mathbf{x}) = -\frac{Ze^2}{r}, \tag{4.232}$$

where Z is the atomic number, e is the electron charge, and r is the distance. Define

$$\rho_0 = \left(\frac{2m}{-E}\right)^{1/2} \frac{Ze^2}{\hbar} = \left(\frac{2mc^2}{-E}\right)^{1/2} Z\alpha, \tag{4.233}$$

where $\alpha \equiv \frac{e^2}{\hbar c} \approx \frac{1}{137}$ is the fine structure constant. Eq. (4.210) becomes

$$\rho \frac{\mathrm{d}^2 w}{\mathrm{d}\rho^2} + 2(l+1-\rho)\frac{\mathrm{d}w}{\mathrm{d}\rho} + \left[\rho_0 - 2(l+1)\right] w(\rho) = 0. \tag{4.234}$$

It can be written as Kummer's Equation:

$$x\frac{\mathrm{d}^2 F}{\mathrm{d}x^2} + (c-x)\frac{\mathrm{d}F}{\mathrm{d}x} - aF = 0, \tag{4.235}$$

where

$$x = 2\rho, \quad c = 2(l+1), \quad 2a = 2(l+1) - \rho_0. \tag{4.236}$$

The solution is called the Confluent Hypergeometric Function:

$$F(a;c;x) = 1 + \frac{a}{c}\frac{x}{1!} + \frac{a(a+1)}{c(c+1)}\frac{x^2}{2!} + \cdots, \tag{4.237}$$

so

$$w(\rho) = F\left(l+1-\frac{\rho_0}{2}; 2(l+1); 2\rho\right). \tag{4.238}$$

For large ρ, we have

$$w(\rho) \approx \sum_N \frac{a(a+1)\cdots(2\rho)^N}{c(c+1)\cdots N!} \approx \sum_N \frac{(N/2)^N}{N^N}\frac{(2\rho)^N}{N!} \approx \sum_N \frac{\rho^N}{N!} \approx \exp(\rho). \tag{4.239}$$

To allow the series Eq. (4.237) finite, we must have $a + N = 0$ that leads to $\rho_0 = 2(N+l+1)$, where $N = 0,1,2,\cdots$ and $l = 0,1,2,\cdots$. Define the principal quantum number

$$n \equiv N + l + 1 = 1,2,3,\cdots \tag{4.240}$$

where $l = 0,1,\cdots,n-1$, According to Eq. (4.233), we have

$$\rho_0 = \sqrt{\frac{2mc^2}{-E}} Z\alpha = 2n, \tag{4.241}$$

which leads to the **Balmer formula**

$$E = -\frac{1}{2}mc^2\frac{Z^2\alpha^2}{n^2} = -13.6\times\frac{Z^2}{n^2}\,\mathrm{eV}. \tag{4.242}$$

The level of degeneracy for a state $|nlm\rangle$ is given by

$$\sum_{l=0}^{n-1}(2l+1) = n^2. \tag{4.243}$$

Since $\rho = \kappa r$, where $\kappa = \sqrt{-2mE/\hbar^2}$, we have

$$\frac{1}{\kappa} = \frac{\hbar}{mc\alpha}\frac{n}{Z} = a_0 \frac{n}{Z}, \tag{4.244}$$

Where the **Bohr radius**

$$a_0 \equiv \frac{\hbar}{mc\alpha} = \frac{\hbar^2}{me^2} \tag{4.245}$$

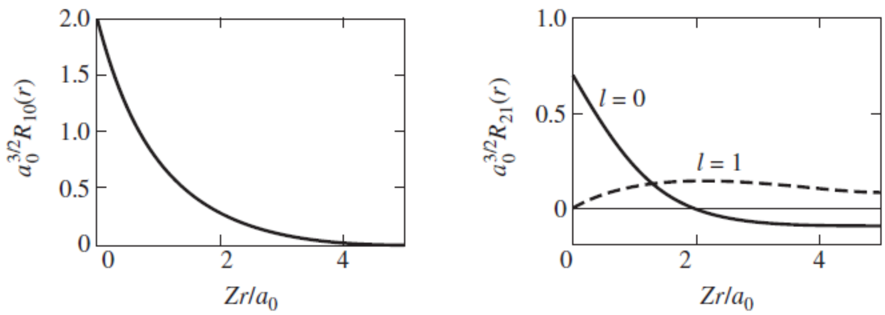
For an electron, $a_0 = 0.53$ Å, which is the typical size of an atom.

