12 Rotations and angular momentum

12.1 Orbital angular momentum

Later in these notes, we will see that the orbital angular momentum operator arises naturally from the transformation properties of wave functions under a rotation. At a more elementary level, however, this operator also crops up as the quantum mechanical counterpart of the classical angular momentum of a mass point (specifically, the angular momentum with respect to the origin of the system of coordinates). For memory, the latter is defined by the equation

$$\mathbf{L}_{\mathrm{cl}} = \mathbf{r} \times \mathbf{p}_{\mathrm{cl}}, \tag{12.1}$$

where $\mathbf{r}$ is the position vector of the mass point and $\mathbf{p}_{\mathrm{cl}}$ is its momentum.

As discussed previously, we can define a position operator $\hat{x}$ and a momentum operator $\hat{p}_x$ for the x-direction, a position operator $\hat{y}$ and a momentum operator $\hat{p}_y$ for the y-direction, and a position operator $\hat{z}$ and a momentum operator $\hat{p}_z$ for the z-direction. These operators can be taken to be the x-, y- and z-components of a vector position operator $\hat{\mathbf{r}}$ and a vector momentum operator $\hat{\mathbf{p}}$:

$$\hat{\mathbf{r}} = \hat{x}\,\hat{\mathbf{x}} + \hat{y}\,\hat{\mathbf{y}} + \hat{z}\,\hat{\mathbf{z}}, \tag{12.2}$$

$$\hat{\mathbf{p}} = \hat{p}_x\,\hat{\mathbf{x}} + \hat{p}_y\,\hat{\mathbf{y}} + \hat{p}_z\,\hat{\mathbf{z}}. \tag{12.3}$$

(As in the rest of these notes, $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$ and $\hat{\mathbf{z}}$ are unit vectors in the x-, y- and z-directions. The hat sign in $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$ and $\hat{\mathbf{z}}$ indicates that these objects are unit vectors, not that they are operators, whereas the hat sign in $\hat{x}$, $\hat{y}$ and $\hat{z}$ indicates that these objects are operators, not that they are unit vectors.)

Likewise, the orbital angular momentum operator, $\hat{\mathbf{L}}$, is a geometric vector whose x-, y- and z-components, denoted $\hat{L}_x$, $\hat{L}_y$ and $\hat{L}_z$, are themselves operators:

$$\hat{\mathbf{L}} = \hat{L}_x\,\hat{\mathbf{x}} + \hat{L}_y\,\hat{\mathbf{y}} + \hat{L}_z\,\hat{\mathbf{z}}. \tag{12.4}$$

This operator is related to the position operator $\hat{\mathbf{r}}$ and to the momentum operator $\hat{\mathbf{p}}$ in the same way as, in Classical Mechanics, the angular momentum of a mass point is related to its position and its momentum:

$$\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}. \tag{12.5}$$

The usual rules of the vector product apply, although the vectors are operators here. $\hat{\mathbf{L}}$ can thus be calculated as a determinant:

$$\hat{\mathbf{L}} = \begin{vmatrix} \hat{\mathbf{x}} & \hat{\mathbf{y}} & \hat{\mathbf{z}} \\ \hat{x} & \hat{y} & \hat{z} \\ \hat{p}_x & \hat{p}_y & \hat{p}_z \end{vmatrix}. \tag{12.6}$$

This gives

$$\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x, \tag{12.7}$$

and similar expressions for $\hat{L}_x$ and $\hat{L}_y$ which can be obtained from Eq. (12.7) by circular permutation of the indices ($x \to y$, $y \to z$, $z \to x$):

$$\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \qquad \hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z. \tag{12.8}$$

The operator $\hat{\mathbf{L}}^2$ also plays an important role in the theory. It is defined as the dot product of $\hat{L}$ with itself, i.e.,

$$\hat{\mathbf{L}}^2 = \hat{\mathbf{L}} \cdot \hat{\mathbf{L}} = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2. \tag{12.9}$$

It is not particularly difficult to deduce from these definitions and from the properties of the position and momentum operators that $\hat{L}_x$, $\hat{L}_y$, $\hat{L}_z$ and $\hat{\mathbf{L}}^2$ are Hermitian and satisfy the following commutation relations:

$$[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z, \quad [\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x, \quad [\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y, \tag{12.10}$$

and furthermore

$$[\hat{L}_x, \hat{\mathbf{L}}^2] = [\hat{L}_y, \hat{\mathbf{L}}^2] = [\hat{L}_z, \hat{\mathbf{L}}^2] = 0. \tag{12.11}$$

Given Eqs. (12.7) and (12.8) and how the momentum operators $\hat{p}_x$, $\hat{p}_y$ and $\hat{p}_z$ are represented, the operators $\hat{L}_z$, $\hat{L}_x$ and $\hat{L}_y$ take on the following forms in the position representation:

$$L_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right), \tag{12.12}$$

$$L_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right), \tag{12.13}$$

$$L_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right). \tag{12.14}$$

☞ Passing to spherical polar coordinates (r, θ, ϕ) brings L_z to a particularly simple form:

$$L_z = -i\hbar\frac{\partial}{\partial\phi}. \tag{12.15}$$

However, somewhat more complicated expressions are found for L_x and L_y:

$$L_x = -i\hbar\left(-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\,\cos\phi\frac{\partial}{\partial\phi}\right), \tag{12.16}$$

$$L_y = -i\hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\,\sin\phi\frac{\partial}{\partial\phi}\right). \tag{12.17}$$

(We define the angles θ and ϕ in the usual way in Physics: θ is measured from the positive z-axis and ϕ is measured in the xy-plane from the positive x-axis. L_x, L_y and L_z do not depend on r or on derivatives with respect to r.)

☞ In the position representation, the Hamiltonian of a particle of mass m and potential energy $V(r)$ can be written as $-(\hbar^2/2m)\,\nabla^2 + V(r)$. In Cartesian coordinates,

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}, \tag{12.18}$$

whereas in spherical polar coordinates,

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\,\frac{\partial}{\partial r} + \frac{1}{r^2}\,\frac{\partial^2}{\partial \theta^2} + \frac{\cot\theta}{r^2}\,\frac{\partial}{\partial \theta} + \frac{1}{r^2\sin^2\theta}\,\frac{\partial^2}{\partial \phi^2}. \tag{12.19}$$

This last equation can be somewhat simplified, and made more transparent, by using the fact that

$$\mathbf{L}^2 = L_x^2 + L_y^2 + L_z^2 = -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\,\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\,\frac{\partial^2}{\partial\phi^2}\right). \tag{12.20}$$

Namely,

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\,\frac{\partial}{\partial r} - \frac{1}{\hbar^2}\,\frac{\mathbf{L}^2}{r^2}. \tag{12.21}$$

Therefore

$$H = -\frac{\hbar^2}{2m}\,\nabla^2 + V(r) = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\,\frac{\partial}{\partial r}\right) + \frac{\mathbf{L}^2}{2mr^2} + V(r). \tag{12.22}$$

Note that we take the potential to be central. I.e., we assume that $V(r)$ depends only on the distance of the particle to the origin, not on its angular position. Such potentials are said to be central because the corresponding classical force, $-\nabla V$, is a vector directed towards or away from a fixed point (the origin), the "centre of force". Remember that in Classical Mechanics the angular momentum vector $\mathbf{L}_{\rm cl}$ is a constant of motion if the potential is central. Since H depends on θ and ϕ only through $\hat{L}^2$, that $\hat{L_z}$ commutes with $\hat{L}^2$ and that $\hat{L}^2$ and $\hat{L}_z$ do not depend on r, $\hat{L}^2$ and $\hat{L}_z$ commute H. These two operators thus correspond to quantum mechanical constants of motion if the potential is central (see Section 11.4).

It is interesting to compare the Hamiltonian given by Eq. (12.22) with the classical Hamiltonian for the same system,

$$H_{\rm cl} = \frac{1}{2m}\,p_r^2 + \frac{|\mathbf{L}_{\rm cl}|^2}{2mr^2} + V(r), \tag{12.23}$$

where p_r is the generalized momentum conjugate to the radial variable r. In Quantum Mechanics as in Classical Mechanics, the radial motion of the particle is affected both by the potential energy $V(r)$ and by an "angular momentum barrier", $\mathbf{L}^2/(2mr^2)$ in the quantum case or $|\mathbf{L}|^2/(2mr^2)$ in the classical case, which plays the role of an additional potential energy.

