3 Angular Momentum and Spin

In this chapter we review the notions surrounding the different forms of angular momenta in quantum mechanics, including the spin angular momentum, which is entirely quantum mechanical in nature.

Some of the material presented in this chapter is taken from Auletta, Fortunato and Parisi, Chap. 6 and Cohen-Tannoudji, Diu and Laloë, Vol. II, Chaps. IX and X.

3.1 Orbital Angular Momentum

Orbital angular momentum is as fundamental in quantum mechanics as it is in classical mechanics. In quantum mechanics, when applied to the realms of atoms and molecules, it can come in many different forms and flavours. For example, in molecular quantum mechanics the electronic angular momentum (for the motion of electrons about the atomic nuclei) and the rotational angular momentum (for the motions of nuclei about the molecular centre of mass) arise in the analysis of such systems.

We define the quantum mechanical orbital angular momentum in the same manner as its classical counterpart

$$\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}, \tag{3.1}$$

with $\hat{\mathbf{r}}$ and $\hat{\mathbf{p}}$ the position and linear momentum observables, respectively. It follows that in quantum mechanics, the orbital angular momentum is also an observable. If we introduce the components $\hat{x}_j$ and $\hat{p}_j$ for the position and linear momentum, where $j = 1, 2, 3$ (i.e., in Cartesian coordinates $\hat{x}_1 = \hat{x}$, $\hat{x}_2 = \hat{y}$ and $\hat{x}_3 = \hat{z}$, and similarly for $\hat{p}_j$), such that

$$\hat{\mathbf{x}} = \sum_j \mathbf{e}_j \hat{x}_j \tag{3.2}$$

$$\hat{\mathbf{p}} = \sum_j \mathbf{e}_j \hat{p}_j, \tag{3.3}$$

with $\mathbf{e}_j$ the different unit basis vectors, then

$$\begin{aligned}\hat{\mathbf{L}} &= \sum_{j,k} \left(\mathbf{e}_j \times \mathbf{e}_k\right) \hat{x}_j \hat{p}_k \\ &= \sum_{j,k} \left(\sum_i \mathbf{e}_i \varepsilon_{ijk}\right) \hat{x}_j \hat{p}_k\end{aligned}$$

$$= \sum_{i,j,k} \mathbf{e}_i \varepsilon_{ijk} \hat{x}_j \hat{p}_k. \tag{3.4}$$

In equation (3.4) we have introduced the elements of the very important ***Levi-Civita tensor*** ε_{ijk}, which are defined as follows

$$\varepsilon_{ijk} = \begin{cases} +1 & \text{, even permutation of } ijk \ (123, 231, 312) \\ -1 & \text{, odd permutation of } ijk \ (213, 132, 321) \\ 0 & \text{, if } i = j, j = k \text{ or } j = k. \end{cases} \tag{3.5}$$

This tensor is particularly useful for expressing the elements of a vectorial cross-product (i.e., $(\mathbf{a} \times \mathbf{b})_i = \sum_{j,k} \varepsilon_{ijk} a_j b_k$), and it is also related to the Kronecker delta (and thus the scalar product) through

$$\sum_i \varepsilon_{ijk} \varepsilon_{imn} = \delta_{jm} \delta_{kn} - \delta_{jn} \delta_{km}. \tag{3.6}$$

It is straightforward through equation (3.6) to verify that $[\mathbf{a} \times (\mathbf{b} \times \mathbf{c})]_j = (\mathbf{a} \cdot \mathbf{c})\, \mathbf{b}_j - (\mathbf{a} \cdot \mathbf{b})\, \mathbf{c}_j$.

Coming back to equation (3.4), since it is also the case that

$$\hat{\mathbf{L}} = \sum_i \mathbf{e}_i \hat{L}_i, \tag{3.7}$$

it then follows that

$$\hat{L}_i = \sum_{j,k} \varepsilon_{ijk} \hat{x}_j \hat{p}_k. \tag{3.8}$$

There are several important and useful commutation relations involving the (orbital) angular momentum, we derive some here. First, the commutations with the position and linear momentum components

$$\begin{aligned} \left[\hat{x}_j, \hat{L}_k\right] &= \sum_{m,n} \varepsilon_{kmn} \left[\hat{x}_j, \hat{x}_m \hat{p}_n\right] \\ &= \sum_{m,n} \varepsilon_{kmn} \left(\hat{x}_m \left[\hat{x}_j, \hat{p}_n\right] + \left[\hat{x}_j, \hat{x}_m\right] \hat{p}_n\right) \\ &= i\hbar \sum_{m,n} \varepsilon_{kmn} \hat{x}_m \delta_{jn} \\ &= i\hbar \sum_m \varepsilon_{jkm} \hat{x}_m, \end{aligned} \tag{3.9}$$

and

$$\begin{aligned}
\left[\hat{p}_j, \hat{L}_k\right] &= \sum_{m,n} \varepsilon_{kmn} \left[\hat{p}_j, \hat{x}_m \hat{p}_n\right] \\
&= \sum_{m,n} \varepsilon_{kmn} \left(\hat{x}_m \left[\hat{p}_j, \hat{p}_n\right] + \left[\hat{p}_j, \hat{x}_m\right] \hat{p}_n\right) \\
&= -i\hbar \sum_{m,n} \varepsilon_{kmn} \hat{p}_n \delta_{jm} \\
&= i\hbar \sum_{n} \varepsilon_{jkn} \hat{p}_n \qquad (3.10)
\end{aligned}$$

where $[\hat{x}_j, \hat{p}_k] = i\hbar\delta_{jk}$ was used for both derivations. For the commutation between components of the angular momentum

$$\begin{aligned}
\left[\hat{L}_j, \hat{L}_k\right] &= \sum_{m,n} \left[\varepsilon_{jmn} \hat{x}_m \hat{p}_n, \hat{L}_k\right] \\
&= \sum_{m,n} \varepsilon_{jmn} \left(\hat{x}_m \left[\hat{p}_n, \hat{L}_k\right] + \left[\hat{x}_m, \hat{L}_k\right] \hat{p}_n\right) \\
&= i\hbar \sum_{m,n,r} \varepsilon_{jmn} \left(\hat{x}_m \varepsilon_{nkr} \hat{p}_r + \varepsilon_{mkr} \hat{x}_r \hat{p}_n\right) \\
&= i\hbar \sum_{m,n,r} \left(-\varepsilon_{njm} \varepsilon_{nrk} \hat{x}_m \hat{p}_r + \varepsilon_{mnj} \varepsilon_{mkr} \hat{x}_r \hat{p}_n\right) \\
&= i\hbar \left[-\sum_{m,r} \left(\delta_{jr}\delta_{mk} - \delta_{jk}\delta_{mr}\right) \hat{x}_m \hat{p}_r + \sum_{n,r} \left(\delta_{nk}\delta_{jr} - \delta_{nr}\delta_{jk}\right) \hat{x}_r \hat{p}_n\right] \\
&= i\hbar \left(-\sum_{m,r} \delta_{jr}\delta_{mk} \hat{x}_m \hat{p}_r + \sum_{n,r} \delta_{nk}\delta_{jr} \hat{x}_r \hat{p}_n\right) \\
&= i\hbar \sum_{n,r} \left(\delta_{jr}\delta_{kn} - \delta_{jn}\delta_{kr}\right) \hat{x}_r \hat{p}_n \\
&= i\hbar \sum_{n,r} \varepsilon_{ijk} \varepsilon_{irn} \hat{x}_r \hat{p}_n \\
&= i\hbar \sum_{i} \varepsilon_{ijk} \hat{L}_i, \qquad (3.11)
\end{aligned}$$

where equations (3.6) and (3.9)-(3.10) were used. Considering the square of the angular momentum

$$\begin{aligned}
\left[\hat{L}^2, \hat{L}_j\right] &= \sum_{k} \left[\hat{L}_k \hat{L}_k, \hat{L}_j\right] \\
&= \sum_{k} \left(\hat{L}_k \left[\hat{L}_k, \hat{L}_j\right] + \left[\hat{L}_k, \hat{L}_j\right] \hat{L}_k\right)
\end{aligned}$$

$$
\begin{aligned}
&= i\hbar \sum_{i,k} \varepsilon_{ikj} \left(\hat{L}_k \hat{L}_i + \hat{L}_i \hat{L}_k \right) \\
&= i\hbar \sum_{i,k} \left(\varepsilon_{ikj} \hat{L}_k \hat{L}_i + \varepsilon_{kij} \hat{L}_k \hat{L}_i \right) \\
&= i\hbar \sum_{i,k} \varepsilon_{ikj} \left(\hat{L}_k \hat{L}_i - \hat{L}_k \hat{L}_i \right) \\
&= \hat{0}. \qquad (3.12)
\end{aligned}
$$