According to Eq. (4.170), the hydrogen-atom wave functions can be written as

$$\psi_{nlm}(\mathbf{x}) = \langle \mathbf{x} | nlm \rangle = R_{nl}(r) Y_l^m(\theta, \phi), \tag{4.246}$$

where

$$R_{nl}(r) = \frac{\left(\frac{2Zr}{na_0}\right)^l}{(2l+1)!} \exp\left(-\frac{Zr}{na_0}\right) \sqrt{\left(\frac{2Z}{na_0}\right)^3 \frac{(n+l)!}{2n(n-l-1)!}} \times F\left(-n+l+1; 2l+2; \frac{2Zr}{na_0}\right). \tag{4.247}$$



Radial wave functions for the Coulomb potential and principal quantum numbers $n = 1$ (left) and $n = 2$ (right).

4.4.5 Addition of Angular Momenta

We start by looking at two simple examples:

(1) For a realistic description of a particle considering both the position and spin degrees of freedom, the base ket

$$|\mathbf{x}', \pm\rangle = |\mathbf{x}'\rangle \otimes |\pm\rangle, \tag{4.248}$$

where any operator in the space spanned by $\{|\mathbf{x}'\rangle\}$ commutes with any operator spanned by $|\pm\rangle$.

The rotation operator still has the form $\exp(-i\mathbf{J}\cdot\hat{\mathbf{n}}\phi/\hbar)$, but the generator of rotation

$$\mathbf{J} = \mathbf{L} + \mathbf{S}. \tag{4.249}$$

More precisely, it should be written as

$$\mathbf{J} = \mathbf{L} \otimes 1 + 1 \otimes \mathbf{S}, \tag{4.250}$$

where the 1 in $\mathbf{L} \otimes 1$ stands for the identity operator in the infinite-dimensional ket space spanned by the position eigenkets, and the 1 in $1 \otimes \mathbf{S}$ stands for the identity operator in the spin space. Because **L** and **S** commute, we can write

$$\mathscr{D}(R) = \mathscr{D}^{(\text{orb})}(R)\mathscr{D}^{(\text{spin})}(R) = \exp\left(-i\frac{\mathbf{L}\cdot\hat{\mathbf{n}}\phi}{\hbar}\right) \otimes \exp\left(-i\frac{\mathbf{S}\cdot\hat{\mathbf{n}}\phi}{\hbar}\right). \tag{4.251}$$

The corresponding wave function is written as

$$\langle \mathbf{x}', \pm | \alpha \rangle = \psi_{\pm}(\mathbf{x}') = \begin{pmatrix} \psi_{+}(\mathbf{x}') \\ \psi_{-}(\mathbf{x}') \end{pmatrix}. \tag{4.252}$$

Instead of $|\mathbf{x}'\rangle$, we may use the simultaneous eigenkets of $\mathbf{L}^2$ and L_z, $|nlm\rangle$, with eigenvalues $\hbar^2 l(l+1)$ and $m_l \hbar$, respectively. For the spin part, $|\pm\rangle$ are eigenkets of $\mathbf{S}^2$ and S_z with eigenvalues $3\hbar^2/4$ and $\pm\hbar/2$, respectively. Therefore, we can expand the state ket in terms of simultaneous eigenket of $(\mathbf{L}^2, \mathbf{S}^2, L_z, S_z)$ or $(\mathbf{J}^2, J_z, \mathbf{L}^2, \mathbf{S}^2)$.

(2) For two spin ½ particles with the orbital degree of freedom suppressed, the total spin operator can be written as

$$\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2 = \mathbf{S}_1 \otimes 1 + 1 \otimes \mathbf{S}_2 . \tag{4.253}$$

We have the commutation relations

$$\begin{aligned} &[S_{1x}, S_{2y}] = 0, \cdots \\ &[S_{1x}, S_{1y}] = i\hbar S_{1z}, [S_{2x}, S_{2y}] = i\hbar S_{2z}, \cdots \end{aligned}, \tag{4.254}$$

which lead to the commutation relation for the total spin operator

$$[S_x, S_y] = i\hbar S_z . \tag{4.255}$$

The eigenvalues of the various spin operators are

$$\begin{aligned} \mathbf{S}^2 = (\mathbf{S}_1 + \mathbf{S}_2)^2 \quad &: s(s+1)\hbar^2 \\ S_z = S_{1z} + S_{2z} \quad &: m\hbar \\ S_{1z} \quad &: m_1\hbar \\ S_{2z} \quad &: m_2\hbar \end{aligned} . \tag{4.256}$$

An arbitrary spin state of two spin ½ particles can be expanded in terms of $(S_{1z,} S_{2z})$ or $(\mathbf{S}^2, S_z)$.

