V Spherical coordinates and Spherical Harmonics

1. We will now derive the eigenstates of the total angular momentum and z-component of angular momentum. That is we will find what the exact functional forms of the *ket* vectors $|l, m\rangle$ are that we have been talking about for so long. In particular we will solve and obtain exact solutions to Eqs. (IV.0.13) and (IV.0.14).

2. Recall Eqs. (IV.0.13) and (IV.0.14) are:

$$\mathbf{L}^2 |l, m\rangle = \hbar^2 l(l+1) |l, m\rangle \quad l = 0, 1, 2, 3, \cdots \tag{V.0.18}$$

and

$$\mathbf{L}_z |l, m\rangle = \hbar m |l, m\rangle \quad m = \pm l, \pm(l-1), \pm(l-2), \cdots, 0 \tag{V.0.19}$$

We will find here the coordinate representation for the *ket* vectors $|l, m\rangle$ and also prove our assertion regarding the eigenvalues.

3. First:

$$
\begin{aligned}
\mathbf{L}_x &= yp_z - zp_y = -\imath\hbar \left[y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y} \right] \\
\mathbf{L}_y &= zp_x - xp_z = -\imath\hbar \left[z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z} \right] \\
\mathbf{L}_z &= xp_y - yp_x = -\imath\hbar \left[x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} \right]
\end{aligned}
\tag{V.0.20}
$$

4. In an atom there is spherical symmetry. That is there is symmetry about a central point, the nucleus. Hence, to use this spherical symmetry we would like to transform to a coordinate system that looks like a sphere (the spherical coordinate system).

5. Note: In all areas where mathematics plays a role the symmetry of the problem is exploited to rewrite the problem in the most convenient coordinate system. In our case for an atomic system the spherical coordinate system turns out to be the most convenient. It may not look very convenient to you over the next couple of pages but you will understand at the end of this exercise as to why it is convenient.

$$
\begin{aligned}
x &= r\sin\theta\cos\phi \\
y &= r\sin\theta\sin\phi \\
z &= r\cos\theta \\
r^2 &= x^2 + y^2 + z^2 \\
\cos\theta &= \frac{z}{r} = \frac{z}{\sqrt{x^2 + y^2 + z^2}} \\
\tan\phi &= \frac{y}{x}
\end{aligned}
\tag{V.0.21}
$$

6. We need appropriate expressions for $\frac{\partial}{\partial x}$, $\frac{\partial}{\partial y}$ and $\frac{\partial}{\partial z}$ in terms of r, θ and ϕ so that we can express the angular momentum operators in the this new coordinate system.

7. We will use the chain rule for differentiation:

$$
\frac{\partial}{\partial x} = \left[\frac{\partial r}{\partial x}\right]_{y,z} \frac{\partial}{\partial r} + \left[\frac{\partial \theta}{\partial x}\right]_{y,z} \frac{\partial}{\partial \theta} + \left[\frac{\partial \phi}{\partial x}\right]_{y,z} \frac{\partial}{\partial \phi}
\tag{V.0.22}
$$

where we have used the fact that (x, y, z) are all functions of (r, θ, ϕ) and vice versa as seen in Eqs. (V.0.21). Also, the symbol $\left[\frac{\partial r}{\partial x}\right]_{y,z}$ means a "constrained" partial derivative. That is while differentiating r with respect to x we want to hold θ and ϕ constant.

8. In a similar fashion we can write down:

$$
\begin{aligned}
\frac{\partial}{\partial y} &= \left[\frac{\partial r}{\partial y}\right]_{x,z} \frac{\partial}{\partial r} + \left[\frac{\partial \theta}{\partial y}\right]_{x,z} \frac{\partial}{\partial \theta} + \left[\frac{\partial \phi}{\partial y}\right]_{x,z} \frac{\partial}{\partial \phi} \\
\frac{\partial}{\partial z} &= \left[\frac{\partial r}{\partial z}\right]_{x,y} \frac{\partial}{\partial r} + \left[\frac{\partial \theta}{\partial z}\right]_{x,y} \frac{\partial}{\partial \theta} + \left[\frac{\partial \phi}{\partial z}\right]_{x,y} \frac{\partial}{\partial \phi}
\end{aligned}
\tag{V.0.23}
$$

All we are going to do is use Eqs. (V.0.21) to obtain suitable expressions for $\frac{\partial}{\partial x}$, $\frac{\partial}{\partial y}$ and $\frac{\partial}{\partial z}$ in terms of (r, θ, ϕ) and use these to express the angular momentum operators. So lets do it.