12.2 Spin

Physicists became aware in the 1920s that many quantum systems have an angular-momentum like property, distinct from the orbital angular momentum. At first, it was theorized that this property could be related to some kind of self-rotation of the particles forming these systems, a bit as if electrons, protons, etc, were spinning tops. This property became referred to as "spin" for that reason. It was soon realized that associating spin to an actual rotation is completely incorrect — an electron is *not* a spinning top — but the word "spin" kept being used. The modern understanding of spin is that this property has nothing to do with an actual motion and has no analogue in Classical Mechanics.

There is a relation with the orbital angular momentum, though, in that spin is a dynamical variable described by a Hermitian vector operator whose components obey the same commutation relations as those of the orbital angular momentum operator $\hat{\mathbf{L}}$. We denote this vector operator by $\hat{\mathbf{S}}$ and its x-, y- and z-components by $\hat{S}_x$, $\hat{S}_y$ and $\hat{S}_z$:

$$\hat{\mathbf{S}} = \hat{S}_x\,\hat{\mathbf{x}} + \hat{S}_y\,\hat{\mathbf{y}} + \hat{S}_z\,\hat{\mathbf{z}}. \tag{12.24}$$

As for the orbital angular momentum,

$$[\hat{S}_x, \hat{S}_y] = i\hbar\hat{S}_z, \quad [\hat{S}_y, \hat{S}_z] = i\hbar\hat{S}_x, \quad [\hat{S}_z, \hat{S}_x] = i\hbar\hat{S}_y, \tag{12.25}$$

and also

$$[\hat{S}_x, \hat{\mathbf{S}}^2] = [\hat{S}_y, \hat{\mathbf{S}}^2] = [\hat{S}_z, \hat{\mathbf{S}}^2] = 0, \tag{12.26}$$

with the operator $\hat{\mathbf{S}}^2$ being the dot product of $\hat{S}$ with itself:

$$\hat{\mathbf{S}}^2 = \hat{\mathbf{S}} \cdot \hat{\mathbf{S}} = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2. \tag{12.27}$$

However, the commutation relations for $\hat{S}_x$, $\hat{S}_y$ and $\hat{S}_z$ cannot be derived from those of the position and momentum operators, in contrast to those of $\hat{L}_x$, $\hat{L}_y$ and $\hat{L}_z$. We will see that they can be obtained from the rotational properties of quantum states.

It is important to understand that spin is unrelated to position, momentum or orbital angular momentum. Thus

$$[\hat{\mathbf{r}}, \hat{\mathbf{S}}] = [\hat{\mathbf{p}}, \hat{\mathbf{S}}] = [\hat{\mathbf{L}}, \hat{\mathbf{S}}] = 0. \tag{12.28}$$

Spin is sometimes described as an "intrinsic angular momentum", i.e., an angular momentum which is not defined with respect to a particular point. (Note the contrast with the orbital angular momentum: since $\mathbf{r}$ is the position vector with respect to the origin, $\mathbf{r} \times \mathbf{p}$ depends on the choice of the origin.)

12.3 Rotations and rotation operators

First, a fact of fundamental importance:

Rotations about different axes do not commute.

I.e., the order in which rotations are made matters when they are made about different axes.

☞ Should you have any doubt about the above statement, try this experiment: Define two orthogonal axes, fixed with respect to the room, e.g., a vertical axis and a horizontal axis. Take a book, and rotate it first by 90 deg about the vertical axis and then by 90 deg about the horizontal axis. Note its new position. Then start again with the book in the same initial position as before, but now rotate it first by 90 deg about the horizontal axis and then by 90 deg about the vertical axis. Its new position won't be the same as what you found in the first sequence of rotations...

Clearly, rotations about a *same* axis do commute. For example, rotating a book by 20 deg about the vertical axis and then by 30 deg about the same axis is the same as rotating it first by 30 deg and then by 20 deg.

☞ As an exception to the general rule that rotations about different axes do not commute, a rotation by 180 deg commutes with a rotation by 180 deg about a perpendicular axis.

☞ Any rotation in 3D space can be described by a 3×3 matrix. For example, rotating a point by an angle α about the x-axis changes its coordinates from (x, y, z) to (x', y', z'), with

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\alpha & -\sin\alpha \\ 0 & \sin\alpha & \cos\alpha \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} . \tag{12.29}$$

Rotations about the y- or z-axes can be represented similarly. Let us denote the corresponding rotation matrices by $\mathsf{R}_x(\alpha)$, $\mathsf{R}_y(\alpha)$ and $\mathsf{R}_z(\alpha)$:

$$\mathsf{R}_x(\alpha) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\alpha & -\sin\alpha \\ 0 & \sin\alpha & \cos\alpha \end{pmatrix} , \tag{12.30}$$

$$\mathsf{R}_y(\alpha) = \begin{pmatrix} \cos\alpha & 0 & \sin\alpha \\ 0 & 1 & 0 \\ -\sin\alpha & 0 & \cos\alpha \end{pmatrix} , \tag{12.31}$$

$$\mathsf{R}_z(\alpha) = \begin{pmatrix} \cos\alpha & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} . \tag{12.32}$$

Remember that the positive sense of rotation is given by the right-hand rule: imagine that you grip the rotation axis with your right hand, your thumb pointing in the positive direction of that axis. The direction in which your fingers then curl in the positive direction of rotation.

☞ The following, rather obvious facts are also worth noting in view of their importance in the mathematical theory of these transformations:

- Rotating an object several times, about the same axis or about different axes, always amounts to rotating it once: the product of two rotations is also a rotation.
- Composing rotations is associative: Doing a rotation A, then a rotation B and then a third rotation C can be described as first doing the resultant of A and B and then C, or first doing A and then the resultant of B and C.
- There is a "neutral rotation" (a rotation by a zero angle about any axis). Composing any rotation A with that identity rotation gives A.
- Any rotation has an inverse, such that doing a rotation and then its inverse rotation amounts to no change at all (the zero rotation).

These four facts mean that these transformations form a group with respect to the composition of rotations (in the mathematical meaning of the word group).

As noted above, rotating a point transforms its coordinates, and this transformation can be represented by a certain 3×3 matrix. Matrices representing these rotations have three special features: they are real (not complex), their transpose equal their inverse, and their determinant is 1. A real invertible matrix whose transpose is its inverse is said to be orthogonal (or unitary since for a real matrix the transpose is the same as the conjugate transpose). Orthogonal matrices of unit determinant form a group under matrix multiplication: the product of two such matrices is also an orthogonal matrix of unit determinant, matrix multiplication is associative, the identity matrix is an orthogonal matrix of unit determinant, and any such matrix has an inverse, which is also an orthogonal matrix of unit determinant. This group is called SO(3) (SO stands for "special orthogonal", the word special referring to the condition that the determinant is 1). Transformations of coordinates amounting to a rotation are in 1 to 1 correspondance with elements of SO(3).

SO(3) is related to the group SU(2), the group of the unitary 2×2 complex matrices of unit determinant. In fact general rotations in 3D space are best described by SU(2) matrices rather than by SO(3) matrices. An explanation of why this is the case would require a lengthy

mathematical analysis of rotations, as would a detailed account of the mathematics of these 2×2 matrices and their relationship with SO(3) matrices. We just note that these two descriptions may differ significantly for finite rotations, but they don't for infinitesimal rotations (rotations by an infinitesimal angle). For example, it is possible to show that Eqs. (12.30–12.32) imply that

$$\mathsf{R}_y(-\epsilon)\mathsf{R}_x(-\epsilon)\mathsf{R}_y(\epsilon)\mathsf{R}_x(\epsilon) = \mathsf{R}_z(-\epsilon^2) + \mathcal{O}(\epsilon^3), \tag{12.33}$$

where the symbol $\mathcal{O}(\epsilon^3)$ means that terms cubic and of higher order in ϵ have been neglected. (See the homework problem QT2.6 for details.) Eq. (12.33) is a relation between the SO(3) matrices of Eqs. (12.30–12.32). However, exactly the same relation would be obtained for the SU(2) matrices describing the same rotations.

☞ An active rotation of an object is a rotation within a fixed system of coordinates (fixed, e.g., with respect to the room): the rotation changes the actual position of the object with respect to both the room and the axes of the coordinate system. By contrast, a passive rotation would be a rotation of the system of coordinates with respect to the room with no actual change in the position the object. The coordinates of points of this object change under a passive rotation as well as under an active rotation, although usually not in the same way. We only consider active rotations in these notes.

