Chapter 7a – Hydrogen Atom and Angular Momentum

Angular Momentum Theory

Definitions:
\[ \hat{L}_x = yP_z - zP_y \]
\[ \hat{L}_y = zP_x - xP_z \]
\[ \hat{L}_z = xP_y - yP_x \]
\[ \hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \]

We know:
\[ [r_{\alpha}, P_{\beta}] = i\hbar \delta_{\alpha\beta} \]

Derive fundamental commutation relations, for angular momentum
\[ [\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z \]
\[ [\hat{L}_z, \hat{L}_x] = i\hbar \hat{L}_y \]
\[ [\hat{L}_y, \hat{L}_z] = i\hbar \hat{L}_x \]
\[ \hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 \]

More definitions
\[ \hat{L}_+ = \hat{L}_x + i\hat{L}_y \]
\[ \hat{L}_- = \hat{L}_x - i\hat{L}_y \]

Derive:
\[ \hat{L}^2 = \hat{L} \cdot \hat{L} + \hat{L}_+^2 + \hbar \hat{L}_z \]
\[ = \hat{L}_+ \hat{L}_- + \hat{L}_+^2 + \hbar \hat{L}_z \]
\[ [\hat{L}_z, \hat{L}_+] = \hbar \hat{L}_+ \quad [\hat{L}_z, \hat{L}_-] = -\hbar \hat{L}_- \]
\[ \hat{L}_+ \hat{L}_- = \hat{L}_+ \hat{L}_- + \hbar \hat{L}_z \]
\[ [\hat{L}^2, \hat{L}_x] = [\hat{L}^2, \hat{L}_y] = [\hat{L}^2, \hat{L}_z] = [\hat{L}^2, \hat{L}_+] = [\hat{L}^2, \hat{L}_-] = 0 \]
Before we discuss further let me list a few useful tricks when dealing with commutators.

1) \[
\left[ \hat{A}, \hat{B} \right] = -\left[ \hat{B}, \hat{A} \right]
\]

2) a. \[
\left[ c\hat{A}, \hat{B} \right] = c\left[ \hat{A}, \hat{B} \right] \quad \text{(pull c in front of everything)}
\]

b. if \( \hat{C} \) commutes with \( \hat{A} \) and \( \hat{B} \) then
\[
\left[ \hat{A}\hat{C}, \hat{B} \right] = \hat{A}\left[ \hat{C}, \hat{B} \right] = \hat{C}\left[ \hat{A}, \hat{B} \right]
\]

3) For any operators \( \hat{A}, \hat{B}, \hat{C} \):

a. \[
\left[ \hat{A}\hat{B}, \hat{C} \right] = \hat{A}\left[ \hat{B}, \hat{C} \right] + \left[ \hat{A}, \hat{C} \right] \hat{B}
\]

b. \[
\left[ \hat{A}, \hat{B}\hat{C} \right] = \left[ \hat{A}, \hat{B} \right] \hat{C} + \hat{B}\left[ \hat{A}, \hat{C} \right]
\]

4) \[
\left[ \hat{A}, \hat{B} + \hat{C} \right] = \left[ \hat{A}, \hat{B} \right] + \left[ \hat{A}, \hat{C} \right]
\]

Proofs are easy:

e.g. \[
\left[ \hat{A}, \hat{B}\hat{C} \right] = \hat{A}\hat{B}\hat{C} - \hat{B}\hat{C}\hat{A}
\]
\[
= \hat{A}\hat{B}\hat{C} - \hat{B}\hat{A}\hat{C} + BAC - BCA
\]
\[
= \left[ \hat{A}, \hat{B} \right] \hat{C} + \hat{B}\left[ \hat{A}, \hat{C} \right]
\]

\[\Rightarrow\] Derive commutation relations easily:

\[
\left[ \hat{L}_x, \hat{L}_y \right] = \left[ yP_z - zP_y, zP_x - xP_z \right]
\]
\[
= \left[ yP_z, zP_x \right] - \left[ yP_z, xP_z \right] - \left[ zP_y, zP_x \right] + \left[ zP_y, xP_z \right]
\]
\[
= yP_x \left[ P_z, z \right] - yx \left[ P_z, P_x \right] - P_y \left[ P_x, z \right] + xP_y \left[ z, P_z \right]
\]
\[
= i\hbar \left( xP_y - yP_x \right) = i\hbar \hat{L}_z
\]

\[\Rightarrow\] No derivatives, not acting on a function. Just use tricks!

