

ANGULAR MOMENTUM IN QUANTUM MECHANICS. ¹

1. ORBITAL ANGULAR MOMENTUM $\hat{\mathbf{L}}$ & ITS COMMUTATORS.

For a classical particle with linear momentum \mathbf{p} and position vector \mathbf{r} , the **Orbital Angular Momentum** is:

$$\mathbf{L}_{cl} = \mathbf{r} \times \mathbf{p}. \tag{1}$$

To find the quantum mechanical orbital angular momentum we follow the rules for quantising a classical problem: replace all classical dynamical variables by the appropriate operator,

$$\mathbf{p} \rightarrow \hat{\mathbf{p}} = -i\hbar\nabla = -i\hbar\left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right) \tag{2}$$

$$\text{and } \mathbf{r} \rightarrow \hat{\mathbf{r}} = \mathbf{r} = (x, y, z), \tag{3}$$

giving the **QM Orbital Angular Momentum Operator**:

$$\hat{\mathbf{L}} = \mathbf{r} \times \hat{\mathbf{p}} = -i\hbar\mathbf{r} \times \nabla, \tag{4}$$

or, in cartesian components,²

$$\hat{L}_x = y\hat{p}_z - z\hat{p}_y = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right), \tag{5}$$

$$\hat{L}_y = z\hat{p}_x - x\hat{p}_z = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right), \tag{6}$$

$$\hat{L}_z = x\hat{p}_y - y\hat{p}_x = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right). \tag{7}$$

First we note that, as befits an observable dynamical variable, $\hat{\mathbf{L}}$ is a Hermitian operator because both \mathbf{r} and $\hat{\mathbf{p}}$ are Hermitian,

$$\hat{L}_i^\dagger = \hat{L}_i, \quad i = 1, 2, 3 \tag{8}$$

Next we study the commutation relations between the three components of the angular momentum operator using the canonical commutation relations. These state that coordinates commute with alien components of the momentum operator, but do not commute with their own, $[\hat{x}_i, \hat{p}_j] = i\hbar\delta_{ij}$, and that coordinates commute with coordinates and momenta with momenta, $[\hat{x}_i, \hat{x}_j] = 0$, $[\hat{p}_i, \hat{p}_j] = 0$:

¹This topic is quite long and complicated. I recommend that you first look at the summary section at the end, p.21, and then work through the material several times, looking through the summary at regular intervals. Your primary aim should be to understand the *results* given in the summary. The detailed derivations and discussion are to create that understanding by showing where the results come from. There are, of course, several techniques and concepts of considerable importance in the derivations, so they should not be skipped.

²I remember the cross-product by drawing a circle in my mind with the components x, y, z arranged clockwise. The components of the cross-product, reading from left to right in the equation, always occur in cyclic order (ie. clockwise order) for the first (positive sign) term and anti-cyclic for the second (negative sign) term. Thus, for the z-component L_z , you start the cyclic sequence with z , giving $z \rightarrow x \rightarrow y$, giving $L_z = xp_y \dots$; the anti-cyclic one is $z \rightarrow y \rightarrow x$, giving $L_z = xp_y - yp_x$. This is just another way of expressing the rule based on the determinant, but it's easier to keep in your head without the need to write down any intermediate steps.

$$\begin{aligned}
[\widehat{L}_x, \widehat{L}_y] &= [(y\widehat{p}_z - z\widehat{p}_y), (z\widehat{p}_x - x\widehat{p}_z)] \text{ and using the distributive law for commutators,} \\
&= [y\widehat{p}_z, z\widehat{p}_x] - [y\widehat{p}_z, x\widehat{p}_z] - [z\widehat{p}_y, z\widehat{p}_x] + [z\widehat{p}_y, x\widehat{p}_z] \\
&= y\widehat{p}_x[\widehat{p}_z, z] - 0 - 0 + x\widehat{p}_y[z, \widehat{p}_z] \text{ taking out factors which commute;} \\
&= (x\widehat{p}_y - y\widehat{p}_x)[z, \widehat{p}_z], \\
&= i\hbar(x\widehat{p}_y - y\widehat{p}_x), \text{ using } [z, \widehat{p}_z] = i\hbar \\
&= i\hbar\widehat{L}_z.
\end{aligned} \tag{9}$$

Similarly for the other possible commutators, giving

$$[\widehat{L}_x, \widehat{L}_y] = i\hbar\widehat{L}_z, \tag{10}$$

$$[\widehat{L}_z, \widehat{L}_x] = i\hbar\widehat{L}_y, \tag{11}$$

$$[\widehat{L}_y, \widehat{L}_z] = i\hbar\widehat{L}_x. \tag{12}$$

Notice that the commutators give $+i\hbar$ when, reading from left to right, the components are in cyclic order just as in a cross product. Indeed, these commutators can be written in an even more succinct form as a cross product:

$$\widehat{\mathbf{L}} \times \widehat{\mathbf{L}} = i\hbar\widehat{\mathbf{L}}. \tag{13}$$

This form of the commutators shows how unintuitive non-commuting operators can be: the cross product of two parallel ordinary vectors vanishes, but not when they are operators and their components don't commute!

The physical consequences of this failure to commute are remarkable and follow from the generalised Heisenberg uncertainty relation

$$\begin{aligned}
\Delta A \Delta B &\geq \frac{1}{2} |\langle [\widehat{A}, \widehat{B}] \rangle|, \\
&\neq 0 \quad \text{if } [\widehat{A}, \widehat{B}] \neq 0.
\end{aligned} \tag{14}$$

Hence only one component, conventionally taken to be \widehat{L}_z , can be measured with perfect precision ($\Delta L_z = 0$). Once this measurement has been performed, we can learn nothing whatever about the other two components ($\Delta L_x \neq 0$ and $\Delta L_y \neq 0$) because the operator \widehat{L}_z commutes with neither \widehat{L}_x nor \widehat{L}_y . Formally we can say that an eigenstate of \widehat{L}_z cannot also be an eigenstate of either \widehat{L}_x or \widehat{L}_y .