We start by looking at how wave functions transform when we map each point of space to its image by a rotation about the x-axis. Consider, e.g., an atom of hydrogen in a state described by a wave function $\psi(x, y, z)$, ignoring spin. At a point P of coordinates (x_P, y_P, z_P), the value of this wave function is a certain complex number $\psi(x_P, y_P, z_P)$. The rotation maps P to a point P' of coordinates (x'_P, y'_P, z'_P). In general, the value of the wave function $\psi(x, y, z)$ at P' differs from its value at P. However, we can define a function $\psi'(x, y, z)$ whose value at P' is the same as the value of $\psi(x, y, z)$ at P. How to do this is simple: we take $\psi'(x, y, z)$ to be the function whose value at the point of coordinate (x, y, z) is $\psi(x'', y'', z'')$, where (x'', y'', z'') are the coordinates of the point sent to the point (x, y, z) by the rotation [e.g., (x'', y'', z'') would be (x_P, y_P, z_P) if (x, y, z) was (x'_P, y'_P, z'_P)]. Clearly, if $\psi(x, y, z)$ describes an atomic state oriented in the z-direction (e.g., the $2\mathrm{p}_{m=0}$ state), $\psi'(x, y, z)$ describes a state oriented in a different direction but otherwise identical to that described by $\psi(x, y, z)$.

Passing from $\psi(x, y, z)$ to $\psi'(x, y, z)$ is a transformation. Formally,

$$\psi'(x, y, z) = R_x(\alpha)\psi(x, y, z), \tag{12.34}$$

where $R_x(\alpha)$ is a certain operator corresponding to a rotation by an angle α about the x-axis. This operator is potentially quite complicated, as we want

Eq. (12.34) to apply to any wave function $\psi(x, y, z)$, not just one in particular. We will see how to construct this operator shortly. However, at this stage we simply note that $R_x(\alpha = 0)$ must be the identity operator since a rotation by a zero angle amounts to no rotation at all. Moreover, the rotation operator for a rotation by an infinitesimal angle $\mathrm{d}\alpha$ must differ from the identity operator only infinitesimally. I.e., there must be an operator L_x such that

$$R_x(\mathrm{d}\alpha) = 1 - (i/\hbar)L_x\,\mathrm{d}\alpha. \tag{12.35}$$

(The factor of $-i/\hbar$ multiplying L_x has been introduced for later convenience.) Hence, for an infinitesimal rotation,

$$\psi'(x, y, z) = [1 - (i/\hbar)L_x\,\mathrm{d}\alpha]\,\psi(x, y, z). \tag{12.36}$$

Remarkably, it follows from this that

$$L_x = -i\hbar\left(y\,\frac{\partial}{\partial z} - z\,\frac{\partial}{\partial y}\right). \tag{12.37}$$

Thus L_x is nothing else than the x-component of the orbital angular momentum operator in the position representation. Rotations about the y-axis or the z-axis can be treated in the same way: operators L_y and L_z can be introduced in terms of which the corresponding rotation operators $R_y(\alpha)$ and $R_z(\alpha)$ reduce to $1 - (i/\hbar)L_y\,\mathrm{d}\alpha$ and $1 - (i/\hbar)L_z\,\mathrm{d}\alpha$ for infinitesimal rotations, and the same reasoning identifies L_y and L_z with the respective components of the orbital angular momentum operator in the position representation. Note that here we did not assume from the start that L_x, L_y and L_z are the three components of the cross product of the position operator and the momentum operator, as we did in Section 12.1. Instead, we have obtained these three operators entirely from an analysis of how wave functions transform under a rotation.

☞ The reader is referred to the model solution of Problem QT2.6 for the principle of the calculation leading to Eq. (12.37).

The wave function $\psi'(x, y, z)$ thus describes a state which is rotated about the x-axis compared to the state described by the wave function $\psi(x, y, z)$. In a sense, going from $\psi(x, y, z)$ to $\psi'(x, y, z)$ is "rotating the atom" from one orientation to another. Imagine an experiment in which the atom is excited from the ground state to the $2\mathrm{p}_{m=0}$ state by a laser beam whose electric field component is oriented in the z-direction (you will study this process in the level 3 QM course). Let $\psi(x, y, z)$ be the corresponding wave function. Arranging for the electric field component of the laser to be oriented in a direction rotated by an angle α about the x-axis will instead lead to an excited state oriented in that different direction. This state can be described by the wave function $\psi'(x, y, z)$. The two

states $\psi(x,y,z)$ and $\psi'(x,y,z)$ thus differ by a rotation $\mathcal{R}$ of the apparatus used to prepare them. Moreover, any prediction one can make about the results of measurements on the atom in the state $\psi(x,y,z)$ are exactly the same as those for measurements on the atom in the state $\psi'(x,y,z)$, provided the measuring apparatus is also rotated by $\mathcal{R}$.

This carries over to more general systems, even to systems which are not amenable to a description in terms of functions of x, y, and z. Imagine an experiment in which a certain quantum system can be prepared and measured with the apparatus either in an orientation A or in an orientation B differing from A by a rotation. Any quantum state $|\psi\rangle$ relevant for measurements made with the apparatus in the orientation A has a counterpart $|\psi'\rangle$ for measurements made with the apparatus in the orientation B. How each of the states $|\psi\rangle$ is related to the "rotated state" $|\psi'\rangle$ depends on the axis and the angle of the rotation which brings the apparatus from one orientation to the other. This transformation can be expressed by the equation

$$|\psi'\rangle = \hat{R}_{\hat{\mathbf{n}}}(\alpha)|\psi\rangle, \tag{12.38}$$

where $\hat{R}_{\hat{\mathbf{n}}}(\alpha)$ is a certain operator corresponding to a rotation by an angle α about an axis pointing in the direction of the unit vector $\hat{\mathbf{n}}$. In particular, we can introduce the operators $\hat{R}_x(\alpha)$, $\hat{R}_y(\alpha)$ and $\hat{R}_z(\alpha)$ corresponding to a rotation by an angle α about the x-, y- or z-axis.

Since $|\psi\rangle \equiv |\psi'\rangle$ for a rotation by a zero angle, the operator $\hat{R}_{\hat{\mathbf{n}}}(\alpha)$ must differ infinitesimally from the identity operator if α is infinitesimal. The usual way of stating this property is to introduce an α-independent Hermitian operator $\hat{J}_{\hat{\mathbf{n}}}$ and write $\hat{R}_{\hat{\mathbf{n}}}(\mathrm{d}\alpha) = \hat{I} - (i/\hbar)\hat{J}_{\hat{\mathbf{n}}}\,\mathrm{d}\alpha$. In particular, $\hat{R}_x(\mathrm{d}\alpha) = \hat{I} - (i/\hbar)\hat{J}_x\,\mathrm{d}\alpha$, $\hat{R}_y(\mathrm{d}\alpha) = \hat{I} - (i/\hbar)\hat{J}_y\,\mathrm{d}\alpha$ and $\hat{R}_z(\mathrm{d}\alpha) = \hat{I} - (i/\hbar)\hat{J}_z\,\mathrm{d}\alpha$. Since the identity operator has no physical dimensions, the operators $\hat{J}_{\hat{\mathbf{n}}}$, $\hat{J}_x$, $\hat{J}_y$ and $\hat{J}_z$ must have the same physical dimensions as $\hbar$, i.e., the physical dimensions of an angular momentum. (These operators are, of course, angular momentum operators. The letters J and j are commonly used to refer to general angular momentum operators. In Atomic Physics they are also used to refer specifically to the sum of the orbital angular momentum operator and the spin operator, but here they simply refer to a general, unspecified, angular momentum.)

As seen in the homework problem QT2.6, it follows from the commutation relation between 3D rotations that the three operators $\hat{J}_x$, $\hat{J}_y$ and $\hat{J}_z$ do not commute with each other, and instead that

$$[\hat{J}_x, \hat{J}_y] = i\hbar\hat{J}_z, \quad [\hat{J}_y, \hat{J}_z] = i\hbar\hat{J}_x, \quad [\hat{J}_z, \hat{J}_x] = i\hbar\hat{J}_y. \tag{12.39}$$

☞ The detail of the calculations leading to this key result can be found in the model solution of this problem.

