11 Angular Momentum Theory

In this chapter we will develop the quantum theory of angular momentum. As in classical mechanics, working with angular momentum requires that we leave the one-dimensional space in which we have been working so far, with all the complications that this entails.

For two- or three-dimensional problems, the notion of angular momentum is not only very useful, but to a large extent necessary. In QM, this importance is accentuated by at least three facts: (i) central problems are of particular interest (the problem of the H atom is paradigmatic); (ii) many particles have an intrinsic angular momentum (the spin); and (iii) the physics of angular momentum involves features such as the so-called *space quantization*, that have no classical analog but are essential for describing the behavior of quantum systems, even the simplest atom. Moreover, since angular momentum is described by an operator, studying its properties gives us another opportunity to learn how to deal with the quantum formalism.

11.1 Orbital Angular Momentum. Spherical Harmonics

We saw in Section 8.7.2 that the orbital angular momentum operator $\widehat{\boldsymbol{L}}$ can be defined in QM precisely as in classical theory,

$$\widehat{\boldsymbol{L}} = \widehat{\boldsymbol{r}} \times \widehat{\boldsymbol{p}}. \tag{11.1}$$

If you have not read that section, take Eq. (11.1) as the definition. Note that $\widehat{\boldsymbol{r}} \times \widehat{\boldsymbol{p}} = -\widehat{\boldsymbol{p}} \times \widehat{\boldsymbol{r}}$ in classical physics, so there is no problem with the order of the factors when moving from the classical to the quantum case. In Cartesian coordinates, the components of $\widehat{\boldsymbol{L}}$ are

$$\widehat{L}_i = \varepsilon_{ijk} j{:}x_j \widehat{x} \widehat{p}_k = -i\hbar \varepsilon_{ijk} x_j \frac{\partial}{\partial x_k} \tag{11.2}$$

(summing over repeated indices is understood; ε_{ijk} is the totally anti-symmetric 3-D Levi–Civita tensor). In spherical coordinates we have

$$\widehat{\boldsymbol{L}} = -i\hbar \left(\widehat{\mathbf{a}}_\varphi \frac{\partial}{\partial \theta} - \widehat{\mathbf{a}}_\theta \frac{1}{\sin\theta} \frac{\partial}{\partial \varphi} \right), \tag{11.3}$$

whence $\widehat{\boldsymbol{L}}$ commutes with functions of r and of $\partial/\partial r$, that is,

$$\left[\widehat{\boldsymbol{L}}, f\left(r, \frac{\partial}{\partial r} \right) \right] = 0. \tag{11.4}$$

This feature will prove very useful.

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We will now study the commutation properties of $\widehat{\boldsymbol{L}}$ with different dynamical variables. We start with the following equations in Cartesian coordinates,

$$[x_i, P(\widehat{p})] = i\hbar\frac{\partial P}{\partial \widehat{p}_i}, \quad [\widehat{p}_i, Q(\widehat{x})] = -i\hbar\frac{\partial Q}{\partial \widehat{x}_i}. \tag{11.5}$$

From the first expression it follows that

$$[x_i\widehat{p}_j, P(\widehat{p})] = x_i\widehat{p}_j P(\widehat{p}) - P(\widehat{p})x_i\widehat{p}_j = (x_i P - P x_i)\widehat{p}_j = i\hbar\frac{\partial P}{\partial \widehat{p}_i}\widehat{p}_j. \tag{11.6}$$

Interchanging the indices i and j and taking the difference between the two results gives

$$[\widehat{L}_k, P(\widehat{p})] = [x_i\widehat{p}_j - x_j\widehat{p}_i, P(\widehat{p})] = i\hbar\left(\frac{\partial P}{\partial p_i}\widehat{p}_j - \frac{\partial P}{\partial p_j}\widehat{p}_i\right). \tag{11.7}$$

Similarly, from Eq. (11.5) it follows that

$$[x_i\widehat{p}_j, Q(x)] = x_i\widehat{p}_j Q(x) - x_i Q(x)\widehat{p}_j = x_i[\widehat{p}_j, Q(x)] = -i\hbar x_i\frac{\partial Q}{\partial x_j}, \tag{11.8}$$

which gives

$$[\widehat{L}_k, Q(x)] = [x_i\widehat{p}_j - x_j\widehat{p}_i, Q(x)] = -i\hbar\left(x_i\frac{\partial Q}{\partial x_j} - x_j\frac{\partial Q}{\partial x_i}\right). \tag{11.9}$$

In Eqs. (11.7) and (11.9) the indices i, j, k are in cyclic order. As a simple example of application of these results, we calculate the commutators $[\widehat{L}_i, x_j]$ and $[\widehat{L}_i, \widehat{p}_j]$,[1]

$$\begin{aligned}
[\widehat{L}_x, x] &= -i\hbar\left(y\frac{\partial x}{\partial z} - z\frac{\partial x}{\partial y}\right) = 0,\\
[\widehat{L}_x, y] &= -i\hbar\left(y\frac{\partial y}{\partial z} - z\frac{\partial y}{\partial y}\right) = i\hbar z,\\
[\widehat{L}_x, z] &= -i\hbar\left(y\frac{\partial z}{\partial z} - z\frac{\partial z}{\partial y}\right) = -i\hbar y;
\end{aligned} \tag{11.10}$$

$$\begin{aligned}
[\widehat{L}_x, \widehat{p}_x] &= -i\hbar\left(p_y\frac{\partial p_x}{\partial p_z} - p_z\frac{\partial p_x}{\partial p_y}\right) = 0,\\
[\widehat{L}_x, \widehat{p}_y] &= i\hbar\widehat{p}_z, \quad [\widehat{L}_x, \widehat{p}_z] = -i\hbar\widehat{p}_y.
\end{aligned} \tag{11.11}$$

Of particular importance are the commutators of the components of $\widehat{\boldsymbol{L}}$, which we proceed to determine. Since the $\widehat{L}_i$ are linear combinations of components of $\boldsymbol{r}$ and $\widehat{\boldsymbol{p}}$, it follows that they do not commute with each other (we give the Cartesian index the values 1, 2, 3 or x, y, z, as convenient). Specifically,

$$\begin{aligned}
[\widehat{L}_x, \widehat{L}_y] &= [\widehat{L}_x, z\widehat{p}_x] - [\widehat{L}_x, x\widehat{p}_z]\\
&= [\widehat{L}_x, z]\widehat{p}_x - x[\widehat{L}_x, \widehat{p}_z] = -i\hbar y\widehat{p}_x + i\hbar x\widehat{p}_y = i\hbar L_z,
\end{aligned} \tag{11.12}$$

where we have used (11.10) and (11.11). To the commutator

$$[\widehat{L}_x, \widehat{L}_y] = i\hbar\widehat{L}_z \tag{11.13}$$

[1] Note that Eqs. (11.10) and (11.11) are particular cases of the general law $\left[\hat{L}_i, \hat{A}_j\right] = i\hbar\varepsilon_{ijk}\hat{A}_k$ derived in Section 8.7.2.

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we may add the cyclic permutations,

$$[\widehat{L}_y, \widehat{L}_z] = i\hbar\widehat{L}_x, \quad [\widehat{L}_z, \widehat{L}_x] = i\hbar\widehat{L}_y, \tag{11.14}$$

and write the results formally and succinctly as

$$\widehat{\boldsymbol{L}} \times \widehat{\boldsymbol{L}} = i\hbar\widehat{\boldsymbol{L}}. \tag{11.15}$$

(Note that the cross product of a vector by itself is not necessarily zero, if the vector is an operator.)

To calculate the commutator of a component $\widehat{L}_i$ with the operator $\widehat{\boldsymbol{L}}^2$, we write

$$\widehat{\boldsymbol{L}}^2 = \widehat{L}_x^2 + \widehat{L}_y^2 + \widehat{L}_z^2, \tag{11.16}$$

so we get, for example,

$$\begin{aligned}[\widehat{\boldsymbol{L}}^2, \widehat{L}_z] &= [\widehat{L}_x^2 + \widehat{L}_y^2, \widehat{L}_z] \\ &= \widehat{L}_x[\widehat{L}_x, \widehat{L}_z] + [\widehat{L}_x, \widehat{L}_z]\widehat{L}_x + \widehat{L}_y[\widehat{L}_y, \widehat{L}_z] + [\widehat{L}_y, \widehat{L}_z]\widehat{L}_y = 0,\end{aligned} \tag{11.17}$$

i.e.,

$$[\widehat{\boldsymbol{L}}^2, \widehat{L}_i] = 0, \quad i = 1, 2, 3. \tag{11.18}$$

The result just obtained was expected, since $\widehat{\boldsymbol{L}}^2$ is a scalar operator, and thus invariant to rotations of the coordinate system, and the $\widehat{L}_k$ are the generators of such rotations. Since $\widehat{\boldsymbol{L}}^2$ commutes with each component $\widehat{L}_i$, it looks as if simultaneous eigenstates of $\widehat{\boldsymbol{L}}^2$ and the three $\widehat{L}_i$ exist. However, Eqs. (11.13) and (11.14) show that the $\widehat{L}_i$ do not commute with each other, so at most one of them can be fixed in a given state. This means that although all three components are integrals of motion, only one of them can have a well-defined value. Taking, in a purely conventional way, L_z as the variable with a well-defined value, we can construct the simultaneous eigenstate of $\widehat{\boldsymbol{L}}^2$ and $\widehat{L}_z$, namely $|L\, L_z\rangle$, which in general is not an eigenstate of $\widehat{L}_x$ and $\widehat{L}_y$. In fact, by applying Heisenberg's inequality to Eq. (11.13), we obtain

$$\langle(\Delta\widehat{L}_x)^2\rangle\langle(\Delta\widehat{L}_y)^2\rangle \geq \tfrac{1}{4}\hbar^2|\langle\widehat{L}_z\rangle|^2, \tag{11.19}$$

which shows that when $\langle\widehat{L}_z\rangle \neq 0$ (its value is well defined), the components $\widehat{L}_x$ and $\widehat{L}_y$ are necessarily distributed. However, if $\langle\widehat{L}_z\rangle = 0$, all projections of $\widehat{\boldsymbol{L}}$ can be well defined, with $\langle\widehat{L}_x\rangle = \langle\widehat{L}_y\rangle = \langle\widehat{L}_z\rangle = 0$. Let us look at this last case more closely. If $\langle\hat{\boldsymbol{L}}\rangle = 0$ or, what is equivalent,

$$\hat{\boldsymbol{L}}|\psi_0\rangle = 0, \tag{11.20}$$

where $|\psi_0\rangle$ corresponds to the zero eigenvalue of L_i, the three Cartesian components of $\hat{\boldsymbol{L}}$ are well defined (all three eigenvalues are 0). Writing the wave function as $\psi_0(r, \theta, \varphi) = \langle r, \theta, \varphi|\psi_0\rangle$, we see from (11.3) and (11.20) that the following differential equation must hold

$$\left(\widehat{\mathbf{a}}_\varphi \frac{\partial}{\partial\theta} - \widehat{\mathbf{a}}_\theta \frac{1}{\sin\theta}\frac{\partial}{\partial\varphi}\right)\psi_0 = 0, \tag{11.21}$$

whose general solution

$$\psi_0 = \psi(r), \tag{11.22}$$

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does not depend on the angular variables, that is, it is a state with spherical symmetry. These are the so-called s-states, with zero orbital angular momentum. For any other state, assuming that $\widehat{L}_z$ is well defined, the variables $\widehat{L}_x$ and $\widehat{L}_y$ are dispersive.

11.1.1 Dynamics of angular momentum

From Eq. (11.7) with $P(\hat{p}) = \widehat{\boldsymbol{p}}^2/2m$, we see that the three components of the angular momentum commute with the kinetic-energy operator,

$$\left[\hat{L}_x, \frac{\widehat{\boldsymbol{p}}^2}{2m}\right] = \frac{i\hbar}{2m}\left(\frac{\partial \widehat{\boldsymbol{p}}^2}{\partial p_y}\widehat{p}_z - \frac{\partial \widehat{\boldsymbol{p}}^2}{\partial p_z}\widehat{p}_y\right) = \frac{i\hbar}{m}\left(\widehat{p}_y\widehat{p}_z - \widehat{p}_z\widehat{p}_y\right) = 0, \tag{11.23}$$

or in vector form,

$$\left[\widehat{\boldsymbol{L}}, \frac{\widehat{\boldsymbol{p}}^2}{2m}\right] = 0. \tag{11.24}$$

On the other hand, applying Eq. (11.9) to the potential energy, we get

$$[\widehat{L}_x, V(\boldsymbol{r})] = -i\hbar\left(y\frac{\partial V}{\partial z} - z\frac{\partial V}{\partial y}\right) = i\hbar(yF_z - zF_y), \tag{11.25}$$

where $F_i = -\partial V/\partial x_i$ is the external force. Since $yF_z - zF_y$ is the x-component of the momentum of the external force (or torque) $\widehat{\boldsymbol{M}}$,

$$\widehat{\boldsymbol{M}} = \widehat{\boldsymbol{r}} \times \widehat{\boldsymbol{F}}, \tag{11.26}$$

we can write the preceding result in vector form,

$$[\widehat{\boldsymbol{L}}, V(\boldsymbol{r})] = i\hbar\widehat{\boldsymbol{M}}. \tag{11.27}$$

Adding Eqs. (11.24) and (11.27) and introducing the Hamiltonian $\widehat{H} = \widehat{\boldsymbol{p}}^2/2m + V(\boldsymbol{r})$ gives

$$[\widehat{\boldsymbol{L}}, \widehat{H}] = i\hbar\widehat{\boldsymbol{M}}. \tag{11.28}$$

This equation shows that if the external force exerts a torque $\boldsymbol{M}$ on the particle, $\widehat{\boldsymbol{L}}$ does not commute with the Hamiltonian. Combining Eq. (11.28) with the Heisenberg equation of motion applied to $\widehat{\boldsymbol{L}}$ (writing $\dot{\widehat{\boldsymbol{L}}} = \widehat{\dot{\boldsymbol{L}}}$),

$$i\hbar\dot{\widehat{\boldsymbol{L}}} = [\widehat{\boldsymbol{L}}, \widehat{H}], \tag{11.29}$$

we obtain the law of evolution of the angular momentum

$$\frac{d\widehat{\boldsymbol{L}}}{dt} = \widehat{\boldsymbol{M}}, \tag{11.30}$$

which has the same form as the corresponding classical law. We see that $\widehat{\boldsymbol{M}}$ is the cause of the evolution of $\widehat{\boldsymbol{L}}$.