\[
\left[ \hat{L}_x, \hat{L}_y \right] = \left[ \hat{L}_x^2, \hat{L}_x \right] + \left[ \hat{L}_y^2, \hat{L}_x \right] + \left[ \hat{L}_z^2, \hat{L}_x \right]
\]
\[
= 0 + \hat{L}_y \left[ \hat{L}_y, \hat{L}_x \right] + \left[ \hat{L}_y, \hat{L}_x \right] \hat{L}_y + \hat{L}_x \left[ \hat{L}_z, \hat{L}_x \right] + \left[ \hat{L}_z, \hat{L}_x \right] \hat{L}_z
\]
\[
= \hat{L}_x \hat{L}_y - \hat{L}_y \hat{L}_x + \hat{L}_z \hat{L}_y + \hat{L}_y \hat{L}_z = 0
\]

\[
\hat{L}_- \hat{L}_+ + \hat{L}_z^2 + i\hbar \hat{L}_z = \left( \hat{L}_x - i\hat{L}_y \right) \left( \hat{L}_x + i\hat{L}_y \right) + \hat{L}_z^2 + i\hbar \hat{L}_z
\]
\[
= \hat{L}_x^2 + \hat{L}_z^2 + i \left( \hat{L}_x \hat{L}_y - \hat{L}_y \hat{L}_x \right) + \hat{L}_z^2 + i\hbar \hat{L}_z
\]
\[
= \hat{L}_x^2 + i \left( \hbar \hat{L}_z \right) + \hbar \hat{L}_z = \hat{L}_x^2
\]
\[
[\hat{L}_z, \hat{L}_-] = [\hat{L}_z, \hat{L}_x - i\hat{L}_y] = [\hat{L}_z, \hat{L}_x] - i[\hat{L}_z, \hat{L}_y] = i\hbar\hat{L}_y - i(-i\hbar\hat{L}_x) = -\hbar(\hat{L}_x - i\hat{L}_y) = -\hbar\hat{L}_-
\]

Next we will derive the spectrum (eigenvalues and eigenfunctions) using only commutation relations. \([\hat{L}^2, \hat{L}_z] = 0 \rightarrow \hat{L}^2, \hat{L}_z\) have a set of common eigenfunctions. Let us denote these common eigenfunctions (for now) as \(g_{a,b}\)

\[
\hat{L}^2 g_{a,b} = a g_{a,b}, \quad \hat{L}_z g_{a,b} = b g_{a,b}
\]

Because \(\hat{L}^2 = L_x^2 + L_y^2 + L_z^2\)

Proof: \(\langle \psi | \hat{L}^2 | \psi \rangle \geq 0\) for any \(\psi\) (use Hermiticity \(\hat{L}_z\))

Next: if \(g_{a,b}\) is eigenfunction of \(\hat{L}^2, \hat{L}_z\), then so is \(\hat{L}_+ g_{a,b}\)

Proof: \(\hat{L}^2 (\hat{L}_+ g_{a,b}) = \hat{L}_+ \hat{L}^2 g_{a,b} = a \hat{L}_+ g_{a,b}\)

\(\hat{L}_z (\hat{L}_+ g_{a,b}) = \hat{L}_+ \hat{L}_z g_{a,b} + \hat{L}_+ \hat{L}_z g_{a,b} = (b + \hbar) \hat{L}_+ g_{a,b}\)

\(\hat{L}_+ g_{a,b}\): same eigenvalue of \(\hat{L}^2\), raised eigenvalue \(b + \hbar\) of \(\hat{L}_z\) (or: \(\hat{L}_+ g_{a,b} = 0\))

\(\hat{L}^2 (\hat{L}_- g_{a,b}) = \hat{L}_- \hat{L}^2 g_{a,b} = a \hat{L}_- g_{a,b}\)

\(\hat{L}_z (\hat{L}_- g_{a,b}) = \hat{L}_- \hat{L}_z g_{a,b} - \hbar \hat{L}_- g_{a,b} = (b - \hbar) \hat{L}_- g_{a,b}\)

\(\hat{L}_+, \hat{L}_-\): ladder operators

\[
\begin{array}{c}
\hat{L}_- \\
\vdots \\
\hat{L}_a, b \\
\hat{L}_- \\
\hat{L}_+ \\
\end{array}
\]

Same eigenvalue \(a\)
When do the ladder operators terminate?