1. The $\{m_1, m_2\}$ representation based on the eigenkets of $(S_{1z,} S_{2z})$:

$$|++\rangle, \quad |+-\rangle, \quad |-+\rangle, \quad |--\rangle, \tag{4.257}$$

where + stands for $m_i = 1/2$ and – stands for $m_i = -1/2$, $i = 1, 2$.

2. The $\{s, m\}$ representation (or the triplet-singlet representation) based on the eigenkets of $(\mathbf{S}^2, S_z)$:

$$|s = 1, m = \pm 1\rangle, \quad |s = 0, m = 0\rangle. \tag{4.258}$$

The relationship between the two base kets is:

$$
\begin{aligned}
&\left| s=1, m=1 \right\rangle = \left| ++ \right\rangle \\
&\left| s=1, m=0 \right\rangle = \frac{1}{\sqrt{2}}\left(\left| +- \right\rangle + \left| -+ \right\rangle \right) \\
&\left| s=1, m=-1 \right\rangle = \left| -- \right\rangle \\
&\left| s=0, m=0 \right\rangle = \frac{1}{\sqrt{2}}\left(\left| +- \right\rangle - \left| -+ \right\rangle \right)
\end{aligned}
. \tag{4.259}
$$

The **formal theory of angular-momentum addition** can be systematically developed as follows. Considering two angular-momentum operators J_1 and J_2 in different subspaces. They satisfy the following commutation relations:

$$
\begin{aligned}
&\left[J_{1i}, J_{1j} \right] = i\hbar \varepsilon_{ijk} J_{1k} \\
&\left[J_{2i}, J_{2j} \right] = i\hbar \varepsilon_{ijk} J_{2k} \\
&\left[J_{1k}, J_{2l} \right] = 0
\end{aligned}
, \tag{4.260}
$$

and the total $\mathbf{J}$ also satisfies the angular-momentum commutation relations

$$
\left[J_i, J_j \right] = i\hbar \varepsilon_{ijk} J_k . \tag{4.261}
$$

(1) If we choose simultaneous eigenkets of $\left(\mathbf{J}_1^2, \mathbf{J}_2^2, J_{1z}, J_{2z} \right)$, denoted by $\left| j_1 j_2; m_1 m_2 \right\rangle$, the defining equations are

$$
\begin{aligned}
&\mathbf{J}_1^2 \left| j_1 j_2; m_1 m_2 \right\rangle = j_1 \left(j_1 + 1 \right) \hbar^2 \left| j_1 j_2; m_1 m_2 \right\rangle \\
&J_{1z} \left| j_1 j_2; m_1 m_2 \right\rangle = m_1 \hbar \left| j_1 j_2; m_1 m_2 \right\rangle \\
&\mathbf{J}_2^2 \left| j_1 j_2; m_1 m_2 \right\rangle = j_2 \left(j_2 + 1 \right) \hbar^2 \left| j_1 j_2; m_1 m_2 \right\rangle \\
&J_{2z} \left| j_1 j_2; m_1 m_2 \right\rangle = m_2 \hbar \left| j_1 j_2; m_1 m_2 \right\rangle
\end{aligned}
. \tag{4.262}
$$

(2) If we choose simultaneous eigenkets of $\left(\mathbf{J}^2, \mathbf{J}_1^2, \mathbf{J}_2^2, J_z \right)$, denoted by $\left| j_1 j_2; jm \right\rangle$, the defining equations are

$$
\begin{aligned}
&\mathbf{J}_1^2 \left| j_1 j_2; jm \right\rangle = j_1 \left(j_1 + 1 \right) \hbar^2 \left| j_1 j_2; jm \right\rangle \\
&\mathbf{J}_2^2 \left| j_1 j_2; jm \right\rangle = j_2 \left(j_2 + 1 \right) \hbar^2 \left| j_1 j_2; jm \right\rangle \\
&\mathbf{J}^2 \left| j_1 j_2; jm \right\rangle = j \left(j + 1 \right) \hbar^2 \left| j_1 j_2; jm \right\rangle \\
&J_z \left| j_1 j_2; jm \right\rangle = m \hbar \left| j_1 j_2; jm \right\rangle
\end{aligned}
. \tag{4.263}
$$