However, there is a further twist to the story: the *square* of the angular momentum, $\widehat{\mathbf{L}}^2$ commutes with \widehat{L}_z . Hence the *length* of the angular momentum vector *can also* be measured with perfect precision along with its z -component. To prove this we consider separately each term in $\widehat{\mathbf{L}}^2$, which is defined as

$$\widehat{\mathbf{L}}^2 = \widehat{L}_x^2 + \widehat{L}_y^2 + \widehat{L}_z^2. \tag{15}$$

First,³

$$\begin{aligned}
[\widehat{L}_x^2, \widehat{L}_z] &= \widehat{L}_x[\widehat{L}_x, \widehat{L}_z] + [\widehat{L}_x, \widehat{L}_z]\widehat{L}_x \\
&= -i\hbar(\widehat{L}_x\widehat{L}_y + \widehat{L}_y\widehat{L}_x) \text{ using } [\widehat{L}_x, \widehat{L}_z] = -i\hbar\widehat{L}_y,
\end{aligned} \tag{16}$$

³Using the identity obtained by adding and subtracting $\widehat{A}\widehat{B}\widehat{A}$ from

$$\begin{aligned}
[\widehat{A}^2, \widehat{B}] &= \widehat{A}^2\widehat{B} - \widehat{B}\widehat{A}^2 \\
&= \widehat{A}\widehat{A}\widehat{B} - \widehat{A}\widehat{B}\widehat{A} + \widehat{A}\widehat{B}\widehat{A} - \widehat{B}\widehat{A}\widehat{A} \\
&= \widehat{A}(\widehat{A}\widehat{B} - \widehat{B}\widehat{A}) + (\widehat{A}\widehat{B} - \widehat{B}\widehat{A})\widehat{A} \\
&= \widehat{A}[\widehat{A}, \widehat{B}] + [\widehat{A}, \widehat{B}]\widehat{A}
\end{aligned}$$

Similarly,

$$\begin{aligned} [\widehat{L}_y^2, \widehat{L}_z] &= \widehat{L}_y[\widehat{L}_y, \widehat{L}_z] + [\widehat{L}_y, \widehat{L}_z]\widehat{L}_y \\ &= +i\hbar(\widehat{L}_y\widehat{L}_x + \widehat{L}_x\widehat{L}_y), \quad \text{using } [\widehat{L}_y, \widehat{L}_z] = i\hbar\widehat{L}_x \end{aligned} \quad (17)$$

while, finally and obviously, \widehat{L}_z commutes with its own square,

$$[\widehat{L}_z^2, \widehat{L}_z] = 0 \quad (18)$$

Adding eqs. (16), (17), and (18), shows that $\widehat{\mathbf{L}}^2$ indeed commutes with \widehat{L}_z :

$$[\widehat{\mathbf{L}}^2, \widehat{L}_y] = [\widehat{L}_x^2, \widehat{L}_y] + [\widehat{L}_y^2, \widehat{L}_y] + [\widehat{L}_z^2, \widehat{L}_y] = 0 \quad (19)$$

Similar calculations for the other components give the same result, which we can summarise as:

$$[\widehat{\mathbf{L}}^2, \widehat{L}_i] = 0, \quad \text{for all } i = 1, 2, 3 \quad (20)$$

Since we have chosen to measure \widehat{L}_z exactly, the relevant commutator is $[\widehat{\mathbf{L}}^2, \widehat{L}_z] = 0$ ($i = 3$), which shows that we can also measure $\widehat{\mathbf{L}}^2$ exactly: it is possible to measure exactly both the length *and* one component of the angular momentum vector, but at the price of knowing *nothing whatever* about the other two components. This can be illustrated with Figure 1, which shows a vector of known length and projection onto the z -axis, but which can have any position on the circle obtained by rotating the vector around the z -axis. In formal terms our result tells us that eigenfunctions of \widehat{L}_z are also eigenfunctions of $\widehat{\mathbf{L}}^2$, but not of \widehat{L}_x nor of \widehat{L}_y . Of course the choice of \widehat{L}_z rather than \widehat{L}_x or \widehat{L}_y is an *arbitrary convention*; the point is that *only one* may be chosen from the three components because the corresponding operators do not commute.

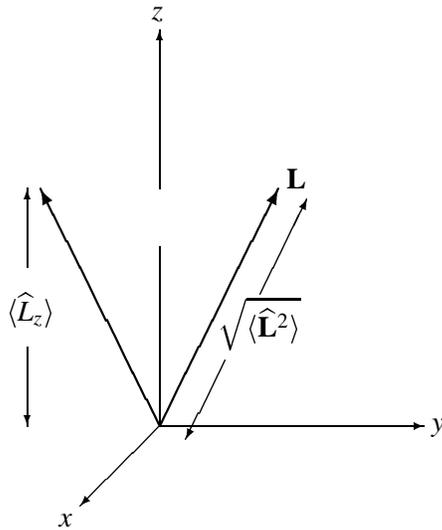


Figure 1: Picturing what can be measured exactly. This quasi-classical picture is not to be taken too literally - for an eigenstate $\langle \widehat{L}_z \rangle$ and $\langle \widehat{\mathbf{L}}^2 \rangle$ are the eigenvalues of the corresponding operators. \mathbf{L} is a quasi-classical vector representing the quantum mechanical angular momentum.

2. REPRESENTING \hat{L} IN SPHERICAL POLARS.⁴

In many physical applications, such as the quantum mechanics of the hydrogen atom, we either have exact or approximate spherical symmetry. This, together with angular momentum's association with rotation, demands that we consider writing down the angular momentum operators in spherical polar coordinates; this also leads to a great simplification and a recognition that the orbital angular momentum operators only involve the angular variables θ and ϕ .

In cartesian coordinates the orthogonal x -, y -, and z -axes, are fixed and lie along the orthogonal unit vectors $\mathbf{e}_x = \mathbf{i}$, $\mathbf{e}_y = \mathbf{j}$, and $\mathbf{e}_z = \mathbf{k}$; but in spherical polar coordinates the unit vectors, \mathbf{e}_r , \mathbf{e}_θ , and \mathbf{e}_ϕ , although orthogonal, vary in direction with the direction of the position vector \mathbf{r} as may be seen by inspecting Figure 2. Any vector may be written as an expansion in terms of these so-called **basis vectors**:

$$\mathbf{V} = \mathbf{i}V_x + \mathbf{j}V_y + \mathbf{k}V_z \quad (21)$$

$$= \mathbf{e}_r V_r + \mathbf{e}_\theta V_\theta + \mathbf{e}_\phi V_\phi \quad (22)$$

special cases being the position vector,

$$\mathbf{r} = \mathbf{i}x + \mathbf{j}y + \mathbf{k}z \quad (23)$$

$$= \mathbf{e}_r r \quad (24)$$

and the gradient operator,

$$\nabla = \mathbf{i} \frac{\partial}{\partial x} + \mathbf{j} \frac{\partial}{\partial y} + \mathbf{k} \frac{\partial}{\partial z}, \quad (25)$$

$$= \mathbf{e}_r \frac{\partial}{\partial r} + \mathbf{e}_\theta \frac{1}{r} \frac{\partial}{\partial \theta} + \mathbf{e}_\phi \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi}. \quad (26)$$

Of course you could just look up this last expression in a maths text book, but the following argument shows that it is almost obvious: The gradient involves differentials with respect to the 3 orthogonal infinitesimal distances: dx, dy, dz for cartesian coordinates and, as inspection of Figure 3 shows, $dr, r d\theta, r \sin \theta d\phi$ for spherical polars.