use \( a > b^2; \quad b^2 < a \) \[ \hat{L}_* g_{a,b_{\text{max}}} = 0 \]

\[ \hat{L}_- g_{a,b_{\text{max}}} = (\hat{L}_- \hat{L}_+ + \hat{L}_z^2 + \hbar \hat{L}_z) g_{a,b_{\text{max}}} \]

\[ = 0 + b_{\text{max}}^2 + \hbar b_{\text{max}} = a \]

\[ \rightarrow b_{\text{max}} = \hbar \rightarrow a = \hbar^2 l(l+1) \]

At the other end:

\[ \hat{L}_- g_{a,b_{\text{min}}} = 0 \]

\[ \hat{L}_- g_{a,b_{\text{min}}} = (\hat{L}_- \hat{L}_+ + \hat{L}_z^2 - \hbar \hat{L}_z) g_{a,b_{\text{min}}} \]

\[ = (b_{\text{min}}^2 + \hbar b_{\text{min}}) = a = \hbar^2 l(l+1) \]

\[ \rightarrow b_{\text{min}} = -\hbar \]

Hence from purely the commutation relations we find

\[ a = l(l+1)\hbar^2 \]

\[ b = \hbar(-l,-l+1,-l+2,...l-2,l-1,l) \]

\[ 2l+1 \text{ states associated with } a = l(l+1)\hbar^2 \]

There are 2 possibilities for such a structure:

A: \( l \) is integer

B: \( l \) is a half integer

<table>
<thead>
<tr>
<th>( l )</th>
<th>( l(l+1) )</th>
<th>( m = -l...l )</th>
<th>Degen</th>
<th>Spatial name</th>
<th>Spin name</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>s</td>
<td>Singlet</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>-1,0,1</td>
<td>3</td>
<td>p</td>
<td>Triplet</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>-2,-1,0,1,2</td>
<td>5</td>
<td>d</td>
<td>Quintet</td>
</tr>
<tr>
<td>3</td>
<td>12</td>
<td>-3,-2,-1,0,1,2,3</td>
<td>7</td>
<td>f</td>
<td>Septet</td>
</tr>
<tr>
<td>( \frac{1}{2} )</td>
<td>( \frac{3}{4} )</td>
<td>-( \frac{1}{2},\frac{1}{2},\frac{1}{2} )</td>
<td>2</td>
<td>-</td>
<td>Doublet</td>
</tr>
<tr>
<td>( \frac{3}{2} )</td>
<td>( \frac{15}{4} )</td>
<td>-( \frac{3}{2},\frac{1}{2},\frac{3}{2},\frac{3}{2} )</td>
<td>4</td>
<td>-</td>
<td>Quartet</td>
</tr>
<tr>
<td>( \frac{5}{2} )</td>
<td>( \frac{35}{4} )</td>
<td>-( \frac{5}{2},\frac{3}{2},\frac{1}{2},\frac{3}{2},\frac{3}{2},\frac{3}{2} )</td>
<td>6</td>
<td>-</td>
<td>Sextet</td>
</tr>
</tbody>
</table>
When do spin-multiples show up?
- Electron in spin $\frac{1}{2}$ particle
- Nuclear spin; many nuclear spin states are possible
- Many electron states: triplet, quartet, doublet excited states.

We have used only the commutation relations $[L_x, L_y] = i\hbar L_z$ and $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$ to derive the eigenvalues for $\hat{L}^2$ and $\hat{L}_z$ operators. Any set of 3 operators that satisfy the commutation relations will yield the same ‘spectrum’

$$\hat{L}^2 \rightarrow \hbar^2 l(l+1)$$
$$\hat{L}_z \rightarrow mh \quad m = -l, -l+1, ... , l-1, l$$

We can do more, if we go back to our original problem, using the $\theta, \phi$ representation of operators.

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi}$$

$$\hat{L}^2 = \hbar^2 \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \phi}{\partial \phi^2} \right]$$

One can also derive expressions for $\hat{L}_s$ and $\hat{L}_-$

$$\hat{L}_s = \hbar e^{i\phi} \left[ \frac{\partial}{\partial \theta} + i \frac{\cos \theta}{\sin \theta} \frac{\partial}{\partial \phi} \right]$$

$$\hat{L}_- = \hbar e^{-i\phi} \left[ \frac{\partial}{\partial \theta} - i \frac{\cos \theta}{\sin \theta} \frac{\partial}{\partial \phi} \right]$$

It is easy to find eigenfunctions for $\hat{L}_z$

$$-i\hbar \frac{\partial}{\partial \phi} f(\phi) = mh f(\phi) \quad \rightarrow \quad f(\phi) = e^{im\phi}$$