The derivation may seem to be based on a (a priori reasonable) assumption that if $\mathsf{R}_1(\alpha_1)$ and $\mathsf{R}_2(\alpha_2)$ are two rotation matrices describing geometric rotations of points in 3D space, and $R_1(\alpha_1)$ and $R_2(\alpha_2)$ are the corresponding rotation operators, then $R_2(\alpha_2)R_1(\alpha_1)$ is the rotation operator corresponding to the geometric rotation described by the matrix $\mathsf{R}_2(\alpha_2)\mathsf{R}_1(\alpha_1)$. In fact, this assumption would not be correct in general. It is correct for the transformations of wave functions discussed earlier, though, and it is always correct if the angles α_1 and α_2 are infinitesimal (which is the case considered in the derivation). The issue is related to an important mathematical detail alluded to above, which is that the geometric rotations of points in 3D space are described by elements of the group SO(3) (the group of the orthogonal 3×3 real matrices with determinant equal to 1) whereas the rotation operators transforming quantum states are represented by elements of the related group SU(2) (the group of the unitary 2×2 complex matrices with determinant equal to 1).

☞ A position vector $\mathbf{r}$ is transformed into the vector $\mathbf{r}+\mathrm{d}\mathbf{r} = \mathbf{r}+\hat{\mathbf{n}}\times\mathbf{r}\,\mathrm{d}\alpha$ by an infinitesimal rotation of angle $\mathrm{d}\alpha$ about an axis in the direction of the unit vector $\hat{\mathbf{n}}$. If the x-, y- and z-components of $\hat{\mathbf{n}}$ are, respectively, $\sin\Theta\cos\Phi$, $\sin\Theta\sin\Phi$ and $\cos\Theta$, then

$$\mathbf{r}+\mathrm{d}\mathbf{r} = \mathbf{r}+\sin\Theta\cos\Phi\,(\hat{\mathbf{x}}\times\mathbf{r})\,\mathrm{d}\alpha+\sin\Theta\sin\Phi\,(\hat{\mathbf{y}}\times\mathbf{r})\,\mathrm{d}\alpha+\cos\Theta\,(\hat{\mathbf{z}}\times\mathbf{r})\,\mathrm{d}\alpha. \tag{12.40}$$

Correspondingly,

$$\hat{R}_{\hat{\mathbf{n}}}(\mathrm{d}\alpha) = \hat{I} - (i/\hbar)\left(\sin\Theta\cos\Phi\,\hat{J}_x + \sin\Theta\sin\Phi\,\hat{J}_y + \cos\Theta\,\hat{J}_z\right)\mathrm{d}\alpha. \tag{12.41}$$

Thus $\hat{J}_{\hat{\mathbf{n}}} = \hat{\mathbf{n}}\cdot\hat{\mathbf{J}}$ with $\hat{\mathbf{J}} = \hat{J}_x\hat{\mathbf{x}} + \hat{J}_y\hat{\mathbf{y}} + \hat{J}_z\hat{\mathbf{z}}$.

☞ Because the norm of the ket $|\psi'\rangle = \hat{R}_{\hat{\mathbf{n}}}(\alpha)|\psi\rangle$ ought to be the same as the norm of the ket $|\psi\rangle$, the rotation operator $\hat{R}_{\hat{\mathbf{n}}}(\alpha)$ must be unitary:

$$\hat{R}^\dagger_{\hat{\mathbf{n}}}(\alpha)\hat{R}_{\hat{\mathbf{n}}}(\alpha) = \hat{R}_{\hat{\mathbf{n}}}(\alpha)\hat{R}^\dagger_{\hat{\mathbf{n}}}(\alpha) = \hat{I}. \tag{12.42}$$

For infinitesimal rotations,

$$\hat{R}_{\hat{\mathbf{n}}}(\mathrm{d}\alpha) = \hat{I} - (i/\hbar)\hat{J}_{\hat{\mathbf{n}}}\,\mathrm{d}\alpha, \qquad \hat{R}^\dagger_{\hat{\mathbf{n}}}(\mathrm{d}\alpha) = \hat{I} + (i/\hbar)\hat{J}^\dagger_{\hat{\mathbf{n}}}\,\mathrm{d}\alpha, \tag{12.43}$$

and therefore, ignoring terms quadratic in $\mathrm{d}\alpha$,

$$\hat{R}^\dagger_{\hat{\mathbf{n}}}(\mathrm{d}\alpha)\hat{R}_{\hat{\mathbf{n}}}(\mathrm{d}\alpha) = \hat{R}_{\hat{\mathbf{n}}}(\mathrm{d}\alpha)\hat{R}^\dagger_{\hat{\mathbf{n}}}(\mathrm{d}\alpha) = \hat{I} - (i/\hbar)\left(\hat{J}_{\hat{\mathbf{n}}} - \hat{J}^\dagger_{\hat{\mathbf{n}}}\right)\mathrm{d}\alpha. \tag{12.44}$$

In view of Eq. (12.42), it must be the case that $\hat{J}_{\hat{\mathbf{n}}} = \hat{J}^\dagger_{\hat{\mathbf{n}}}$: the angular momentum operators are self-adjoint.

Spin vs. orbital angular momentum

Depending on the system, the operators $\hat{J}_x$, $\hat{J}_y$ and $\hat{J}_z$, and more generally $\hat{J}_{\hat{\mathbf{n}}}$ could be spin operators, orbital angular momentum operators, or sums of spin operators and orbital angular momentum operators.

The operator $\hat{J}_x\,\hat{\mathbf{x}} + \hat{J}_y\,\hat{\mathbf{y}} + \hat{J}_z\,\hat{\mathbf{z}}$ can be identified with the spin operator $\hat{\mathbf{S}}$ if the system has no spatial extension (i.e., it is a point particle such as an electron). As seen above, it can be identified with the orbital angular momentum operator $\hat{\mathbf{L}}$ if the system has a spatial extension but no spin. The relevant angular momentum operators for extended systems of non-zero spin are the sum of a spin operator and an orbital angular momentum operator.

Infinitesimal generators and finite rotations

We have seen that for rotation by an *infinitesimal* angle α,

$$\hat{R}_{\hat{\mathbf{n}}}(\alpha) = \hat{I} - (i/\hbar)\hat{J}_{\hat{\mathbf{n}}}\,\alpha. \tag{12.45}$$

One says that the angular momentum operator $\hat{J}_{\hat{\mathbf{n}}}$ is the infinitesimal generator of the rotations about the axis $\hat{\mathbf{n}}$ in the Hilbert space of the state vectors of the system.

Eq. (12.45) does not apply to the case of a *finite* rotation angle. Instead, for any finite or infinitesimal value of α,

$$\hat{R}_{\hat{\mathbf{n}}}(\alpha) = \exp\big(-i\alpha\hat{J}_{\hat{\mathbf{n}}}/\hbar\big). \tag{12.46}$$

Remember that the exponential of an operator is defined by its Taylor series (see Section 3.3). Here,

$$\exp\big(-i\alpha\hat{J}_{\hat{\mathbf{n}}}/\hbar\big) = \hat{I} + \Big(-i\frac{\alpha}{\hbar}\Big)\,\hat{J}_{\mathbf{n}} + \frac{1}{2!}\Big(-i\frac{\alpha}{\hbar}\Big)^2\,\hat{J}^2_{\mathbf{n}} + \frac{1}{3!}\Big(-i\frac{\alpha}{\hbar}\Big)^3\,\hat{J}^3_{\mathbf{n}} + \cdots \tag{12.47}$$

Thus Eqs. (12.45) and (12.46) are consistent up to first order in α.

☞ The momentum operator is the infinitesimal generator of translations in space: as seen in a workshop problem,

$$\exp(-ix_0P/\hbar)\psi(x) = \psi(x - x_0), \tag{12.48}$$

where x_0 is a length and $P = -i\hbar\,\mathrm{d}/\mathrm{d}x$.

Likewise, the Hamiltonian is the infinitesimal generator of translations in time (see Section 11.2 of these notes).

12.4 Symmetries and conservation laws

Compare the ket $|\psi\rangle$ representing the state of a molecule oriented in one direction to the ket $|\psi'\rangle$ representing exactly the same state but rotated by an angle α about an axis $\hat{\mathbf{n}}$ (e.g., about the x-axis). These two kets are related to each other by the equation

$$|\psi'\rangle = \hat{R}_{\hat{\mathbf{n}}}(\alpha)|\psi\rangle, \tag{12.49}$$

where $\hat{R}_{\hat{\mathbf{n}}}(\alpha)$ is a rotation operator. This operator transforms ket vectors of the unrotated system into ket vectors of the rotated system, and is the same for any ket vector (i.e., $\hat{R}_{\hat{\mathbf{n}}}(\alpha)$ does not depend on $|\psi\rangle$).