In spherical polars the momentum operator is therefore

$$\hat{\mathbf{p}} = -i\hbar \nabla \quad (27)$$

$$= \mathbf{e}_r \hat{p}_r + \mathbf{e}_\theta \hat{p}_\theta + \mathbf{e}_\phi \hat{p}_\phi, \quad (28)$$

$$= -i\hbar \left(\mathbf{e}_r \frac{\partial}{\partial r} + \mathbf{e}_\theta \frac{1}{r} \frac{\partial}{\partial \theta} + \mathbf{e}_\phi \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi} \right), \quad (29)$$

enabling us to identify the polar components of the momentum operator:

$$\hat{p}_r = -i\hbar \frac{\partial}{\partial r}, \quad \hat{p}_\theta = -i\hbar \frac{1}{r} \frac{\partial}{\partial \theta}, \quad \hat{p}_\phi = -i\hbar \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi}. \quad (30)$$

To find an expression for the orbital angular momentum operator we need the cross product of the vector $\mathbf{r} = r\mathbf{e}_r$ with the momentum operator. This brings in the cross products of the unit vector \mathbf{e} with all three

⁴You may find this section somewhat intimidating at a first reading. First read through the summary Sections 5 at the end of this chapter then work through the material several times, referring to the summary at the end of each reading. If you still feel it's beyond you then just skim the material and take the results on trust. As long as you understand the meaning of the results in the summary you should be able to follow the subsequent developments.

orthogonal unit vectors. These can be found by inspecting Figure 2 and using the right–hand rule for the cross–product:

$$\mathbf{e}_r \times \mathbf{e}_r = 0, \quad (31)$$

$$\mathbf{e}_r \times \mathbf{e}_\theta = \mathbf{e}_\varphi, \quad (32)$$

$$\mathbf{e}_r \times \mathbf{e}_\varphi = -\mathbf{e}_\theta, \quad (33)$$

making it easy to obtain the angular momentum operator in spherical polar coordinates,

$$\begin{aligned} \hat{\mathbf{L}} &:= \mathbf{r} \times \hat{\mathbf{p}} \\ &= (r\mathbf{e}_r) \times (\mathbf{e}_r \hat{p}_r + \mathbf{e}_\theta \hat{p}_\theta + \mathbf{e}_\varphi \hat{p}_\varphi) \\ &= r(\mathbf{e}_\varphi \hat{p}_\theta - \mathbf{e}_\theta \hat{p}_\varphi) \\ &= -i\hbar \left(\mathbf{e}_\varphi \frac{\partial}{\partial \theta} - \mathbf{e}_\theta \frac{1}{\sin \theta} \frac{\partial}{\partial \varphi} \right), \end{aligned} \quad (34)$$

Where we have used our previous results for the cross products and the momentum operators. This expression immediately shows the important property alluded to above: **the orbital angular momentum operator only acts on the angular variables.** Thus for a potential not depending on direction, ie. a **central potential** with $V(\mathbf{r}) \equiv V(r, \theta, \varphi) = V(r)$, **the angular momentum commutes with the potential:**

$$\text{For a central potential:} \quad [\hat{\mathbf{L}}, V(r)] = 0 \quad (35)$$

which means that each component and any power of the angular momentum commutes with the potential:

$$\text{For a central potential:} \quad [\hat{L}_i, V(r)] = 0 \quad i = 1, 2, 3 \quad (36)$$

$$\text{and} \quad [\hat{\mathbf{L}}^2, V(r)] = 0 \quad (37)$$

We conclude this section by giving expressions for the orbital angular momentum operators $\hat{L}_x, \hat{L}_y, \hat{L}_z$ and $\hat{\mathbf{L}}^2$ in spherical polars. For this we need to find the projections of the unit vectors $\mathbf{e}_r, \mathbf{e}_\theta$ and \mathbf{e}_φ onto the $x-, y-,$ and $z-$ axes. The details are given in Appendix A and Figure 4.

$$\mathbf{e}_r = \mathbf{i} \sin \theta \cos \varphi + \mathbf{j} \sin \theta \sin \varphi + \mathbf{k} \cos \theta \quad (38)$$

$$\mathbf{e}_\theta = \mathbf{i} \cos \theta \cos \varphi + \mathbf{j} \cos \theta \sin \varphi - \mathbf{k} \sin \theta. \quad (39)$$

$$\mathbf{e}_\varphi = -\mathbf{i} \sin \varphi + \mathbf{j} \cos \varphi. \quad (40)$$

Having established the projections of vectors $\mathbf{e}_r, \mathbf{e}_\theta$ and \mathbf{e}_φ onto the $x-, y-, z-$ axes we can simply rewrite the angular momentum vector in eq. (34), using the above equations, as:

$$\begin{aligned} \hat{\mathbf{L}} &= -i\hbar \left(\mathbf{e}_\varphi \frac{\partial}{\partial \theta} - \mathbf{e}_\theta \frac{1}{\sin \theta} \frac{\partial}{\partial \varphi} \right), \\ &= -i\hbar \left\{ \mathbf{i} \left(-\sin \varphi \frac{\partial}{\partial \theta} - \frac{\cos \theta}{\sin \theta} \cos \varphi \frac{\partial}{\partial \varphi} \right) + \mathbf{j} \left(\cos \varphi \frac{\partial}{\partial \theta} - \frac{\cos \theta}{\sin \theta} \sin \varphi \frac{\partial}{\partial \varphi} \right) + \mathbf{k} \frac{\sin \theta}{\sin \theta} \frac{\partial}{\partial \varphi} \right\}, \\ &= -i\hbar \left\{ -\mathbf{i} \left(\sin \varphi \frac{\partial}{\partial \theta} + \cot \theta \cos \varphi \frac{\partial}{\partial \varphi} \right) + \mathbf{j} \left(\cos \varphi \frac{\partial}{\partial \theta} - \cot \theta \sin \varphi \frac{\partial}{\partial \varphi} \right) + \mathbf{k} \frac{\partial}{\partial \varphi} \right\}, \end{aligned} \quad (41)$$

Hence we identify the three cartesian components of angular momentum:

$$\hat{L}_x = i\hbar \left(\sin \varphi \frac{\partial}{\partial \theta} + \cot \theta \cos \varphi \frac{\partial}{\partial \varphi} \right) \quad (42)$$

$$\hat{L}_y = -i\hbar \left(\cos \varphi \frac{\partial}{\partial \theta} - \cot \theta \sin \varphi \frac{\partial}{\partial \varphi} \right) \quad (43)$$

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \varphi} \quad (44)$$

Note particularly the very simple form taken by \widehat{L}_z - this is a consequence of the fact that L_z is the component of rotation about the z -axis, ie. in a plane parallel to the $x-y$ plane; this clearly corresponds to only the azimuthal angle φ varying. We can obtain the operator as follows by referring to Figure 3:

$$\begin{aligned}\widehat{L}_z &= (\text{lever arm projected onto } x-y \text{ plane})(\widehat{\mathbf{p}} \text{ projected onto } x-y \text{ plane}) \\ &= (r \sin \theta)(\widehat{p}_\varphi) \\ &= (r \sin \theta)\left(-i\hbar \frac{1}{r \sin \theta} \frac{\partial}{\partial \varphi}\right) \\ &= -i\hbar \frac{\partial}{\partial \varphi}\end{aligned}$$