For radial or central forces (for which $\widehat{\boldsymbol{M}} = 0$), $\hat{H}$ and $\widehat{\boldsymbol{L}}$ commute and therefore have common eigenvectors. The reason for this result is that in this case the Hamiltonian is invariant with respect to rotations of the coordinate system and therefore invariant with respect to the generator of rotations, $\hat{\boldsymbol{L}}$.

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When $\langle \widehat{\boldsymbol{M}} \rangle \neq 0$, we can use Eq. (8.73) to determine a characteristic time of evolution τ_L of the angular momentum. If $\langle \Delta L \rangle$ represents the standard deviation of $\widehat{\boldsymbol{L}}$ in the given state, we have

$$\tau_L = \frac{\langle \Delta L \rangle}{|\langle \widehat{\boldsymbol{M}} \rangle|}. \tag{11.31}$$

Therefore, according to the Mandelstam–Tamm inequality (8.75) applied to L,

$$\langle (\Delta \widehat{H})^2 \rangle \left\langle \left(\frac{\Delta \widehat{L}}{d\langle \widehat{L} \rangle / dt} \right)^2 \right\rangle \geq \tfrac{1}{4}\hbar^2, \tag{11.32}$$

the evolution time τ_L is not arbitrarily short but is bounded from below by the standard deviation of the energy.

11.1.2 Spherical harmonics and their eigenvalues

We will now establish the differential equations for the eigenfunctions and eigenvalues of the orbital angular-momentum operators. It is convenient to use spherical coordinates for this purpose, since the angular-momentum operator commutes with the variable r and acts only on the angular variables θ and φ, so it is a function of only these two variables.

We look for simultaneous eigenfunctions of $\widehat{\boldsymbol{L}}^2$ and one of its components, say, $\widehat{L}_z$, so the equations to solve are

$$\widehat{\boldsymbol{L}}^2 Y(\theta, \varphi) = \hbar^2 \lambda Y(\theta, \varphi), \tag{11.33}$$

$$\widehat{L}_z Y(\theta, \varphi) = \hbar m Y(\theta, \varphi), \tag{11.34}$$

where $Y(\theta, \varphi)$ are the eigenfunctions, and the eigenvalues λ and m are dimensionless parameters to be determined. From (11.3) squared, we get

$$\begin{aligned} \widehat{\boldsymbol{L}}^2 &= -\hbar^2 \left(\widehat{\mathbf{a}}_\varphi \partial_\theta - \frac{\widehat{\mathbf{a}}_\theta}{\sin\theta} \partial_\varphi \right)^2 \\ &= -\hbar^2 \left[\widehat{\mathbf{a}}_\varphi \cdot \partial_\theta (\widehat{\mathbf{a}}_\varphi \partial_\theta) - \widehat{\mathbf{a}}_\varphi \cdot \partial_\theta \left(\frac{\widehat{\mathbf{a}}_\theta}{\sin\theta} \partial_\varphi \right) \right. \\ &\quad \left. - \frac{\widehat{\mathbf{a}}_\theta}{\sin\theta} \cdot \partial_\varphi (\widehat{\mathbf{a}}_\varphi \partial_\theta) + \frac{\widehat{\mathbf{a}}_\theta}{\sin\theta} \cdot \partial_\varphi \left(\frac{\widehat{\mathbf{a}}_\theta}{\sin\theta} \partial_\varphi \right) \right]. \end{aligned} \tag{11.35}$$

From the expressions for $\widehat{\mathbf{a}}_r, \widehat{\mathbf{a}}_\theta$ and $\widehat{\mathbf{a}}_\varphi$ in terms of the Cartesian unit vectors $\widehat{\mathbf{a}}_x, \widehat{\mathbf{a}}_y, \widehat{\mathbf{a}}_z$,

$$\widehat{\mathbf{a}}_r = \widehat{\mathbf{a}}_x \sin\theta \cos\varphi + \widehat{\mathbf{a}}_y \sin\theta \sin\varphi + \widehat{\mathbf{a}}_z \cos\theta, \tag{11.36}$$

$$\widehat{\mathbf{a}}_\theta = \widehat{\mathbf{a}}_x \cos\theta \cos\varphi + \widehat{\mathbf{a}}_y \cos\theta \sin\varphi - \widehat{\mathbf{a}}_z \sin\theta, \tag{11.37}$$

$$\widehat{\mathbf{a}}_\varphi = -\widehat{\mathbf{a}}_x \sin\varphi + \widehat{\mathbf{a}}_y \cos\varphi, \tag{11.38}$$

it follows that

$$\begin{aligned} \partial_\theta \widehat{\mathbf{a}}_\varphi &= 0, \qquad \partial_\theta \widehat{\mathbf{a}}_\theta = -\widehat{\mathbf{a}}_r, \\ \partial_\varphi \widehat{\mathbf{a}}_\theta &= \widehat{\mathbf{a}}_\varphi \cos\theta, \qquad \partial_\varphi \widehat{\mathbf{a}}_\varphi = -\widehat{\mathbf{a}}_r \sin\theta - \widehat{\mathbf{a}}_\theta \cos\theta. \end{aligned} \tag{11.39}$$

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Plugging these results into Eq. (11.35) we get

$$\widehat{\boldsymbol{L}}^2 = -\hbar^2\left[\partial_\theta^2 + \frac{\cos\theta}{\sin\theta}\partial_\theta + \frac{1}{\sin^2\theta}\partial_\varphi^2\right]$$
$$= -\hbar^2\left[\frac{1}{\sin^2\theta}\partial_\varphi^2 + \frac{1}{\sin\theta}\partial_\theta(\sin\theta\partial_\theta)\right]. \tag{11.40}$$

To construct the operator $\widehat{L}_z$ we project the $\widehat{\boldsymbol{L}}$ given by Eq. (11.3) in the z-direction,

$$\widehat{L}_z = -i\hbar\widehat{\mathbf{a}}_z \cdot \left(\widehat{\mathbf{a}}_\varphi\partial_\theta - \frac{\widehat{\mathbf{a}}_\theta}{\sin\theta}\partial_\varphi\right). \tag{11.41}$$

Since from Eqs. (11.37) and (11.38) it follows that $\widehat{\mathbf{a}}_z \cdot \widehat{\mathbf{a}}_\varphi = 0, \quad \widehat{\mathbf{a}}_z \cdot \widehat{\mathbf{a}}_\theta = -\sin\theta$, the result is

$$\widehat{L}_z = -i\hbar\partial_\varphi. \tag{11.42}$$

With (11.40) and (11.42), the eigenvalue equations (11.33) and (11.34) take the form

$$\frac{\partial Y}{\partial\varphi} = imY, \tag{11.43}$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2} = -\lambda Y. \tag{11.44}$$

The solution of this pair of equations is simplified by first solving Eq. (11.43) for $\widehat{L}_z$,

$$Y(\theta,\varphi) = \Theta(\theta)e^{im\varphi}. \tag{11.45}$$

For this to be a physical (i.e., single-valued) solution, its value must be the same for φ and $\varphi + 2\pi m$, where

$$|m| = 0, 1, 2, \ldots \tag{11.46}$$

Therefore the eigenvalues $\hbar m$ of $\widehat{L}_z$ are *integer* multiples, positive or negative, of $\hbar$: $0, \pm\hbar, \pm 2\hbar, \ldots$ Since the z-direction is arbitrary, the result must be understood in the sense that the projection of the orbital momentum in any given direction is quantized, so that the eigenvalues of the operator $\mathbf{n}\cdot\widehat{\boldsymbol{L}}$, where $\mathbf{n}$ is a unit vector in that direction, are $0, \pm\hbar, \pm 2\hbar, \ldots$ This is the so-called *space quantization*,[2] perhaps one of the most counterintuitive concepts in QM. For historical reasons (related to its important applications, see Section 12.7), the quantum number m is called the *magnetic quantum number*.

Substituting (11.45) in Eq. (11.44), we get

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta - \frac{m^2}{\sin^2\theta}\Theta + \lambda\Theta = 0. \tag{11.47}$$

We recognize here the *Legendre differential equation*, which has a solution for all values of the parameter λ. In general, however, such solutions diverge for some value of the variable θ within the interval $(0,\pi)$, so they are physically inadmissible. Equation (11.47) has regular solutions in $(0,\pi)$ for $m \geq 0$ if and only if

$$\lambda = l(l+1), \quad l \geq |m| \tag{11.48}$$

[2] This term does not refer to the quantization of space of course, but to the possible values of the angular-momentum projections in a given direction.

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with l an integer, $l = 0, 1, 2, \ldots$ This means that also the magnitude of the orbital angular momentum is quantized.[3]

The appropriate solutions of Eq. (11.47) are the associated Legendre polynomials $\Theta(\theta) = P_l^m(x)$, with $x = \cos\theta$, which can be obtained using the Rodrigues formula

$$P_l^m(x) = \frac{l}{2^l l!}(1-x^2)^{m/2}\frac{d^{l+m}}{dx^{l+m}}(x^2-1)^l. \tag{11.49}$$

These functions are orthogonal with respect to the index l,

$$\int_{-1}^{1} P_l^m(x)P_{l'}^m(x)dx = \frac{2}{2l+1}\,\frac{(l+m)!}{(l-m)!}\delta_{ll'}, \tag{11.50}$$

while the factor $e^{im\varphi}$ in Eq. (11.45) takes care of the orthogonality with respect to the index m. It is thus established that the simultaneous eigenfunctions of $\boldsymbol{L}^2$ and $\widehat{L}_z$ are the *spherical harmonics* $Y_l^m(\theta,\varphi) \sim P_l^m(\cos\theta)e^{im\varphi}$. Using formula (11.50) it is not difficult to show that the $Y's$ normalized over the entire solid angle are

$$Y_l^m(\theta,\varphi) = \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}}(-)^m P_l^m(\cos\theta)e^{im\varphi}, \tag{11.51}$$

for $m \geq 0$.[4]

For $m < 0$ we write

$$Y_l^m = (-)^m Y_l^{-m*}. \tag{11.52}$$

The functions Y_l^m thus defined form an orthonormal set, so for $-l \leq m \leq l$ they give

$$\int_0^{2\pi}\int_0^{\pi} Y_l^{m*}(\theta,\varphi)Y_{l'}^{m'}(\theta,\varphi)\sin\theta d\theta d\varphi = \delta_{ll'}\delta_{mm'}. \tag{11.53}$$

Spherical harmonics have a well-defined parity. To determine it, we observe from Fig. 11.1 that when the coordinates are reflected with respect to the origin, the angles θ and φ change to

$$\theta \to \theta' = \pi - \theta; \quad \varphi \to \varphi' = \varphi + \pi, \tag{11.54}$$

$$x = \cos\theta \to \cos(\pi - \theta) = -\cos\theta = -x, \tag{11.55}$$

which gives a factor $(-1)^{l+m}$; the function Y is then affected by the factor $(-1)^{l+2m} = (-1)^l$. We write this as an eigenvalue equation for the parity operator,

$$\widehat{P}Y_l^m(\theta,\varphi) = (-)^l Y_l^m(\theta,\varphi), \tag{11.56}$$

to show explicitly that the parity of the spherical harmonics is that of the angular momentum l,

$$P = (-1)^l. \tag{11.57}$$

[3] It is customary to speak of the magnitude of the angular momentum in units of $\hbar$.

[4] Different conventions are used in the literature for defining both the normalization of spherical harmonics and their normalization condition. For example, the normalization factor of Eq. (11.51) may vary from one text to another. The definition of spherical harmonics for negative m can also vary between different authors. The present one is used in the book by Condon and Shortley (1935), which is a very common reference.