Suppose that a measurement of the energy of this molecule would be made, e.g., by recording the energy of the photon(s) it emits when de-exciting to the ground state. The energy is a physical quantity which does not have a direction (it is not vectorial). The values that could be obtained in this measurement and the probability of obtaining each of them should therefore be exactly the same in the state $|\psi'\rangle$ as in the state $|\psi'\rangle$, since these two states only differ in their orientation. (This might not be true if the molecule interacted, e.g., with an external electric or magnetic field, which would break the rotational symmetry of space and make $|\psi\rangle$ and $|\psi'\rangle$ unequivalent; we assume that this is not the case here.) In particular, the expectation value of the Hamiltonian must be the same in the rotated system as in the unrotated system. In other words,

$$\langle\psi'|\hat{H}|\psi'\rangle = \langle\psi|\hat{H}|\psi\rangle \tag{12.50}$$

if the system is invariant under rotation. It is possible to deduce from this that $\hat{J}_{\hat{\mathbf{n}}}$ commutes with $\hat{H}$ (and similarly for any other rotation axis).

☞ Proof: As shown earlier, rotation operators are unitary operators. Therefore $\hat{R}^{\dagger}_{\hat{\mathbf{n}}}(\alpha) = \hat{R}^{-1}_{\hat{\mathbf{n}}}(\alpha)$, and since a rotation by $-\alpha$ undoes a rotation by α, $\hat{R}^{-1}_{\hat{\mathbf{n}}}(\alpha) = \hat{R}_{\hat{\mathbf{n}}}(-\alpha)$. Thus

$$\langle\psi'| = \langle\psi|\hat{R}^{\dagger}_{\hat{\mathbf{n}}}(\alpha) = \langle\psi|\hat{R}^{-1}_{\hat{\mathbf{n}}}(\alpha) = \langle\psi|\hat{R}_{\hat{\mathbf{n}}}(-\alpha). \tag{12.51}$$

As seen above, $\hat{R}_{\hat{\mathbf{n}}}(\pm\alpha)$ can be taken to be equal to $\hat{I} \mp i\alpha\hat{J}_{\hat{\mathbf{n}}}/\hbar$ if the angle α is infinitesimally small, with $\hat{J}_{\hat{\mathbf{n}}}$ the component of the angular momentum operator in the $\hat{\mathbf{n}}$ direction and $\hat{I}$ the identity operator. Denoting this infinitesimal angle by ϵ, we can therefore write

$$\begin{aligned}\langle\psi'|\hat{H}|\psi'\rangle &= \langle\psi|\left[\left(\hat{I} + \frac{i\epsilon}{\hbar}\,\hat{J}_{\hat{\mathbf{n}}}\right)\right]\hat{H}\left[\left(\hat{I} - \frac{i\epsilon}{\hbar}\,\hat{J}_{\hat{\mathbf{n}}}\right)\right]|\psi\rangle \\ &= \langle\psi|\hat{H} + \frac{i\epsilon}{\hbar}\,\hat{J}_{\hat{\mathbf{n}}}\hat{H} - \frac{i\epsilon}{\hbar}\,\hat{H}\hat{J}_{\hat{\mathbf{n}}} + \frac{\epsilon^2}{\hbar^2}\,\hat{J}_{\hat{\mathbf{n}}}\hat{H}\hat{J}_{\hat{\mathbf{n}}}|\psi\rangle. \end{aligned} \tag{12.52}$$

Neglecting the term of order ϵ^2 compared to the terms of order ϵ on account that ϵ is infinitesimally small, we obtain

$$\begin{aligned}\langle\psi'|\hat{H}|\psi'\rangle &= \langle\psi|\hat{H} + \frac{i\epsilon}{\hbar}\,\hat{J}_{\hat{\mathbf{n}}}\hat{H} - \frac{i\epsilon}{\hbar}\,\hat{H}\hat{J}_{\hat{\mathbf{n}}}|\psi\rangle \\ &= \langle\psi|\hat{H} + \frac{i\epsilon}{\hbar}\,[\hat{J}_{\hat{\mathbf{n}}}\hat{H} - \hat{H}\hat{J}_{\hat{\mathbf{n}}}]|\psi\rangle \\ &= \langle\psi|\hat{H}|\psi\rangle + \frac{i\epsilon}{\hbar}\,\langle\psi|[\hat{J}_{\hat{\mathbf{n}}}, \hat{H}]|\psi\rangle. \qquad (12.53)\end{aligned}$$

In view of Eq. (12.50), $\langle\psi|[\hat{J}_{\hat{\mathbf{n}}}, \hat{H}]|\psi\rangle$ must be zero. Since this must be the case for *any* state vector $|\psi\rangle$, we can conclude that $[\hat{J}_{\hat{\mathbf{n}}}, \hat{H}] = 0$. □

We see that the requirement that an isolated system is invariant under rotation, which stems from the isotropy of space (space is identical in any direction), implies that the angular momentum operator commutes with the Hamiltonian, hence that the angular momentum is a constant of motion (see Section 11.4).

This relationship between the symmetry of the system (here, invariance under rotation) and the existence of a conserved quantity (here, the angular momentum vector) is in fact very general. For example, momentum is conserved if the system is invariant under a spatial translation, and energy is conserved if the system is invariant under a "time translation", $t \to t + \tau$ with τ constant (there is invariance under a "time translation" in the absence of any time-dependent interaction).

12.5 Angular momentum operators

A vector operator

$$\hat{\mathbf{J}} = \hat{J}_x\,\hat{\mathbf{x}} + \hat{J}_y\,\hat{\mathbf{y}} + \hat{J}_z\,\hat{\mathbf{z}} \qquad (12.54)$$

is said to be an angular momentum operator if its three components $\hat{J}_x$, $\hat{J}_y$ and $\hat{J}_z$ are Hermitian and satisfy the commutation relations

$$[\hat{J}_x, \hat{J}_y] = i\hbar\hat{J}_z, \quad [\hat{J}_y, \hat{J}_z] = i\hbar\hat{J}_x, \quad [\hat{J}_z, \hat{J}_x] = i\hbar\hat{J}_y. \qquad (12.55)$$

The orbital angular momentum operator $\hat{\mathbf{L}}$ and the spin operator $\hat{\mathbf{S}}$ are particular instances of angular momentum operators.

- Angular momenta are often denoted by the letter J. Accordingly, in this section we use J to denote general angular momentum operators. This letter is also often used to represent, specifically, the "total angular momentum operator" $\hat{\mathbf{L}} + \hat{\mathbf{S}}$; what we cover here applies to $\hat{\mathbf{L}} + \hat{\mathbf{S}}$ as well as to any other angular momentum operator.

- Knowing that $[\hat{J}_x, \hat{J}_y] = i\hbar\hat{J}_z$, the other commutation relations can be obtained by circular permutation of the indices ($x \to y$, $y \to z$, $z \to x$).

We denote by $\hat{\mathbf{J}}^2$ the dot product of the operator $\hat{\mathbf{J}}$ with itself:

$$\hat{\mathbf{J}}^2 = \hat{\mathbf{J}} \cdot \hat{\mathbf{J}} = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2. \tag{12.56}$$

It is not difficult to show that the commutation relations satisfied by $\hat{J}_x$, $\hat{J}_y$ and $\hat{J}_z$ imply that these three operators commute with $\hat{\mathbf{J}}^2$:

$$[\hat{J}_x, \hat{\mathbf{J}}^2] = [\hat{J}_y, \hat{\mathbf{J}}^2] = [\hat{J}_z, \hat{\mathbf{J}}^2] = 0. \tag{12.57}$$

Like $\hat{J}_x$, $\hat{J}_y$ and $\hat{J}_z$, $\hat{\mathbf{J}}^2$ is a Hermitian operator.

Since $\hat{\mathbf{J}}^2$ and $\hat{J}_z$ commute, any eigenvector of $\hat{\mathbf{J}}^2$ can be written as a linear combination of normalized ket vectors $|j, m\rangle$ that are eigenvectors of *both* $\hat{\mathbf{J}}^2$ and $\hat{J}_z$ (see Section 5.3). The following is found, after rather long calculations:

1. The eigenvalues of $\hat{\mathbf{J}}^2$ are $j(j+1)\hbar^2$, where j is a non-negative integer (0, 1, 2,...) or half-integer (1/2, 3/2, 5/2,...). In particular,

$$\hat{\mathbf{J}}^2|j, m\rangle = j(j+1)\hbar^2|j, m\rangle. \tag{12.58}$$

2. The eigenvalues of $\hat{\mathbf{J}}_z$ are $m\hbar$, where m is an integer (0, $\pm$1, $\pm$2,...) or half-integer ($\pm$1/2, $\pm$3/2, $\pm$5/2,...). In the case of simultaneous eigenvectors of $\hat{\mathbf{J}}^2$ and $\hat{J}_z$, the possible values of j and m are restricted to be in the range $-j \leq m \leq j$, with m running from $-j$ to j by integer step. Therefore, for any of the $|j, m\rangle$'s,

$$\hat{J}_z|j, m\rangle = m\hbar|j, m\rangle \tag{12.59}$$

   with m equal to $-j$, $-j+1$,..., $j-1$ or j.