There is no particularly easy way to obtain $\widehat{\mathbf{L}}^2$, because \mathbf{e}_θ and \mathbf{e}_φ both depend on θ and φ ; this contrasts with the constant unit vectors \mathbf{i} , \mathbf{j} , and \mathbf{k} . But the answer derived in Appendix C is quite simple:

$$\widehat{\mathbf{L}}^2 = -\hbar^2 \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right\}. \quad (45)$$

This is a remarkable result: apart from the factor $-\hbar^2$, and a missing $1/r^2$, this is just the angular part of the del-squared operator in spherical polars,

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right\}. \quad (46)$$

$$= \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right\}. \quad (47)$$

Recalling the kinetic energy part of the Hamiltonian

$$\widehat{KE} = \frac{\widehat{\mathbf{p}}^2}{2m} \quad (48)$$

$$= -\frac{\hbar^2}{2m} \nabla^2 \quad (49)$$

we immediately see that this can be written in terms of the squared angular momentum as

$$\widehat{KE} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{\widehat{\mathbf{L}}^2}{2m r^2} \quad (50)$$

In the following section we explain how we might have guessed this simple result from a knowledge of the *classical* kinetic energy.

3. CLASSICAL & QUANTUM KINETIC ENERGIES.

To appreciate the important result for the kinetic energy obtained in the previous section let us first consider the classical case. Resolve the total momentum vector along and perpendicular to \mathbf{r} ⁵

$$\mathbf{p} = \mathbf{p}_r + \mathbf{p}_\perp \quad (51)$$

Since these are orthogonal and, of course, *commuting* classical vectors,

$$\mathbf{p}_r \cdot \mathbf{p}_\perp = \mathbf{p}_\perp \cdot \mathbf{p}_r = 0. \quad (52)$$

Looking at Figure 5 we see that the lever arm of \mathbf{p}_\perp about the origin is r so that the magnitude of the orbital angular momentum is

$$L_{cl} = r p_\perp, \quad \text{and therefore,} \quad \mathbf{p}_\perp^2 = \frac{\mathbf{L}_{cl}^2}{r^2}, \quad (53)$$

Hence we easily obtain the *classical Kinetic energy* as the sum of linear and rotational energies:

$$(KE)_{cl} = \frac{\mathbf{p}^2}{2m} = \frac{(\mathbf{p}_r + \mathbf{p}_\perp)^2}{2m} = \frac{p_r^2}{2m} + \frac{\mathbf{L}_{cl}^2}{2mr^2} \quad (54)$$

where we used $\mathbf{p}_r^2 = \mathbf{p}_r \cdot \mathbf{p}_r = p_r^2$. To obtain the QM form one might be tempted to simply replace p_r and L_{cl} by the quantum mechanical operators. This would be wrong: the quantum mechanical calculation is altogether more tricky because the two momentum operators don't commute,

$$\hat{\mathbf{p}}_r \cdot \hat{\mathbf{p}}_\perp \neq \hat{\mathbf{p}}_\perp \cdot \hat{\mathbf{p}}_r, \quad \text{with} \quad \hat{\mathbf{p}}_r \cdot \hat{\mathbf{p}}_\perp = 0 \quad \text{but} \quad \hat{\mathbf{p}}_\perp \cdot \hat{\mathbf{p}}_r = -2i\hbar \frac{\hat{p}_r}{r} \neq 0. \quad (55)$$

This shows itself through the fact that although all the unit vectors are independent of r , they all vary with the angles θ and φ .⁶ In Appendix B we show how to calculate this additional term $\hat{\mathbf{p}}_\perp \cdot \hat{\mathbf{p}}_r$. Recalling the expression for the r -component of the momentum operator,

$$\hat{p}_r = -i\hbar \frac{\partial}{\partial r} \quad \text{and hence,} \quad \hat{p}_r^2 = -\hbar^2 \frac{\partial^2}{\partial r^2} \quad (56)$$

the full **Quantum Mechanical KE operator** becomes:

$$\widehat{KE} = \frac{\widehat{\mathbf{p}}^2}{2m} \quad (57)$$

$$= \frac{\hat{p}_r^2}{2m} - i\hbar \frac{\hat{p}_r}{mr} + \frac{\widehat{\mathbf{L}}^2}{2mr^2} \quad (58)$$

$$= -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{\widehat{\mathbf{L}}^2}{2mr^2} \quad (59)$$

$$= -\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{\widehat{\mathbf{L}}^2}{2mr^2} \quad (60)$$

This expression shows a close resemblance to the classical expression for the KE, eq. (54): the additional term, $-i\hbar \hat{p}_r / mr$, is clearly of quantum origin because it has an explicit factor of \hbar even before we use a particular representation for the operator. It arises from the non-commuting operators and corresponds to the 'extra' term $(2/r)\partial/\partial r$ which we failed to discover by unthinkingly translating the classical formula

⁵Where the momentum vector along \mathbf{r} is $\mathbf{p}_r = \mathbf{e}_r p_r$, and the one perpendicular to \mathbf{r} is $\mathbf{p}_\perp = \mathbf{e}_\theta p_\theta + \mathbf{e}_\varphi p_\varphi$

⁶See Appendix A for a full discussion

into operator form. This expression will be important in our study of the hydrogen atom. For the present we note that the Hamiltonian now takes the form,

$$\hat{H} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{\hat{\mathbf{L}}^2}{2mr^2} + V(r) \quad \text{for a central potential.} \quad (61)$$

This form for the Hamiltonian in *any* central potential immediately demonstrates that it commutes with all the angular momentum operators \hat{L}_i and $\hat{\mathbf{L}}^2$. This is because \hat{L}_i and $\hat{\mathbf{L}}^2$, (a) only act on the angular variables θ, ϕ , and therefore do not effect any r -dependent terms, and (b) commute with the operator $\hat{\mathbf{L}}^2$ and hence they commute with $\hat{\mathbf{L}}^2/2mr^2$ and other r -dependent terms in the Hamiltonian. Hence we find the important results,

$$[\hat{H}, \hat{L}_i] = 0 \quad i = 1, 2, 3 \quad (62)$$

For a Central Potential

$$[\hat{H}, \hat{\mathbf{L}}^2] = 0 \quad (63)$$

which imply that **eigenstates of energy are also eigenstates of \hat{L}_z and $\hat{\mathbf{L}}^2$** . Recall that once we have chosen to make our energy eigenstates also eigenfunctions of \hat{L}_z they cannot be eigenfunctions of \hat{L}_x and \hat{L}_y because these don't commute with \hat{L}_z .