Boundary Condition $f(\phi + 2\pi) = f(\phi)$

$$m = e^{im\phi}, e^{im2\pi} = 1$$

$\rightarrow m$ is an integer

The periodic boundary condition is the reason that we do not know how to represent spin functions:

$$-i\hbar \frac{\partial}{\partial \phi} e^{\frac{i\phi}{2}} = \frac{1}{2} \hbar e^{\frac{i\phi}{2}}$$

$\rightarrow$ eigenvalue $\frac{1}{2} \hbar$, but rotating $\phi$ over $2\pi$, the function $e^{\frac{i\phi}{2}}$ changes ‘sign’!
Let us return to eigenfunctions of $\hat{L}_z$ and $\hat{L}_-$. These eigenfunctions are denoted

$$Y_l^m(\theta, \varphi) = P_l^m(\theta)e^{im\varphi}$$

$P_l^m(\theta)$ are called the ‘associated Legendre’ polynomials. They will be seen to be polynomials in $\sin \theta$, $\cos \theta$. We can easily generate them using the ladder operators.

The highest $m = l$ function in the multiplet has to satisfy

$$\hat{L}_+ Y_l^l(\theta, \varphi) = 0$$

$$Y_l^l(\theta, \varphi) = P_l^l(\theta)e^{il\varphi}$$

$$\hat{L}_+ P_l^l(\theta)e^{il\varphi} = \hbar e^{il\varphi} \left[ \frac{\partial}{\partial \theta} + i \frac{\cos \theta}{\sin \theta} \frac{\partial}{\partial \varphi} \right] P_l^l(\theta)e^{il\varphi}$$

$$0 = \hbar e^{i(l+1)\varphi} \left[ \frac{\partial P_l^l(\theta)}{\partial \theta} - l \frac{\cos \theta}{\sin \theta} P_l^l(\theta) \right]$$

The solution to this equation is

$$P_l^l(\theta) = (\sin \theta)^l = \sin^l(\theta)$$

since

$$l(\sin \theta)^{l-1} \cos \theta - l \frac{\cos \theta}{\sin \theta} (\sin \theta)^l = 0$$

Hence we have found the highest $m = l$ function $Y_l^l(\theta)$, for any $l$

$$Y_l^l(\theta) = (\sin \theta)^l e^{il\varphi} \quad l = 0, 1, 2, 3, 4, \ldots$$

All the other functions can be generated by differentiation: acting with

$$\hat{L}_- = \hbar e^{-il\varphi} \left[ \frac{\partial}{\partial \theta} - i \frac{\cos \theta}{\sin \theta} \frac{\partial}{\partial \varphi} \right] \rightarrow \text{yields other functions in multiplet}$$

Eg. To generate the p-functions ($l = 1$)

$$Y_1^1 = \sin \theta e^{i\varphi}$$

$$Y_0^0 \sim \hbar e^{-i\varphi} \left( \cos \theta + \frac{\cos \theta}{\sin \theta} \sin \theta \right) e^{i\varphi} \sim \cos \theta$$

$$Y_{-1}^0 : \hbar e^{-i\varphi} \left[ -\sin \theta - 0 \right] \sim \sin \theta e^{-i\varphi}$$

This procedure works for all $l$. I did not worry about normalization.

In general one finds that $P_l^m(\theta)$ only depends on $|m|$, hence the $\theta$-part of $Y_l^m(\theta)$ and $Y_{-l}^{-m}(\theta)$ are the same. Then one can combine the functions.
\[
\frac{1}{2} \left( Y_i^m(\theta, \varphi) + Y_i^{-m}(\theta, \varphi) \right) = P_i^{|m|}(\theta) \frac{e^{\text{imp}} + e^{-\text{imp}}}{2} = P_i^{|m|}(\theta) \cos \varphi
\]

And
\[
\frac{1}{2i} \left( Y_i^m(\theta, \varphi) - Y_i^{-m}(\theta) \right) = \ldots = P_i^{|m|}(\theta) \sin \varphi
\]

Using the new linear combination we get
\[
\sin \theta \cos \varphi \sim \frac{x}{r} \rightarrow p_x
\]
\[
\cos \theta \sim \frac{z}{r} \rightarrow p_z
\]
\[
\sin \theta \sin \varphi \sim \frac{y}{r} \rightarrow p_y
\]

The \( Y_i^m(\theta, \varphi) \) are then related to the usual Cartesian angular momentum functions (atomic orbitals).