3. $\langle j, m|j', m'\rangle = 0$ if $j \neq j'$ or $m \neq m'$ since eigenvectors belonging to different eigenvalues of a Hermitian operator are always orthogonal. Thus

$$\langle j, m|j', m'\rangle = \delta_{jj'}\delta_{mm'}. \tag{12.60}$$

For example, in the case of an orbital angular momentum operator, the operators $\hat{J}_z$ and $\hat{\mathbf{J}}^2$ correspond, in the position representation, to the operators L_z and $\mathbf{L}^2 = L_x^2 + L_y^2 + L_z^2$, and the eigenvectors $|j, m\rangle$ to the spherical harmonics $Y_{lm}(\theta, \phi)$:

$$\mathbf{L}^2 Y_{lm}(\theta, \phi) = l(l+1)\hbar^2 Y_{lm}(\theta, \phi), \tag{12.61}$$

$$L_z Y_{lm}(\theta, \phi) = m\hbar Y_{lm}(\theta, \phi), \tag{12.62}$$

with $l = 0, 1, 2, \ldots$ (half-integer values of l are not allowed) and $-l \leq m \leq l$. The spherical harmonics are thus simultaneous eigenfunctions of $\mathbf{L}^2$ and L_z.

☞ Whereas j can in general be a half-integer as well as an integer, in the specific case of the orbital angular momentum this quantum number (usually denoted by l for an orbital angular momentum) can only be an integer. An in-depth analysis of why this must be so is beyond the scope of the course.

☞ The choice of $\hat{J}_z$, rather than another component of $\hat{\mathbf{J}}$, for defining the basis vectors $|j,m\rangle$ is purely conventional (however, it is a time-honoured convention and everybody abides by). There is nothing special about the z-direction. Instead of $\hat{J}_z$, one could use, for example, the component $\hat{J}_{\hat{\mathbf{n}}}$ of $\hat{\mathbf{J}}$ in an arbitrary direction defined by the unit vector $\hat{\mathbf{n}}$ ($\hat{J}_{\hat{\mathbf{n}}} = \hat{\mathbf{n}}\cdot\hat{\mathbf{J}}$). All what we said above about $\hat{J}_z$ also applies to $\hat{J}_{\hat{\mathbf{n}}}$: irrespective of the direction $\hat{\mathbf{n}}$, $\hat{J}_{\hat{\mathbf{n}}}$ commutes with $\hat{\mathbf{J}}^2$, the eigenvalues of $\hat{J}_{\hat{\mathbf{n}}}$ are $m\hbar$ with $m = 0$, $\pm 1/2$, ± 1, etc., one can construct a basis of the Hilbert space with simultaneous eigenvectors of $\hat{\mathbf{J}}^2$ and $\hat{J}_{\hat{\mathbf{n}}}$, and for these eigenvectors $-j \le m \le j$. However, if $\hat{\mathbf{n}}$ is not in the z-direction, these simultaneous eigenvectors of $\hat{\mathbf{J}}^2$ and $\hat{J}_{\hat{\mathbf{n}}}$ in general will not be the same as the eigenvectors of $\hat{\mathbf{J}}^2$ and $\hat{J}_z$ defined above.

☞ Rotating an eigenvector of $\hat{J}_{\hat{\mathbf{n}}}$ by an angle α about the axis $\hat{\mathbf{n}}$ simply multiplies this eigenvector by a phase factor $\exp(-im\alpha)$. For example, rotate the state $|j,m\rangle$ about the z-axis: Since $\hat{J}_z|j,m\rangle = \hbar m|j,m\rangle$, $\hat{R}_z(\alpha)|j,m\rangle = \exp(-i\alpha\hat{J}_z/\hbar)|j,m\rangle = \exp(-i\alpha m)|j,m\rangle$. Intriguingly, this means that if j (and thus m) is a half integer, then a rotation by 2π transforms $|j,m\rangle$ into $-|j,m\rangle$: only a 4π rotation brings $|j,m\rangle$ back to itself...

☞ How do the eigenvectors of $\hat{\mathbf{J}}^2$ transform under a rotation? As stated above, $\hat{\mathbf{J}}^2$ commutes with the projection of $\hat{\mathbf{J}}$ on any direction: $[\hat{\mathbf{J}}^2, \hat{J}_{\hat{\mathbf{n}}}] = 0$ for any direction $\hat{\mathbf{n}}$. Since these two operators commute, $\hat{J}_{\hat{\mathbf{n}}}$ transforms any eigenvector of $\hat{\mathbf{J}}^2$ into an eigenvector of $\hat{\mathbf{J}}^2$ belonging to the same eigenvalue (see Section 3.11 of these notes). In other words, if $\hat{\mathbf{J}}^2|\psi\rangle = j(j+1)\hbar^2|\psi\rangle$, then the vector $\hat{J}_{\hat{\mathbf{n}}}|\psi\rangle$ is also an eigenvector of $\hat{\mathbf{J}}^2$ and

$$\hat{\mathbf{J}}^2\big(\hat{J}_{\hat{\mathbf{n}}}|\psi\rangle\big) = j(j+1)\hbar^2\big(\hat{J}_{\hat{\mathbf{n}}}|\psi\rangle\big) \tag{12.63}$$

for the same value of j.

A consequence of this fact is that rotations transform any eigenvector of $\hat{\mathbf{J}}^2$ into an eigenvector of $\hat{\mathbf{J}}^2$ belonging to the same eigenvalue. For example, a p-state of an atom of hydrogen remains a p-state under a rotation.

Proof: A rotation by an angle α about a direction $\hat{\mathbf{n}}$ transforms a ket vector $|\psi\rangle$ into a ket vector $|\psi'\rangle = \hat{R}_{\hat{\mathbf{n}}}(\alpha)$. In view of Eq. (12.46),

$$|\psi'\rangle = \exp\big(-i\alpha\hat{J}_{\hat{\mathbf{n}}}/\hbar\big)|\psi\rangle. \tag{12.64}$$

Since $\hat{J}_{\hat{\mathbf{n}}}$ commutes with $\hat{\mathbf{J}}^2$, any power of $\hat{J}_{\hat{\mathbf{n}}}$ also commutes with $\hat{\mathbf{J}}^2$. Therefore $\exp(-i\alpha\hat{J}_{\hat{\mathbf{n}}}/\hbar)$ also commutes with $\hat{\mathbf{J}}^2$. Hence, if $\hat{\mathbf{J}}^2|\psi\rangle = j(j+1)\hbar^2|\psi\rangle$, then, for any rotation angle α and any rotation axis $\hat{\mathbf{n}}$,

$$\hat{\mathbf{J}}^2\big(\hat{R}_{\hat{\mathbf{n}}}(\alpha)|\psi\rangle\big) = j(j+1)\hbar^2\big(\hat{R}_{\hat{\mathbf{n}}}(\alpha)|\psi\rangle\big), \tag{12.65}$$

which means that the rotated eigenvector $|\psi'\rangle = \hat{R}_{\hat{\mathbf{n}}}(\alpha)|\psi\rangle$ is also an eigenvector of $\hat{\mathbf{J}}^2$ corresponding to the same quantum number j. □

☞ The operators $\hat{J}_+$ and $\hat{J}_-$, defined as $\hat{J}_\pm = \hat{J}_x \pm i\hat{J}_y$ both commute with $\hat{\mathbf{J}}^2$. However, they do not commute with each other and they are not Hermitian — in fact, $\hat{J}_+ = \hat{J}_-^\dagger$. These two operators play the role of ladder operators for angular momentum. In particular, one finds, through algebraic methods, that

$$\hat{J}_+|j,m\rangle = [j(j+1) - m(m+1)]^{1/2}\,\hbar|j,m+1\rangle, \tag{12.66}$$

$$\hat{J}_-|j,m\rangle = [j(j+1) - m(m-1)]^{1/2}\,\hbar|j,m-1\rangle, \tag{12.67}$$

with $\hat{J}_+|j,j\rangle = 0$ and $\hat{J}_-|j,-j\rangle = 0$.