9. We recall:

$$
\begin{aligned}
x &= r\sin\theta\cos\phi \\
y &= r\sin\theta\sin\phi \\
z &= r\cos\theta \\
r^2 &= x^2 + y^2 + z^2 \\
\cos\theta &= \frac{z}{r} = \frac{z}{\sqrt{x^2 + y^2 + z^2}} \\
\tan\phi &= \frac{y}{x}
\end{aligned}
\tag{V.0.24}
$$

10. Using Eqs. (V.0.24) we have:

$$2r \left[\frac{\partial r}{\partial x} \right]_{y,z} = 2x = 2r \sin\theta \cos\phi$$

$$\left[\frac{\partial r}{\partial x} \right]_{y,z} = \sin\theta \cos\phi \tag{V.0.25}$$

$$-\sin\theta \left[\frac{\partial \theta}{\partial x} \right]_{y,z} = -\frac{z}{r^2}\frac{2x}{2r} = -\frac{r\cos\theta}{r^3} r\sin\theta\cos\phi$$

$$\left[\frac{\partial \theta}{\partial x} \right]_{y,z} = \frac{\cos\theta \cos\phi}{r} \tag{V.0.26}$$

$$\frac{1}{\cos^2\phi} \left[\frac{\partial \phi}{\partial x} \right]_{y,z} = -\frac{y}{x^2}$$

$$\left[\frac{\partial \phi}{\partial x} \right]_{y,z} = -\frac{r\sin\theta\sin\phi}{r^2\sin^2\theta\cos^2\phi} = -\frac{\sin\phi}{r\sin\theta} \tag{V.0.27}$$

11. We need to use these in Eq. (V.0.22) to obtain $\frac{\partial}{\partial x}$ in terms of (r, θ, ϕ).

12. Using Eqs (V.0.25), (V.0.26) and (V.0.27) in Eq. (V.0.22) we can get an expression for $\frac{\partial}{\partial x}$.

$$\begin{aligned}\frac{\partial}{\partial x} &= \left[\frac{\partial r}{\partial x} \right]_{y,z} \frac{\partial}{\partial r} + \left[\frac{\partial \theta}{\partial x} \right]_{y,z} \frac{\partial}{\partial \theta} + \left[\frac{\partial \phi}{\partial x} \right]_{y,z} \frac{\partial}{\partial \phi} \\ &= \sin\theta\cos\phi \frac{\partial}{\partial r} + \frac{\cos\theta\cos\phi}{r}\frac{\partial}{\partial \theta} - \frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial \phi}\end{aligned} \tag{V.0.28}$$

13. In a similar fashion we will get the expressions for $\frac{\partial}{\partial y}$ and $\frac{\partial}{\partial z}$:

14. **Homework: Work out** $\left[\frac{\partial r}{\partial y} \right]_{x,z}, \left[\frac{\partial \theta}{\partial y} \right]_{x,z}, \left[\frac{\partial \phi}{\partial y} \right]_{x,z}, \left[\frac{\partial r}{\partial z} \right]_{x,y}, \left[\frac{\partial \theta}{\partial z} \right]_{x,y}, \left[\frac{\partial \phi}{\partial z} \right]_{x,y}.$

15. **Homework: Using these partial derivatives and using Eqs. (V.0.23) show that:**

$$\begin{aligned}\frac{\partial}{\partial y} &= \left[\frac{\partial r}{\partial y} \right]_{x,z} \frac{\partial}{\partial r} + \left[\frac{\partial \theta}{\partial y} \right]_{x,z} \frac{\partial}{\partial \theta} + \left[\frac{\partial \phi}{\partial y} \right]_{x,z} \frac{\partial}{\partial \phi} \\ &= \sin\theta\sin\phi \frac{\partial}{\partial r} + \frac{\cos\theta\sin\phi}{r}\frac{\partial}{\partial \theta} + \frac{\cos\phi}{r\sin\theta}\frac{\partial}{\partial \phi}\end{aligned} \tag{V.0.29}$$

$$\begin{aligned}\frac{\partial}{\partial z} &= \left[\frac{\partial r}{\partial z} \right]_{x,y} \frac{\partial}{\partial r} + \left[\frac{\partial \theta}{\partial z} \right]_{x,y} \frac{\partial}{\partial \theta} + \left[\frac{\partial \phi}{\partial z} \right]_{x,y} \frac{\partial}{\partial \phi} \\ &= \cos\theta \frac{\partial}{\partial r} - \frac{\sin\theta}{r}\frac{\partial}{\partial \theta}\end{aligned} \tag{V.0.30}$$

