

Lecture 10: Orbital angular momentum

Reading: Atkins and Friedman, Molecular Quantum Mechanics, 5th ed., Chapter 4.

Although spin is a distinct physical quantity, it shares some mathematical properties with orbital angular momentum. Historically, the modern theory of spin was inspired by this analogy. This lecture reviews the relevant concepts from chemical spectroscopy courses.

1. Rotational symmetry of free space

Empirical evidence indicates that, in the absence of external fields, empty space is isotropic. Therefore, the energy of an isolated physical system should not be changed by a static rotation:

$$|\psi\rangle \rightarrow \hat{R}|\psi\rangle \Rightarrow E = \langle\psi|\hat{H}|\psi\rangle = \langle\psi|\hat{R}^\dagger\hat{H}\hat{R}|\psi\rangle \quad (1)$$

where $\hat{R}$ is necessarily a *unitary* (conjugate-transpose equals inverse) operator that performs the rotation; the hat indicates a linear integrodifferential operator, we will derive its explicit form today.

Eq (1) holds for any wavefunction, it must therefore hold for the corresponding operators:

$$\hat{H} = \hat{R}^\dagger\hat{H}\hat{R} \Rightarrow \hat{H} = \hat{R}^{-1}\hat{H}\hat{R} \Rightarrow [\hat{H}, \hat{R}] = 0 \quad (2)$$

where the square bracket denotes a commutator $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$. This leads to a conservation law for the observable associated with the rotation operator $\hat{R}$:

$$\frac{d}{dt}\langle\psi|\hat{R}|\psi\rangle = \left(\frac{d}{dt}\langle\psi|\right)\hat{R}|\psi\rangle + \langle\psi|\hat{R}\left(\frac{d}{dt}|\psi\rangle\right) = \dots = i\langle\psi|[\hat{H}, \hat{R}]|\psi\rangle = 0 \quad (3)$$

This is a special case of *Noether's theorem*: every differentiable symmetry of the Hamiltonian of a physical system with conservative forces has a corresponding conservation law.

2. Rotation operators

Let us find out, from the physical point of view, what the conserved quantity $\langle\psi|\hat{R}|\psi\rangle$ in Eq (3) is. We start with the operator for a *positive* (counterclockwise) and *active* (of the object, not the coordinate system) rotation of the wavefunction by an angle α around the Z axis:

$$\psi(\varphi - \alpha) = \exp\left(-\alpha \frac{\partial}{\partial \varphi}\right)\psi(\varphi) \Rightarrow \hat{R}_Z(\alpha) = \exp\left(-\alpha \frac{\partial}{\partial \varphi}\right) \quad (4)$$

where the identity on the left is proven using Taylor series:

$$\exp\left(-\alpha \frac{\partial}{\partial \varphi}\right)\psi(\varphi) = \left[\sum_{n=0}^{\infty} \frac{(-\alpha)^n}{n!} \frac{\partial^n}{\partial \varphi^n}\right]\psi(\varphi) = \sum_{n=0}^{\infty} \frac{\psi^{(n)}(\varphi)}{n!} (-\alpha)^n = \psi(\varphi - \alpha) \quad (5)$$

The Cartesian expression for $\partial/\partial\varphi$ follows from the definition of polar coordinates and the chain rule:

$$\begin{cases} x = r \cos \varphi; \\ y = r \sin \varphi; \end{cases} \quad \frac{\partial f}{\partial \varphi} = \frac{\partial f}{\partial x} \frac{\partial x}{\partial \varphi} + \frac{\partial f}{\partial y} \frac{\partial y}{\partial \varphi} = r \cos \varphi \frac{\partial f}{\partial y} - r \sin \varphi \frac{\partial f}{\partial x} = \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x}\right)f \quad (6)$$

After running similar mathematics for rotations around X and Y axes, we arrive at the expressions for the active counter-clockwise Cartesian *rotation operators*:

$$\hat{R}_{\{X,Y,Z\}}(\alpha) = \exp\left(-i\hat{L}_{\{X,Y,Z\}}\alpha\right) \quad (7)$$

where the presence of the complex unit is historical. The operators under the exponential are called (for deeper algebraic reasons that we cannot cover in this module) *rotation generators*:

$$\hat{L}_X = -i \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right); \quad \hat{L}_Y = -i \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right); \quad \hat{L}_Z = -i \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \quad (8)$$

3. Angular momentum operators

From the physical point of view, the rotation generators in Eq (8) are angular momentum operators; this may be seen from classical physics. For the angular momentum of a point particle with a coordinate vector $\mathbf{r} = (x \ y \ z)^T$ and a momentum vector $\mathbf{p} = (p_X \ p_Y \ p_Z)^T$:

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} = \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ x & y & z \\ p_X & p_Y & p_Z \end{vmatrix} = \begin{pmatrix} yp_Z - zp_Y \\ zp_X - xp_Z \\ xp_Y - yp_X \end{pmatrix} = \begin{pmatrix} L_X \\ L_Y \\ L_Z \end{pmatrix} \quad (9)$$

The quantisation procedure in this case amounts to replacing the canonical variables $\mathbf{r}$ and $\mathbf{p}$ with the corresponding quantum mechanical operators, which are:

$$\begin{aligned} \hat{p}_X &= -i \frac{\partial}{\partial x}, & \hat{p}_Y &= -i \frac{\partial}{\partial y}, & \hat{p}_Z &= -i \frac{\partial}{\partial z} \\ \hat{x} &= x, & \hat{y} &= y, & \hat{z} &= z \end{aligned} \quad (10)$$

When the substitutions are made, the resulting *angular momentum operators* match those in Eq (8):

$$\hat{L}_X = -i \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right); \quad \hat{L}_Y = -i \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right); \quad \hat{L}_Z = -i \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \quad (11)$$

They turn up whenever a physical system has rotational dynamics or symmetry.