12.6 Matrix representation of angular momentum operators

Simultaneous eigenvectors of both $\hat{\mathbf{J}}^2$ and $\hat{J}_z$ were introduced in the previous section (the normalized kets $|j,m\rangle$). Recall that $\hat{\mathbf{J}}^2$ and $\hat{J}_z$ are Hermitian operators, that $\hat{\mathbf{J}}^2|j,m\rangle = j(j+1)\hbar^2|j,m\rangle$ and $\hat{\mathbf{J}}_z|j,m\rangle = m\hbar|j,m\rangle$, that such simultaneous eigenvectors exist for m ranging from $-j$ to j by integer steps (hence, for a given value of j, m can take $2j+1$ different values) and that $\langle j,m|j',m'\rangle = \delta_{jj'}\delta_{mm'}$. The set

$$\{|0,0\rangle, |1/2,-1/2\rangle, |1/2,1/2\rangle, |1,-1\rangle, |1,0\rangle, |1,1\rangle, |3/2,-3/2\rangle, \ldots\}$$

thus forms an orthonormal basis of the relevant Hilbert space.

☞ Writing this, we implicitly assumed that the quantum numbers j and m suffice to identify each of the simultaneous eigenvectors $|j,m\rangle$ uniquely. This is not always the case. For example, the $2\mathrm{p}_{m=0}$ and $3\mathrm{p}_{m=0}$ states of atomic hydrogen are linearly independent although they both have $l=1$ and $m=0$ (remember that for the orbital angular momentum operator $\hat{\mathbf{L}}$, the quantum number j is usually denoted l). Instead of $|j,m\rangle$, one could write $|j,m,\tau\rangle$, where τ is a quantum number or a set of quantum numbers such that two kets $|j,m,\tau\rangle$ and $|j,m,\tau'\rangle$ differing by these additional quantum numbers are always orthogonal. Doing so would complicate the notation further, and therefore we do not do it here.

Since $\langle j', m'|j, m\rangle = 0$ when $j' \neq j$ and since an eigenvector of $\hat{\mathbf{J}}^2$ is transformed by $\hat{J}_z$ into an eigenvector of $\hat{\mathbf{J}}^2$ corresponding to the same value of j, $\langle j', m'|\hat{J}_z|j, m\rangle = 0$ if $j \neq j'$. In fact, this is the case for any component of $\hat{\mathbf{J}}$: e.g., $\langle j', m'|\hat{J}_x|j, m\rangle = \langle j', m'|\hat{J}_y|j, m\rangle = 0$ if $j \neq j'$. It thus makes sense to consider each value of j separately, and for a given j represent J_x, J_y and J_z by $(2j+1) \times (2j+1)$ matrices in a basis formed by the $2j+1$ eigenvectors $|j, m\rangle$ with $m = -j, \ldots, j$. Therefore these operators have 1-dimensional representations (for $j = 0$), 2-dimensional representations (for $j = 1/2$), 3-dimensional representations (for $j = 1$), etc.

The Pauli matrices

The $j = 1/2$ case is particularly important because electrons, quarks, protons and neutrons are spin-1/2 particles. As mentioned previously, spin corresponds to an angular momentum operator $\hat{\mathbf{S}}$. The eigenvalues of $\hat{\mathbf{S}}^2$ are $s(s+1)\hbar^2$ with $s = 0,\ 1/2,\ 1, \ldots$ The electron, the proton and the neutron are said to be spin-1/2 particles because the kets representing their quantum state are always eigenvectors of $\hat{\mathbf{S}}^2$ with $s = 1/2$ (otherwise these kets would be physically incorrect).

Let us consider the more general case of an angular momentum operator $\hat{\mathbf{J}}$ and of a system in an eigenstate of $\hat{\mathbf{J}}^2$ with eigenvalue $j = 1/2$. When $j = 1/2$, the quantum number m has only two possible values in simultaneous eigenstates of $\hat{\mathbf{J}}^2$ and $\hat{J}_z$, i.e., $-1/2$ and $1/2$. The J_x, J_y and J_z operators are thus represented by 2×2 matrices in that case.

It is customary to work in the basis $\{|1/2, 1/2\rangle, |1/2, -1/2\rangle\}$. (Note the order of the basis vectors in that set; the matrices representing the relevant operators would be different if we would work in the $\{|1/2, -1/2\rangle, |1/2, 1/2\rangle\}$ basis.) For memory, the two basis vectors $|1/2, 1/2\rangle$ and $|1/2, -1/2\rangle$ are such that

$$\hat{J}_z|1/2, \pm 1/2\rangle = \pm\frac{\hbar}{2}|1/2, \pm 1/2\rangle. \tag{12.68}$$

Alternative notations for $|1/2, 1/2\rangle$ (the "state of spin up") and $|1/2, -1/2\rangle$ (the "state of spin down") are $|+\rangle$ and $|-\rangle$, $|\chi_+\rangle$ and $|\chi_-\rangle$, and $|\uparrow\rangle$ and $|\downarrow\rangle$:

$$|1/2, 1/2\rangle = |+\rangle = |\chi_+\rangle = |\uparrow\rangle, \qquad |1/2, -1/2\rangle = |-\rangle = |\chi_-\rangle = |\downarrow\rangle. \tag{12.69}$$

(The terms "spin up" and "spin down" are conventional and do not reflect a particular orientation with respect to the vertical direction.)

The matrix J_z representing $\hat{J}_z$ in the $\{|+\rangle, |-\rangle\}$ basis is therefore diagonal. Specifically,

$$\mathsf{J}_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{12.70}$$

It can be shown that $\hat{J}_x$ and $\hat{J}_y$ are represented by the following matrices in this basis (see Worksheet 9 for a proof):

$$\mathsf{J}_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad \mathsf{J}_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}. \tag{12.71}$$

J_x, J_y and J_z are often written in terms of the Pauli matrices σ_x, σ_y and σ_z:

$$\mathsf{J}_x = (\hbar/2)\sigma_x, \qquad \mathsf{J}_y = (\hbar/2)\sigma_y, \qquad \text{and} \qquad \mathsf{J}_z = (\hbar/2)\sigma_z, \tag{12.72}$$

where

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{12.73}$$

Any $j = 1/2$ eigenvector of $\hat{\mathbf{J}}^2$ can be written as a linear combination of the vectors $|+\rangle$ and $|-\rangle$. Namely, if $|\psi\rangle$ is such that $\hat{\mathbf{J}}^2|\psi\rangle = j(j+1)\hbar^2|\psi\rangle$ with $j = 1/2$, then there always exists two complex numbers α and β such that

$$|\psi\rangle = \alpha|+\rangle + \beta|-\rangle. \tag{12.74}$$

This ket vector is represented by the column vector

$$\begin{pmatrix} \langle +|\psi\rangle \\ \langle -|\psi\rangle \end{pmatrix}$$

in the $\{|+\rangle, |-\rangle\}$ basis. Since $\langle +|+\rangle = \langle -|-\rangle = 1$ and $\langle +|-\rangle = \langle +|-\rangle = 0$,

$$\begin{pmatrix} \langle +|\psi\rangle \\ \langle -|\psi\rangle \end{pmatrix} = \begin{pmatrix} \alpha \\ \beta \end{pmatrix}. \tag{12.75}$$

In particular, the states of spin up and spin down, $|+\rangle$ and $|-\rangle$, are represented, respectively, by the column vectors

$$\begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \text{and} \qquad \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

12.7 The Clebsch-Gordan coefficients

Consider a system formed by two electrons, electron 1 and electron 2. Electron 1 can be, e.g., in the state of spin up, which we will now write $|+\rangle_1$ with the subscript 1 indicating that this ket vector pertains to the state of that electron. Likewise, electron 2 can be, e.g., in the state of spin down, $|-\rangle_2$. We can

represent the joint state of these two electrons by the symbol $|+\rangle_1|-\rangle_2$. (Recall that this symbol does not represent a product like a product of numbers or a dot product of geometrical vectors; as is explained in Part 7 of these notes, it represents a quantum state in which electron 1 is in the state $|+\rangle_1$ and electron 2 in the state $|-\rangle_2$.) Other possibilities for this bipartite system include $|+\rangle_1|+\rangle_2$, representing a state in which both electrons are in a state of spin up, and also $|-\rangle_1|+\rangle_2$ and $|-\rangle_1|-\rangle_2$. However, by virtue of the principle of superposition, the state of this system can also be a linear combination of $|+\rangle_1|+\rangle_2$, $|+\rangle_1|-\rangle_2$, $|-\rangle_1|+\rangle_2$ and $|-\rangle_1|-\rangle_2$. In general, the two-electron system can be in a joint spin state represented by the ket vector

$$|\psi\rangle_{12} = \alpha|+\rangle_1|+\rangle_2 + \beta|+\rangle_1|-\rangle_2 + \gamma|-\rangle_1|+\rangle_2 + \delta|-\rangle_1|-\rangle_2, \tag{12.76}$$

where α, β, γ and δ are four complex numbers.