and

$$
\begin{aligned}
\left[\hat{L}^2, \hat{x}_j\right] &= \sum_k \left[\hat{L}_k \hat{L}_k, \hat{x}_j\right] \\
&= \sum_k \left(\hat{L}_k \left[\hat{L}_k, \hat{x}_j\right] + \left[\hat{L}_k, \hat{x}_j\right] \hat{L}_k \right) \\
&= -i\hbar \sum_{i,k} \left(\hat{L}_k \varepsilon_{ijk} \hat{x}_i + \varepsilon_{ijk} \hat{x}_i \hat{L}_k \right) \\
&= -i\hbar \sum_{i,k} \varepsilon_{ijk} \left(2\hat{x}_i \hat{L}_k - \left[\hat{x}_i, \hat{L}_k\right] \right) \\
&= \sum_{i,k} \left(2i\hbar \varepsilon_{ijk} \hat{x}_k \hat{L}_i - \varepsilon_{ijk} \hbar^2 \sum_m \varepsilon_{ikm} \hat{x}_m \right) \\
&= 2 \left(i\hbar \sum_{i,k} \varepsilon_{jki} \hat{x}_k \hat{L}_i + \hbar^2 \hat{x}_j \right) \qquad (3.13)
\end{aligned}
$$

since $\sum_{k,i} \varepsilon_{ijk}\varepsilon_{ikm} = \sum_k \left(\delta_{jk}\delta_{km} - \delta_{jm}\delta_{kk}\right) = -2\delta_{jm}$, while similarly

$$
\left[\hat{L}^2, \hat{p}_j\right] = 2 \left(i\hbar \sum_{i,k} \varepsilon_{jki} \hat{p}_k \hat{L}_i + \hbar^2 \hat{p}_j \right), \qquad (3.14)
$$

A little more work will establish that (see the Second Problem List)

$$
\begin{aligned}
\left[\hat{L}^2, \hat{x}_j \hat{x}_k\right] &= 2 \left[i\hbar \sum_{m,n} \left(\hat{x}_j \varepsilon_{kmn} + \hat{x}_k \varepsilon_{jmn}\right) \hat{x}_m \hat{L}_n - \hbar^2 \left(\hat{x}^2 \delta_{jk} - 3\hat{x}_j \hat{x}_k \right) \right] \qquad (3.15) \\
\left[\hat{L}^2, \hat{p}_j \hat{p}_k\right] &= 2 \left[i\hbar \sum_{m,n} \left(\hat{p}_j \varepsilon_{kmn} + \hat{p}_k \varepsilon_{jmn}\right) \hat{p}_m \hat{L}_n - \hbar^2 \left(\hat{p}^2 \delta_{jk} - 3\hat{p}_j \hat{p}_k \right) \right], \qquad (3.16)
\end{aligned}
$$

which also imply that $\left[\hat{L}^2, \hat{x}^2\right] = \left[\hat{L}^2, \hat{p}^2\right] = 0$. Finally, we find using equations (3.9)-(3.10)

$$\left[\hat{L}_j, \hat{x}^2\right] = 0 \quad (3.17)$$
$$\left[\hat{L}_j, \hat{p}^2\right] = 0. \quad (3.18)$$

3.2 Eigenvalues of the Angular Momentum

The fact that the three components of the angular momentum $\hat{L}_x$, $\hat{L}_y$, $\hat{L}_z$ commute with its square $\hat{L}^2$, from equation (3.12), implies that we can find a common set of eigenvectors $\{|\psi\rangle\}$ for $\hat{L}^2$ and one component of $\hat{\mathbf{L}}$ (the three components cannot share the same eigenvectors since they do not commute with each other; see equation (3.11)). This can be verified as follows. If a is an eigenvector of $\hat{L}^2$ and $|\psi\rangle$ one of its eigenvector, then

$$\begin{aligned}\hat{L}^2\hat{L}_j\,|\psi\rangle &= \hat{L}_j\left(\hat{L}^2\,|\psi\rangle\right) \\ &= a\hat{L}_j\,|\psi\rangle \end{aligned} \quad (3.19)$$

implies that the ket $\hat{L}_j\,|\psi\rangle$ is also a eigenvector of $\hat{L}^2$. If this eigenvalue is non-degenerate, then $\hat{L}_j\,|\psi\rangle = b\,|\psi\rangle$, with b a constant, and $|\psi\rangle$ is also an eigenvector of $\hat{L}_j$ (and b its corresponding eigenvalue). Similarly, we can assert that $\hat{L}^2\,|\psi\rangle$ is an eigenvector of $\hat{L}_j$ by swapping the order of the two operators in the first line of equation (3.19); they, therefore, share the same set of eigenvectors. It is common to choose $\hat{L}_j = \hat{L}_z$ and we denote by $\left\{\left|l^2, m\right\rangle\right\}$ for the set of eigenvectors, with l^2 and m the ***quantum numbers*** associated to $\hat{L}^2$ and $\hat{L}_z$, respectively. As a matter of fact, we set $l^2\hbar^2$ as an eigenvalue of $\hat{L}^2$ and $m\hbar$ one for $\hat{L}_z$ (although both l^2 and m still need to be determined).

We now introduce the ***raising and lowering operators***

$$\hat{L}_\pm = \hat{L}_x \pm i\hat{L}_y \quad (3.20)$$

for which the following commutation relations can easily be established

$$\begin{aligned}\left[\hat{L}_z, \hat{L}_\pm\right] &= \left[\hat{L}_z, \hat{L}_x\right] \pm i\left[\hat{L}_z, \hat{L}_y\right] \\ &= i\hbar\left(\hat{L}_y \mp i\hat{L}_x\right) \\ &= \pm\hbar\hat{L}_\pm \end{aligned} \quad (3.21)$$
$$\left[\hat{L}^2, \hat{L}_\pm\right] = 0, \quad (3.22)$$

from equations (3.11) and (3.13). Using equation (3.21) we can calculate that

$$\begin{aligned}\hat{L}_z\hat{L}_\pm\left|l^2, m\right\rangle &= \left(\hat{L}_\pm\hat{L}_z \pm \hbar\hat{L}_\pm\right)\left|l^2, m\right\rangle \\ &= (m \pm 1)\,\hat{L}_\pm\left|l^2, m\right\rangle \end{aligned} \quad (3.23)$$

which implies that whenever $\hat{L}_{\pm}$ acts on a eigenvector it transforms it to another eigenvector of eigenvalue $(m \pm 1)\hbar$ for $\hat{L}_z$. It is therefore apparent that $\hat{L}_{\pm}$ are ***ladders operators*** that will allow us to span the whole set of eigenvectors associated to a given eigenvalue $l^2\hbar^2$ (i.e., since $\hat{L}_{\pm}$ commutes with $\hat{L}^2$ it shares the same eigenvectors). Moreover, we deduce that m must have lower and upper bounds, since the following relation must be obeyed

$$m\hbar \leq \sqrt{l^2\hbar^2}. \tag{3.24}$$

If we denote the upper and lower bounds of m as m_+ and m_-, respectively, then we can write

$$\hat{L}_{\pm} \left| l^2, m_{\pm} \right\rangle = 0. \tag{3.25}$$

Furthermore, we have

$$\begin{aligned} \hat{L}_{\mp}\hat{L}_{\pm} \left| l^2, m_{\pm} \right\rangle &= \left(\hat{L}_x^2 + \hat{L}_y^2 \pm i \left[\hat{L}_x, \hat{L}_y \right] \right) \left| l^2, m_{\pm} \right\rangle \\ &= \left(\hat{L}^2 - \hat{L}_z^2 \mp \hbar \hat{L}_z \right) \left| l^2, m_{\pm} \right\rangle \\ &= \left(l^2 - m_{\pm}^2 \mp m_{\pm} \right) \hbar^2 \left| l^2, m_{\pm} \right\rangle \\ &= 0. \end{aligned} \tag{3.26}$$

From this result we obtain the two equations

$$l^2 - m_-^2 + m_- = 0 \tag{3.27}$$
$$l^2 - m_+^2 - m_+ = 0 \tag{3.28}$$

from which we can take the difference and transform it to

$$(m_+ + m_-)(m_+ - m_- + 1) = 0. \tag{3.29}$$

The term in the second set of parentheses must be greater than zero because $m_+ \geq m_-$, which implies that the term within the first set of parentheses must cancel and

$$m_+ = -m_- \tag{3.30}$$
$$m_+ - m_- = 2\ell, \tag{3.31}$$

where 2ℓ has to be some positive integer number, since $m_+ - m_-$ corresponds to the number of times (i.e., 2ℓ times) $\hat{L}_{\pm}$ is applied to $\left| l^2, m_{\mp} \right\rangle$ to span the whole set of kets. It is now clear from equation (3.31) that $m_+ = \ell$ and from equation (3.28)

$$l^2 = \ell (\ell + 1). \tag{3.32}$$

Furthermore, equation (3.23) and (3.30)-(3.31) tell us that m is quantized and can either be an integer with

$$m = -\ell, -\ell + 1, \ldots, -1, 0, 1, \ldots, \ell - 1, \ell \tag{3.33}$$

or a half-integer such that

$$m = -\ell, -\ell + 1, \ldots, -\frac{1}{2}, \frac{1}{2}, \ldots, \ell - 1, \ell. \tag{3.34}$$