4. QUANTISING ORBITAL ANGULAR MOMENTUM.

We are now in a position to *prove* that the eigenvalues of $\hat{\mathbf{L}}^2$ and \hat{L}_z are quantised. Since in a central potential, eigenstates of these two operators are also eigenstates of energy, we therefore see that an electron in a state of definite energy will also be in an eigenstate of $\hat{\mathbf{L}}^2$ and \hat{L}_z :

$$\text{If } \hat{H}\psi_E(\mathbf{r}) = E\psi_E(\mathbf{r}), \quad (64)$$

$$\text{then } \hat{\mathbf{L}}^2\psi_E(\mathbf{r}) = \hbar^2\ell(\ell+1)\psi_E(\mathbf{r}) \quad \ell = 0, 1, 2, \dots, \quad (65)$$

$$\text{and } \hat{L}_z\psi_E(\mathbf{r}) = \hbar m\psi_E(\mathbf{r}) \quad m = -\ell, -\ell+1, \dots, 0, \dots, \ell-1, \ell. \quad (66)$$

(We will show later that there is also the possibility of ℓ -values $1/2, 3/2, 5/2, \dots$ for angular momentum in general, including spin, but not for *orbital* angular momentum.) From the above summary we see that the electron wave function should not only carry the energy label E (or equivalently the quantum number n , as in the infinite square well, harmonic oscillator or the hydrogen atom), but also those corresponding to the angular momentum, $\psi_{E,\ell,m}$, or $\psi_{n,\ell,m}$.

There are two approaches to demonstrating the quantisation of angular momentum:

APPROACH (1), by seeking directly the eigenfunctions of $\hat{\mathbf{L}}^2$ and \hat{L}_z . I will motivate this approach physically by showing how the eigenvalue equations arise in seeking the energy eigenfunctions for a particle in a central potential. We will apply this later to our study of the hydrogen atom.

APPROACH (2), by treating the angular momentum operators as abstract entities defined entirely by their commutation relations. It is this approach which reveals the possibility of non-integer quantum numbers ℓ and m and which enables us to handle the purely quantum mechanical phenomenon of spin.

4.1 APPROACH (1): THE EIGENFUNCTIONS & EIGENVALUES OF ORBITAL ANGULAR MOMENTUM OPERATORS.

We could start our discussion by seeking directly the eigenfunctions of $\widehat{\mathbf{L}}^2$ and \widehat{L}_z . Looking back at the representations of these two operators in spherical polars, eqs. (44) & (45), we notice that \widehat{L}_z only operates on the variable φ , eq. (44), so that its eigenfunctions are functions of φ ,

$$\widehat{L}_z \Phi_m(\varphi) = m\hbar \Phi_m(\varphi), \quad (67)$$

$$\text{ie. } -i\hbar \frac{\partial \Phi_m(\varphi)}{\partial \varphi} = m\hbar \Phi_m(\varphi), \quad (68)$$

The solution to this equation is simple and unique:

$$\Phi_m(\varphi) = e^{im\varphi}, \quad (69)$$

but there is nothing yet to tell us the value of m , the **azimuthal quantum number**; for this we need to introduce some further physical information.

In contrast, the operator $\widehat{\mathbf{L}}^2$, eq. (45), operates on both θ and φ , so that its eigenfunctions depend on both variables; we will also find that the eigenfunctions depend on m as well as the \mathbf{L}^2 eigenvalue ℓ :

$$\widehat{\mathbf{L}}^2 Y_{\ell m}(\theta, \varphi) = \hbar^2 \ell(\ell+1) Y_{\ell m}(\theta, \varphi) \quad (70)$$

Again, at this stage, there is nothing to tell us the value of the quantum number ℓ .

To introduce the physics we consider a particle in a central potential $V(r)$ and we proceed to solve the TDSE in the obviously appropriate spherical coordinate system:

$$\widehat{H}(r, \theta, \varphi) \psi_E(r, \theta, \varphi) = E \psi_E(r, \theta, \varphi), \quad (71)$$

which we can write more explicitly as,

$$\left\{ -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{\widehat{\mathbf{L}}^2}{2mr^2} + V(r) \right\} \psi_E(r, \theta, \varphi) = E \psi_E(r, \theta, \varphi) \quad (72)$$

or in its full glory,

$$\left\{ -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) - \frac{\hbar^2}{2mr^2} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right] + V(r) \right\} \psi_E = E \psi_E \quad (73)$$

Separation of variables: To solve this equation we first notice that the angular dependent terms are very nearly separated from the r -dependent ones; all we have to do is multiply by r^2 to achieve the full separation. This suggests that a way to find the solutions is to try to find one in the form

$$\boxed{\psi_E(r, \theta, \varphi) = R(r)Y(\theta, \varphi)} \quad (74)$$

Substituting into the TISE and multiplying by $2mr^2/R(r)Y(\theta, \varphi)$ we obtain

$$\begin{aligned} \frac{r^2}{R(r)} \left\{ \hbar^2 \left(\frac{d^2 R(r)}{dr^2} + \frac{2}{r} \frac{dR(r)}{dr} \right) \right\} + (E - V(r))2mr^2 &= -\frac{1}{Y(\theta, \varphi)} \widehat{\mathbf{L}}^2 Y(\theta, \varphi) \\ &= \frac{-\hbar^2}{Y(\theta, \varphi)} \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y(\theta, \varphi)}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y(\theta, \varphi)}{\partial \varphi^2} \right\}. \end{aligned}$$

This equation must hold for *all* values of the three *independent* variables r, θ and φ ; but the left side is only a function of r , the right only a function of θ and φ . They can only possibly be equal for *arbitrary*

choices of r, θ and φ if they don't vary at all, ie. they are constant. We call this constant, which has the *dimensions* of \hbar^2

$$\hbar^2 \ell(\ell + 1)$$

for convenience, where ℓ is an unknown dimensionless constant.⁷ Thus we obtain the **radial equation** whose solution depends on the precise form of the potential,

$$-\frac{\hbar^2}{2m} \left(\frac{d^2 R(r)}{dr^2} + \frac{2}{r} \frac{dR(r)}{dr} \right) + \left(V(r) + \frac{\hbar^2 \ell(\ell + 1)}{2mr^2} \right) R(r) = E R(r), \quad (75)$$

and the angular equation *which is independent of the potential*:

$$\hat{\mathbf{L}}^2 Y(\theta, \varphi) = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right] Y(\theta, \varphi) = \hbar^2 \ell(\ell + 1) Y(\theta, \varphi). \quad (76)$$

Something remarkable has happened: the differential operator which operates on the function $Y(\theta, \varphi)$ is none other than our recent acquaintance, $\hat{\mathbf{L}}^2$, and this equation is nothing but the statement that $Y(\theta, \varphi)$ **is an eigenfunction of the angular momentum operator $\hat{\mathbf{L}}^2$** , with the corresponding eigenvalue being the constant $\hbar^2 \ell(\ell + 1)$:

$$\boxed{\hat{\mathbf{L}}^2 Y(\theta, \varphi) = \hbar^2 \ell(\ell + 1) Y(\theta, \varphi)} \quad (77)$$