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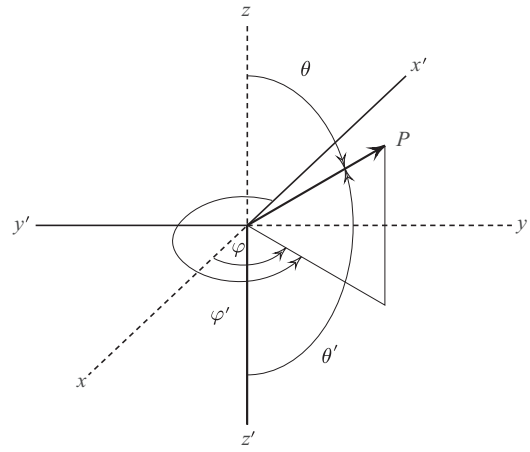


Figure 11.1 Upon reflection of the coordinates with respect to the origin, the angles θ and φ change to $\pi - \theta$ and $\varphi + \pi$, respectively.

11.1.3 Angular momentum dispersion

From the Heisenberg inequalities and the commutation relations (11.10) it follows that

$$\langle(\Delta\widehat{L}_z)^2\rangle\langle(\Delta y)^2\rangle \geq \tfrac{1}{4}\hbar^2\langle x\rangle^2, \tag{11.58}$$

$$\langle(\Delta\widehat{L}_x)^2\rangle\langle(\Delta y)^2\rangle \geq \tfrac{1}{4}\hbar^2\langle z\rangle^2, \tag{11.59}$$

and so on. From the first inequality we see that the eigenstates of $\widehat{L}_z$ necessarily have $\langle x\rangle = 0$ and $\langle y\rangle = 0$ (this second condition follows from the first by symmetry). The second inequality tells us that in such a case $\langle z\rangle \neq 0$, as expected for $\langle L_z\rangle \neq 0$. In other words, there is rotation about the z-axis. Therefore, an eigenstate of $\langle L_z\rangle \neq 0$ means precession around z.

This is confirmed by Eq. (11.48), the meaning of which can be understood as follows. The maximum value of the projection of $\widehat{\boldsymbol{L}}$ in any given direction is $\hbar m_{\max} = \hbar l$, according to (11.48); from $|\langle\widehat{\boldsymbol{L}}\rangle|_{\max} = \langle\widehat{L}_z\rangle_{\max} = \hbar l$ it follows that $\langle(\Delta\widehat{\boldsymbol{L}})^2\rangle_{\min} = \langle\widehat{\boldsymbol{L}}^2\rangle - \left(\langle\widehat{\boldsymbol{L}}\rangle_{\max}\right)^2 = \hbar^2 l(l+1) - \hbar^2 l^2 = \hbar^2 l$. In other words, if $l \neq 0$, the angular momentum *always* precesses around some axis. It is this inevitable precession that causes the x- and y-components to change continuously, albeit averaging to zero, as can be seen in Fig. 11.2. From Eq. (11.19) and the figure, we see that when $\langle L_z\rangle$ is maximum, the dispersions on the xy-plane are minimum, which allows us to write

$$\left[\langle(\Delta\widehat{L}_x)^2\rangle\langle(\Delta\widehat{L}_y)^2\rangle\right]_{\min} = \tfrac{1}{4}\hbar^2\langle\widehat{L}_z\rangle^2_{\max} = \tfrac{1}{4}\hbar^4 l^2. \tag{11.60}$$

Since $\langle\widehat{L}_x\rangle = \langle\widehat{L}_y\rangle = 0$, $\langle(\Delta\widehat{L}_x)^2\rangle_{\min} = \langle\widehat{L}_x^2\rangle_{\min} = \frac{1}{2}\hbar^2 l$, and therefore,

$$\langle\widehat{L}_x^2 + \widehat{L}_y^2\rangle_{\min} = \hbar^2 l. \tag{11.61}$$

Consequently,

$$\langle\widehat{\boldsymbol{L}}^2\rangle = \langle\widehat{L}_x^2 + \widehat{L}_y^2\rangle_{\min} + \langle\widehat{L}_z^2\rangle_{\max} = \hbar^2 l + \hbar^2 l^2 = \hbar^2 l(l+1), \tag{11.62}$$

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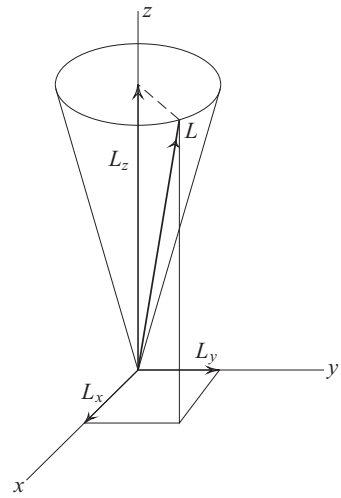


Figure 11.2 For eigenstates of L_z, the angular-momentum vector precesses around the z-axis, with its x- and y-components oscillating periodically around the origin.

which confirms that the term $\hbar^2 l$ in the eigenvalue of $\widehat{\boldsymbol{L}}^2$ comes from the precession of the angular momentum around the quantization axis, that is, from the variances $\langle(\Delta\widehat{L}_x)^2\rangle$ and $\langle(\Delta\widehat{L}_y)^2\rangle$.

In this analysis we have assumed that the averages over the ensemble coincide with the averages over time, obtained by following a single particle. For example, in Fig. 11.2 we can see that as the particle describes an orbit, $\widehat{L}_x$ takes on different values, positive and negative, so that the average over one revolution (one period) is zero. But we can interpret the drawing differently, by considering that it corresponds to a particle at a given moment, and that at that *same moment* other particles of the ensemble would be in other possible positions of the orbit. In this case, the average of $\widehat{L}_x$ over the ensemble is zero. If we stick to this second view, the whole preceding description will be consistent, but we will have to reinterpret Fig.11.2, understanding that there are infinitely many vectors $\boldsymbol{L}$ coexisting in the ensemble, uniformly distributed around the circumference. If we prefer the temporal interpretation, then we will have to propose that $\langle\widehat{L}_x\rangle = \overline{L_x}^t$, where the time average refers to a single particle. As mentioned earlier, this equality means that the system has ergodic properties (equivalence of the ensemble average and the individual time average).

It is customary to refer to states with $l = 0$ as s states, with $l = 1$ as p states, and so on, the order of the letters s, p, d, f, g, corresponding to $0, 1, 2, 3, 4, 5$; hereafter the order is alphabetical. The current use of the letters s (sharp), p (principal), d (diffusive), f (fundamental)… is nothing more than a legacy of the prequantum spectroscopic tradition.

Exercise E11.1. An action-angle Heisenberg inequality

In the Heisenberg–Robertson inequality (8.54) one obtains by taking $\hat{A} = \varphi$, $\hat{B} = L_z = -i\hbar(\partial/\partial\varphi)$

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$$\Delta_\psi \varphi \Delta_\psi L_z \geq \frac{1}{2}\hbar. \tag{11.63}$$

Check the validity of this expression.

Solution. Since $\Delta\varphi \leq 2\pi$, for (11.63) to be valid it is required that $\Delta_\psi \hat{L}_z \geq \hbar/4\pi$, which is violated if ψ is chosen as one of the eigenfunctions $Y_l^m(\theta, \varphi)$ of L_z. This contradiction shows that the inequality (11.63) is only valid under restricted conditions. The difficulty arises from the fact that the inequalities (8.53) and (8.54) hold only if the two operators $\hat{A}$ and $\hat{B}$ are Hermitian; but $\hat{L}_z$ is only Hermitian in the space of periodic functions of φ with period 2π. Indeed, it follows from

$$\int \psi_1^* \hat{L}_z \psi_2 d\varphi = -i\hbar \int \psi_1^* \frac{\partial \psi_2}{\partial \varphi} d\varphi = -i\hbar \psi_1^* \psi_2 |_0^{2\pi} + i\hbar \int \psi_2 \frac{\partial \psi_1^*}{\partial \varphi} d\varphi \tag{11.64}$$

that the Hermiticity condition holds if and only if the integrated term vanishes, which in general only happens if ψ_1 and ψ_2 have period 2π. In the previous case, this condition is not met, since the function $\varphi Y_{lm}(\theta, \varphi)$ is not periodic in φ.

To obtain a correct inequality that replaces (11.63), we can proceed in several ways; one of them is the following. Let us take a periodic function A of φ with period 2π, otherwise arbitrary; then $A(\varphi) = A(\varphi + 2\pi)$. Since $[\hat{A}, \hat{L}_z] = i\hbar A'$, from the inequality (8.53) we get

$$\Delta_\psi A \Delta \hat{L}_z \geq \frac{1}{2}\hbar \mid \langle A' \rangle \mid, \tag{11.65}$$

that is,

$$\Delta_A \varphi \Delta \hat{L}_z \geq \frac{1}{2}\hbar, \tag{11.66}$$

where

$$\Delta_A \varphi = \sqrt{\frac{\langle (\Delta A)^2 \rangle}{\mid \langle dA/d\varphi \rangle \mid}}. \tag{11.67}$$

We conclude that an inequality of the Mandelstam–Tamm type is the correct form of the Heisenberg inequality for angle variables. Alternatively, we can give a correct form to Eq. (11.63) by replacing φ with the periodic function $A = \varphi \bmod 2\pi$. A Fourier expansion gives

$$A = \pi + i \sum_{-\infty}^{\infty} \frac{1}{k} e^{ik\varphi}, \qquad (k \neq 0), \tag{11.68}$$

and therefore, $A' = -\sum e^{ik\varphi}$ $(k \neq 0)$. Replacing A and A' in Eq. (11.65) gives the desired inequality. Note that A' is highly singular, since for $\varphi \neq 2\pi n, n = 0, 1, 2, \ldots$, it is zero, but for $\varphi = 2\pi n$ it is equal to $-\infty$. These singularities are the ones that cancel $\langle A' \rangle$ when calculating the expectation value of eigenstates of $\hat{L}_z$. Conversely, in the initial calculation with $A = \varphi$ we have $\langle A' \rangle = 1$, and the inconsistency is produced.

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11.2 Radial Hamiltonian for Central Forces

We have seen that when the external force is central (or radial), the Hamiltonian commutes with $\widehat{\boldsymbol{L}}^2$ and with $\widehat{L}_z$, so that there are simultaneous eigenfunctions of these three operators. In this section we will find the general form of these eigenfunctions, which are of great theoretical importance.

In the spherical-coordinate system, the Laplacian operator is

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}. \tag{11.69}$$

Using Eq. (11.40), we can rewrite this operator in the form

$$\widehat{\boldsymbol{p}}^2 = -\hbar^2\nabla^2 = -\frac{\hbar^2}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\widehat{\boldsymbol{L}}^2. \tag{11.70}$$

This suggests writing

$$\widehat{\boldsymbol{p}}^2 = \widehat{p}_r^2 + \frac{\widehat{\boldsymbol{L}}^2}{r^2}, \tag{11.71}$$

where $\widehat{p}_r$ represents the *canonical momentum conjugate to* r. Since

$$\boldsymbol{r}\cdot\hat{\boldsymbol{p}} = -i\hbar r\frac{\partial}{\partial r}, \tag{11.72}$$

using (11.70), we can write the square of $\widehat{p}_r$ in the form

$$\widehat{p}_r^2 = -\frac{\hbar^2}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) = -\frac{\hbar^2}{r^2}\left[\left(r\frac{\partial}{\partial r}\right)\left(r\frac{\partial}{\partial r}\right) + r\frac{\partial}{\partial r}\right], \tag{11.73}$$

or alternatively,

$$\widehat{p}_r^2 = \frac{1}{r^2}[(\boldsymbol{r}\cdot\hat{\boldsymbol{p}})^2 - i\hbar(\boldsymbol{r}\cdot\hat{\boldsymbol{p}})]. \tag{11.74}$$

From this it follows that

$$\widehat{p}_r = \frac{1}{r}(\boldsymbol{r}\cdot\hat{\boldsymbol{p}} - i\hbar) = -i\hbar\left(\frac{\partial}{\partial r} + \frac{1}{r}\right). \tag{11.75}$$

This is the canonical conjugate momentum of the variable r (see Problem 11.7).

Exercise E11.2. Conjugate momentum of the radial variable *r*

Guided by the correspondence with the classical variable p_r, derive the correct quantum expression for the momentum operator conjugate to the variable r.

Solution. The canonical conjugate momentum of r in classical mechanics is $p_r = \frac{1}{r}\boldsymbol{p}\cdot\boldsymbol{r}$. Taking into account that $\hat{\boldsymbol{p}}$ and $\hat{\boldsymbol{r}}$ do not commute, we propose a linear combination of the form

$$\hat{p}_r = \lambda\widehat{\boldsymbol{p}}\cdot\frac{\widehat{\boldsymbol{r}}}{r} + (1-\lambda)\frac{\hat{\boldsymbol{r}}}{r}\cdot\widehat{\boldsymbol{p}}, \tag{11.76}$$

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with λ to be determined, to correspond to the preceding formula. It is easy to see that this $\hat{p}_r$ is Hermitian only for $\lambda = 1/2$, which gives the symmetric combination

$$\widehat{p}_r = \tfrac{1}{2}\left(\widehat{\boldsymbol{p}}\cdot\frac{\widehat{\boldsymbol{r}}}{r} + \frac{\widehat{\boldsymbol{r}}}{r}\cdot\widehat{\boldsymbol{p}}\right). \tag{11.77}$$

A little algebra using the basic commutator $\left[\hat{x}_i, \hat{p}_j\right] = i\hbar\delta_{ij}$ (or alternatively, Eq. (11.70)) shows that this expression is equivalent to the one given in (11.75). Since we want the eigenvalues of $\hat{p}_r$ to be real, the final result is unique.

