CHEM6154 - Week 21 - Lecture 1: Angular momentum

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

Angular momentum in quantum mechanics

It stands to reason that, in the absence of external fields and perturbations, the result of an experiment on a physical system should not depend on the choice of coordinates. In other words, it is reasonable to assume that *space itself is uniform and isotropic*. In particular, the energy of a physical system should not be changed by static coordinate translations and rotations:

$$\begin{array}{lll} |\psi\rangle \to \hat{T}|\psi\rangle & \Rightarrow & \langle\psi|\hat{T}^{\dagger}\hat{H}\hat{T}|\psi\rangle = \langle\psi|\hat{H}|\psi\rangle \\ |\psi\rangle \to \hat{R}|\psi\rangle & \Rightarrow & \langle\psi|\hat{R}^{\dagger}\hat{H}\hat{R}|\psi\rangle = \langle\psi|\hat{H}|\psi\rangle \end{array} \tag{1}$$

where $\hat{T}$ is an operator that performs coordinate system translation and $\hat{R}$ is a rotation operator. Because the relations above hold for any wavefunction, they must hold for the corresponding operators. Therefore, both $\hat{T}$ and $\hat{R}$ commute with the Hamiltonian:

$$\begin{array}{lllll} \hat{T}^{\dagger}\hat{H}\hat{T} = \hat{H} & \Rightarrow & \hat{T}^{-1}\hat{H}\hat{T} = \hat{H} & \Rightarrow & \left[\hat{H},\hat{T}\right] = 0 \\ \hat{R}^{\dagger}\hat{H}\hat{R} = \hat{H} & \Rightarrow & \hat{R}^{-1}\hat{H}\hat{R} = \hat{H} & \Rightarrow & \left[\hat{H},\hat{R}\right] = 0 \end{array} \tag{2}$$

This leads to the conservation of the corresponding observables:

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

We will now find out what these observables are. Let us derive the operator for a positive (counter clockwise) rotation of the wavefunction (not the coordinate system) by a small angle φ in the XY plane:

$$\begin{array}{c} \left\{ \begin{array}{l} \hat{R}(\varphi): x \to +x\cos\varphi + y\sin\varphi \\ \hat{R}(\varphi): y \to -x\sin\varphi + y\cos\varphi \\ \hat{R}(\varphi): z \to z \end{array} \right. \\ \hat{R}(\varphi)\left|\psi(x,y,z)\right\rangle = \left|\psi(x\cos\varphi + y\sin\varphi, -x\sin\varphi + y\cos\varphi, z)\right\rangle \end{array} \tag{4}$$

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

$$\hat{R}(\varphi)|\psi\rangle = \hat{R}(0)|\psi\rangle + \left[\frac{\partial}{\partial\varphi}\hat{R}(\varphi)|\psi\rangle\right]_{\varphi=0}\varphi + O(\varphi^2) \tag{5}$$

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

$$\left[\frac{\partial}{\partial\varphi}\hat{R}(\varphi)|\psi\rangle\right]_{\varphi=0} = \left[\frac{\partial}{\partial\varphi}\left|\psi(x\cos\varphi + y\sin\varphi, -x\sin\varphi + y\cos\varphi, z)\right\rangle\right]_{\varphi=0} = \ldots = \left(y\frac{\partial}{\partial x} - x\frac{\partial}{\partial y}\right)|\psi\rangle \tag{6}$$

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:

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

These operators are actually *angular momentum operators* – the definition of angular momentum of a point particle with a coordinate vector $\vec{r}=\begin{pmatrix}x & y & z\end{pmatrix}$ and a momentum vector $\vec{p}=\begin{pmatrix}p_{\mathrm{X}} & p_{\mathrm{Y}} & p_{\mathrm{Z}}\end{pmatrix}$ given in classical mechanics is:

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

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

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

with the result that the operators corresponding to the three components of the angular momentum vector become:

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

These operators make an appearance whenever a physical system has rotational dynamics or symmetry. Two more types of angular momentum operators will be useful later. One is the *total momentum operator* – the sum of squares of $\hat{L}_{\mathrm{X}}$, $\hat{L}_{\mathrm{Y}}$ and $\hat{L}_{\mathrm{Z}}$:

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

It corresponds to the squared norm of the total angular momentum. The other type is raising and lowering operators, defined as:

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

These are non-Hermitian operators that we will use for manipulating angular momentum eigenfunctions. It is easy to demonstrate by direct inspection that the following relations also hold:

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

Commutation and uncertainty relations

Many equations that we will encounter later in the course involve operator commutators, *i.e.* combinations of the following general form:

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

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

$$[\hat{L}_X,\hat{L}_Y]=i\hat{L}_Z,\qquad [\hat{L}_Y,\hat{L}_Z]=i\hat{L}_X,\qquad [\hat{L}_Z,\hat{L}_X]=i\hat{L}_Y \tag{16}$$

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

$$[\hat{L}^2,\hat{L}_X]=0,\quad [\hat{L}^2,\hat{L}_Y]=0,\quad [\hat{L}^2,\hat{L}_Z]=0 \tag{17}$$

For commutators involving raising and lowering operators we similarly get:

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

Angular momentum eigenfunctions

Because the angular momentum operators derived above correspond to 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 and we shall simply state here that the eigenfunctions exist and are known as *spherical harmonics* $Y_{lm}(\theta,\varphi)$:

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

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

$$\begin{cases}\hat{L}^2\left|l,m\right\rangle=l(l+1)\left|l,m\right\rangle\\ \hat{L}_Z\left|l,m\right\rangle=m\left|l,m\right\rangle\end{cases} \tag{21}$$

and only addressed in terms of their properties under the action of specific operators – the explicit trigonometric form of these functions is rarely required in practice. In the angular momentum research jargon, the l quantum number is called *total momentum* and m is known as *projection*.

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

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

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

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

More specifically (the coefficient may be derived from the properties of spherical harmonics):

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

It is not possible to raise or lower a state beyond the range specified in Equation (20) for the projection quantum number:

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

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