Remember that at this point we know nothing about the numerical value of ℓ . Incidentally, it's not too surprising that this equation occurs in this problem: for a central potential $\hat{\mathbf{L}}^2$ commutes with the Hamiltonian, and therefore eigenstates of energy - in this case $\psi_E = R(r)Y(\theta, \varphi)$ - are also eigenstates of $\hat{\mathbf{L}}^2$. We now anticipate that the wave function is also an eigenstate of \hat{L}_z because this operator also commutes with \hat{H} . To see that this is so we now separate the eigenvalue equation for $Y(\theta, \varphi)$ by trying a solution of the form:

$$\boxed{Y(\theta, \varphi) = \Theta(\theta) \Phi(\varphi)}. \quad (78)$$

Substituting into the equation, multiplying by $\sin^2 \theta / \Theta \Phi$ and isolating the φ -dependent terms on the right we obtain the separated form,

$$\frac{1}{\Theta(\theta)} \sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta(\theta)}{d\theta} \right) + \ell(\ell + 1) \sin^2 \theta = -\frac{1}{\Phi(\varphi)} \frac{d^2 \Phi(\varphi)}{d\varphi^2}. \quad (79)$$

Once again we see that this equation must hold for all values of the *independent* variables θ and φ , so that the left and right sides must be a constant. Calling this as yet unknown dimensionless constant m^2 , we obtain for the θ equation:

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta(\theta)}{d\theta} \right) + \left[\ell(\ell + 1) - \frac{m^2}{\sin^2 \theta} \right] \Theta(\theta) = 0. \quad (80)$$

This is the **associated Legendre equation** whose *finite* solutions, known as the **associated Legendre functions**, are well-studied and are labelled by the values of the two constants ℓ and m :

$$\Theta(\theta) = P_\ell^m(\cos \theta). \quad (81)$$

The φ equation is very simple:

$$\frac{d^2 \Phi(\varphi)}{d\varphi^2} = -m^2 \Phi(\varphi). \quad (82)$$

The solutions are of the general form

$$\Phi(\varphi) = e^{im\varphi}, \quad (83)$$

⁷At this stage we have no idea whatever what the value of ℓ is and we are just anticipating the *form* that will come out of subsequent discussion. The discussion would go exactly the same way if we called this constant A, α, β or anything else.

which is also a solution of the eigenvalue equation,

$$\boxed{\widehat{L}_z \Phi(\varphi) = \hbar m \Phi(\varphi)}. \quad (84)$$

Indeed, if we act on this last equation with \widehat{L}_z we simply obtain $-\hbar^2$ times eq. (82):

$$\widehat{L}_z^2 \Phi(\varphi) = -\hbar^2 \frac{d^2 \Phi(\varphi)}{d\varphi^2} = \hbar^2 m^2 \Phi(\varphi), \quad (85)$$

thereby confirming that $\hbar m$ is the eigenvalue of \widehat{L}_z and that $\Phi_m(\varphi)$ its eigenfunction. Thus we have explicitly verified that eigenfunctions of the Hamiltonian for a central potential are also eigenfunctions of \widehat{L}^2 and \widehat{L}_z .

Applying Physical conditions to the wave function: We now impose the physically reasonable restriction that **the wave function be single-valued**; this is certainly consistent with the probability interpretation of the wave function.⁸ Since φ and $\varphi + 2\pi$ correspond to the same physical point, we require

$$\Phi(\varphi + 2\pi) = \Phi(\varphi), \quad (86)$$

which immediately shows that **m must be an integer**:

$$m = 0, \pm 1, \pm 2, \pm 3, \dots \quad (87)$$

Thus do we obtain the **quantisation of the z -component of orbital angular momentum**: \widehat{L}_z has quantised eigenvalues $\hbar m, m = 0, \pm 1, \pm 2, \pm 3, \dots$

We now return to the θ -equation which can be simplified by using the variable $w = \cos \theta$ ⁹

$$\left[(1-w^2) \frac{d^2}{dw^2} - 2w \frac{d}{dw} + \ell(\ell+1) - \frac{m^2}{1-w^2} \right] P_\ell^{|m|}(w) = 0 \quad (88)$$

This can be solved by the series method: as with the harmonic oscillator, it turns out that a physically acceptable wave function, finite at $\cos \theta = \pm 1$, only results if the series terminates after a finite number of terms. This imposes a relationship between ℓ and m :

$$\begin{aligned} \ell &= 0, 1, 2, \dots & \text{and for each } \ell, m \text{ has } (2\ell + 1) \text{ allowed values,} \\ m &= -\ell, -\ell + 1, \dots, 0, \dots, \ell - 1, \ell. \end{aligned} \quad (89)$$

The angular momentum vector, in units of \hbar , is a vector of length $\sqrt{\ell(\ell+1)}$; the only permissible orientations of the vector being those for which its projection onto the z -axis have the values $m = -\ell, -\ell + 1, \dots, \ell$. Thus for $\ell = 1$ there are 3 allowed m -values, $m = -1, 0, 1$; for $\ell = 2$ there are 5 allowed values, $m = -2, -1, 0, 1, 2$. Figure 6 illustrates these rules and emphasises the fact that \widehat{L}_x and \widehat{L}_y are indeterminate by showing the angular momentum vector as having any orientation corresponding to rotations about the z -axis.¹⁰

4.1.1 ORTHONORMALITY OF ANGULAR MOMENTUM EIGENSTATES:

⁸This argument for single-valuedness of ψ is not generally valid, but is correct for *orbital* angular momentum. In fact, since the physical quantity is the probability density $|\psi|^2 \propto |\Phi(\varphi)|^2$, we only require *it* to be single-valued. This only makes m real. The operator approach will show that $2\ell + 1 = \text{integer}$, which implies that $m = 1/2$ is also possible - a value appropriate for electron spin. So the the spin wave functions for the electron are double-valued!

⁹That the solution of this equation is independent of the *sign* of m is obvious because the equation contains m only in the form m^2 . Thus $P_\ell^m = P_\ell^{-m} = P_\ell^{|m|}$

¹⁰Note also the rather peculiar characteristic of the rules which never have the vector pointing precisely along the z -axis! This is because the vector has length $\sqrt{\ell(\ell+1)}$ rather than the value ℓ obtained from Bohr's original theory.