11.2.1 The radial Schrödinger equation

Using Eq. (11.71), we can write the Hamiltonian for a central problem in the form

$$\widehat{H} = \frac{\widehat{p}_r^2}{2m} + \frac{\widehat{\boldsymbol{L}}^2}{2mr^2} + V(r). \tag{11.78}$$

Therefore, there are simultaneous eigenstates $|nlm\rangle$ of the Hamiltonian $\hat{H}$ (with principal quantum number n), $\widehat{\boldsymbol{L}}^2$ (with orbital angular-momentum quantum number l) and $\hat{L}_z$ (with magnetic quantum number m). Furthermore, since the angular dependence of the Hamiltonian is restricted to the term containing $\widehat{\boldsymbol{L}}^2$, the wave function $\psi_{nlm}(r,\theta,\varphi) \equiv \langle r\theta\varphi|nlm\rangle$, that is, the coordinate representation of the vector $|nlm\rangle$, can be factored as the product of a radial function $R_n(r)$ and the angular function, that is, the spherical harmonic $Y_l^m(\theta,\varphi)$. In fact, if we write

$$\psi_{nlm}(r,\theta,\varphi) = R_{nl}(r)Y_l^m(\theta,\varphi) \tag{11.79}$$

and substitute in the Schrödinger equation, using

$$\widehat{\boldsymbol{L}}^2 Y_l^m = \hbar^2 l(l+1)Y_l^m, \tag{11.80}$$

we get

$$\widehat{H}\psi = \left[\frac{\widehat{p}_r^2}{2m} + \frac{\hbar^2 l(l+1)}{2mr^2} + V(r)\right] R(r)Y_l^m = ER(r)Y_l^m. \tag{11.81}$$

Omitting the common factor Y_l^m, which is now irrelevant, this equation reduces to the *radial Schrödinger equation*,

$$\left[\frac{\widehat{p}_r^2}{2m} + \frac{\hbar^2 l(l+1)}{2mr^2} + V(r)\right] R(r) = ER(r). \tag{11.82}$$

Three observations are worth making. First, the factorization just done is independent of $V(r)$, so the spherical harmonics are the angular wave functions of *any* central problem. Second, the effective potential that appears in the radial equation is the sum of $V(r)$ and the term $\hbar^2 l(l+1)/2mr^2$, which represents the so-called *centrifugal barrier* that prevents the particles from approaching the potential-generating center (the nucleus of an atom, for example) without limit. This centrifugal repulsion is only canceled out when the angular momentum is zero. Finally, the eigenstates of $\widehat{H}$ are degenerate with respect to m, since the eigenvalues of the energy depend in general on l, but not on m, which does not appear in Eq. (11.82) This allowed us to write $R(r)$

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in the explicit form $R_{nl}(r)$ in Eq. (11.79). In the next chapter we will use the radial equation (11.82) to solve several important problems, including that of the H atom.

Exercise E11.3. Particle flow for a central-force problem

Show that if the particles move under the action of a central potential, in an energy and angular momentum eigenstate, the flow is purely equatorial.

Solution. In spherical coordinates, the components of the particle flow vector are (we write M for the particle mass)

$$j_r = \frac{i\hbar}{2M}\left(\psi\frac{\partial\psi^*}{\partial r} - \psi^*\frac{\partial\psi}{\partial r}\right), \qquad j_\theta = \frac{i\hbar}{2Mr}\left(\psi\frac{\partial\psi^*}{\partial\theta} - \psi^*\frac{\partial\psi}{\partial\theta}\right), \tag{11.83}$$

$$j_\varphi = \frac{i\hbar}{2Mrsin\theta}\left(\psi\frac{\partial\psi^*}{\partial\varphi} - \psi^*\frac{\partial\psi}{\partial\varphi}\right). \tag{11.84}$$

From Eqs. (11.79) and (11.45) it follows that the energy and angular momentum eigenfunction for a central problem can be written in the form

$$\psi = R(r)\Theta(\theta)e^{im\varphi}, \tag{11.85}$$

where $R(r)$ and $\Theta(\theta)$ are real; therefore, the only nonzero component of the flow is

$$j_\varphi = \frac{\hbar}{M}\frac{R^2(r)\Theta^2(\theta)}{r\sin\theta}m = \frac{\hbar}{M}\frac{\rho(r,\theta)}{r\sin\theta}m. \tag{11.86}$$

This result represents a net average circulation around the polar axis of the particles with angular momentum projection $\hbar m$.

Exercise E11.4. Schrödinger equation in curvilinear coordinates

According to Eqs. (11.73) and (11.75), the operator representing p_r is not simply $-i\hbar(\partial/\partial r)$, so that the contribution of the radial component to the energy is not simply $(-\hbar^2/2m)(\partial^2/\partial r^2)$. This shows that care must be taken when defining operators in curvilinear coordinates. Derive the Schrödinger equation in an arbitrary curvilinear coordinate system.

Solution. Consider the transition from the Cartesian coordinate system to an arbitrary curvilinear one $\{u_i\}$. Suppose that the coordinate transformation is $x_k = f_k(u_i)$; it follows that

$$\dot{x}_k = \sum_i \frac{\partial f_k}{\partial u_i}\dot{u}_i \tag{11.87}$$

and the kinetic energy becomes (various particles are considered, whose masses can be different)

$$T = \frac{1}{2}\sum_k m_k\dot{x}_k^2 = \frac{1}{2}\sum_{i,j,k} m_k\frac{\partial f_k}{\partial u_i}\frac{\partial f_k}{\partial u_j}\dot{u}_i\dot{u}_j = \frac{1}{2}\sum_{i,j} g_{ij}\dot{u}_i\dot{u}_j, \tag{11.88}$$

where the metric tensor of the transformation is given by $g_{ij}(u_k) = \sum_k m_k\frac{\partial f_k}{\partial u_i}\frac{\partial f_k}{\partial u_j}$.

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The coefficients of the velocities in the last expression of (11.88), which play the role of the effective masses, are now a function of the coordinates. If you want to quantize this expression, you have the problem of defining the order in which, for example, the powers of the u_i and the factor $\dot{u}_i$ in (11.87) should appear. The easiest way to proceed is to express the problem in Cartesian coordinates, quantize, and then return to the curvilinear coordinate system. To write the Schrödinger equation correctly, however, it is sufficient to write the kinetic energy precisely in the form (11.88), where the components of the metric tensor are given by the structure of the square of the line element in the new coordinate system,

$$ds^2 = \sum_{i,j} g_{ij} du_i du_j, \qquad T = \frac{1}{2} m \left(\frac{ds}{dt}\right)^2 = \frac{1}{2} \sum_{i,j} g_{ij} \dot{u}_i \dot{u}_j. \tag{11.89}$$

If g is the determinant of the matrix $g_{ij}(u_s)$, and the matrix inverse is $(g_{ij})^{-1} = g^{ij}$, then the Laplacian in the u_k coordinate system is (in any number of dimensions; if there are N equal particles, the sum goes up to $3N$)

$$\nabla^2 = \frac{1}{\sqrt{g}} \sum_{i,j} \frac{\partial}{\partial u_i} \left(\sqrt{g} g^{ij} \frac{\partial}{\partial u_j} \right). \tag{11.90}$$

This is precisely the method used earlier to write the Hamiltonian in spherical coordinates. In fact, in this case

$$ds^2 = dr^2 + r^2 d\theta^2 + r^2 sin^2\theta d\varphi^2 = \sum_{i,j} g_{ij} du_i du_j, \tag{11.91}$$

from which it follows that the matrix g of the metric tensor is diagonal, with elements

$$g_{11} = 1, \qquad g_{22} = r^2, \qquad g_{33} = r^2 sin^2\theta, \qquad g_{12} = g_{13} = g_{23} = 0, \tag{11.92}$$

and therefore

$$g^{11} = 1, \quad g^{22} = r^{-2}, \quad g^{33} = (r sin\theta)^{-2}, \quad g^{12} = g^{13} = g^{23} = 0, \quad g = r^4 sin^2\theta. \tag{11.93}$$

Substituting these values into the expression for the Laplacian leads directly to Eq. (11.69). The Schrödinger equation for particles of equal mass in the curvilinear u_k coordinate system is then

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{1}{\sqrt{g}} \sum_{i,j} \frac{\partial}{\partial u_i} \left(\sqrt{g} g^{ij} \frac{\partial}{\partial u_j} \right) \psi + V(u_i)\psi. \tag{11.94}$$

11.3 Matrix Representation of the Angular Momentum. The Pauli Matrices

So far we have concentrated on the study of the angular momentum associated with the *orbital* motion of particles. However, it is a fact that elementary particles (electron,

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proton, neutron, etc.) have, in addition to mass and charge, other properties associated with quantum numbers, among which the *spin* angular momentum stands out.

Particles in general can have an "internal" angular momentum and an associated quantum number. While the orbital angular momentum can only be an integer multiple of $\hbar$, the spin can be an integer or half-integer of $\hbar$. For example, electrons and nucleons (protons and neutrons) have spin $\hbar/2$, pions have spin 0, photons have spin $\hbar$, and so on. The coordinate representation we have used so far turns out to be too restrictive, since it excludes from the outset both the possibility of an intrinsic angular momentum and of half-integer values for it. The theory must therefore be generalized to include spin.

Following the preceding arguments, the total angular momentum $\widehat{\boldsymbol{J}}$ (which we will simply call angular momentum when there is no confusion) is generally defined as the sum of orbital and spinorial contributions,

$$\widehat{\boldsymbol{J}} = \widehat{\boldsymbol{L}} + \widehat{\boldsymbol{S}}. \tag{11.95}$$

The definition $\boldsymbol{r} \times \widehat{\boldsymbol{p}}$ only applies to the orbital part of $\widehat{\boldsymbol{J}}$, and the commutation properties of $\widehat{L}_i$ with $\widehat{L}_j$ and with $\widehat{\boldsymbol{L}}^2$ were obtained from the definition of $\widehat{\boldsymbol{L}}$. We will now use the fact that the commutation relations are independent of the representation. Therefore, we define the angular-momentum operator as the vector operator whose components satisfy the following commutation relations,

$$[J_i, \widehat{J}_j] = i\hbar\varepsilon_{ijk}\widehat{J}_k, \tag{11.96}$$

$$[\widehat{\boldsymbol{J}}^2, \widehat{J}_i] = 0. \qquad i = 1, 2, 3, \tag{11.97}$$

write a common eigenstate of $\widehat{\boldsymbol{J}}^2$ and $\widehat{J}_z$ – which, as we know from (11.96), is neither an eigenstate of $\hat{J}_x$ nor of $\widehat{J}_y$ – as $|jm\rangle$, and call j the (total) angular momentum quantum number and m, the quantum number corresponding to the z-projection of the angular momentum. The eigenvalue equations now take the form

$$\widehat{\boldsymbol{J}}^2|jm\rangle = \hbar^2\lambda|jm\rangle, \tag{11.98}$$

$$\widehat{J}_z|jm\rangle = \hbar m|jm\rangle, \tag{11.99}$$

where the eigenvalue λ will obviously be a function of j, which must reduce to $l(l+1)$ when $\widehat{\boldsymbol{J}}$ is reduced to $\widehat{\boldsymbol{L}}$ (i.e., when the spin is zero).

We now determine the possible values of j and m and construct a matrix representation of the angular-momentum operators in the basis $|jm\rangle$. The calculation is an excellent, simple example of the pure matrix methods of QM, in the style of those developed with the advent of matrix mechanics.

11.3.1 Matrix elements of angular-momentum components

The matrix elements of $\widehat{\boldsymbol{J}}^2$ and $\widehat{J}_z$ are immediately obtained, since according to (11.98) and (11.99), these matrices are diagonal,

$$\langle j'm'|\widehat{\boldsymbol{J}}^2|jm\rangle = \hbar^2\lambda\langle j'm'|jm\rangle = \hbar^2\lambda\delta_{jj'}\delta_{mm'}, \tag{11.100}$$

$$\langle j'm'|\widehat{J}_z|jm\rangle = \hbar m\langle j'm'|jm\rangle = \hbar m\delta_{jj'}\delta_{mm'}. \tag{11.101}$$

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To calculate the matrix elements of $\widehat{J}_x$ and $\widehat{J}_y$, it is useful to introduce the linear combinations $\widehat{J}_+$ and $\widehat{J}_-$, defined as follows,

$$\widehat{J}_\pm \equiv \tfrac{1}{\sqrt{2}}(\widehat{J}_x \pm i\widehat{J}_y). \tag{11.102}$$

These are known as raising and lowering operators, for reasons that will become clear in Section 3.2.