Given these results, we will write from now on the set of eigenvectors for $\hat{L}^2$ and $\hat{L}_z$ as $\{|\ell, m\rangle\}$ with

$$\begin{aligned} \hat{L}^2 |\ell, m\rangle &= \ell(\ell + 1)\hbar^2 |\ell, m\rangle & (3.35) \\ \hat{L}_z |\ell, m\rangle &= m\hbar |\ell, m\rangle . & (3.36) \end{aligned}$$

We know from our previous discussion focusing on equation (3.23) that $\hat{L}_\pm |\ell, m\rangle \propto |\ell, m \pm 1\rangle$. Then considering the following, we have (using the projector $\sum_{k=-\ell}^{\ell} |\ell, k\rangle\langle \ell, k| = \hat{P}_\ell$)

$$\begin{aligned} \left\langle \ell, m \middle| \hat{L}_\mp \hat{L}_\pm \middle| \ell, m \right\rangle &= \sum_{k=-\ell}^{\ell} \left\langle \ell, m \middle| \hat{L}_\mp \middle| \ell, k \right\rangle \left\langle \ell, k \middle| \hat{L}_\pm \middle| \ell, m \right\rangle \\ &= \left\langle \ell, m \middle| \hat{L}_\mp \middle| \ell, m \pm 1 \right\rangle \left\langle \ell, m \pm 1 \middle| \hat{L}_\pm \middle| \ell, m \right\rangle \\ &= \left| \left\langle \ell, m \pm 1 \middle| \hat{L}_\pm \middle| \ell, m \right\rangle \right|^2 , \end{aligned} \tag{3.37}$$

since $\left(\hat{L}_\pm |\ell, m\rangle\right)^\dagger = \langle \ell, m| \hat{L}_\mp$. On the other hand we also have (see equation (3.26))

$$\begin{aligned} \left\langle \ell, m \middle| \hat{L}_\mp \hat{L}_\pm \middle| \ell, m \right\rangle &= \left\langle \ell, m \middle| \hat{L}^2 - \hat{L}_z^2 \mp \hbar \hat{L}_z \middle| \ell, m \right\rangle \\ &= \left[\ell(\ell + 1) - m(m \pm 1)\right]\hbar^2, \end{aligned} \tag{3.38}$$

which with equation (3.37) implies that

$$\hat{L}_\pm |\ell, m\rangle = \sqrt{\ell(\ell + 1) - m(m \pm 1)}\hbar |\ell, m \pm 1\rangle . \tag{3.39}$$

It also follows that

$$\begin{aligned} \hat{L}_\mp \hat{L}_\pm |\ell, m\rangle &= \sqrt{\ell(\ell + 1) - (m \pm 1)(m \pm 1 \mp 1)}\sqrt{\ell(\ell + 1) - m(m \pm 1)}\hbar^2 |\ell, m\rangle \\ &= \left[\ell(\ell + 1) - m(m \pm 1)\right]\hbar^2 |\ell, m\rangle \\ &= \left[(\ell \mp m)(\ell \pm m + 1)\right]\hbar^2 |\ell, m\rangle . \end{aligned} \tag{3.40}$$

Alternatively, we can write the matrix elements associated to the different angular momentum observables

$$
\begin{aligned}
\left\langle \ell, m \middle| \hat{L}^2 \middle| \ell, m \right\rangle &= \ell(\ell+1)\hbar^2 && (3.41)\\
\left\langle \ell, m \middle| \hat{L}_z \middle| \ell, m \right\rangle &= m\hbar && (3.42)\\
\left\langle \ell, m\pm 1 \middle| \hat{L}_\pm \middle| \ell, m \right\rangle &= \sqrt{\ell(\ell+1) - m(m\pm 1)}\hbar && (3.43)\\
\left\langle \ell, m \middle| \hat{L}_\mp \hat{L}_\pm \middle| \ell, m \right\rangle &= \left[(\ell \mp m)(\ell \pm m + 1)\right]\hbar^2. && (3.44)
\end{aligned}
$$

All other matrix elements are null.

Exercise 3.1. Write the matrix representations for $\hat{L}_z$, $\hat{L}_\pm$ and $\hat{L}^2$ for $\ell = 0, 1/2$ and 1.

Solution.

The dimension of the subspace (or the matrices) associated to a given ℓ is determined by the number of values the quantum number m can take. Referring to equations (3.33)-(3.34) we find that m takes $2\ell+1$ values as it goes from $-\ell$ to ℓ with unit steps.

i) For $\ell = 0$ the dimension is $2\ell+1 = 1$ and the only matrix elements are $L_z = L_\pm = L^2 = 0$ and.

ii) For $\ell = 1/2$ the dimension is $2\ell+1 = 2$. Using the following basis representation for the eigenvectors

$$
\left|\tfrac{1}{2}, -\tfrac{1}{2}\right\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \quad \left|\tfrac{1}{2}, \tfrac{1}{2}\right\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{3.45}
$$

equations (3.41)-(3.43), we have

$$
\begin{aligned}
\hat{L}_z &= \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} && (3.46)\\
\hat{L}_+ &= \hbar\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} && (3.47)\\
\hat{L}_- &= \hbar\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} && (3.48)\\
\hat{L}^2 &= \frac{3}{4}\hbar^2\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. && (3.49)
\end{aligned}
$$

We can also readily verify from these matrices that $\hat{L}^2 = \frac{1}{2}\left(\hat{L}_+\hat{L}_- + \hat{L}_-\hat{L}_+\right) + \hat{L}_z^2$

iii) For $\ell = 1$ the dimension is $2\ell+1 = 3$ and with

$$
|1, -1\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}, \quad |1, 0\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \quad |1, 1\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \tag{3.50}
$$

we have

$$\hat{L}_z = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad (3.51)$$

$$\hat{L}_+ = \hbar \begin{pmatrix} 0 & \sqrt{2} & 0 \\ 0 & 0 & \sqrt{2} \\ 0 & 0 & 0 \end{pmatrix} \quad (3.52)$$

$$\hat{L}_- = \hbar \begin{pmatrix} 0 & 0 & 0 \\ \sqrt{2} & 0 & 0 \\ 0 & \sqrt{2} & 0 \end{pmatrix} \quad (3.53)$$

$$\hat{L}^2 = 2\hbar^2 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \quad (3.54)$$

3.3 Eigenfunctions of the Angular Momentum

To derive the eigenfunctions we start by writing down the action of the different angular momentum operators on a wave function $\psi(\mathbf{r})$ with (see equation (1.84))

$$\begin{aligned} \left\langle \mathbf{r} \middle| \hat{L}_x \middle| \psi \right\rangle &= \langle \mathbf{r} \,|\, \hat{y}\hat{p}_z - \hat{z}\hat{p}_y \,|\, \psi \rangle \\ &= -i\hbar \left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y} \right) \psi(\mathbf{r}) \end{aligned} \quad (3.55)$$

$$\begin{aligned} \left\langle \mathbf{r} \middle| \hat{L}_y \middle| \psi \right\rangle &= \langle \mathbf{r} \,|\, \hat{z}\hat{p}_x - \hat{x}\hat{p}_z \,|\, \psi \rangle \\ &= -i\hbar \left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial y} \right) \psi(\mathbf{r}) \end{aligned} \quad (3.56)$$

$$\begin{aligned} \left\langle \mathbf{r} \middle| \hat{L}_z \middle| \psi \right\rangle &= \langle \mathbf{r} \,|\, \hat{x}\hat{p}_y - \hat{y}\hat{p}_x \,|\, \psi \rangle \\ &= -i\hbar \left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} \right) \psi(\mathbf{r}). \end{aligned} \quad (3.57)$$

Within the present context, where the three components of the angular momentum have the same standing (i.e., no particular orientation is linked to a symmetry), we would do well to use spherical coordinates, which are related to the Cartesian coordinates through

$$x = r\sin(\theta)\cos(\phi) \quad (3.58)$$

$$y = r\sin(\theta)\sin(\phi) \quad (3.59)$$

$$z = r\cos(\theta). \quad (3.60)$$

We must express the Cartesian partial derivatives in equations (3.55)-(3.57) in terms of spherical coordinates. There are several ways to accomplish this, but we will proceed as follows. We can use the chain rule for the total differential of a Cartesian coordinate dx_i as a functions of the spherical coordinates α_j $(= r, \theta, \phi)$

$$dx_i = \sum_j \frac{\partial x_i}{\partial \alpha_j} d\alpha_j \tag{3.61}$$

and then write it down in matrix form

$$\begin{aligned}
\begin{pmatrix} dx \\ dy \\ dz \end{pmatrix} &= \begin{pmatrix} \frac{\partial x}{\partial r} & \frac{\partial x}{\partial \theta} & \frac{\partial x}{\partial \phi} \\ \frac{\partial y}{\partial r} & \frac{\partial y}{\partial \theta} & \frac{\partial y}{\partial \phi} \\ \frac{\partial z}{\partial r} & \frac{\partial z}{\partial \theta} & \frac{\partial z}{\partial \phi} \end{pmatrix} \begin{pmatrix} dr \\ d\theta \\ d\phi \end{pmatrix} \\
&= \begin{pmatrix} \sin(\theta)\cos(\phi) & r\cos(\theta)\cos(\phi) & -r\sin(\theta)\sin(\phi) \\ \sin(\theta)\sin(\phi) & r\cos(\theta)\sin(\phi) & r\sin(\theta)\cos(\phi) \\ \cos(\theta) & -r\sin(\theta) & 0 \end{pmatrix} \begin{pmatrix} dr \\ d\theta \\ d\phi \end{pmatrix}
\end{aligned} \tag{3.62}$$