We have now shown that the wave function depends on the energy and on the quantum numbers ℓ, m ; in fact if we look at the equations satisfied by $R(r)$ and $Y(\theta, \varphi)$ we see that the former depends only on E and ℓ , $R(r) = R_{E\ell}(r)$, while the latter does not involve E at all, but *does* depend on both ℓ and m , $Y(\theta, \varphi) = Y_{\ell m}(\theta, \varphi)$. Thus we should write the energy eigenstates not as $\Psi_E(\mathbf{r})$ but as:

$$\boxed{\Psi_{E\ell m}(\mathbf{r}) = R_{E\ell}(r) Y_{\ell m}(\theta, \varphi)}. \quad (90)$$

To be a physically acceptable wave function $\Psi_{E\ell m}(\mathbf{r})$ must also be normalised:

$$\boxed{\int |\Psi_{E\ell m}(\mathbf{r})|^2 d^3x = 1}, \quad \text{where the 3-D volume element, Figure 7, is } d^3x \equiv r^2 \sin\theta d\theta d\varphi dr, \quad (91)$$

or, in full detail (note especially the factor of r^2),

$$\int_0^\infty r^2 dr \int_0^{2\pi} d\varphi \int_0^\pi \sin\theta d\theta |\Psi_{E\ell m}(\mathbf{r})|^2 = 1. \quad (92)$$

A convenient shorthand for the angular integration variable is the solid angle notation, $d\Omega \equiv \sin\theta d\theta d\varphi$, with the accompanying shorthand for the integration itself:

$$\int d\Omega \equiv \int_0^{2\pi} d\varphi \int_0^\pi \sin\theta d\theta \quad (93)$$

It is conventional and convenient to normalise the **spherical harmonics**,¹¹

$$Y_{\ell m}(\theta, \varphi) \equiv N_{\ell m} P_\ell^{|m|}(\cos\theta) e^{im\varphi}, \quad (94)$$

$$\int |Y_{\ell m}(\theta, \varphi)|^2 d\Omega = 1, \quad (95)$$

which means that, to normalise the wave function $\Psi_{E\ell m}(\mathbf{r})$ the radial wave function $R_{E\ell}(r)$ is normalised only when multiplied by r^2 :¹²

$$\int_0^\infty |R_{E\ell}(r)|^2 r^2 dr = 1. \quad (96)$$

As expected for eigenfunctions of Hermitian operators, the spherical harmonics are orthonormal:

$$\int Y_{\ell' m'}^*(\theta, \varphi) Y_{\ell m}(\theta, \varphi) d\Omega = \delta_{\ell' \ell} \delta_{m' m} \quad (97)$$

Moreover the most general solution to the TISE equation is a linear combination of spherical harmonics: they constitute a **complete set** of functions for which the expansion theorem holds. Thus the angular part of any wave function may be expanded in terms of eigenfunctions of \widehat{L}^2 and \widehat{L}_z :

$$\Psi(r, \theta, \varphi) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{+\ell} c_{\ell, m} \Psi_{E\ell}(r) Y_{\ell m}(\theta, \varphi), \quad (98)$$

¹¹The normalising factor, with a conventional but arbitrary phase factor $(-1)^m$, is

$$N_{\ell m} = (-1)^m \left[\frac{(2\ell+1)(\ell-m)!}{4\pi(\ell+m)!} \right]^{1/2}.$$

¹²This is important for the physical interpretation of plots of the radial wave function: one normally plots $|rR_{E\ell}(r)|^2$ because this represents the physical probability density at a distance r from the origin. Of course we must remember that this is then modulated by the direction-dependent angular wave function $|Y_{\ell m}(\theta, \varphi)|^2$ factor to give the full spatial dependence of the probability density.

where the coefficients $c_{\ell,m}$ play the same role as the c_n in our general discussion of the expansion theorem. Normalisation of this state requires,

$$\sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{+\ell} |c_{\ell,m}|^2 = 1, \quad (99)$$

which tells us that the $|c_{\ell,m}|^2$ are probabilities. Thus, for a system in the normalised state $Y(\theta, \varphi)$ a measurement of both the square and z -component of orbital angular momentum yields, with probability $|c_{\ell,m}|^2$; one of the eigenvalues $\hbar^2 \ell(\ell + 1)$ of $\widehat{\mathbf{L}}^2$ and one of the eigenvalues, $\hbar m, m \equiv m_{\ell} = -\ell, -\ell + 1, \dots, \ell - 1, \ell$, of \widehat{L}_z corresponding to that ℓ -value; immediately after the measurement which gave the values (ℓ, m) the wave function will be $Y_{\ell m}(\theta, \varphi)$. If *only* the squared angular momentum is measured, yielding $\hbar^2 \ell(\ell + 1)$, then the probability for this outcome is the sum over the possible, but unmeasured m_{ℓ} -values, $\sum_{m=-\ell}^{+\ell} |c_{\ell,m}|^2$.

If we are concerned with a state of *definite* total orbital angular momentum, then it must be an eigenstate of $\widehat{\mathbf{L}}^2$, fixing the value of the quantum number ℓ . This is a frequently used special case of the more general expansion theorem in eq. (98). The angular part of the wave function would then be:

$$Y_{(\ell)}(\theta, \varphi) = \sum_{m=-\ell}^{+\ell} c_m Y_{\ell m}(\theta, \varphi), \quad \text{where} \quad \sum_{m=-\ell}^{+\ell} |c_m|^2 = 1, \quad (100)$$

For a system in this normalised state the outcome of a measurement of $\widehat{\mathbf{L}}^2$ will certainly yield $\hbar^2 \ell(\ell + 1)$; but a measurement of \widehat{L}_z will yield one of its eigenvalues, $\hbar m, m \equiv m_{\ell} = -\ell, -\ell + 1, \dots, \ell - 1, \ell$, with probability $|c_m|^2$; if the outcome is $\hbar m$ then immediately after the measurement the wave function will be $Y_{\ell m}(\theta, \varphi)$.

4.1.2 PLOTTING THE SPHERICAL HARMONICS - THE SHAPES OF ATOMS.

Before we deal with the operator approach to angular momentum, let us briefly examine the properties of the spherical harmonics with a view to its application in understanding the shapes of atoms. Since the relevant angular part of the quantum mechanical probability density (per unit solid angle, $d\Omega = \sin\theta d\theta d\varphi$) is independent of the azimuthal angle φ ,

$$\begin{aligned} |Y_{\ell m}(\theta, \varphi)|^2 &= N_{\ell m}^2 |P_{\ell}^{|m|}|^2 |e^{im\varphi}|^2 \\ &= N_{\ell m}^2 \left[P_{\ell}^{|m|} \right]^2, \end{aligned} \tag{101}$$

we see that all systems with a central potential have rotational symmetry about the z -axis. Put another way, a plot of the angular probability distribution can always be pictured as a 2-dimensional figure rotated about the z -axis; examples of the first few are shown in Figures 8a and 8b. The first three angular momentum eigenfunctions are also tabulated in Table 1; notice that the states have definite parity which, being $(-1)^{\ell}$, alternates in a nearly familiar manner.¹³ Of course this is another example of our theorem that eigenstates of energy are also eigenstates of parity if the potential is symmetric, $V(-\mathbf{r}) = V(\mathbf{r})$. This is trivially satisfied for a central potential because under a mirror reflection the *length* r of the vector \mathbf{r} doesn't change.

Figure 9: Illustrating the parity transformation in spherical polar coordinates.