Since the $\widehat{J}_i$ are Hermitian, it follows that $\widehat{J}_+^\dagger = \widehat{J}_-$ and $\widehat{J}_-^\dagger = \widehat{J}_+$. Here we have another important example of very commonly used operators that are not Hermitian, but one is the adjoint of the other, as happened with the $\hat{a}^\dagger, \hat{a}$ operators of the HO. Using (11.96) and (11.97) it is possible to prove the following commutation properties

$$\left[\widehat{\boldsymbol{J}}^2, \widehat{J}_\pm\right] = 0, \tag{11.103}$$

$$\left[\widehat{J}_z, \widehat{J}_\pm\right] = \pm\hbar\widehat{J}_\pm, \tag{11.104}$$

$$\left[\widehat{J}_+, \widehat{J}_-\right] = \hbar\widehat{J}_z. \tag{11.105}$$

In addition, we have the identities

$$\widehat{J}_+\widehat{J}_- = \tfrac{1}{2}\left(\widehat{\boldsymbol{J}}^2 - \widehat{J}_z(\widehat{J}_z - \hbar)\right), \tag{11.106}$$

$$\widehat{J}_-\widehat{J}_+ = \tfrac{1}{2}\left(\widehat{\boldsymbol{J}}^2 - \widehat{J}_z(\widehat{J}_z + \hbar)\right). \tag{11.107}$$

Note that these two equations can be rewritten in the following useful form (keep them handy),

$$\widehat{\boldsymbol{J}}^2 = 2\widehat{J}_+\widehat{J}_- + \widehat{J}_z^2 - \hbar\widehat{J}_z, \tag{11.108}$$

$$\widehat{\boldsymbol{J}}^2 = 2\widehat{J}_-\widehat{J}_+ + \widehat{J}_z^2 + \hbar\widehat{J}_z. \tag{11.109}$$

The difference of these two expressions gives Eq. (11.105). From (11.98), (11.99), and (11.106), it follows that

$$\widehat{J}_+\widehat{J}_-|jm\rangle = \tfrac{1}{2}\hbar^2[\lambda - m(m-1)]|jm\rangle, \tag{11.110}$$

while (11.107) gives

$$\widehat{J}_-\widehat{J}_+|jm\rangle = \tfrac{1}{2}\hbar^2[\lambda - m(m+1)]|jm\rangle, \tag{11.111}$$

from which it follows that

$$\langle jm|\widehat{J}_+^\dagger\widehat{J}_+|jm\rangle = \langle jm|\widehat{J}_-\widehat{J}_+|jm\rangle = \tfrac{1}{2}\hbar^2[\lambda - m(m+1)] \geq 0$$

(the inequality follows from Eq. (8.43)), whence

$$\lambda - m(m+1) \geq 0. \tag{11.112}$$

Analogously, from (11.110) we obtain

$$\lambda - m(m-1) \geq 0. \tag{11.113}$$

Rewriting the first inequality in the form $\lambda \geq m(m+1)$ and adding 1/4 to both sides, we get

$$\lambda + \tfrac{1}{4} \geq m^2 + m + \tfrac{1}{4} = \left(m + \tfrac{1}{2}\right)^2. \tag{11.114}$$

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We now define a number j by the formula

$$j + \tfrac{1}{2} = \sqrt{\lambda + \tfrac{1}{4}}. \tag{11.115}$$

To investigate the meaning of j we get λ from this equation,

$$\lambda = \left(j + \tfrac{1}{2}\right)^2 - \tfrac{1}{4} = j(j+1), \tag{11.116}$$

which is just the generalization of Eq. (11.48) to the angular momentum j, so that we identify the parameter j in (11.115) with the quantum number j and the eigenvalues of $\boldsymbol{J}^2$ with $\hbar^2 j(j+1)$. Using (11.115), Eq. (11.114) becomes $\left(j + \frac{1}{2}\right)^2 \geq \left(m + \frac{1}{2}\right)^2$, that is,

$$j + \tfrac{1}{2} \geq |m + \tfrac{1}{2}|. \tag{11.117}$$

If $m \geq -\frac{1}{2}$, then $j \geq m$; if $m < -\frac{1}{2}$, then $m \geq -(j+1)$. Combining both results, we get

$$-j - 1 \leq m \leq j. \tag{11.118}$$

Analogously, (11.113) can be analyzed to conclude that

$$-j \leq m \leq j + 1. \tag{11.119}$$

Both expressions (11.118) and (11.119) must be satisfied, so that

$$-j \leq m \leq j. \tag{11.120}$$

Note that, as before, $m_{\max} = j \leq \sqrt{j(j+1)}$, so that the notion of precession must be extended to any angular momentum $j \neq 0$. Later we will determine the values that j and m can take.

We now turn to the construction of the matrix elements of $\widehat{J}_x$ and $\widehat{J}_y$. Since $\widehat{J}_+$ commutes with $\widehat{\boldsymbol{J}}^2$, every matrix element of $\left[\widehat{J}_+, \widehat{\boldsymbol{J}}^2\right]$ is zero, that is,

$$\langle j'm'|\widehat{\boldsymbol{J}}^2 J_+ - \widehat{J}_+ \widehat{\boldsymbol{J}}^2 |jm\rangle = \hbar^2(\lambda' - \lambda)\langle j'm'|\widehat{J}_+|jm\rangle = 0, \tag{11.121}$$

where $\lambda = j(j+1), \lambda' = j'(j'+1)$. An analogous result is obtained for $\widehat{J}_-$ by taking the adjoint of the previous expression. We conclude that if $j \neq j'$, the matrix elements of $\widehat{J}_+$ and $\widehat{J}_-$ are zero. Using (11.102) and (11.99) we can synthetically write

$$\langle j'm'|\widehat{J}_s|jm\rangle \sim \delta_{jj'}, \quad \text{for } s = x, y, z, +, -, \tag{11.122}$$

which tells us that all matrix elements of $\widehat{J}_s$ between states corresponding to different values of j are zero, as is the case with $\widehat{\boldsymbol{J}}^2$. Therefore, the Hilbert space of angular momentum is partitioned into rotation-invariant orthogonal subspaces, each with a well-defined value of j. The fact that the subspaces of a given j are invariant with respect to rotation means that when a rotation is performed, only the vectors belonging to one such subspace are mixed with each other. Therefore, in the following we will consider matrix elements between states with the same j; only the projections m, m' may be different.

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Using the commutator between $\widehat{J}_z$ and $\widehat{J}_+$, (11.104), we now write $\hbar\langle jm'|\widehat{J}_+|jm\rangle = \langle jm'|\widehat{J}_z\widehat{J}_+ - \widehat{J}_+\widehat{J}_z|jm\rangle = \hbar(m'-m)\langle jm'|\widehat{J}_+|jm\rangle$, that is, $(m'-m-1)\langle jm'|\widehat{J}_+|jm\rangle = 0$. The general solution of this equation is

$$\langle jm'|\widehat{J}_+|jm\rangle = \hbar C_{jm}\delta_{m',m+1}, \tag{11.123}$$

where the coefficient C_{jm} remains to be determined. Taking the adjoint we get

$$\langle jm|\widehat{J}_-|jm'\rangle = \hbar C^*_{jm}\delta_{m',m+1}, \tag{11.124}$$

or, interchanging the indices m and m',

$$\langle jm'|\widehat{J}_-|jm\rangle = \hbar C^*_{jm-1}\delta_{m'+1,m}. \tag{11.125}$$

To determine C_{jm} we turn to the matrix element of $\widehat{J}_-\widehat{J}_+$, obtained from (11.111) with λ given by (11.116). Inserting an expansion of the unit in terms of the projectors $|jm'\rangle\langle jm'|$, and using (11.123) and (11.124), we obtain

$$\begin{aligned}\langle jm|\widehat{J}_-\widehat{J}_+|jm\rangle &= \tfrac{1}{2}\hbar^2[j(j+1)-m(m+1)]\\ &= \sum_{j'm'}\langle jm|\widehat{J}_-|j'm'\rangle\langle j'm'|\widehat{J}_+|jm\rangle = \sum_{m'}\langle jm|\widehat{J}_-|jm'\rangle\langle jm'|\widehat{J}_+|jm\rangle\\ &= \hbar^2\sum_{m'}C^*_{jm}\delta_{m',m+1}C_{jm}\delta_{m',m+1} = \hbar^2|C_{jm}|^2,\end{aligned} \tag{11.126}$$

that is,

$$\begin{aligned}|C_{jm}|^2 &= \tfrac{1}{2}[j(j+1)-m(m+1)]\\ &= \tfrac{1}{2}[j(j+1)+jm-m(m+1)-mj] = \tfrac{1}{2}(j+m+1)(j-m).\end{aligned} \tag{11.127}$$

The phase is not determined by the above relations, so it is chosen arbitrarily; the most common convention, which we will adopt here, is to take C_{jm} to be real and positive, that is,

$$C_{jm} = \sqrt{\tfrac{1}{2}(j+m+1)(j-m)}. \tag{11.128}$$

Substitution of this value in (11.123) and (11.125) gives the full matrix elements of $\widehat{J}_+$ and $\widehat{J}_-$,

$$\begin{aligned}\langle j,m+1|\widehat{J}_+|j,m\rangle &= \hbar\sqrt{\tfrac{1}{2}(j+m+1)(j-m)},\\ &= \hbar\sqrt{\tfrac{1}{2}\big[(j+1)j-(m+1)m\big]},\end{aligned} \tag{11.129}$$

$$\begin{aligned}\langle j,m-1|\widehat{J}_-|j,m\rangle &= \hbar\sqrt{\tfrac{1}{2}(j+m)(j-m+1)},\\ &= \hbar\sqrt{\tfrac{1}{2}\big[(j+1)j-(m-1)m\big]}.\end{aligned} \tag{11.130}$$

All other matrix elements of these operators are zero. From (11.129) and the definitions of $\widehat{J}_+$ and $\widehat{J}_-$, (11.102), we get the nonzero matrix elements of $\widehat{J}_x$ and $\widehat{J}_y$. Collecting results,

$$\langle j,m\pm1|\widehat{J}_x|j,m\rangle = \tfrac{1}{2}\hbar\sqrt{(j\mp m)(j\pm m+1)}, \tag{11.131}$$

$$\langle j,m\pm1|\widehat{J}_y|j,m\rangle = \mp i\tfrac{1}{2}\hbar\sqrt{(j\mp m)(j\pm m+1)}, \tag{11.132}$$

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$$\langle jm'|\widehat{J}_z|jm\rangle = \hbar m\delta_{mm'}, \tag{11.133}$$

$$\langle jm'|\widehat{\mathbf{J}}^2|jm\rangle = \hbar^2 j(j+1)\delta_{mm'}. \tag{11.134}$$

This completes the construction of the matrix representation of the angular-momentum operators.

11.3.2 Angular-momentum raising and lowering operators

We now show that the $\widehat{J}_\pm$ are raising and lowering operators acting on m, which in turn allows us to determine the possible values of j and m. To do this, we express the effect of $\widehat{J}_+$ on $|jm\rangle$ in the general form

$$\widehat{J}_+|jm\rangle = \sum_{m'} B_{jm'}|jm'\rangle. \tag{11.135}$$

From this and (11.123) it follows that

$$\langle jm''|\widehat{J}_+|jm\rangle = \sum_{m'} B_{jm'}\delta_{m'm''} = B_{jm''} = \hbar C_{jm}\delta_{m'',m+1}. \tag{11.136}$$

Substituting into the previous expression the value of the coefficients $B_{jm'}$ just obtained, we get

$$\widehat{J}_+|jm\rangle = \sum_{m'} \hbar C_{jm}\delta_{m',m+1}|jm'\rangle,$$

$$\widehat{J}_+|jm\rangle = \hbar C_{jm}|j,m+1\rangle, \tag{11.137}$$

so that the operator $\widehat{J}_+$ effectively increases the value of the projection m by one. Similarly, we can see that $\widehat{J}_-$ decreases the value of m by one,

$$\widehat{J}_-|jm\rangle = \hbar C_{j,m-1}|j,m-1\rangle. \tag{11.138}$$

The states with different m can be generated from the state with the minimum m (which is $-j$) by repeated application of the raising operator. Since each application of $\widehat{J}_+$ increases the value of m by one, m can only vary in unit steps, taking the values $-j, -j+1, -j+2, \ldots, j-1, j$. The number of steps needed to cover all possible values of m, from $m = -j$ to $m = j$, is $2j$, and we get

$$\widehat{J}_+|j,-j\rangle = \hbar C_{j,-j}|j,-j+1\rangle,$$
$$\left(\widehat{J}_+\right)^2|j,-j\rangle = \hbar^2 C_{j,-j}C_{j,-j+1}|j,-j+2\rangle,$$
$$\ldots$$
$$\left(\widehat{J}_+\right)^{2j}|j,-j\rangle = \hbar^{2j} C_{j,-j}C_{j,-j+1}\ldots C_{j,j}|jj\rangle. \tag{11.139}$$

Since the total number of steps is an integer, j can take integer values $0, 1, 2, \ldots$ or half-integer values $1/2, 3/2, \ldots$ In this way, we verify that the theory covers all the cases of interest, allowing both the integer orbital momentum and the integer or half-integer spinor momentum to be taken into account. We have thus fully determined the angular-momentum operators and their eigenvalues.