Because

$$
\mathbf{J}^2 = \mathbf{J}_1^2 + \mathbf{J}_2^2 + 2 J_{1z} J_{2z} + J_{1+} J_{2-} + J_{1-} J_{2+} , \tag{4.264}
$$

we have

$$
\left[\mathbf{J}^2, J_z \right] = 0 , \tag{4.265}
$$

but

$$
\left[\mathbf{J}^2, J_{1z} \right] \neq 0, \quad \left[\mathbf{J}^2, J_{2z} \right] \neq 0 . \tag{4.266}
$$

The two bases are connected by the unitary transformation:

$$
\left| j_1 j_2; jm \right\rangle = \sum_{m_1} \sum_{m_2} \left| j_1 j_2; m_1 m_2 \right\rangle \left\langle j_1 j_2; m_1 m_2 \middle| j_1 j_2; jm \right\rangle , \tag{4.267}
$$

The elements of the transformation matrix $\langle j_1 j_2; m_1 m_2 | j_1 j_2; jm \rangle$ are **Clebsch-Gordan coefficients**, which can also be written in terms of the **Wigner's 3-j symbol**:

$$\langle j_1 j_2; m_1 m_2 | j_1 j_2; jm \rangle = (-1)^{j_1 - j_2 + m} \sqrt{2j+1} \begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & -m \end{pmatrix}. \tag{4.268}$$

They have the following important properties:

(1) The coefficients vanish unless

$$m = m_1 + m_2 . \tag{4.269}$$

Proof: Note that

$$(J_z - J_{1z} - J_{2z}) | j_1 j_2; jm \rangle = 0 . \tag{4.270}$$

Multiplying $\langle j_1 j_2; m_1 m_2 |$ on the left, we obtain

$$(m - m_1 - m_2) \langle j_1 j_2; m_1 m_2 | j_1 j_2; jm \rangle = 0 . \tag{4.271}$$

Therefore, unless $m = m_1 + m_2$, $\langle j_1 j_2; m_1 m_2 | j_1 j_2; jm \rangle = 0$.

(2) The coefficients vanish unless $|j_1 - j_2| \le j \le j_1 + j_2$.

Proof: Because $\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2$, this is obviously true if the dimensionalities of the spanned spaces are the same. For $\{ | j_1 j_2; jm \rangle \}$, let $j_1 \ge j_2$, the dimensionality is

$$\begin{aligned} N &= \sum_{j=j_1-j_2}^{j_1+j_2} (2j+1) \\ &= \frac{1}{2} \left[\{ 2(j_1 - j_2) + 1 \} + \{ 2(j_1 + j_2) + 1 \} \right] (2j_2 + 1) , \\ &= (2j_1 + 1)(2j_2 + 1) \end{aligned} \tag{4.272}$$

which is just the dimensionality of $\{ | j_1 j_2; m_1 m_2 \rangle \}$.

(3) The Clebsch-Gordan coefficients form a real unitary matrix, so we have the orthogonality condition

$$\sum_j \sum_m \langle j_1 j_2; m_1 m_2 | j_1 j_2; jm \rangle \langle j_1 j_2; m_1' m_2' | j_1 j_2; jm \rangle = \delta_{m_1 m_1'} \delta_{m_2 m_2'} \tag{4.273}$$

and

$$\sum_{m_1} \sum_{m_2} \langle j_1 j_2; m_1 m_2 | j_1 j_2; jm \rangle \langle j_1 j_2; m_1 m_2 | j_1 j_2; j' m' \rangle = \delta_{jj'} \delta_{mm'} . \tag{4.274}$$

By setting $j' = j$, $m' = m = m_1 + m_2$, we then obtain

$$\sum_{m_1} \sum_{m_2 = m - m_1} \left| \langle j_1 j_2; m_1 m_2 | j_1 j_2; jm \rangle \right|^2 = 1 , \tag{4.275}$$

which is just the normalization condition for $| j_1 j_2; jm \rangle$.