On the other hand, the partial derivatives can be written as

$$\begin{aligned}
\frac{\partial}{\partial x_i} &= \sum_j \frac{\partial \alpha_j}{\partial x_i} \frac{\partial}{\partial \alpha_j} \\
&= \sum_j \left(\frac{\partial x_i}{\partial \alpha_j} \right)^{-1} \frac{\partial}{\partial \alpha_j},
\end{aligned} \tag{3.63}$$

where $(\partial x_i / \partial \alpha_j)^{-1}$ is the inverse of the matrix of equation (3.62) since

$$\begin{aligned}
\sum_i \frac{\partial \alpha_j}{\partial x_i} \frac{\partial x_i}{\partial \alpha_k} &= \frac{\partial \alpha_j}{\partial \alpha_k} \\
&= \delta_{jk}.
\end{aligned} \tag{3.64}$$

We should note that since dx_i is an element of a column vector, then $\partial / \partial x_i$ is an element of a row vector (or a covector). Therefore, calculating the inverse of matrix of equation (3.62) we find[1]

$$\begin{pmatrix} \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \end{pmatrix} = \begin{pmatrix} \frac{\partial}{\partial r} & \frac{\partial}{\partial \theta} & \frac{\partial}{\partial \phi} \end{pmatrix} \begin{pmatrix} \sin(\theta)\cos(\phi) & \sin(\theta)\sin(\phi) & \cos(\theta) \\ \frac{1}{r}\cos(\theta)\cos(\phi) & \frac{1}{r}\cos(\theta)\sin(\phi) & -\frac{1}{r}\sin(\theta) \\ -\frac{1}{r}\frac{\sin(\phi)}{\sin(\theta)} & \frac{1}{r}\frac{\cos(\phi)}{\sin(\theta)} & 0 \end{pmatrix}, \tag{3.65}$$

[1] The inverse of a matrix is the transpose of its adjoint, divided by its determinant (the adjoint is the matrix made of the cofactors).

which implies that

$$\frac{\partial}{\partial x} = \sin(\theta)\cos(\phi)\frac{\partial}{\partial r} + \frac{1}{r}\cos(\theta)\cos(\phi)\frac{\partial}{\partial \theta} - \frac{1}{r}\frac{\sin(\phi)}{\sin(\theta)}\frac{\partial}{\partial \phi} \tag{3.66}$$

$$\frac{\partial}{\partial y} = \sin(\theta)\sin(\phi)\frac{\partial}{\partial r} + \frac{1}{r}\cos(\theta)\sin(\phi)\frac{\partial}{\partial \theta} + \frac{1}{r}\frac{\cos(\phi)}{\sin(\theta)}\frac{\partial}{\partial \phi} \tag{3.67}$$

$$\frac{\partial}{\partial z} = \cos(\theta)\frac{\partial}{\partial r} - \frac{1}{r}\sin(\theta)\frac{\partial}{\partial \theta}. \tag{3.68}$$

Inserting equations (3.66)-(3.68) and (3.58)-(3.60) into equations (3.55)-(3.57) we find

$$\hat{L}_x \Rightarrow i\hbar\left(\sin(\phi)\frac{\partial}{\partial \theta} + \cos(\phi)\cot(\theta)\frac{\partial}{\partial \phi}\right) \tag{3.69}$$

$$\hat{L}_y \Rightarrow i\hbar\left(-\cos(\phi)\frac{\partial}{\partial \theta} + \sin(\phi)\cot(\theta)\frac{\partial}{\partial \phi}\right) \tag{3.70}$$

$$\hat{L}_z \Rightarrow -i\hbar\frac{\partial}{\partial \phi}, \tag{3.71}$$

as well as

$$\hat{L}_\pm \Rightarrow \hbar e^{\pm i\phi}\left(\pm\frac{\partial}{\partial \theta} + i\cot(\theta)\frac{\partial}{\partial \phi}\right) \tag{3.72}$$

$$\hat{L}^2 \Rightarrow -\hbar^2\left[\frac{1}{\sin(\theta)}\frac{\partial}{\partial \theta}\left(\sin(\theta)\frac{\partial}{\partial \theta}\right) + \frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial \phi^2}\right] \tag{3.73}$$

$$\Rightarrow -\hbar^2\left[\frac{\partial^2}{\partial \theta^2} + \cot(\theta)\frac{\partial}{\partial \theta} + \frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial \phi^2}\right]. \tag{3.74}$$

The eigenvalue problem for $\hat{L}^2$ and $\hat{L}_z$ then lead to the following differential equations

$$-\left[\frac{\partial^2}{\partial \theta^2} + \cot(\theta)\frac{\partial}{\partial \theta} + \frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial \phi^2}\right]\psi(r,\theta,\phi) = \ell(\ell+1)\psi(r,\theta,\phi) \tag{3.75}$$

$$-i\frac{\partial}{\partial \phi}\psi(r,\theta,\phi) = m\psi(r,\theta,\phi). \tag{3.76}$$

But since these equations are purely angular in nature and do not depend on r, we can express the wave function as a product of radial and angular functions

$$\psi(r,\theta,\phi) = R(r)\,Y_{\ell m}(\theta,\phi), \tag{3.77}$$

with the required normalization property

$$\int_0^\infty |R(r)|^2 r^2 dr = 1 \tag{3.78}$$

$$\int_0^{2\pi} d\phi \int_0^\pi |Y_{\ell m}(\theta, \phi)|^2 \sin(\theta)\, d\theta = 1. \tag{3.79}$$

The separation of variable expressed in equation (3.77) transform the set of differential equations to be solved to

$$-\left[\frac{\partial^2}{\partial\theta^2} + \cot(\theta)\frac{\partial}{\partial\theta} + \frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial\phi^2}\right] Y_{\ell m}(\theta, \phi) = \ell(\ell+1)\, Y_{\ell m}(\theta, \phi) \tag{3.80}$$

$$-i\frac{\partial}{\partial\phi} Y_{\ell m}(\theta, \phi) = m Y_{\ell m}(\theta, \phi). \tag{3.81}$$

The solution of this system of equations is rendered easier upon the realization that equation (3.81) allows for a further separation of the two angular variables. More precisely, we can set

$$Y_{\ell m}(\theta, \phi) = F_{\ell m}(\theta)\, e^{im\phi}. \tag{3.82}$$

The functions $Y_{\ell m}(\theta, \phi)$ are called ***spherical harmonics*** and form a basis in the corresponding two-dimensional angular space, which implies that they must possess a closure relation

$$\begin{aligned}\sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell} Y_{\ell m}(\theta, \phi)\, Y_{\ell m}^*(\theta', \phi') &= \delta\left[\cos(\theta) - \cos(\theta')\right]\delta(\phi - \phi') \\ &= \frac{1}{\sin(\theta)}\delta(\theta - \theta')\,\delta(\phi - \phi')\end{aligned} \tag{3.83}$$

beyond their ***orthonormality condition***

$$\int_0^{2\pi} d\phi \int_0^\pi Y_{\ell' m'}^*(\theta, \phi)\, Y_{\ell m}(\theta, \phi) \sin(\theta)\, d\theta = \delta_{\ell'\ell}\delta_{m'm}. \tag{3.84}$$

Any function $f(\theta, \phi)$ can therefore be expanded with a series of spherical harmonics

$$f(\theta, \phi) = \sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell} c_{\ell m} Y_{\ell m}(\theta, \phi), \tag{3.85}$$

with the coefficients of the expansion given by

$$c_{\ell m} = \int_0^{2\pi} d\phi \int_0^\pi Y_{\ell m}^*(\theta, \phi)\, f(\theta, \phi) \sin(\theta)\, d\theta. \tag{3.86}$$

Although we will not demonstrate this here, the solution of equation (3.75), given equation (3.82), can be obtained by setting, for example, $m = \ell$ and applying equation (3.72) for $\hat{L}_+$ to show that

$$Y_{\ell\ell}(\theta, \phi) = c_\ell \sin^\ell(\theta), \tag{3.87}$$

and then successively act with $\hat{L}_-$ to recover the functions $Y_{\ell m}(\theta, \phi)$. Here are some examples of spherical harmonics for the three lowest values of ℓ

$$\begin{aligned}
Y_{0,0}(\theta,\phi) &= \frac{1}{\sqrt{4\pi}} && (3.88)\\
Y_{1,0}(\theta,\phi) &= \sqrt{\frac{3}{4\pi}}\cos(\theta) && (3.89)\\
Y_{1,\pm1}(\theta,\phi) &= \mp\sqrt{\frac{3}{8\pi}}\sin(\theta)\, e^{\pm i\phi} && (3.90)\\
Y_{2,0}(\theta,\phi) &= \sqrt{\frac{5}{16\pi}}\left[3\cos^2(\theta) - 1\right] && (3.91)\\
Y_{2,\pm1}(\theta,\phi) &= \mp\sqrt{\frac{15}{8\pi}}\sin(\theta)\cos(\theta)\, e^{\pm i\phi} && (3.92)\\
Y_{2,\pm2}(\theta,\phi) &= \sqrt{\frac{15}{32\pi}}\sin^2(\theta)\, e^{\pm i2\phi}. && (3.93)
\end{aligned}$$

Exercise 3.2. The diatomic molecule. Let us consider two atoms of masses m_1 and m_2 that are bound together into a diatomic molecule. Express the Hamiltonian as a function of the angular momentum of the system. We assume that the distance r_0 between the two nuclei is constant.