For a given j, the matrices must contain the $2j+1$ possible values of m from $-j$ to $+j$ in unit steps, so they must be square matrices with $2j+1$ rows and columns. The

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corresponding $2j+1$ basis vectors, $|j,-j\rangle, |j,-j+1\rangle, \ldots, |j,\, j-1\rangle, |j,\, j\rangle$, can be selected as

$$|j,j\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \\ \vdots \end{pmatrix}; \quad |j,j-1\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \\ \vdots \end{pmatrix}; \quad |j,j-2\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \\ \vdots \end{pmatrix}, \quad \text{and so on.} \tag{11.140}$$

The matrices $\widehat{J}_z$ and $\widehat{\boldsymbol{J}}^2$ take the diagonal form

$$\widehat{J}_z = \hbar \begin{pmatrix} j & 0 & 0 & \cdots \\ 0 & j-1 & 0 & \cdots \\ \vdots & \vdots & \ddots & \cdots \\ 0 & 0 & 0 & -j \end{pmatrix}, \quad \widehat{\boldsymbol{J}}^2 = \hbar^2 j(j+1) \begin{pmatrix} 1 & 0 & 0 & \cdots \\ 0 & 1 & 0 & \cdots \\ 0 & 0 & 1 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}, \tag{11.141}$$

while the matrices representing $\widehat{J}_x$ and $\widehat{J}_y$ have their nonzero elements shifted by one unit to either side of the main diagonal. If we denote the nonzero elements schematically by C_s, the structure of $\widehat{J}_x$, for example, is

$$\widehat{J}_x = \frac{\hbar}{2} \begin{pmatrix} 0 & C_a & 0 & 0 & \cdots \\ C_a & 0 & C_b & 0 & \cdots \\ 0 & C_b & 0 & C_c & \cdots \\ 0 & 0 & C_c & 0 & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix} \tag{11.142}$$

and similarly for $\widehat{J}_y$, but with imaginary elements.

11.3.3 The spin angular momentum 1/2: Pauli matrices

We will use the above results to construct the angular-momentum operators for spin 1/2. The results obtained here will be fundamental for studying important problems in which the electron spin in particular plays a relevant role, but they also apply to other particles with spin 1/2.

To study spin 1/2, we take $l=0$ and $\widehat{\boldsymbol{J}} = \widehat{\boldsymbol{S}}$, with $j = s = 1/2$. The projection m can only take the values $m = \pm 1/2$ so the spinor space is two-dimensional. In the matrix representation the basis vectors are

$$|+\rangle \equiv |\tfrac{1}{2}, \tfrac{1}{2}\rangle \to \begin{pmatrix} 1 \\ 0 \end{pmatrix}; \quad |-\rangle \equiv |\tfrac{1}{2}, -\tfrac{1}{2}\rangle \to \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \tag{11.143}$$

Thus, the wave function of an electron (or any particle with spin 1/2), called a spinor, has two components, each corresponding to one of the possible projections of the spin in spin space.

The general state consists of a superposition of states ψ_+ with spin up $|+\rangle$ and states ψ_- with spin down $|-\rangle$, which we write as

$$|\psi\rangle = \psi_+|+\rangle + \psi_-|-\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}\psi_+ + \begin{pmatrix} 0 \\ 1 \end{pmatrix}\psi_- = \begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix}. \tag{11.144}$$

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By taking another spinor $|\varphi\rangle$ with components φ_+ and φ_-, we can construct the scalar product (the result is a pseudo-scalar, not a scalar)

$$\langle\varphi|\psi\rangle = \begin{pmatrix} \varphi_+^* & \varphi_-^* \end{pmatrix} \begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix} = \varphi_+^*\psi_+ + \varphi_-^*\psi_-. \tag{11.145}$$

In particular, with $\psi = \varphi$ we get

$$\langle\psi|\psi\rangle = |\psi_+|^2 + |\psi_-|^2 = \rho_+ + \rho_-. \tag{11.146}$$

Suppose that ψ_+, ψ_- are in the coordinate representation; then the particle density in the configuration space is given by the sum of the densities corresponding to spin up and spin down, with no interference between them. Note that $\langle\psi|\psi\rangle$ is a scalar in spin space, but *not* necessarily the square of the norm; it is the density associated with ψ, since the vectors in this section refer exclusively to spin space, and their coefficients are wave functions in other spaces, such as $\psi_\pm = \psi_\pm(\boldsymbol{x}, t)$.

According to Eqs. (11.141) and (11.142), the matrices $\hat{S}_x$, $\hat{S}_y$ and $\hat{S}_z$ have the form

$$\hat{S}_x = \tfrac{1}{2}\hbar\begin{pmatrix} 0 & C_1 \\ C_1 & 0 \end{pmatrix}, \quad \hat{S}_y = \tfrac{1}{2}\hbar\begin{pmatrix} 0 & iC_2 \\ -iC_2 & 0 \end{pmatrix}, \quad \hat{S}_z = \tfrac{1}{2}\hbar\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \tag{11.147}$$

with the coefficients C_1, C_2 obtained from Eqs. (11.131) and (11.132). For example, if C_1 corresponds to $m = -1/2$ (upper sign in Eq. (11.131)), then $C_1 = 1$. Completing the calculations gives

$$\hat{S}_x = \tfrac{1}{2}\hbar\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{S}_y = \tfrac{1}{2}\hbar\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \hat{S}_z = \tfrac{1}{2}\hbar\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{11.148}$$

It is usual to write these results in terms of the Hermitian *Pauli matrices* $\hat{\sigma}_i$, which were introduced in Section 3.7, that is,

$$\hat{\boldsymbol{S}} = \tfrac{1}{2}\hbar\hat{\boldsymbol{\sigma}}, \tag{11.149}$$

where

$$\hat{\sigma}_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \hat{\sigma}_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \hat{\sigma}_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{11.150}$$

These matrices together with the identity matrix form a complete set of linearly independent 2×2 operators in the 2D Hilbert space, and any operator in this space can be written as a linear combination of them. Using (11.148) and (11.150) in combination with the fundamental commutation rules of angular-momentum operators (11.96), we obtain the commutation rules

$$\left[\hat{\sigma}_i, \hat{\sigma}_j\right] = 2i\varepsilon_{ijk}\hat{\sigma}_k. \tag{11.151}$$

Furthermore, from the definition (11.96) we can immediately verify that the square of each Pauli matrix is the unit,

$$\hat{\sigma}_i^2 = \mathbb{I}. \tag{11.152}$$

These two properties can be summarized in the following expression, which is *specific* of Pauli matrices,

$$\hat{\sigma}_i\hat{\sigma}_j = \mathbb{I}\delta_{ij} + i\varepsilon_{ijk}\hat{\sigma}_k. \tag{11.153}$$

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The raising and lowering operators for spin $\frac{1}{2}$ are

$$\widehat{\sigma}_+ = \tfrac{1}{\sqrt{2}}\left(\hat{\sigma}_1 + i\hat{\sigma}_2\right) = \sqrt{2}\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \quad \widehat{\sigma}_- = \sqrt{2}\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}, \tag{11.154}$$

and the projection operators are

$$\hat{P}^+ = |+\rangle\langle+| = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}, \quad \hat{P}^- = |-\rangle\langle-| = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}. \tag{11.155}$$

For further properties of Pauli matrices, see Section 3.7 and Exercise E4.7.

For reference, the angular momentum matrices for $j = 1$ are (see Problem 11.10):

$$\hat{J}_x = \frac{\hbar}{\sqrt{2}}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \; \hat{J}_y = \frac{\hbar}{\sqrt{2}}\begin{pmatrix} 0 & -i & 0 \\ i & 0 & -i \\ 0 & i & 0 \end{pmatrix}, \; \hat{J}_z = \hbar\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}. \tag{11.156}$$

In the coordinate representation, the three angular components of the wave function for $l = 1$, corresponding to $m = 1, 0, -1$, are the spherical harmonics Y_1^1, Y_1^0 and Y_1^{-1}, respectively.

11.4 Addition of Two Angular Momenta

There are quantum systems whose components can eventually stop interacting. For example, an atomic electron can be removed by a photon, or an atomic nucleus can decay into different parts that no longer interact, and so on. In some cases the elements into which the system is split do not even have an existence of their own before the decay, but are created during the very process that produces the decay; this happens, for example, when photons in an external field give rise to an electron–positron pair.

Here we study the case where the quantum system can be considered to be effectively composed of parts, each of which has a well-defined angular momentum. An example would be an atom composed of electrons and the nucleus. We then ask for the possible values of the angular momentum of the whole system. It is clear that we can pose the problem in the reverse sense: given the angular-momentum state of the composite system, we ask about the possible angular momentum states of its constituent parts. Due to the mathematical complexity of the problem, we will restrict ourselves to the case of only two parts; the analysis of systems with three or more constituents can be found in the literature.

From a physical point of view, the problem is interesting for several reasons. To get a qualitative idea of the situation, we note that the results of the previous section are general, that is, they apply to any quantum system, simple or complex. In particular, this means that the angular momenta of both the parts and the whole are constrained to be integers or half-integers. When two arbitrary angular momenta $\widehat{\boldsymbol{J}}_1$ and $\widehat{\boldsymbol{J}}_2$ are coupled, the resulting angular momentum $\widehat{\boldsymbol{J}} = \widehat{\boldsymbol{J}}_1 + \widehat{\boldsymbol{J}}_2$ must be an integer or half-integer. This indicates the existence of strong "interaction" phenomena between the different angular momenta of the system, so that the eigenstates that finally emerge as

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the product of all the interactions obey laws as singular as that of the spatial quantization of the angular momenta (total or partial). For example, we will see that in the stationary state of an atomic system, two electrons are coupled in such a way that their total spin is only 0 or 1. From the mathematical point of view, the problem of the coupling of two angular momenta J_1 and J_2 corresponds to the construction of the Hilbert-space product $\mathcal{H}_{J_1} \otimes \mathcal{H}_{J_2}$ and its decomposition into rotation-invariant subspaces.

11.4.1 Clebsch–Gordan coefficients

Our purpose is to express the eigenstates of the total angular momentum in terms of the eigenstates of its components. First, we note that the angular-momentum operators of each particle operate on different variables – that is, they act in different spaces – so they commute with each other,

$$[\widehat{J}_{1k}, \widehat{J}_{2l}] = 0 \quad (k, l = 1, 2, 3, +, -). \tag{11.157}$$

For the rest, the commutation properties of $\widehat{J}_{1i}$ and $\widehat{J}_{2i}$ are the usual ones, Eqs. (11.96) and (11.97). We will consider that each subsystem is in an angular-momentum eigenstate, with eigenvalues (j_1, m_1) and (j_2, m_2), respectively. Thus,

$$\widehat{\boldsymbol{J}}_i^2 |j_i m_i\rangle = \hbar^2 j_i(j_i + 1)|j_i m_i\rangle, \quad i = 1, 2. \tag{11.158}$$

The angular-momentum operator of the system is

$$\widehat{\boldsymbol{J}} = \widehat{\boldsymbol{J}}_1 + \widehat{\boldsymbol{J}}_2, \tag{11.159}$$

with projection on the z-axis given by

$$\widehat{J}_z = \widehat{J}_{1z} + \widehat{J}_{2z}, \tag{11.160}$$

and square angular momentum

$$\widehat{\boldsymbol{J}}^2 = \widehat{\boldsymbol{J}}_1^2 + \widehat{\boldsymbol{J}}_2^2 + 2\widehat{\boldsymbol{J}}_1 \cdot \widehat{\boldsymbol{J}}_2. \tag{11.161}$$

Since $\widehat{J}_z$ commutes with $\widehat{\boldsymbol{J}}_1^2$ and with $\widehat{\boldsymbol{J}}_2^2$, there are simultaneous eigenfunctions of the four operators $\widehat{\boldsymbol{J}}_1^2, \widehat{\boldsymbol{J}}_2^2, \widehat{\boldsymbol{J}}^2, \widehat{J}_z$. To construct them we proceed as follows. We call $|j_1 j_2 j m\rangle$ the state vector with the quantum numbers j_1, j_2, j, m corresponding to well-defined values of $\widehat{\boldsymbol{J}}_1^2, \widehat{\boldsymbol{J}}_2^2, \widehat{\boldsymbol{J}}^2, \widehat{J}_z$, respectively. We can then write, introducing an expansion in terms of the basis $|j_1 m_1\rangle|j_2 m_2\rangle$ for given j_1 and j_2 (remember that $|j_1 m_1\rangle$ and $|j_2 m_2\rangle$ are vectors in different spaces),

$$\begin{aligned} |j_1 j_2 j m\rangle &= \sum_{m_1 m_2} |j_1 m_1\rangle|j_2 m_2\rangle\langle j_1 m_1|\langle j_2 m_2|j_1 j_2 j m\rangle \\ &= \sum_{m_1 m_2} (j_1 j_2 m_1 m_2|j m)|j_1 m_1\rangle|j_2 m_2\rangle. \end{aligned} \tag{11.162}$$

The coefficients of the expansion

$$(j_1 j_2 m_1 m_2|j m) \equiv \langle j_1 m_1|\,\langle j_2 m_2|\,j_1 j_2 j m\rangle \tag{11.163}$$

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are called *Clebsch–Gordan coefficients*[5] (hereafter C-G coefficients).[6] These coefficients are the elements of a unitary matrix that transforms the representation in which the angular momentum of each subsystem and its z-component are fixed, into another in which the angular momentum of the composite system and its projection m are fixed.

