CHEM6154 - Week 21 - Lecture 1: Angular momentum

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

1. Angular momentum in quantum mechanics

Empirical evidence suggests 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:

$$\psi \to \hat{R}\psi \quad \Rightarrow \quad \langle\psi|\hat{R}^\dagger\hat{H}\hat{R}|\psi\rangle = \langle\psi|\hat{H}|\psi\rangle \tag{1}$$

where $\hat{R}$ is an operator that performs the rotation. Because the relation above holds for any wavefunction, it must hold for the corresponding operators:

$$\hat{R}^\dagger\hat{H}\hat{R} = \hat{H} \quad \Rightarrow \quad \hat{R}^{-1}\hat{H}\hat{R} = \hat{H} \quad \Rightarrow \quad \left[\hat{H},\hat{R}\right] = 0 \tag{2}$$

This leads to a conservation law for the observable associated with $\hat{R}$:

$$\frac{d}{dt}\langle\psi|\hat{R}|\psi\rangle = \ldots = i\langle\psi|\left[\hat{H},\hat{R}\right]|\psi\rangle = 0 \tag{3}$$

Let us find out what this observable is. We start with the operator for a positive (counterclockwise) rotation of the wavefunction (not the coordinate system) by a small angle φ in the XY plane:

$$\begin{cases} \hat{R}(\varphi): x \to x' = x\cos\varphi + y\sin\varphi \\ \hat{R}(\varphi): y \to y' = -x\sin\varphi + y\cos\varphi \\ \hat{R}(\varphi): z \to z' = z \end{cases}$$
$$\hat{R}(\varphi)\psi(x,y,z) = \psi(x',y',z') \tag{4}$$

Because the angle φ is small, we can use a Taylor expansion to second term around $\varphi = 0$:

$$\psi(x',y',z') = \psi(x,y,z) + \left[\frac{\partial}{\partial\varphi}\psi(x',y',z')\right]_{\varphi=0}\varphi + O\left(\varphi^2\right) \tag{5}$$

The derivative in the square brackets is computed using the chain rule:

$$\begin{aligned} \left[\frac{\partial}{\partial\varphi}\psi(x',y',z')\right]_{\varphi=0} &= \left[\frac{\partial\psi}{\partial x'}\frac{\partial x'}{\partial\varphi} + \frac{\partial\psi}{\partial y'}\frac{\partial y'}{\partial\varphi} + \frac{\partial\psi}{\partial z'}\frac{\partial z'}{\partial\varphi}\right]_{\varphi=0} = \\ = \left[\frac{\partial\psi}{\partial x'}(-x\sin\varphi + y\cos\varphi) + \frac{\partial\psi}{\partial y'}(-x\cos\varphi - y\sin\varphi)\right]_{\varphi=0} &= \left(y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y}\right)\psi(x,y,z) \end{aligned} \tag{6}$$

We therefore find the following expression for the operator performing a rotation by an infinitesimal angle $d\varphi$ around the Z axis:

$$\hat{R}(d\varphi)|\psi\rangle = \left[1 - i\hat{L}_{\mathrm{Z}}d\varphi\right]|\psi\rangle \qquad \hat{L}_{\mathrm{Z}} = -i\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \tag{7}$$

A similar treatment can demonstrate that small rotations in the YZ and XZ planes are performed by:

$$\hat{L}_{\mathrm{X}} = -i\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right); \qquad \hat{L}_{\mathrm{Y}} = -i\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \tag{8}$$

Let us compare these expressions to those of angular momentum of a point particle with a coordinate vector $\vec{r} = \begin{pmatrix} x & y & z \end{pmatrix}$ and a momentum vector $\vec{p} = \begin{pmatrix} p_{\mathrm{X}} & p_{\mathrm{Y}} & p_{\mathrm{Z}} \end{pmatrix}$ in classical mechanics:

$$\vec{L}=\vec{r}\times\vec{p}=\begin{vmatrix}\vec{i} & \vec{j} & \vec{k}\\ x & y & z\\ p_\text{X} & p_\text{Y} & p_\text{Z}\end{vmatrix}=\begin{pmatrix}yp_\text{Z}-zp_\text{Y}\\ zp_\text{X}-xp_\text{Z}\\ xp_\text{Y}-yp_\text{X}\end{pmatrix}=\begin{pmatrix}L_\text{X}\\ L_\text{Y}\\ L_\text{Z}\end{pmatrix} \tag{9}$$

The quantisation procedure in this case amounts to replacing all quantities in this definition with the corresponding quantum mechanical operators, which are:

$$\hat{p}_\text{X}=-i\frac{\partial}{\partial x},\quad \hat{p}_\text{Y}=-i\frac{\partial}{\partial y},\quad \hat{p}_\text{Z}=-i\frac{\partial}{\partial z},\quad \hat{x}=x,\quad \hat{y}=y,\quad \hat{z}=z \tag{10}$$