With j_1, j_2, and j fixed, the coefficients with different m_1 and m_2 are related to each other by **recursion relations**. Starting with

$$J_{\pm}\left| j_1 j_2; jm\right\rangle = \left(j_{1\pm} + j_{2\pm}\right)\sum_{m_1}\sum_{m_2}\left| j_1 j_2; m_1 m_2\right\rangle\left\langle j_1 j_2; m_1 m_2 \right| \left. j_1 j_2; jm\right\rangle \tag{4.276}$$

and using Eqs. (4.138) and (4.139), we obtain

$$\begin{aligned}&\sqrt{(j\mp m)(j\pm m+1)}\left| j_1 j_2; j, m\pm 1\right\rangle \\ &= \sum_{m_1'}\sum_{m_2'}\left(\sqrt{(j_1\mp m_1')(j_1\pm m_1'+1)}\left| j_1 j_2; m_1'\pm 1, m_2'\right\rangle + \sqrt{(j_2\mp m_2')(j_2\pm m_2'+1)}\left| j_1 j_2; m_1', m_2'\pm 1\right\rangle\right). \\ &\times\left\langle j_1 j_2; m_1' m_2' \right| \left. j_1 j_2; jm\right\rangle\end{aligned} \tag{4.277}$$

Multiplying by $\left\langle j_1 j_2; m_1 m_2\right|$ on the left and using orthonormality, the nonvanishing contributions from the right-hand side are possible only with

$$m_1 = m_1' \pm 1, \quad m_2 = m_2' \tag{4.278}$$

for the first term and

$$m_1 = m_1', \quad m_2 = m_2' \pm 1 \tag{4.279}$$

for the second term. So we finally reach the recursion relations:

$$\begin{aligned}&\sqrt{(j\mp m)(j\pm m+1)}\left\langle j_1 j_2; m_1 m_2 \right| \left. j_1 j_2; j, m\pm 1\right\rangle \\ &= \sqrt{(j_1\mp m_1+1)(j_1\pm m_1)}\left\langle j_1 j_2; m_1\mp 1, m_2 \right| \left. j_1 j_2; jm\right\rangle \;. \\ &+\sqrt{(j_2\mp m_1+1)(j_2\pm m_2)}\left\langle j_1 j_2; m_1, m_2\mp 1 \right| \left. j_1 j_2; jm\right\rangle\end{aligned} \tag{4.280}$$

Because the $J_{\pm}$ operators have shifted the m-values, the nonvanishing condition Eq. (4.269) for the Clesch-Gordan coefficients has now become (when applied to Eq. (4.280))

$$m_1 + m_2 = m \pm 1 \,. \tag{4.281}$$

The recursion relations Eq. (4.280), along with the normalization condition Eq. (4.275), almost uniquely determine all Clebsh-Gordan coefficients, subject to certain sign conventions to be specified.

An important example is adding the orbital and spin-angular momenta of a single spin ½ particle. We have

$$\begin{aligned} j_1 &= l, & m_1 &= m_l, \\ j_2 &= s = \frac{1}{2}, & m_2 &= m_s = \pm\frac{1}{2} \,. \end{aligned} \tag{4.282}$$

The allowed j values are

$$j = \begin{cases} l \pm \dfrac{1}{2}, & l > 0 \\ \dfrac{1}{2}, & l = 0 \end{cases} . \tag{4.283}$$

Using the fact that

$$m_1 = m_l = m - \frac{1}{2}, \quad m_2 = m_s = \frac{1}{2}, \tag{4.284}$$

according to Eq. (4.280) (lower sign), we work out for the case $j = l + \frac{1}{2}$ to obtain

$$\sqrt{\left(l+\frac{1}{2}+m+1\right)\left(l+\frac{1}{2}-m\right)}\left\langle m-\frac{1}{2},\frac{1}{2}\middle| l+\frac{1}{2},m\right\rangle \\ =\sqrt{\left(l+m+\frac{1}{2}\right)\left(l-m+\frac{1}{2}\right)}\left\langle m+\frac{1}{2},\frac{1}{2}\middle| l+\frac{1}{2},m+1\right\rangle , \tag{4.285}$$

which just moves horizontally by one unit:

$$\left\langle m-\frac{1}{2},\frac{1}{2}\middle| l+\frac{1}{2},m\right\rangle = \sqrt{\frac{\left(l+m+\frac{1}{2}\right)}{\left(l+m+\frac{3}{2}\right)}}\left\langle m+\frac{1}{2},\frac{1}{2}\middle| l+\frac{1}{2},m+1\right\rangle . \tag{4.286}$$