Because of (11.160), the addition over m_1 and m_2 in the preceding expression can only be performed over the values that satisfy the condition

$$m = m_1 + m_2. \tag{11.165}$$

To determine the values of j that can be realized with the given values of j_1 and j_2, first note that the maximum possible m is

$$m_{\max} = (m_1 + m_2)_{\max} = j_1 + j_2, \tag{11.166}$$

which is only realized with the state $|j_1, j_1\rangle|j_2, j_2\rangle$ and corresponds to $j = j_1 + j_2$ with $m = j$. The next value of m,

$$m_{\max} - 1 = j_1 + j_2 - 1, \tag{11.167}$$

can be obtained with the states $|j_1,\ j_1 - 1\rangle|j_2, j_2\rangle$ and $|j_1, j_1\rangle|j_2,\ j_2 - 1\rangle$, whose linear combinations allow us to construct states with $j = j_1 + j_2$ and with $j = j_1 + j_2 - 1$; we conclude that this last value of j is also realized. Repeating this procedure, we can continue to reduce the value of j, while maintaining the possibility of constructing states with the given basis, until we reach the value $j = |j_1 - j_2|$, after which it is not possible to continue. Therefore, the possible values of j generated by the pair j_1, j_2 are the integers or semi-integers that differ by unit steps and satisfy the triangle relation,

$$|j_1 - j_2| \leq j \leq j_1 + j_2. \tag{11.168}$$

11.4.1.1 Some properties of the C–G coefficients

The usual phase convention is

$$\langle j_1, j_2, j_1, j - j_1 | jj \rangle \quad \text{real and positive.} \tag{11.169}$$

With this convention, all C-G coefficients are real, so the transformation matrix is not only unitary but also orthogonal ($U^T = U^{-1}$). The orthogonality condition implies the two equalities

$$\sum_{jm} (j_1 j_2 m_1 m_2 | jm)(j_1 j_2 m_1' m_2' | jm) = \delta_{m_1 m_1'} \delta_{m_2 m_2'} \tag{11.170}$$

$$\sum_{m_1 m_2} (j_1 j_2 m_1 m_2 | jm)(j_1 j_2 m_1 m_2 | j' m') = \delta_{jj'} \delta_{mm'}. \tag{11.171}$$

[5] Alfred Clebsch (1833–1872) was a Prussian mathematician; Paul Gordan (1837–1912) was a German mathematician, Emmy Noether's doctoral supervisor.

[6] These coefficients have different names in the literature; they are also called also Wigner coefficients or simply vector addition coefficients. Sometimes the definitions are slightly modified and, more often, the conventions regarding their arbitrary phases are changed. Certain coefficients proportional to C-G are often used because they are more symmetric; these are the *3-j symbols*, defined as

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \frac{(-1)^{j_1 - j_2 - m_3}}{(2j_3 + 1)^{1/2}} (j_1 j_2 m_1 m_2 | j_3, -m_3). \tag{11.164}$$

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Using these properties, we can invert (11.162) to obtain

$$|j_1 m_1\rangle|j_2 m_2\rangle = \sum_{j,m} (j_1 j_2 m_1 m_2|jm)|j_1 j_2 jm\rangle. \tag{11.172}$$

It is possible, although tedious, to determine the C-G coefficients using general procedures. For example, from the expression whose validity is directly derived from (11.162),

$$\widehat{J}_\pm|j_1 j_2 jm\rangle = \sum_{m_1 m_2} (j_1 j_2 m_1 m_2|jm)(\widehat{J}_{1\pm} + \widehat{J}_{2\pm})|j_1 m_1\rangle|j_2 m_2\rangle, \tag{11.173}$$

one obtains with the help of Eqs. (11.137), (11.138) and (11.172)

$$\begin{aligned}\sqrt{(j \pm m + 1)(j \mp m)}(j_1 j_2 m_1 m_2|j, m \pm 1) \\ = \sqrt{(j_1 \mp m_1 + 1)(j_1 \pm m_1)}(j_1 j_2, m_1 \pm 1, m_2|jm) \\ + \sqrt{(j_2 \mp m_2 + 1)(j_2 \pm m_2)}(j_1, j_2, m_1, m_2 \pm 1|jm).\end{aligned} \tag{11.174}$$

For $m = j$ and the upper sign, the left side vanishes, which gives a series of relations between the coefficients $(j_1 j_2 m_1 m_2|jj)$. Using the coefficient given in (11.169) as a reference, all the others are obtained from these relations and are in fact real. If we now take the lower sign, we obtain successively the coefficients for $m = j - 1$, $j - 2$, and so on. This method was used by G. Racah[7] to obtain an explicit expression for the C-G coefficients, which is extremely complicated, so we will omit it. Note that Eq. (11.174) is sufficient to obtain all the C-G coefficients. Its detailed derivation and use can be studied in one of the specialized texts (references at the end of the chapter).

11.4.1.2 Calculation of some C-G coefficients

With the twofold purpose of gaining some experience with the algebra involved – without going into its computational difficulties – and of obtaining results that will be very useful to us later, we will calculate the coupling coefficients for two angular momenta 1/2 from first principles (in particular we will not use equations like (11.174)).

As follows from the triangle relation (11.168), if $j_1 = j_2 = \frac{1}{2}$ the possible values of j are 0 and 1 (antiparallel and parallel spins, respectively), giving rise to four states that are grouped naturally into a singlet with $j = 0$ and $m = 0$, and a triplet with $j = 1$ and $m = 1, 0, -1$.[8] These are the invariant subspaces of dimensions 1 and 3 respectively of the product space $2 \otimes 2 = 3 \oplus 1$.[9] The three states belonging to $j = 1$ are symmetric with respect to the exchange of particles 1 and 2, Eqs. (11.175, 11.177, 11.181), while the (singlet) state belonging to $j = 0$ is antisymmetric, Eq. (11.182). Since rotation does not change these symmetry properties, the decomposition $3 \oplus 1$ yields rotation-invariant subspaces; in other words, the components of the triplet mix with each other under rotation, but not with that of the singlet and vice versa.

[7] Giulio Racah (1909–1965) was an Italian–Israeli physicist and mathematician.

[8] The terms singlet and triplet have a spectroscopic origin: while the singlet state gives rise to a single spectral line, the triplet state gives rise to a triplet splitting of the spectral lines when the system is subjected to a magnetic field.

[9] The notation used refers to summation and multiplication, respectively, in Hilbert space.

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We will denote the vectors of the composite states as $|c;jm\rangle \equiv |j_1 j_2 jm\rangle$, where the c reminds us of the composite system; when there is no danger of confusion, we will omit the c. Let us first analyze the triplet. The state $|jm\rangle = |11\rangle$ can only be obtained with the values $m_1 = m_2 = \frac{1}{2}$, so we have (in products of kets, the first ket refers to particle 1 and the second to particle 2)

$$|11\rangle = |+\rangle|+\rangle. \tag{11.175}$$

In more explicit notation we would write this equation in the form

$$|c;11\rangle = \left|\tfrac{1}{2}\tfrac{1}{2}11\right\rangle = \left|\tfrac{1}{2}\tfrac{1}{2}\right\rangle\left|\tfrac{1}{2}\tfrac{1}{2}\right\rangle. \tag{11.176}$$

Similarly, the state with $j = 1, m = -1$ can only be obtained from the projections $-\frac{1}{2}$ of j_1 and j_2,

$$|1\,,-1\rangle = |-\rangle|-\rangle. \tag{11.177}$$

The remaining state of the triplet, $|10\rangle$, has two components, the states with $m_1 = \frac{1}{2}$, $m_2 = -\frac{1}{2}$, and with $m_1 = -\frac{1}{2}$, $m_2 = \frac{1}{2}$. We can obtain it by applying $J_- \equiv \widehat{J}_{1-} + \widehat{J}_{2-}$ to $|11\rangle$ or $\widehat{J}_+ \equiv \widehat{J}_{1+} + \widehat{J}_{2+}$ to $|1,-1\rangle$. For example,

$$\widehat{J}_+|1\,,-1\rangle = C_{1,-1}|10\rangle = \left(\widehat{J}_{1+} + \widehat{J}_{2+}\right)|-\rangle|-\rangle = \left(\widehat{J}_{1+}|-\rangle\right)|-\rangle + |-\rangle\left(\widehat{J}_{2+}|-\rangle\right). \tag{11.178}$$

Using (11.137) we get

$$C_{1,-1}|10\rangle = C_{\frac{1}{2},-\frac{1}{2}}|+\rangle|-\rangle + C_{\frac{1}{2},-\frac{1}{2}}|-\rangle|+\rangle. \tag{11.179}$$

We calculate the coefficients using (11.128),

$$\frac{C_{\frac{1}{2},-\frac{1}{2}}}{C_{1,-1}} = \sqrt{\frac{\left(\frac{1}{2}-\frac{1}{2}+1\right)\left(\frac{1}{2}+\frac{1}{2}\right)}{(1-1+1)(1+1)}} = \frac{1}{\sqrt{2}}, \tag{11.180}$$

and finally we get

$$|10\rangle = \frac{1}{\sqrt{2}}\Big(|+\rangle|-\rangle + |-\rangle|+\rangle\Big). \tag{11.181}$$

To construct the singlet state $|00\rangle$, we note that it is a linear combination of the same states that make up $|10\rangle$, and that it must be orthogonal to the latter. It is a simple exercise to show that

$$|00\rangle = \frac{1}{\sqrt{2}}\Big(|+\rangle|-\rangle - |-\rangle|+\rangle\Big). \tag{11.182}$$

With this, all coupling coefficients for $j_1 = j_2 = \frac{1}{2}$ have been determined. Later, when we deal with two-electron problems (such as the He atom, or Bell states), we will have the opportunity to use these important results.

We will solve a second example that generalizes the previous one and gives us results that will also be used later. This is the coupling between an arbitrary angular momentum j_1 and the spin angular momentum $j_2 = s = 1/2$. The calculation is greatly simplified by using the following equality, which can be derived from the given definitions,

$$\widehat{\boldsymbol{J}}^2 = (\widehat{\boldsymbol{J}}_1 + \widehat{\boldsymbol{S}})^2 = \widehat{\boldsymbol{J}}_1^2 + \hat{\boldsymbol{S}}^2 + 2\widehat{J}_{1z}\widehat{S}_z + 2\widehat{J}_{1+}\widehat{S}_- + 2\widehat{J}_{1-}\widehat{S}_+. \tag{11.183}$$

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Note that this equality contains the following,

$$\widehat{\boldsymbol{J}}_1 \cdot \widehat{\boldsymbol{S}} = \widehat{J}_{1z}\widehat{S}_z + \widehat{J}_{1+}\widehat{S}_- + \widehat{J}_{1-}\widehat{S}_+. \tag{11.184}$$

More generally, for two arbitrary angular momenta $\widehat{\boldsymbol{J}}_1$ and $\widehat{\boldsymbol{J}}_2$,

$$\widehat{\boldsymbol{J}}_1 \cdot \widehat{\boldsymbol{J}}_2 = \widehat{J}_{1z}\widehat{J}_{2z} + \widehat{J}_{1+}\widehat{J}_{2-} + \widehat{J}_{1-}\widehat{J}_{2+}. \tag{11.185}$$

These expressions are very useful in practice and should be kept in mind when performing calculations involving two angular momenta.