Solution.

Let us start with the classical version of the problem. We set the origin at the centre of mass of the system, which implies that the positions of the nuclei (positive, by definition) are given by

$$\begin{aligned}
r_1 &= \frac{m_2}{m_1 + m_2} r_0 && (3.94)\\
r_2 &= \frac{m_1}{m_1 + m_2} r_0. && (3.95)
\end{aligned}$$

The kinetic energy of the molecule is entirely in the form of rotational motion (relative to the centre of mass) and can be expressed with

$$T = \frac{1}{2} I \omega^2, \tag{3.96}$$

where ω is angular velocity about an axis perpendicular to the axis of symmetry and I the moment of inertia (about the same axis)

$$
\begin{aligned}
I &= m_1 r_1^2 + m_2 r_2^2 \\
&= m_{\mathrm{r}} r_0^2,
\end{aligned} \tag{3.97}
$$

with the reduced mass $m_{\mathrm{r}} = m_1 m_2 / (m_1 + m_2)$.

As is well known, for such a system there is correspondence between linear and rotational motions, where the mass, velocity and linear momentum make way to the moment of inertia, angular velocity and angular momentum

$$
\mathbf{L} = I\boldsymbol{\omega}. \tag{3.98}
$$

It follows that the classical Hamiltonian can be written as

$$
H_0 = \frac{L^2}{2I}, \tag{3.99}
$$

which is similar in form to the Hamiltonian of a free particle. The transition to the quantum mechanical version of the problem is straightforward and yields the corresponding Hamiltonian

$$
\hat{H}_0 = \frac{\hat{L}^2}{2I}. \tag{3.100}
$$

The eigenvectors of this Hamiltonian consist of the set $\{|\ell, m\rangle\}$ previously derived, with the corresponding eigenvalues

$$
E_\ell = \frac{\hbar^2}{2I}\ell(\ell+1), \tag{3.101}
$$

which are $2\ell+1$ times degenerate since the energy is independent of m. We find that the energy difference between two adjacent energy levels is given by

$$
\begin{aligned}
\Delta E_{\ell+1,\ell} &= \frac{\hbar^2}{2I}\left[(\ell+1)(\ell+2) - \ell(\ell+1)\right] \\
&= \frac{\hbar^2}{I}(\ell+1).
\end{aligned} \tag{3.102}
$$

Transitions between these states will be accompanied by the emission or absorption of a photon of frequency (when the two atoms forming the molecules are different, these are the only allowed molecular transitions for an electric dipole interaction)

$$
\begin{aligned}
\nu_{\ell+1,\ell} &= \frac{\Delta E_{\ell+1,\ell}}{h} \\
&= 2B(\ell+1),
\end{aligned} \tag{3.103}
$$

with the rotational constant $B = h/\left(8\pi^2 I\right)$.

3.4 The Spin Intrinsic Angular Momentum

If we consider a classical electron of charge q and mass m_{e} exhibiting some orbital motion in an atom of molecule, then we can calculate it magnetic moment μ by the product of the associated electric current and the area contained within the circuit traced by the charge. Assuming a circular orbit we have

$$\begin{aligned}\mu &= q\frac{\omega}{2\pi}\cdot\pi r^2 \\ &= \frac{q}{2m_{\mathrm{e}}}m_{\mathrm{e}}vr \\ &= \frac{q}{2m_{\mathrm{e}}}L, \end{aligned} \tag{3.104}$$

where we used $v = \omega r$ for the orbital speed. We therefore see that the magnetic moment of the electron is proportional to its angular momentum. When the atom or molecule is subjected to an external magnetic (induction) field $\mathbf{B}$ the Hamiltonian of the system can be written

$$H = H_0 - \boldsymbol{\mu}\cdot\mathbf{B}, \tag{3.105}$$

where H_0 is the Hamiltonian of the free atom or molecule (i.e., when unperturbed by the external field) and we have generalized the field-matter interaction using the total (vectorial) magnetic moment $\boldsymbol{\mu}$, which potentially contains a contribution from all the components (i.e., particles) of the systems.

If we now define the magnetic field as being oriented along the z-axis, i.e., $\mathbf{B} = B\mathbf{e}_z$, then for the simple case where only one electron contributes to the total magnetic moment

$$H = H_0 - \frac{\mu_{\mathrm{B}}}{\hbar}L_z B, \tag{3.106}$$

with the ***Bohr magneton***

$$\mu_{\mathrm{B}} = \frac{q\hbar}{2m_{\mathrm{e}}}. \tag{3.107}$$

We now transition to the quantum world and write

$$\begin{aligned}\hat{H} &= \hat{H}_0 - \hat{\boldsymbol{\mu}}\cdot\mathbf{B} \\ &= \hat{H}_0 - \frac{\mu_{\mathrm{B}}}{\hbar}\hat{L}_z B, \end{aligned} \tag{3.108}$$

where we still treat the magnetic field as a classical entity (for that reason analyses such as this one area often called "semi-classical"). Assuming that $\hat{H}_0$ has the set $\{|\ell, m\rangle\}$ for its eigenvector with the eigenvalue, say, $E_{\ell,m}$, we find that the interaction with the magnetic field changes this energy by an amount

$$\Delta E_{\ell,m} = -\mu_{\mathrm{B}} m B. \tag{3.109}$$

We therefore find that the energy of the system is altered by a quantity that is proportional to the ***magnetic quantum number*** m and the external magnetic field. This is a very important example as it clearly shows that the $2\ell + 1$ times degenerate $|\ell, m\rangle$ state is lifted by the presence of the magnetic field. For an atom or molecule, this implies that a spectral line associated with the ***principal quantum number*** ℓ should split into $2\ell + 1$ separate ***fine structure*** lines. This is the so-called ***normal Zeeman effect***.[2]

Although this effect is observed experimentally, it does not take account for all possible results. For example, for systems where $\ell = 0$ (and therefore $m = 0$) it is found (e.g., for the hydrogen atom) that there can still exist a spectral splitting, contrary to what would be expected through equation (3.109). For this reason, this is called the ***anomalous Zeeman effect***.

It was found that this effect could be explained if one postulates that the electron (and other particles) possesses an ***intrinsic angular momentum*** or ***spin*** $\hat{\mathbf{S}}$, to which an intrinsic magnetic moment is associated

$$\hat{\boldsymbol{\mu}}_{\mathrm{s}} = \gamma \frac{\mu_{\mathrm{B}}}{\hbar} \hat{\mathbf{S}}, \tag{3.110}$$

where $\gamma \simeq 2$ for the electron. Comparison with equations (3.104) and (3.107) reveals that the electron spin has a ***gyromagnetic ratio*** that is (approximately) twice that of its orbital angular momentum.

Although the existence of the electron spin can be demonstrated from the (relativistic) Dirac equation, we can incorporate it in our formalism for non-relativistic quantum mechanics through the addition of a new postulates to the ones introduced in Chapter 1.

3.4.1 Seventh Postulate

The spin operator is an intrinsic angular momentum with commutation relations similar to those obtained for the orbital angular momentum, i.e.,

$$\left[\hat{S}_j, \hat{S}_k\right] = i\hbar \sum_i \varepsilon_{ijk} \hat{S}_i \tag{3.111}$$

$$\left[\hat{S}^2, \hat{S}_j\right] = \hat{0}. \tag{3.112}$$

The spin possesses its own space, along with its eigenvectors $|s, m_s\rangle$ and associated eigenvalues such that

$$\hat{S}^2 |s, m_s\rangle = s(s+1)\hbar^2 |s, m_s\rangle \tag{3.113}$$

$$\hat{S}_z |s, m_s\rangle = m_s \hbar |s, m_s\rangle . \tag{3.114}$$

[2] Although we have considered a "one-electron" atom (at least, as far as the external interaction is concerned), this formalism can be extended to any quantum mechanical system possessing a magnetic moment. For example, the case of the diatomic molecule considered previously is an example where such considerations can come into play.