This procedure can be continued until m_l reaches l. So the maximum possible value

$$\left\langle m-\frac{1}{2},\frac{1}{2}\middle| l+\frac{1}{2},m\right\rangle = \sqrt{\frac{\left(l+m+\frac{1}{2}\right)}{\left(l+m+\frac{3}{2}\right)}}\sqrt{\frac{\left(l+m+\frac{3}{2}\right)}{\left(l+m+\frac{5}{2}\right)}}\left\langle m+\frac{3}{2},\frac{1}{2}\middle| l+\frac{1}{2},m+2\right\rangle \\ \vdots \\ =\sqrt{\frac{l+m+\frac{1}{2}}{2l+1}}\left\langle l,\frac{1}{2}\middle| l+\frac{1}{2},l+\frac{1}{2}\right\rangle . \tag{4.287}$$

When both m_l and m_s take the maximal values of l and $\frac{1}{2}$, $m=m_l+m_s=l+\frac{1}{2}$, and the corresponding $j=l+\frac{1}{2}$. So $\left| m_l=l,m_s=\frac{1}{2}\right\rangle$ must be equal to $\left| j=l+\frac{1}{2},m=l+\frac{1}{2}\right\rangle$ up to a phase factor. By choosing the phase factor to be real and positive, we have

$$\left\langle l,\frac{1}{2}\middle| l+\frac{1}{2},l+\frac{1}{2}\right\rangle =1. \tag{4.288}$$

Putting into Eq. (4.287), we obtain

$$\left\langle m-\frac{1}{2},\frac{1}{2}\middle| l+\frac{1}{2},m\right\rangle = \sqrt{\frac{l+m+\frac{1}{2}}{2l+1}} . \tag{4.289}$$

Because the transformation matrix with fixed m from the (m_l,m_s) basis to the (j,m) basis is expected to have the form

$$\begin{pmatrix} \cos\alpha & \sin\alpha \\ -\sin\alpha & \cos\alpha \end{pmatrix}, \tag{4.290}$$

let $\cos\alpha$ to be Eq. (4.289), then

$$\sin^2\alpha = 1-\frac{l+m+\frac{1}{2}}{2l+1}=\frac{l-m+\frac{1}{2}}{2l+1}. \tag{4.291}$$

Therefore, Eq. (4.290) can be written as

$$\begin{pmatrix} \sqrt{\dfrac{l+m+\frac{1}{2}}{2l+1}} & \sqrt{\dfrac{l-m+\frac{1}{2}}{2l+1}} \\ -\sqrt{\dfrac{l-m+\frac{1}{2}}{2l+1}} & \sqrt{\dfrac{l+m+\frac{1}{2}}{2l+1}} \end{pmatrix}. \tag{4.292}$$

The **spin-angular functions** in two-component form are defined as

$$\begin{aligned} \mathscr{Y}^{j=l\pm 1/2,m} &= \pm\sqrt{\dfrac{l\pm m+\frac{1}{2}}{2l+1}} Y_l^{m-1/2}(\theta,\phi)\chi_+ + \sqrt{\dfrac{l\pm m+\frac{1}{2}}{2l+1}} Y_l^{m+1/2}(\theta,\phi)\chi_- \\ &= \frac{1}{\sqrt{2l+1}} \begin{pmatrix} \pm\sqrt{l\pm m+\frac{1}{2}}\, Y_l^{m-1/2}(\theta,\phi) \\ \sqrt{l\mp m+\frac{1}{2}}\, Y_l^{m+1/2}(\theta,\phi) \end{pmatrix} \end{aligned}. \tag{4.293}$$

They are simultaneous eigenfunctions of $\mathbf{L}^2, \mathbf{S}^2, \mathbf{J}^2, J_z$.

They are also eigenfunctions of $\mathbf{L}\cdot\mathbf{S} = \frac{1}{2}\left(\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2\right)$, whose eigenvalue is

$$\left(\frac{\hbar^2}{2}\right)\left[j(j+1) - l(l+1) - \frac{3}{4}\right] = \begin{cases} \dfrac{l\hbar^2}{2}, & j = l+\dfrac{1}{2} \\ -\dfrac{(l+1)\hbar^2}{2}, & j = l-\dfrac{1}{2} \end{cases}. \tag{4.294}$$