In the lecture notes on angular momentum I work out the \( d \)-functions in this way. You are asked to do it on the assignment.

**The Radial Equation for the Hydrogen Atom**

In spherical coordinates:
\[
\hat{H} = \frac{-\hbar^2}{2\mu} \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{\hat{L}^2}{2\mu r^2} - \frac{e^2}{4\pi \varepsilon_0 r}
\]

\[
\rightarrow \quad \text{try solution} \quad f(r) Y_i^m(\theta,\varphi)
\]

\[
\hat{H} f(r) Y_i^m(\theta,\varphi) = Y_i^m(\theta,\varphi) \left[ \frac{-\hbar^2}{2\mu} \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial f}{\partial r} \right) + \frac{l(l+1)\hbar^2}{2\mu r^2} f(r) - \frac{e^2}{4\pi \varepsilon_0 r} \frac{f(r)}{r} \right]
\]

Or
\[
\frac{-\hbar^2}{2\mu} \frac{2}{r^2} \frac{\partial f}{\partial r} - \frac{\hbar^2}{2\mu} \frac{\partial^2 f}{\partial r^2} + \left( \frac{l(l+1)\hbar^2}{2\mu r^2} - \frac{e^2}{4\pi \varepsilon_0 r} \right) f(r) = Ef(r)
\]

\[
\Rightarrow \quad \text{Multiply through by} \quad \frac{2\mu}{\hbar^2}
\]

Define
\[
\frac{\hbar^2 e^2}{\mu 4\pi \varepsilon_0} = \frac{1}{a_0}
\]

Where \( a_0 \) is the Bohr radius, also define \( \frac{2\mu}{\hbar^2} \cdot E = \varepsilon \)
\[
\frac{d^2 f(r)}{dr^2} + \left( \frac{l(l+1)}{r^2} - \frac{2}{a_0 r} \right) f(r) = \epsilon f(r)
\]

These type of 1d differential equations are easy to solve on a computer. I give a few examples of solutions in my lecture notes on the Hydrogen atom.

The general solution to the Hydrogen atom is:

\[
\psi_{n,l,m}(r, \theta, \phi) = P_{n,l}(r) e^{-r/a_0} Y_{l}^{m}(\theta, \phi)
\]

where \( P_{n,l}(r) = ar^{n-1} + br^{n-2} + \ldots r^l \) is a polynomial in \( r \) having \( n - l - 1 \) radial nodes

\[
E_{n,l} = E_n = \frac{\hbar^2}{2\mu a_0 n^2}
\]

The energies are exactly the same as for the Bohr atom. The theory is very different. This strange coincidence may have held back physics for 10 years! After all the Bohr atom is very different from the description by quantum mechanics (Schrödinger).

The \( Y_{l}^{m}(\theta, \phi) \) themselves have \( l \) angular nodes, and so the total number of nodes associated with wavefunctions with \( E_n \) is always \( n - l - 1 + l = n - 1 \)

<table>
<thead>
<tr>
<th>( n )</th>
<th>( E_n )</th>
<th>Nodes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s</td>
<td>(-E_0)</td>
<td>No nodes</td>
</tr>
<tr>
<td>2s</td>
<td>(-E_0/4)</td>
<td>1 radial, 0 angular</td>
</tr>
<tr>
<td>2p</td>
<td>(-E_0/4)</td>
<td>No radial, 1 angular</td>
</tr>
<tr>
<td>3s</td>
<td>(-E_0/9)</td>
<td>2 radial nodes</td>
</tr>
<tr>
<td>3p</td>
<td>(-E_0/9)</td>
<td>1 radial, 1 angular</td>
</tr>
<tr>
<td>3d</td>
<td>(-E_0/9)</td>
<td>0 radial, 2 angular</td>
</tr>
</tbody>
</table>
To understand radial distribution $\int_{0}^{\infty} dr \int_{0}^{\pi} d\theta \int_{0}^{2\pi} d\varphi |\psi_{n,l,m}(r, \theta, \varphi)|^2 r^2 \sin \theta$

You have been shown before $\sum_{m} |Y_{l}^{m}(\theta, \varphi)|^2 = \text{constant, no } \theta, \varphi \text{ dependence}$

$\rightarrow$ spherically symmetric

$\rightarrow$ justification to look at radial part only, multiplied by $r^2$ volume element.

$\rightarrow$ usual radial distribution, see figure 7.2 in McQuarrie