Returning to the previous problem, we suggest writing

$$|c; j,\, m_1 + \tfrac{1}{2}\rangle = a|j_1, m_1\rangle|+\rangle + b|j_1,\, m_1 + 1\rangle|-\rangle, \tag{11.186}$$

and a similar relationship for composite states with $m = m_1 - \frac{1}{2}$. The possible values of j are $j_1 + \frac{1}{2}$ and $j_1 - \frac{1}{2}$, according to the triangle law. We now apply the operator $\hat{\boldsymbol{J}}^2$ written in the form (11.183) to the last expression, to obtain, using $\langle \hat{\boldsymbol{J}}^2 \rangle = \hbar^2 S(S+1) = \hbar^2 \frac{1}{2}(\frac{3}{2}) = \frac{3}{4}\hbar^2$,

$$\begin{aligned}
\hat{\boldsymbol{J}}^2 |j,\, m_1 + \tfrac{1}{2}\rangle &= \hbar^2 j(j+1) \left| j\,, m_1 + \tfrac{1}{2} \right\rangle \\
&= \hbar^2 j(j+1) \Big[a|j_1, m_1\rangle|+\rangle + b|j_1,\, m_1 + 1\rangle|-\rangle \Big] \\
&= \hbar^2 a \Big[\Big(j_1(j_1+1) + \tfrac{3}{4} + 2m_1 \cdot \tfrac{1}{2} \Big) |j_1 m_1\rangle|+\rangle \\
&\quad + 2C_{j_1 m_1} C_{\frac{1}{2},-\frac{1}{2}} |j_1, m_1 + 1\rangle|-\rangle \Big] \\
&\quad + \hbar^2 b \Big[\Big(j_1(j_1+1) + \tfrac{3}{4} + 2(m_1+1)(-\tfrac{1}{2}) \Big) |j_1,\, m_1 + 1\rangle|-\rangle \\
&\quad + 2C_{j_1 m_1} C_{\frac{1}{2},-\frac{1}{2}} |j_1\, m_1\rangle|+\rangle \Big].
\end{aligned} \tag{11.187}$$

We regroup the terms containing $|j_1 m_1\rangle|+\rangle$ and those containing $|j_1 m_1 + 1\rangle|-\rangle$, which must be cancelled separately. This condition leads to the system of equations

$$\Big[j(j+1) - j_1(j_1+1) - \tfrac{3}{4} - m_1 \Big] a - 2C_{\frac{1}{2},-\frac{1}{2}} C_{j_1 m_1} b = 0, \tag{11.188}$$

$$-2C_{\frac{1}{2},-\frac{1}{2}} C_{j_1 m_1} a + \Big[j(j+1) - j_1(j_1+1) - \tfrac{3}{4} + m_1 + 1 \Big] b = 0. \tag{11.189}$$

It is easy to show that the determinant of this system is zero if and only if j takes the values $j_1 + \frac{1}{2}$ or $j_1 - \frac{1}{2}$, as is expected from the triangle relation. If we take $j = j_1 + \frac{1}{2}$ and substitute it into Eq. (11.188), we obtain the quotient a/b. If we now impose the normalization condition $a^2 + b^2 = 1$, and taking a positive, we get

$$a = \sqrt{\frac{j_1 + m_1 + 1}{2j_1 + 1}}, \quad b = \sqrt{\frac{j_1 - m_1}{2j_1 + 1}}. \tag{11.190}$$

This process is repeated until the four possible states are constructed. The final results are shown in Table 11.1. If we take the case $j_1 = 1/2$ in the table, we recover the C-G coefficients for the coupling studied in the previous example.

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Table 11.1 Clebsch–Gordan coefficients for the coupling of an arbitrary angular momentum j to a spin $1/2$ angular momentum.

	$\left(j_1 \frac{1}{2} m_1 m_2 \mid jm\right)$	
J	$m_2 = \frac{1}{2}$	$m_2 = -\frac{1}{2}$
$j_1 + \frac{1}{2}$	$\left(\frac{j_1+m+\frac{1}{2}}{2j_1+1}\right)^{1/2}$	$\left(\frac{j_1-m+\frac{1}{2}}{2j_1+1}\right)^{1/2}$
$j_1 - \frac{1}{2}$	$-\left(\frac{j_1-m+\frac{1}{2}}{2j_1+1}\right)^{1/2}$	$\left(\frac{j_1+m+\frac{1}{2}}{2j_1+1}\right)^{1/2}$

Exercise E11.5. Scalar nature of the singlet spin state
Show that the entangled state of two spin-1/2 particles,

$$|\Psi\rangle_\lambda = \frac{1}{\left(1+\mid \lambda^2 \mid\right)^{1/2}} [\mid +\rangle \mid -\rangle + \lambda \mid -\rangle \mid +\rangle] \tag{11.191}$$

is a scalar (i.e., invariant against rotation) if and only if $\lambda = -1$, which is the antisymmetric combination upon particle exchange. The importance of entangled states will become clear in Section 14.5.

Solution. Let us consider a new basis $\mid \alpha\rangle$ and $\mid \beta\rangle$, whose axes are oriented at angles θ, ϕ with respect to the original basis $\mid +\rangle$, $\mid -\rangle$. The matrix describing this rotation has the form given by Eq. (8.167) (with the substitution $L \to S = \hbar\sigma/2$); we can write it in the form

$$\hat{T} = \begin{pmatrix} a & b \\ b^* & -a \end{pmatrix}, \qquad a = cos\theta^2, \qquad b = \frac{sin\theta}{2} e^{i\phi/2}. \tag{11.192}$$

Therefore, $\mid \alpha\rangle = \hat{T}|+\rangle = a|+\rangle + b^*|-\rangle$, $\mid \beta\rangle = \hat{T}|-\rangle = b \mid +\rangle - a|-\rangle$, or inverting, $|+\rangle = a|\alpha\rangle + b^*|\beta\rangle$, $|-\rangle = b|\alpha\rangle - a|\beta\rangle$.

We substitute these results into the expression for $|\Psi\rangle_\lambda$ with $N_\lambda = \left(1+\mid \lambda \mid^2\right)^{-1/2}$ and rearrange to obtain

$$\begin{aligned} |\Psi\rangle_\lambda = N_\lambda [|+\rangle|-\rangle + \lambda|-\rangle|+\rangle] = N(1+\lambda)\left[ab|\alpha\rangle|\alpha\rangle - ab^*|\beta\rangle|\beta\rangle\right] \\ + N\left[\left(\mid b \mid^2 - \lambda a^2\right)|\beta\rangle|\alpha\rangle - \left(a^2 - \lambda \mid b \mid^2\right)|\alpha\rangle|\beta\rangle\right]. \end{aligned} \tag{11.193}$$

For $\lambda = -1$ this expression reduces to $(a^2 + |b|^2 = 1)$:

$$|\Psi\rangle_{-1} = \frac{1}{\sqrt{2}}[|\beta\rangle|\alpha\rangle - |\alpha\rangle|\beta\rangle], \tag{11.194}$$

which has exactly the initial form of $|\Psi\rangle$ with $\lambda = -1$. This invariance shows that in (11.191) with $\lambda = -1$ (but only with this value), the orientation of the axes defining the states $|+\rangle$ and $|-\rangle$ is arbitrary. In other words, the vector $|\Psi\rangle_{-1}$ in Eq. (11.194) contains no information about a preferred direction. This means that $|\Psi\rangle_{-1}$ is a scalar with respect to rotation.

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Problems

P11.1 Determine the relationship between the angular momentum defined in two different inertial reference systems when:

a) the systems are at relative rest, with origins separated by a distance $\boldsymbol{a}$,
b) the systems move with constant relative velocity $\boldsymbol{v}$.

P11.2 Prove that

$$[\hat{\mathbf{n}}\cdot\hat{\boldsymbol{L}},\boldsymbol{r}\,]=-i\hbar(\hat{\mathbf{n}}\times\boldsymbol{r}\,),\quad [\hat{\mathbf{n}}\cdot\hat{\boldsymbol{L}},\hat{\boldsymbol{p}}\,]=-i\hbar(\hat{\mathbf{n}}\times\hat{\boldsymbol{p}}\,),\quad [\hat{\mathbf{n}}\cdot\hat{\boldsymbol{L}},\hat{\boldsymbol{L}}\,]=-i\hbar(\hat{\mathbf{n}}\times\hat{\boldsymbol{L}}\,). \tag{11.195}$$

In the preceding expressions, $\hat{\mathbf{n}}$ is a constant unit vector in any direction.

P11.3 Show that the total orbital momentum of a two-particle system can be expressed in terms of the center-of-mass and relative coordinates in the form

$$\hat{\boldsymbol{L}}=\boldsymbol{R}\times\hat{\boldsymbol{P}}+\boldsymbol{r}\times\hat{\boldsymbol{p}}, \tag{11.196}$$

where

$$\boldsymbol{r}=\boldsymbol{r}_1-\boldsymbol{r}_2,\qquad \hat{\boldsymbol{p}}=m\left(\frac{\hat{\boldsymbol{p}}_1}{m_1}-\frac{\hat{\boldsymbol{p}}_2}{m_2}\right),\qquad m=\frac{m_1m_2}{m_1+m_2{}_1},$$
$$\boldsymbol{R}=\frac{m_1\boldsymbol{r}_1+m_2\boldsymbol{r}_2}{M},\qquad \hat{\boldsymbol{P}}=\hat{\boldsymbol{p}}_1+\hat{\boldsymbol{p}}_2,\qquad M=m_1+m_2. \tag{11.197}$$

P11.4 Show that any function that depends only on r is an eigenfunction of $\hat{L}_z$ and $\hat{\boldsymbol{L}}^2$, with both eigenvalues equal to zero, and that any function $g(z,r)$ is an eigenfunction of the z component with zero eigenvalue. Determine the eigenfunction of $\hat{L}_x$ corresponding to zero eigenvalue and angular momentum 1.

P11.5 Calculate the expectation value of the operator $\frac{1}{2}(\hat{L}_x\hat{L}_y+\hat{L}_y\hat{L}_x)$ and its square, in an eigenstate of $\hat{L}^2$ and $\hat{L}_z$.

P11.6 Determine the expression for the eigenfunctions of $\hat{\boldsymbol{L}}^2$ and $\hat{L}_z$ in momentum space.

P11.7 Prove that there is no solution to the eigenvalue problem $\hat{p}_r R(r)=\alpha R(r)$ that satisfies the condition $\lim_{r\to 0} rR(r)=0$. What can be concluded from here?

P11.8 Consider an eigenfunction $\psi_{nlm}(\boldsymbol{r})$ of a radial Hamiltonian and show that

$$\psi'=e^{i\alpha\hat{\mathbf{n}}\cdot\hat{\boldsymbol{L}}/\hbar}\psi_{nlm}(\boldsymbol{r}) \tag{11.198}$$

is an eigenfunction of the Hamiltonian with the same angular momentum l, independent of the value of α and the orientation of the $\hat{\mathbf{n}}$ axis. Is it also an eigenstate of $\hat{L}_z$?

P11.9 Construct the matrices representing the angular-momentum operators for $j=1$ and $j=3/2$.

P11.10 Since $\hat{S}_i$ are the components of a vector, they are transformed under rotation according to the laws of vectors. For example, under rotation around the z-axis by an angle θ, which performs the transformation $\hat{S}\to\hat{S}'$,

$$\hat{S}'_x=\hat{S}_x\cos\theta+\hat{S}_y\sin\theta,\quad \hat{S}'_y=-\hat{S}_x\sin\theta+\hat{S}_y\cos\theta,\quad \hat{S}'_z=\hat{S}_z. \tag{11.199}$$

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Use the commutation rules for $\hat{S}_x$, $\hat{S}_y$, and $\hat{S}_z$ to show that the transformed components $\hat{S}'_x$, $\hat{S}'_y$ and $\hat{S}'_z$ satisfy exactly the same rules.

P11.11 If $\hat{\mathbf{n}}$ is a constant unit vector with direction cosines l, m, n with respect to the x-, y- and z-axes, respectively, show that

$$\hat{\sigma}_{\mathbf{n}} = \hat{\mathbf{n}}\cdot\hat{\sigma} = \begin{pmatrix} n & l-im \\ l+im & -n \end{pmatrix}, \qquad (\hat{\mathbf{n}}\cdot\hat{\sigma})^2 = \mathbb{I}. \tag{11.200}$$

Confirm that the eigenvalues of $\hat{\sigma}_{\mathbf{n}}$ are ± 1. What does this mean?

P11.12 The spin projection of an electron on a certain z-axis is $\hbar/2$. Determine the probability that the projection of this spin on a certain z'-axis have the value $\hbar/2$ or $-\hbar/2$, as well as the average value of this projection.

P11.13 Consider an ion with spin 1, characterized by the Hamiltonian

$$\hat{H} = D\hat{S}_z^2 + E\left(\hat{S}_x^2 + \hat{S}_y^2\right), \tag{11.201}$$

with D and E constant, $D \gg E$. Determine the energy levels.

P11.14 Consider a system of angular momentum 1 represented by the state vector

$$\psi = \frac{1}{\sqrt{26}}\begin{pmatrix} 1 \\ 4 \\ -3 \end{pmatrix}. \tag{11.202}$$

What is the probability that a measurement of $\hat{L}_x$ returns the value zero?

P11.15 Calculate directly the Clebsch–Gordan coefficients for the coupling of angular momenta 1/2 and 1. Compare your results with those in Table 11.1.

P11.16 An orbital angular momentum $\hat{\boldsymbol{L}}$ couples with a spin $\hat{\boldsymbol{S}}$ to produce a state of total angular momentum $\hat{\boldsymbol{J}}$. Find out what angles between the vectors $\hat{\boldsymbol{L}}$ and $\hat{\boldsymbol{S}}$ are allowed by quantum rules.

P11.17 Is it possible for one photon to spontaneously decay into two photons? And into three photons? Explain your answers.

P11.18 The deuteron has spin 1. What are the possible states of spin and total angular momentum of a system of two deuterons when their total orbital angular momentum is L?

P11.19 Consider a spin 1/2 particle confined by a central potential.

a) Determine the wave functions that are simultaneously eigenfunctions of the operators $\hat{\boldsymbol{L}}^2$, $\hat{\boldsymbol{J}}^2$ and $\hat{J}_z = \hat{L}_z + \hat{S}_z$.

b) When an interaction term of the form $\gamma\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}}$ with γ small is added to the Hamiltonian, what are the eigenfunctions of the system?

Bibliographical Notes

A highly recommended reference is the classic book by Condon and Shortley (1964). Specific references on angular momentum are Brink and Satchler (1968), Edmonds (1957), Khersonskii, Moskalev, and Varshalovich (1988), and Hassani (2013).

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