16. Using these:

$$
\begin{aligned}
\mathbf{L}_x &= y p_z - z p_y = -\imath\hbar \left[y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right] \\
&= -\imath\hbar \left[r \sin\theta \sin\phi \left(\cos\theta \frac{\partial}{\partial r} - \frac{\sin\theta}{r} \frac{\partial}{\partial \theta} \right) \right. \\
&\quad - \left. r \cos\theta \left(\sin\theta \sin\phi \frac{\partial}{\partial r} + \frac{\cos\theta \sin\phi}{r} \frac{\partial}{\partial \theta} + \frac{\cos\phi}{r \sin\theta} \frac{\partial}{\partial \phi} \right) \right] \\
&= -\imath\hbar \left[\sin\phi \frac{\partial}{\partial \theta} + \cot\theta \cos\phi \frac{\partial}{\partial \phi} \right]
\end{aligned}
\tag{V.0.31}
$$

$$
\begin{aligned}
\mathbf{L}_y &= z p_x - x p_z = -\imath\hbar \left[z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right] \\
&= -\imath\hbar \left[r \cos\theta \left(\sin\theta \cos\phi \frac{\partial}{\partial r} + \frac{\cos\theta \cos\phi}{r} \frac{\partial}{\partial \theta} - \frac{\sin\phi}{r \sin\theta} \frac{\partial}{\partial \phi} \right) \right. \\
&\quad - \left. r \sin\theta \cos\phi \left(\cos\theta \frac{\partial}{\partial r} - \frac{\sin\theta}{r} \frac{\partial}{\partial \theta} \right) \right] \\
&= -\imath\hbar \left[\cos\phi \frac{\partial}{\partial \theta} - \cot\theta \sin\phi \frac{\partial}{\partial \phi} \right]
\end{aligned}
\tag{V.0.32}
$$

$$
\begin{aligned}
\mathbf{L}_z &= x p_y - y p_x = -\imath\hbar \left[x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right] \\
&= -\imath\hbar \left[r \sin\theta \cos\phi \left(\sin\theta \sin\phi \frac{\partial}{\partial r} + \frac{\cos\theta \sin\phi}{r} \frac{\partial}{\partial \theta} + \frac{\cos\phi}{r \sin\theta} \frac{\partial}{\partial \phi} \right) \right. \\
&\quad - \left. \sin\theta \sin\phi \left(\sin\theta \cos\phi \frac{\partial}{\partial r} + \frac{\cos\theta \cos\phi}{r} \frac{\partial}{\partial \theta} - \frac{\sin\phi}{r \sin\theta} \frac{\partial}{\partial \phi} \right) \right] \\
&= -\imath\hbar \frac{\partial}{\partial \phi}
\end{aligned}
\tag{V.0.33}
$$

17. Using these

$$
\begin{aligned}
\mathbf{L}^2 &= \mathbf{L}_x{}^2 + \mathbf{L}_y{}^2 + \mathbf{L}_z{}^2 \\
&= -\hbar^2 \left(\frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right)
\end{aligned}
\tag{V.0.34}
$$

18. Now we want to solve:

$$
\mathbf{L}^2 \mathcal{Y}(\theta, \phi) = b \mathcal{Y}(\theta, \phi) \tag{V.0.35}
$$
$$
\mathbf{L}_z \mathcal{Y}(\theta, \phi) = a \mathcal{Y}(\theta, \phi) \tag{V.0.36}
$$

We already know that $\mathbf{L}^2$ and $\mathbf{L}_z$ have simultaneous eigenstates.

19. These equations are second order differential equations. We will not go into the details of these solutions.

20. The solutions $\mathcal{Y}(\theta, \phi)$, turn out to have the functional form:

$$
\mathcal{Y}(\theta, \phi) \propto \mathcal{P}_{l,m}(\cos \theta) \exp \{ \imath m \phi \} \tag{V.0.37}
$$

and the eigenvalues $b = \hbar^2 l(l+1)$ and $a = \hbar m$. The functions $\mathcal{P}_{l,m}(\cos \theta)$ are called the *associated Legendre functions* and can be obtained from the following formula:

$$
\mathcal{P}_{l,m}(x) = \frac{1}{2^l l!} \left(1 - x^2 \right)^{|m|/2} \frac{d^{l+|m|}}{dx^{l+|m|}} \left(x^2 - 1 \right)^l \tag{V.0.38}
$$

21. Now, as we will see later (when we study hydrogen atom) the functions $\mathcal{Y}(\theta, \phi)$ turn out to be the angular part of the wavefunction of the hydrogen atom. We will see later on how this looks for at least small values of l and m.