The resulting operators match those in Eqs (7) and (8), these are *angular momentum operators*:

$$\hat{L}_\text{X}=-i\left(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right);\quad \hat{L}_\text{Y}=-i\left(z\frac{\partial}{\partial x}-x\frac{\partial}{\partial z}\right);\quad \hat{L}_\text{Z}=-i\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right) \tag{11}$$

They appear whenever a physical system has rotational dynamics or symmetry. Three more operators will be useful later. One is the *momentum square operator* – the sum of squares of $\hat{L}_\text{X}$, $\hat{L}_\text{Y}$ and $\hat{L}_\text{Z}$:

$$\hat{L}^2=\hat{L}_\text{X}^2+\hat{L}_\text{Y}^2+\hat{L}_\text{Z}^2 \tag{12}$$

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

$$\hat{L}_+=\hat{L}_\text{X}+i\hat{L}_\text{Y}\qquad \hat{L}_-=\hat{L}_\text{X}-i\hat{L}_\text{Y} \tag{13}$$

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

$$\begin{gathered}\hat{L}^2=\hat{L}_-\hat{L}_++\hat{L}_\text{Z}^2+\hat{L}_\text{Z}=\hat{L}_+\hat{L}_-+\hat{L}_\text{Z}^2-\hat{L}_\text{Z}\\ \hat{L}_\text{X}=\frac{\hat{L}_++\hat{L}_-}{2};\qquad \hat{L}_\text{Y}=\frac{\hat{L}_+-\hat{L}_-}{2i}\end{gathered} \tag{14}$$

2. Angular momentum commutation relations

Many equations that we will encounter later in the course involve operator *commutators*:

$$[\hat{L},\hat{S}]=\hat{L}\hat{S}-\hat{S}\hat{L} \tag{15}$$

One can prove by direct inspection from the definitions given in Equation (11) the following *commutation relations* between the angular momentum projection operators:

$$[\hat{L}_\text{X},\hat{L}_\text{Y}]=i\hat{L}_\text{Z},\qquad [\hat{L}_\text{Y},\hat{L}_\text{Z}]=i\hat{L}_\text{X},\qquad [\hat{L}_\text{Z},\hat{L}_\text{X}]=i\hat{L}_\text{Y} \tag{16}$$

One can also show that the total momentum operator commutes with all projection operators:

$$[\hat{L}^2,\hat{L}_\text{X}]=0,\quad [\hat{L}^2,\hat{L}_\text{Y}]=0,\quad [\hat{L}^2,\hat{L}_\text{Z}]=0 \tag{17}$$

For commutators involving raising and lowering operators we similarly get:

$$[\hat{L}^2,\hat{L}_\pm]=0,\qquad [\hat{L}_+,\hat{L}_-]=2\hat{L}_\text{Z},\qquad [\hat{L}_\text{Z},\hat{L}_\pm]=\pm\hat{L}_\pm \tag{18}$$

3. Angular momentum eigenfunctions

Because the angular momentum operators derived above generate three-dimensional rotations, it is natural to seek their eigenfunctions in spherical coordinates. After the transformation from Cartesian to spherical coordinates, the total momentum operator and the Z projection operator become:

$$\hat{L}^2 = -\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) - \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}, \qquad \hat{L}_Z = -i\frac{\partial}{\partial\varphi} \tag{19}$$

The simultaneous diagonalization problem for these operators is analytically cumbersome; we shall simply state here that the eigenfunctions exist and are called *spherical harmonics* $Y_{lm}(\theta,\varphi)$:

$$\begin{cases} \hat{L}^2 Y_{lm}(\theta,\varphi) = l(l+1)Y_{lm}(\theta,\varphi) \\ \hat{L}_Z Y_{lm}(\theta,\varphi) = mY_{lm}(\theta,\varphi) \end{cases} \qquad l \in \mathbb{N},\; m = -l,-l+1,\ldots,l \tag{20}$$

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

$$\begin{cases} \hat{L}^2 |l,m\rangle = l(l+1)|l,m\rangle \\ \hat{L}_Z |l,m\rangle = m|l,m\rangle \end{cases} \qquad |l,m\rangle \equiv Y_{lm}(\theta,\varphi) \tag{21}$$

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*.

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

$$\hat{L}_Z\left(\hat{L}_\pm|l,m\rangle\right) = \left([\hat{L}_Z,\hat{L}_\pm] + \hat{L}_\pm\hat{L}_Z\right)|l,m\rangle = \left(\pm\hat{L}_\pm + \hat{L}_\pm m\right)|l,m\rangle = (m\pm1)\left(\hat{L}_\pm|l,m\rangle\right) \tag{22}$$

At the same time, the l quantum number remains unchanged:

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

More specifically (we skip the voluminous derivation here):

$$\hat{L}_\pm|l,m\rangle = \sqrt{l(l+1) - m(m\pm1)}\,|l,m\pm1\rangle \tag{24}$$

It is not possible to raise or lower the projection beyond the range specified in Eq (20):

$$\hat{L}_+|l,l\rangle = 0 \qquad \hat{L}_-|l,-l\rangle = 0 \tag{25}$$

because the square root in Eq (24) becomes zero.