Furthermore, the complete state of a particle is the direct product of a ket $|\varphi(t)\rangle$, which is a function of its orbital characteristics, etc., and a ket (or a linear combinations of kets) $|s, m_s\rangle$ associated to its spin. Finally, any spin observable commutes with all orbital observables.

For example, the electron has a spin one-half, i.e, $s = 1/2$. We define the basis $|\pm\rangle \equiv \left|\frac{1}{2}, \pm\frac{1}{2}\right\rangle$ with $\langle + \,|\, -\rangle = 0$ and $\langle + \,|\, +\rangle = \langle - \,|\, -\rangle = 1$, and have that

$$\hat{S}^2 |\pm\rangle = \frac{3}{4}\hbar^2 |\pm\rangle \tag{3.115}$$

$$\hat{S}_z |\pm\rangle = \pm\frac{1}{2}\hbar |\pm\rangle . \tag{3.116}$$

The most general ket for the spin state of an electron is therefore

$$|\psi\rangle = c_+ |+\rangle + c_- |-\rangle , \tag{3.117}$$

with $c_\pm$ complex numbers ($|c_+|^2 + |c_-|^2 = 1$). We can also define the raising and lowering operators

$$\hat{S}_\pm = \hat{S}_x \pm i\hat{S}_y, \tag{3.118}$$

which when acting on the basis yield (see equation (3.43))

$$\hat{S}_+ |+\rangle = 0 \tag{3.119}$$

$$\hat{S}_+ |-\rangle = \hbar |+\rangle \tag{3.120}$$

$$\hat{S}_- |+\rangle = \hbar |-\rangle \tag{3.121}$$

$$\hat{S}_- |-\rangle = 0. \tag{3.122}$$

If we associate the following matrices with the spin basis

$$|-\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \quad |+\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \tag{3.123}$$

the we find the following ***Pauli matrices*** $\hat{\sigma}_j$

$$\hat{\sigma}_+ = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \tag{3.124}$$

$$\hat{\sigma}_- = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \tag{3.125}$$

$$\hat{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{3.126}$$

and

$$\hat{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \tag{3.127}$$

$$\hat{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \tag{3.128}$$

when (with $\hat{\boldsymbol{\sigma}} = \mathbf{e}_x\hat{\sigma}_x + \mathbf{e}_y\hat{\sigma}_y + \mathbf{e}_z\hat{\sigma}_z$)

$$\hat{\mathbf{S}} = \frac{\hbar}{2}\hat{\boldsymbol{\sigma}}. \tag{3.129}$$

Also, the matrix for $\hat{S}^2$ is given by

$$\hat{S}^2 = \frac{3}{4}\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \tag{3.130}$$

If, for example, the basis for the electron's position is $\{|\mathbf{r}\rangle\}$, then its compound basis is given by the set of vectors

$$\begin{aligned} |\chi\rangle &= |\mathbf{r}\rangle \otimes |\varepsilon\rangle \\ &= |\mathbf{r}, \varepsilon\rangle, \end{aligned} \tag{3.131}$$

with $\varepsilon = \pm$. And from our earlier spin postulate

$$[\hat{x}_j, \hat{s}_k] = 0, \tag{3.132}$$

as well

$$\hat{x}_j |\mathbf{r}, \varepsilon\rangle = x_j |\mathbf{r}, \varepsilon\rangle \tag{3.133}$$

$$\hat{S}^2 |\mathbf{r}, \varepsilon\rangle = \frac{3}{4}\hbar^2 |\mathbf{r}, \varepsilon\rangle \tag{3.134}$$

$$\hat{S}_z |\mathbf{r}, \varepsilon\rangle = \varepsilon\frac{\hbar}{2} |\mathbf{r}, \varepsilon\rangle, \tag{3.135}$$

while

$$\left\langle \mathbf{r}', \varepsilon' \,\middle|\, \mathbf{r}, \varepsilon \right\rangle = \delta_{\varepsilon'\varepsilon}\delta\left(\mathbf{r}' - \mathbf{r}\right). \tag{3.136}$$

The closure relation for the orbital-spin compound system is given by

$$\sum_{\varepsilon} \int d^3x\, |\mathbf{r}, \varepsilon\rangle\langle \mathbf{r}, \varepsilon| = \hat{1}. \tag{3.137}$$

An arbitrary state vector $|\psi\rangle$ for a compound system can be expanded using the $\{|\mathbf{r}, \varepsilon\rangle\}$ basis in the usual manner

$$\begin{aligned} |\psi\rangle &= \sum_{\varepsilon} \int d^3x \, |\mathbf{r}, \varepsilon\rangle \langle \mathbf{r}, \varepsilon \,|\, \psi\rangle \\ &= \sum_{\varepsilon} \int d^3x \psi_{\varepsilon}(\mathbf{r}) \, |\mathbf{r}, \varepsilon\rangle \,, \end{aligned} \tag{3.138}$$

with $\psi_{\varepsilon}(\mathbf{r}) = \langle \mathbf{r}, \varepsilon \,|\, \psi\rangle$.

3.5 Composition of Angular Momenta

Given a classical system composed of two particles possessing the angular momenta $\mathbf{L}_1$ and $\mathbf{L}_2$, respectively, we know from Newtonian mechanics that the total angular momentum $\mathbf{L} = \mathbf{L}_1 + \mathbf{L}_2$ will be a conserved quantity if the system is not subjected to a net external torque. But the lack of an external torque does not imply the absence of internal torques. For example, the two particles could be interacting and affecting each other's angular momentum. That is, it is possible that $d\mathbf{L}_1/dt \neq 0$ and $d\mathbf{L}_2/dt \neq 0$, however it will be the case (in the absence of a net external torque) that $d\mathbf{L}_1/dt = -d\mathbf{L}_2/dt$, such that $d\mathbf{L}/dt = 0$.

In quantum mechanics we can verify the conservation of the total angular momentum in the following manner. In the case where the two particles do not interact, the total Hamiltonian of the system can be written as the sum of the individual Hamiltonians of the two particles

$$\hat{H}_0 = \hat{H}_1 + \hat{H}_2 \tag{3.139}$$

with $(j = 1, 2)$

$$\hat{H}_j = \frac{\hat{\mathbf{p}}_j^2}{2m_j} + \hat{V}(\hat{r}_j) \,. \tag{3.140}$$

For simplicity we assume that the potential energies $\hat{V}_j$ are only a function of the distance of the corresponding particle to the origin of the system (i.e., $\hat{r}_j = \sqrt{\hat{x}_j^2 + \hat{y}_j^2 + \hat{z}_j^2}$). Because of this dependency it is possible to expand the potential about the origin with a Taylor series in $\hat{x}_j^2$, $\hat{y}_j^2$ and $\hat{z}_j^2$, i.e., $\hat{V} = \hat{V}\left(\hat{x}_j^2, \hat{y}_j^2, \hat{z}_j^2\right)$. With the commutation relations given in equations (3.15)-(3.18), it is straightforward to verify that

$$\begin{aligned} \left[\hat{L}_1^2, \hat{H}_1\right] = \left[\hat{L}_1^2, \hat{H}_2\right] &= 0 &(3.141)\\ \left[\hat{\mathbf{L}}_1, \hat{H}_1\right] = \left[\hat{\mathbf{L}}_1, \hat{H}_2\right] &= 0, &(3.142) \end{aligned}$$

and similarly for $\hat{L}_2^2$ and $\hat{\mathbf{L}}_2$. It follows that the two individual angular momenta and their squares commute with the total Hamiltonian of the system $\hat{H}_0$, and are therefore conserved quantities (see equations (1.181) and (1.188)).