4. Auxiliary angular momentum operators

Three more operators will be useful later. One is the *momentum square operator*:

$$\hat{L}^2 = \hat{L}_X^2 + \hat{L}_Y^2 + \hat{L}_Z^2 \quad (12)$$

This is the quantity that is conserved under any rotation of the reference frame – individual projections may be redistributed, but the sum of squares remains the same.

The other two are *raising and lowering operators*, defined as:

$$\hat{L}_+ = \hat{L}_X + i\hat{L}_Y, \quad \hat{L}_- = \hat{L}_X - i\hat{L}_Y \quad (13)$$

We will use them later to manipulate angular momentum eigenfunctions. It is easy to demonstrate by direct inspection that the following relations also hold:

$$\begin{aligned} \hat{L}^2 &= \hat{L}_- \hat{L}_+ + \hat{L}_Z^2 + \hat{L}_Z = \hat{L}_+ \hat{L}_- + \hat{L}_Z^2 - \hat{L}_Z \\ \hat{L}_X &= \frac{\hat{L}_+ + \hat{L}_-}{2}; & \hat{L}_Y &= \frac{\hat{L}_+ - \hat{L}_-}{2i} \end{aligned} \quad (14)$$

5. Commutation relations

An important property that angular momentum operators share with spin operators is commutation relations. Many equations that we will encounter later in the course involve *commutators*:

$$[\mathbf{A}, \mathbf{B}] = \mathbf{AB} - \mathbf{BA} \quad (15)$$

One can prove by onerous direct inspection from the definitions given in Eq (8) the following *commutation relations* between the angular momentum projection operators:

$$[\hat{L}_x, \hat{L}_y] = i\hat{L}_z, \quad [\hat{L}_y, \hat{L}_z] = i\hat{L}_x, \quad [\hat{L}_z, \hat{L}_x] = i\hat{L}_y \quad (16)$$

One can also show that the momentum square operator commutes with all Cartesian operators:

$$[\hat{L}^2, \hat{L}_x] = 0, \quad [\hat{L}^2, \hat{L}_y] = 0, \quad [\hat{L}^2, \hat{L}_z] = 0 \quad (17)$$

For commutators involving raising and lowering operators we similarly get:

$$[\hat{L}^2, \hat{L}_\pm] = 0, \quad [\hat{L}_+, \hat{L}_-] = 2\hat{L}_z, \quad [\hat{L}_z, \hat{L}_\pm] = \pm\hat{L}_\pm \quad (18)$$

6. Angular momentum eigenfunctions

The angular momentum operators derived above generate three-dimensional rotations, and it is therefore natural to seek their eigenfunctions in spherical coordinates. Commuting operators share eigenfunctions, and the historical convention is to use simultaneous eigenfunctions of $\hat{L}^2$ and $\hat{L}_z$.

The diagonalisation problem for these operators is analytically cumbersome. We shall simply state here that the eigenfunctions exist; Laplace called them *spherical harmonics* $Y_{lm}(\theta, \varphi)$:

$$\begin{cases} \hat{L}^2 Y_{lm}(\theta, \varphi) = l(l+1) Y_{lm}(\theta, \varphi) \\ \hat{L}_z Y_{lm}(\theta, \varphi) = m Y_{lm}(\theta, \varphi) \end{cases} \quad l \in \mathbb{Z}_+, \quad m = -l, -l+1, \dots, l \quad (19)$$

Spherical harmonics are sometimes labelled with their $\hat{L}_z$ and $\hat{L}^2$ eigenvalues:

$$\begin{cases} \hat{L}^2 |l, m\rangle = l(l+1) |l, m\rangle \\ \hat{L}_z |l, m\rangle = m |l, m\rangle \end{cases} \quad |l, m\rangle \equiv Y_{lm}(\theta, \varphi) \quad (20)$$

and only used through their properties under the action of specific operators – their explicit trigonometric form is rarely needed in practice. In the physical sciences jargon, the l quantum number is loosely called *angular momentum* and m is called its *projection*.

7. Properties of raising and lowering operators

Raising and lowering operators got their names because they shift the projection quantum number of angular momentum eigenfunctions $|l, m\rangle$ one click up or down:

$$\hat{L}_\pm |l, m\rangle = \sqrt{l(l+1) - m(m\pm 1)} |l, m\pm 1\rangle \quad (21)$$

We cannot provide the full derivation in this module, but we can at least verify that $\hat{L}_\pm |l, m\rangle$ is proportional to $|l, m\pm 1\rangle$ by looking at the eigenvalues of $\hat{L}_z$ and $\hat{L}^2$:

$$\hat{L}_z (\hat{L}_\pm |l, m\rangle) = ([\hat{L}_z, \hat{L}_\pm] + \hat{L}_\pm \hat{L}_z) |l, m\rangle = (\pm \hat{L}_\pm + \hat{L}_\pm m) |l, m\rangle = (m\pm 1) (\hat{L}_\pm |l, m\rangle) \quad (22)$$

$$\hat{L}^2 (\hat{L}_\pm |l, m\rangle) = \hat{L}_\pm \hat{L}^2 |l, m\rangle = \hat{L}_\pm l(l+1) |l, m\rangle = l(l+1) (\hat{L}_\pm |l, m\rangle) \quad (23)$$

It is not possible to raise or lower the projection beyond the range specified in Eq (19):

$$\hat{L}_+ |l, l\rangle = 0 \quad \hat{L}_- |l, -l\rangle = 0 \quad (24)$$

because the square root in Eq (21) goes to zero.