More general joint angular momentum states of bipartite systems are often encountered in applications. In general, such states can be written in the following way:

$$|\psi\rangle_{12} = \sum_{j_1 m_1 j_2 m_2} c_{j_1 m_1 j_2 m_2} |j_1, m_1\rangle_1 |j_2, m_2\rangle_2, \tag{12.77}$$

where the kets $|j_1, m_1\rangle_1$ pertain to one part of the whole system and the kets $|j_2, m_2\rangle_2$ to the other part. Note that the angular momentum operator $\hat{\mathbf{J}}_1$ acts only on the state vectors pertaining to part 1 of the whole system while $\hat{\mathbf{J}}_2$ acts only on the state vectors pertaining to part 2. For example,

$$\hat{J}_{2z}|\psi\rangle_{12} = \sum_{j_1 m_1 j_2 m_2} c_{j_1 m_1 j_2 m_2} |j_1, m_1\rangle_1 \hat{J}_{2z}|j_2, m_2\rangle_2. \tag{12.78}$$

One can show that under a rotation by an angle α about an axis $\hat{\mathbf{n}}$, $|\psi\rangle_{12} \to |\psi'\rangle_{12} = \hat{R}_{\hat{\mathbf{n}}}(\alpha)|\psi\rangle_{12}$ with

$$\hat{R}_{\hat{\mathbf{n}}}(\alpha) = \exp\big[-i\alpha\big(\hat{\mathbf{n}}\cdot\hat{\mathbf{J}}_1 + \hat{\mathbf{n}}\cdot\hat{\mathbf{J}}_2\big)/\hbar\big]. \tag{12.79}$$

Let $\hat{\mathbf{J}} = \hat{\mathbf{J}}_1 + \hat{\mathbf{J}}_2$. Each component of $\hat{\mathbf{J}}$ is the sum of the corresponding components of $\hat{\mathbf{J}}_1$ and $\hat{\mathbf{J}}_2$:

$$\hat{\mathbf{J}} = \hat{J}_x\,\hat{\mathbf{x}} + \hat{J}_y\,\hat{\mathbf{y}} + \hat{J}_z\,\hat{\mathbf{z}} \tag{12.80}$$

$$\hat{\mathbf{J}}_1 = \hat{J}_{1x}\,\hat{\mathbf{x}} + \hat{J}_{1y}\,\hat{\mathbf{y}} + \hat{J}_{1z}\,\hat{\mathbf{z}} \tag{12.81}$$

$$\hat{\mathbf{J}}_2 = \hat{J}_{2x}\,\hat{\mathbf{x}} + \hat{J}_{2y}\,\hat{\mathbf{y}} + \hat{J}_{2z}\,\hat{\mathbf{z}}, \tag{12.82}$$

with $J_x = J_{1x} + J_{2x}$, $J_y = J_{1y} + J_{2y}$ and $J_z = J_{1z} + J_{2z}$. It is not difficult to show that $\hat{\mathbf{J}}$ is an angular momentum operator, i.e., that $\hat{J}_x$, $\hat{J}_y$ and $\hat{J}_z$ are Hermitian and satisfy the commutation relations

$$[\hat{J}_x, \hat{J}_y] = i\hbar\hat{J}_z, \quad [\hat{J}_y, \hat{J}_z] = i\hbar\hat{J}_x, \quad [\hat{J}_z, \hat{J}_x] = i\hbar\hat{J}_y. \tag{12.83}$$

Since $\hat{\mathbf{J}}$ is an angular momentum operator, each of its components commute with $\hat{\mathbf{J}}^2$. In particular, $[\hat{J}_z, \hat{\mathbf{J}}^2] = 0$. It is not difficult to show that the operators $\hat{\mathbf{J}}_1^2$ and $\hat{\mathbf{J}}_2^2$ also commute with both $\hat{\mathbf{J}}^2$ and $\hat{J}_z$, besides commuting with each other:

$$[\hat{\mathbf{J}}_1^2, \hat{\mathbf{J}}_2^2] = [\hat{\mathbf{J}}_1^2, \hat{\mathbf{J}}^2] = [\hat{\mathbf{J}}_1^2, \hat{\mathbf{J}}^2] = [\hat{J}_z, \hat{\mathbf{J}}_1^2] = [\hat{J}_z, \hat{\mathbf{J}}_2^2] = [\hat{J}_z, \hat{\mathbf{J}}^2] = 0. \tag{12.84}$$

(However, $\hat{\mathbf{J}}^2$ does not commute with J_{1z} or J_{2z}.) Hence, it is possible to construct a basis of simultaneous eigenvectors of $\mathbf{J}_1^2$, $\mathbf{J}_2^2$, $\mathbf{J}^2$ and J_z. We will denote such simultaneous eigenvectors by $|j_1, j_2, J, M\rangle_{12}$. The quantum numbers j_1, j_2, J and M identify the corresponding eigenvalues:

$$\hat{\mathbf{J}}_1^2 |j_1, j_2, J, M\rangle_{12} = j_1(j_1+1)\hbar^2 |j_1, j_2, J, M\rangle_{12}, \tag{12.85}$$

$$\hat{\mathbf{J}}_2^2 |j_1, j_2, J, M\rangle_{12} = j_2(j_2+1)\hbar^2 |j_1, j_2, J, M\rangle_{12}, \tag{12.86}$$

$$\hat{\mathbf{J}}^2 |j_1, j_2, J, M\rangle_{12} = J(J+1)\hbar^2 |j_1, j_2, J, M\rangle_{12}, \tag{12.87}$$

$$\hat{J}_z |j_1, j_2, J, M\rangle_{12} = M\hbar |j_1, j_2, J, M\rangle_{12}. \tag{12.88}$$

For given values of j_1 and j_2, the possible values of J and M in simultaneous eigenvectors of $\mathbf{J}_1^2$, $\mathbf{J}_2^2$, $\mathbf{J}^2$ and $\mathbf{J}_z$ are restricted by the "triangular inequality",

$$|j_1 - j_2| \leq J \leq j_1 + j_2,$$

and by the usual condition that

$$-J \leq M \leq J. \tag{12.89}$$

(Thus J can have any of the following values: $|j_1-j_2|$, $|j_1-j_2|+1$, $|j_1-j_2|+2$,..., j_1+j_2-1, j_1+j_2. For a given J, M can have any of the following values: $-J$, $-J+1$,..., $J-1$, J.)

Each of the eigenvectors $|j_1, j_2, J, M\rangle_{12}$ can be written as a linear combination of the vectors $|j_1, m_1\rangle_1 |j_2, m_2\rangle_2$. The coefficients of this superposition are real numbers called Clebsch-Gordan coefficients (note the spelling: Gordan, not Gordon). Following well established traditions, we will write them $\langle j_1, j_2, m_1, m_2 | J, M\rangle$:

$$|j_1, j_2, J, M\rangle_{12} = \sum_{m_1, m_2} \langle j_1, j_2, m_1, m_2 | J, M\rangle |j_1, m_1\rangle_1 |j_2, m_2\rangle_2. \tag{12.90}$$

Reciprocally,

$$|j_1, m_1\rangle_1 |j_2, m_2\rangle_2 = \sum_J \langle j_1, j_2, m_1, m_2 | J, M\rangle |j_1, j_2, J, M\rangle_{12}. \tag{12.91}$$

It can be shown that the Clebsch-Gordan coefficient $\langle j_1, j_2, m_1, m_2 | J, M\rangle$ is zero when $M \neq m_1 + m_2$ (see Worksheet 9). Therefore, in Eq. (12.90), the double sum runs only over the values of m_1 and m_2 such that $M = m_1 + m_2$, and in Eq. (12.91) M is necessarily equal to $m_1 + m_2$. In both of these equations, the possible values of J are restricted by the triangular inequality mentioned above.