Let us now assume that the two particles interact through an Hamiltonian $\hat{H}_{\text{int}}\left(\left|\hat{\mathbf{r}}_1-\hat{\mathbf{r}}_2\right|\right)$, which is a function of the distance between them (as is usually the case). We now have for the Hamiltonian of the system

$$\hat{H}=\hat{H}_0+\hat{H}_{\text{int}}\left(\left|\hat{\mathbf{r}}_1-\hat{\mathbf{r}}_2\right|\right). \tag{3.143}$$

Because we have

$$\left|\hat{\mathbf{r}}_1-\hat{\mathbf{r}}_2\right|=\sqrt{\left(\hat{x}_1-\hat{x}_2\right)^2+\left(\hat{y}_1-\hat{y}_2\right)^2+\left(\hat{z}_1-\hat{z}_2\right)^2}, \tag{3.144}$$

it follows that, for example (note that $\left[\hat{x}_1,\hat{H}_{\text{int}}\right]=\hat{0}$, etc.),

$$\begin{aligned}\left[\hat{L}_{1z},\hat{H}\right] &= \left[\hat{L}_{1z},\hat{H}_{\text{int}}\right]\\ &= \hat{x}_1\left[\hat{p}_{1y},\hat{H}_{\text{int}}\right]-\hat{y}_1\left[\hat{p}_{1x},\hat{H}_{\text{int}}\right], \qquad (3.145)\end{aligned}$$

which when acting on an arbitrary ket $|\psi\rangle$ and projected on the $\{|\mathbf{r}\rangle\}$ basis yields

$$\begin{aligned}\left\langle\mathbf{r}\left|\left[\hat{L}_{1z},\hat{H}\right]\right|\psi\right\rangle &= -i\hbar\left\{x_1\left[\frac{\partial\left(H_{\text{int}}\psi\right)}{\partial y_1}-H_{\text{int}}\frac{\partial\psi}{\partial y_1}\right]-y_1\left[\frac{\partial\left(H_{\text{int}}\psi\right)}{\partial x_1}-H_{\text{int}}\frac{\partial\psi}{\partial x_1}\right]\right\}\\ &= -i\hbar\left(x_1\frac{\partial H_{\text{int}}}{\partial y_1}-y_1\frac{\partial H_{\text{int}}}{\partial x_1}\right)\psi\\ &= -i\hbar\frac{1}{r}\frac{\partial H_{\text{int}}}{\partial r}\left[x_1\left(y_1-y_2\right)-y_1\left(x_1-x_2\right)\right]\psi \qquad (3.146)\\ &= -i\hbar\frac{1}{r}\frac{\partial H_{\text{int}}}{\partial r}\left(x_1y_2+y_1x_2\right) \qquad (3.147)\\ &\neq 0. \qquad (3.148)\end{aligned}$$

We therefore find that an individual angular momentum does not commute with the Hamiltonian and its eigenvectors can therefore not be advantageously used to diagonalize the $\hat{H}$. It is not a conserved quantity. On the other hand, because of the form of equation (3.144) we find that

$$\begin{aligned}\left\langle\mathbf{r}\left|\left[\hat{L}_{2z},\hat{H}\right]\right|\psi\right\rangle &= -i\hbar\left(x_2\frac{\partial H_{\text{int}}}{\partial y_2}-y_2\frac{\partial H_{\text{int}}}{\partial x_2}\right)\psi\\ &= i\hbar\frac{1}{r}\frac{\partial H_{\text{int}}}{\partial r}\left(x_2y_1+y_2x_1\right)\\ &= -\left\langle\mathbf{r}\left|\left[\hat{L}_{1z},\hat{H}\right]\right|\psi\right\rangle, \qquad (3.149)\end{aligned}$$

which implies that

$$\left\langle\mathbf{r}\left|\left[\hat{L}_{1z}+\hat{L}_{2z},\hat{H}\right]\right|\psi\right\rangle=0. \tag{3.150}$$

Since the same kind of calculations can be done for the x and y components of the individual angular momenta, we conclude that the total angular momentum $\hat{\mathbf{L}} = \hat{\mathbf{L}}_1 + \hat{\mathbf{L}}_2$ commutes with the Hamiltonian, is a conserved quantity and its eigenvectors are shared with the Hamiltonian. Furthermore, the square of the total momentum can be written as $\hat{\mathbf{L}}^2 = \hat{\mathbf{L}}_1^2 + 2\hat{\mathbf{L}}_1 \cdot \hat{\mathbf{L}}_2 + \hat{\mathbf{L}}_2^2$, such that

$$\begin{aligned}\left[\hat{\mathbf{L}}^2, \hat{H}\right] &= \left[\hat{\mathbf{L}}_1^2, \hat{H}\right] + \left[\hat{\mathbf{L}}_2^2, \hat{H}\right] + 2\left[\hat{\mathbf{L}}_1 \cdot \hat{\mathbf{L}}_2, \hat{H}\right] \\ &= 2\left(\hat{\mathbf{L}}_1 \cdot \left[\hat{\mathbf{L}}_2, \hat{H}\right] + \left[\hat{\mathbf{L}}_1, \hat{H}\right] \cdot \hat{\mathbf{L}}_2\right) \\ &= \hat{0}, \end{aligned} \tag{3.151}$$

on the account of equations (3.13)-(3.14). It is therefore clear that we should concentrate on the total angular momentum, and not its individual components, when dealing with a quantum mechanical system.

3.5.1 The Compound System

Before we consider the total angular momentum it will be instructive to combined the two particles (and angular momenta) through the direct product formalism. If the two respective bases for the individual particles and their Hamiltonians (as in the no-interaction case of equations (3.139)) are $\{|\ell_1, m_1\rangle\}$ and $\{|\ell_2, m_2\rangle\}$, then a natural compound base is given by their direct product

$$|\ell_1, m_1\rangle \otimes |\ell_2, m_2\rangle = |\ell_1, \ell_2; m_1, m_2\rangle . \tag{3.152}$$

This compound basis contains $(2\ell_1 + 1)(2\ell_2 + 1)$ eigenvectors of the angular momenta

$$\hat{\mathbb{L}}_1 = \hat{\mathbf{L}}_1 \otimes \hat{1}(2) \tag{3.153}$$
$$\hat{\mathbb{L}}_1^2 = \hat{L}_1^2 \otimes \hat{1}(2) \tag{3.154}$$
$$\hat{\mathbb{L}}_2 = \hat{1}(1) \otimes \hat{\mathbf{L}}_2 \tag{3.155}$$
$$\hat{\mathbb{L}}_2^2 = \hat{1}(1) \otimes \hat{L}_1^2. \tag{3.156}$$

From now on we will drop this notation for the extension of operators from a single to the compound space and use $\hat{\mathbf{L}}_1$ for $\hat{\mathbb{L}}_1$, etc., as there will be no ambiguity in what follows.

The total angular momentum $\hat{\mathbf{L}} = \hat{\mathbf{L}}_1 + \hat{\mathbf{L}}_2$ leads to the commutation relation

$$\left[\hat{L}^2, \hat{L}_z\right] = 0, \tag{3.157}$$

as is the case for a single particle, but also

$$\left[\hat{L}^2, \hat{L}_1^2\right] = 0 \tag{3.158}$$
$$\left[\hat{L}^2, \hat{L}_2^2\right] = 0 \tag{3.159}$$

$$\begin{aligned}\left[\hat{L}_z, \hat{L}_1^2\right] &= 0 && (3.160)\\ \left[\hat{L}_z, \hat{L}_2^2\right] &= 0. && (3.161)\end{aligned}$$

Note, however, that $\left[\hat{L}_{1z}, \hat{L}^2\right] \neq 0$ and $\left[\hat{L}_{2z}, \hat{L}^2\right] \neq 0$. Because of the vanishing commutators of equations (3.157)-(3.161) we have that $\hat{L}_1^2$, $\hat{L}_2^2$, $\hat{L}^2$ and $\hat{L}_z$ share the same eigenvectors (also with the Hamiltonian of equation (3.143)), which we will denote with $\{|\ell, m\rangle\}$ (we omit the the quantum numbers ℓ_1 and ℓ_2 for reasons that will become clearer later on). The action of $\hat{L}^2$ and $\hat{L}_z$ on these eigenvectors is defined to be

$$\begin{aligned}\hat{L}^2 |\ell, m\rangle &= \ell(\ell+1)\hbar^2 |\ell, m\rangle && (3.162)\\ \hat{L}_z |\ell, m\rangle &= m\hbar |\ell, m\rangle, && (3.163)\end{aligned}$$

with m changing by unit steps on the range $m \leq |\ell|$. But we also have, with $\hat{L}_z = \hat{L}_{1z} + \hat{L}_{2z}$,

$$\hat{L}_z |\ell_1, \ell_2; m_1, m_2\rangle = (m_1 + m_2)\hbar |\ell_1, \ell_2; m_1, m_2\rangle, \tag{3.164}$$

which implies that

$$m = m_1 + m_2. \tag{3.165}$$

It is important to realize that different values for m_1, m_2 or m imply a different orientation for the corresponding angular momenta vectors. We therefore expect that there will be several possibilities for both the orientation of the total angular momentum $\hat{\mathbf{L}}$ as well as its magnitude $\ell(\ell+1)\hbar^2$. To get a better sense of this let us consider the case where $\ell_1 = 1$, $m_1 = -1, 0, 1$, and $\ell_2 = 1/2$, $m_2 = -1/2, 1/2$. Equation (3.165) tells us that the following values for m are realized

$$m = \underbrace{\frac{3}{2}, \frac{1}{2},}_{\substack{m_1 = 1\\ m_2 = \pm\frac{1}{2}}} \quad \underbrace{\frac{1}{2}, -\frac{1}{2},}_{\substack{m_1 = 0\\ m_2 = \pm\frac{1}{2}}} \quad \underbrace{-\frac{1}{2}, -\frac{3}{2}}_{\substack{m_1 = -1\\ m_2 = \pm\frac{1}{2}}}. \tag{3.166}$$

These values for the magnetic total quantum number can be grouped as follows to find the realized values for ℓ according to equations (3.162)-(3.163)

$$\begin{aligned}\ell &= \tfrac{3}{2}, \quad m = -\tfrac{3}{2}, -\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{3}{2}\\ \ell &= \tfrac{1}{2}, \quad m = -\tfrac{1}{2}, \tfrac{1}{2}.\end{aligned} \tag{3.167}$$

This result can be generalized to any pair of angular momenta of any kind with

$$\begin{aligned}|\ell_1 - \ell_2| \leq \quad \ell \quad &\leq |\ell_1 + \ell_2| && (3.168)\\ |m| \leq \quad \ell, & && (3.169)\end{aligned}$$

where successive values for ℓ differ by 1.

Now that we have the determined the eigenvalues of $\hat{L}^2$ and $\hat{L}_z$, we need to express the corresponding eigenvectors $|\ell, m\rangle$ as a function the set of $|\ell_1, \ell_2; m_1, m_2\rangle$. The recipe for accomplishing this task is, in principle, simple to apply. One can start with the eigenvector

$$\begin{aligned} |\ell = \ell_1 + \ell_2, m = \ell_1 + \ell_2\rangle &= |\ell_1 + \ell_2, \ell_1 + \ell_2\rangle \\ &= |\ell_1, \ell_2; \ell_1, \ell_2\rangle \end{aligned} \tag{3.170}$$

and then act upon it with the lowering operator

$$\hat{L}_- = \hat{L}_{1-} + \hat{L}_{2-} \tag{3.171}$$

to obtain (see equation (3.39))

$$\hat{L}_- |\ell_1 + \ell_2, \ell_1 + \ell_2\rangle = \sqrt{2(\ell_1 + \ell_2)}\hbar\, |\ell_1 + \ell_2, \ell_1 + \ell_2 - 1\rangle \tag{3.172}$$

or

$$\begin{aligned} |\ell_1 + \ell_2, \ell_1 + \ell_2 - 1\rangle &= \frac{1}{\sqrt{2(\ell_1 + \ell_2)}\hbar}\left(\hat{L}_{1-} + \hat{L}_{2-}\right)|\ell_1, \ell_2; \ell_1, \ell_2\rangle \\ &= \frac{1}{\sqrt{2(\ell_1 + \ell_2)}\hbar}\left(\hbar\sqrt{2\ell_1}\,|\ell_1, \ell_2; \ell_1 - 1, \ell_2\rangle + \hbar\sqrt{2\ell_2}\,|\ell_1, \ell_2; \ell_1, \ell_2 - 1\rangle\right) \\ &= \sqrt{\frac{\ell_1}{\ell_1 + \ell_2}}\,|\ell_1, \ell_2; \ell_1 - 1, \ell_2\rangle + \sqrt{\frac{\ell_2}{\ell_1 + \ell_2}}\,|\ell_1, \ell_2; \ell_1, \ell_2 - 1\rangle . \end{aligned} \tag{3.173}$$

Repeating this process will yield the remaining eigenvectors $|\ell_1 + \ell_2, m\rangle$ belonging to $\ell = \ell_1 + \ell_2$.

We would then proceed to the subspace $\ell = \ell_1 + \ell_2 - 1$, in which the vector $|\ell_1 + \ell_2 - 1, \ell_1 + \ell_2 - 1\rangle$ is unique (non-degenerate) and can only correspond to

$$|\ell_1 + \ell_2 - 1, \ell_1 + \ell_2 - 1\rangle = a\,|\ell_1, \ell_2; \ell_1 - 1, \ell_2\rangle + b\,|\ell_1, \ell_2; \ell_1, \ell_2 - 1\rangle , \tag{3.174}$$

with $|a|^2 + |b|^2 = 1$. However, this eigenvector much be orthogonal to $|\ell_1 + \ell_2, \ell_1 + \ell_2 - 1\rangle$ and from equation (3.173) we have

$$\begin{aligned} \langle \ell_1 + \ell_2, \ell_1 + \ell_2 - 1\,|\,\ell_1 + \ell_2 - 1, \ell_1 + \ell_2 - 1\rangle &= a\sqrt{\frac{\ell_1}{\ell_1 + \ell_2}} + b\sqrt{\frac{\ell_2}{\ell_1 + \ell_2}} \\ &= 0, \end{aligned} \tag{3.175}$$

which admits $a = \sqrt{\ell_1/(\ell_1 + \ell_2)}$ and $b = -\sqrt{\ell_2/(\ell_1 + \ell_2)}$. We thus find that

$$|\ell_1 + \ell_2 - 1, \ell_1 + \ell_2 - 1\rangle = \sqrt{\frac{\ell_1}{\ell_1 + \ell_2}}\,|\ell_1, \ell_2; \ell_1 - 1, \ell_2\rangle - \sqrt{\frac{\ell_2}{\ell_1 + \ell_2}}\,|\ell_1, \ell_2; \ell_1, \ell_2 - 1\rangle . \tag{3.176}$$

We can then repeated apply $\hat{L}_-$ to find the remaining eigenvectors for the $\ell = \ell_1 + \ell_2 - 1$ subspace, and proceed similarly for $\ell = \ell_1 + \ell_2 - 2$, etc.

More generally, we can concisely relate the two basis with the expansions

$$
\begin{aligned}
|\ell, m\rangle &= \sum_{m_1=-\ell_1}^{\ell_1} \sum_{m_2=-\ell_2}^{\ell_2} |\ell_1, \ell_2; m_1, m_2\rangle \langle \ell_1, \ell_2; m_1, m_2 \,|\, \ell, m\rangle \quad (3.177)\\
|\ell_1, \ell_2; m_1, m_2\rangle &= \sum_{\ell=|\ell_1-\ell_2|}^{\ell_1+\ell_2} \sum_{m=-\ell}^{\ell} |\ell, m\rangle \langle \ell, m \,|\, \ell_1, \ell_2; m_1, m_2\rangle \,, \quad (3.178)
\end{aligned}
$$

where the scalar products $\langle \ell_1, \ell_2; m_1, m_2 \,|\, \ell, m\rangle = \langle \ell, m \,|\, \ell_1, \ell_2; m_1, m_2\rangle$ are the so-called ***Clebsch-Gordon coefficients***, for which extensive tables can be found in the literature.

Exercise 3.3. Let us consider the case of the composition of two one-half spins $s_1 = s_2 = 1/2$. Express the eigenvectors $|s, m_s\rangle$ corresponding to $\hat{\mathbf{S}} = \hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2$ as a function of the basis $|s_1, s_2; m_1, m_2\rangle$ associated to $\hat{\mathbf{S}}_1$ and $\hat{\mathbf{S}}_2$.

Solution.

Since $s_1 = s_2$ we will omit these quantum numbers in the basis $\{|s_1, s_2; m_1, m_2\rangle\}$ and write the corresponding eigenvectors as $|\pm, \pm\rangle$, where $\pm$ stands for $m_{1,2} = \pm 1/2$. We start the calculation with $s = m_s = 1$ and write

$$
|1, 1\rangle = |+, +\rangle \,. \quad (3.179)
$$

Using the lowering operator we have

$$
\begin{aligned}
\hat{S}_- |1, 1\rangle &= \sqrt{2}\hbar\, |1, 0\rangle \\
&= \left(\hat{S}_{1-} + \hat{S}_{2-}\right) |+, +\rangle \\
&= \hbar\, |-, +\rangle + \hbar\, |+, -\rangle \quad (3.180)
\end{aligned}
$$

or

$$
|1, 0\rangle = \frac{1}{\sqrt{2}} \left(|-, +\rangle + |+, -\rangle\right). \quad (3.181)
$$

Applying the lowering operator once more we have

$$
\begin{aligned}
|1, -1\rangle &= \frac{1}{\sqrt{2}\hbar} \hat{S}_- |1, 0\rangle \\
&= \frac{1}{\sqrt{2}\hbar} \left(\hat{S}_{1-} + \hat{S}_{2-}\right) \frac{1}{\sqrt{2}} \left(|-, +\rangle + |+, -\rangle\right) \\
&= \frac{1}{\sqrt{2}\hbar} \left(\hbar\, |-, -\rangle + \hbar\, |-, -\rangle\right) \\
&= |-, -\rangle \,. \quad (3.182)
\end{aligned}
$$

The three eigenvectors $\{|1,1\rangle, |1,0\rangle, |1,-1\rangle\}$ form a ***triplet***.

Finally, we set

$$|0,0\rangle = a\,|+,-\rangle + b\,|-,+\rangle\,, \tag{3.183}$$

as it is the only possible linear combination consistent with $m = 0$. This ket is obviously orthogonal to $|1,1\rangle = |+,+\rangle$ and $|1,-1\rangle = |-,-\rangle$, but in order to have $\langle 1,0\,|\,0,0\rangle = 0$ it must be that $a = -b = 1/\sqrt{2}$. The ***singlet*** state is therefore given by

$$|0,0\rangle = \frac{1}{\sqrt{2}}\left(|+,-\rangle - |-,+\rangle\right). \tag{3.184}$$