¹³In fact the mirror reflection of axes, $(x, y, z) \rightarrow (-x, -y, -z)$ only alters the *angles* in spherical polars. From Figure 9 we see that in the reflected coordinate system (a left-handed system) the components of \mathbf{r} change:

$$(r, \theta, \varphi) \rightarrow (r, \pi - \theta, \varphi + \pi) \quad \text{giving} \quad \sin\theta \rightarrow \sin\theta, \quad \cos\theta \rightarrow -\cos\theta,$$

leading to,

$$\begin{aligned} P_{\ell}^{|m|}(\cos\theta) &\rightarrow (-1)^{\ell-|m|} P_{\ell}^{|m|}(\cos\theta) \\ \text{and also,} \quad e^{im\varphi} &\rightarrow e^{i\pi} e^{im\varphi} = (-1)^{|m|} e^{im\varphi}. \end{aligned}$$

Combining these then gives the result quoted: $Y_{\ell m} \rightarrow (-1)^{\ell} Y_{\ell m}$.

Table 1. Angular Momentum Eigenfunctions, $\Psi_{E\ell m}(\mathbf{r}) = R_{E\ell}(r)Y_{\ell m}(\theta, \varphi)$.

Quantum Numbers Parity = $(-1)^\ell$ ℓ m	Associated Legendre Function $P_\ell^{ m }(\cos\theta)$	Azimuthal Function $e^{im\varphi}$	Spherical Harmonic $Y_{\ell m}(\theta, \varphi) = N_{\ell m} P_\ell^{ m } e^{im\varphi}$
0 0	1	1	$Y_{0,0} = \left(\frac{1}{4\pi}\right)^{\frac{1}{2}}$
1 0	$\cos\theta$	1	$Y_{1,0} = \left(\frac{3}{4\pi}\right)^{\frac{1}{2}} \cos\theta$
± 1	$\sin\theta$	$e^{\pm i\varphi}$	$Y_{1,\pm 1} = \mp \left(\frac{3}{8\pi}\right)^{\frac{1}{2}} \sin\theta e^{\pm i\varphi}$
2 0	$\frac{1}{2}(3\cos^2\theta - 1)$	1	$Y_{2,0} = \left(\frac{5}{16\pi}\right)^{\frac{1}{2}} (3\cos^2\theta - 1)$
± 1	$3\sin\theta\cos\theta$	$e^{\pm i\varphi}$	$Y_{2,\pm 1} = \mp \left(\frac{15}{8\pi}\right)^{\frac{1}{2}} \sin\theta\cos\theta e^{\pm i\varphi}$
± 2	$3\sin^2\theta$	$e^{\pm 2i\varphi}$	$Y_{2,\pm 2} = \left(\frac{15}{32\pi}\right)^{\frac{1}{2}} \sin^2\theta e^{\pm 2i\varphi}$
3 0	$\frac{1}{2}(5\cos^3\theta - 3\cos\theta)$	1	$Y_{3,0} = \left(\frac{7}{16\pi}\right)^{\frac{1}{2}} (5\cos^3\theta - 3\cos\theta)$
± 1	$\frac{3}{2}\sin\theta(5\cos^2\theta - 1)$	$e^{\pm i\varphi}$	$Y_{3,\pm 1} = \mp \left(\frac{21}{64\pi}\right)^{\frac{1}{2}} \sin\theta(5\cos^2\theta - 1) e^{\pm i\varphi}$
± 2	$15\sin^2\theta\cos\theta$	$e^{\pm 2i\varphi}$	$Y_{3,\pm 2} = \left(\frac{105}{32\pi}\right)^{\frac{1}{2}} \sin^2\theta\cos\theta e^{\pm 2i\varphi}$
± 3	$15\sin^3\theta$	$e^{\pm 3i\varphi}$	$Y_{3,\pm 3} = \mp \left(\frac{35}{64\pi}\right)^{\frac{1}{2}} \sin^3\theta e^{\pm 3i\varphi}$

- Notes:** (a) The mysterious \mp in the last column are conventional phase factors - see footnote¹.
 (b) The associated Legendre functions are indeed functions of $\cos\theta$ since $\sin\theta = \sqrt{(1 - \cos^2\theta)}$.
 (c) The normalised components of the wave function for a given ℓ are:

$$\Theta_{\ell m}(\cos\theta) = \sqrt{2\pi} N_{\ell m} P_\ell^{|m|}(\cos\theta) \quad \int_{-1}^{+1} \Theta_{\ell m'}(w) \Theta_{\ell m}(w) dw = \delta_{m'm},$$

where $w = \cos\theta$ is the integration variable, the range of integration being $\theta = 0 \rightarrow \pi$,

$$\Phi_m(\varphi) = \frac{1}{\sqrt{2\pi}} e^{im\varphi} \quad \int_0^{2\pi} \Phi_{m'}^*(\varphi) \Phi_m(\varphi) d\varphi = \delta_{m'm},$$

and

$$Y_{\ell m}(\theta, \varphi) = \Theta_{\ell m}(\theta) \Phi_m(\varphi). \quad \int Y_{\ell m'}^*(\theta, \varphi) Y_{\ell m}(\theta, \varphi) d\Omega = \delta_{m'm}.$$

4.2 APPROACH (2): GENERAL ANGULAR MOMENTUM OPERATORS.

One of the great surprises in the history of 20th century physics was the discovery of spin, a form of angular momentum intrinsic to an isolated particle such as an electron. The surprise is that spin cannot be understood quantitatively as the analogue of a spinning top or the earth spinning on its axis - these are really examples of orbital angular momentum in disguise: the material making up a top or the earth is simply orbiting about the spin axis. In fact the electron is known experimentally to be so small that it's impossible to imagine how it could produce its angular momentum $\hbar/2$ by spinning no faster than the speed of light. This is our motivation for studying angular momentum in a purely abstract way, assuming that the *general* angular momentum operator $\hat{\mathbf{J}}$ represents all forms of angular momentum: orbital, when $\hat{\mathbf{J}} = \hat{\mathbf{L}}$; spin, when $\hat{\mathbf{J}} = \hat{\mathbf{S}}$; and situations which occur when spinning particles are also orbiting - such as an electron in an atom - for which the total angular momentum is the vector sum $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$. Without any prior knowledge about the spatial structure of spin, our approach will be purely algebraic: **angular momentum in QM is represented by the Hermitian vector operator $\hat{\mathbf{J}}$ which obeys the commutation relations:**

$$\hat{\mathbf{J}} \times \hat{\mathbf{J}} = i\hbar \hat{\mathbf{J}} \quad \left\{ \begin{array}{l} [\hat{J}_x, \hat{J}_y] = i\hbar \hat{J}_z, \\ [\hat{J}_z, \hat{J}_x] = i\hbar \hat{J}_y, \\ [\hat{J}_y, \hat{J}_z] = i\hbar \hat{J}_x. \end{array} \right. \quad (102)$$

From these equations we can deduce that $\hat{\mathbf{J}}^2$ commutes with all the components of $\hat{\mathbf{J}}$. The proof follows exactly the sequence eqs. (15) to (20) which used only the commutation relations and not the explicit representation of orbital angular momentum:

$$\hat{\mathbf{J}}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2. \quad (103)$$

For each term we use the identity $[\hat{A}^2, \hat{B}] = \hat{A}[\hat{A}, \hat{B}] + [\hat{A}, \hat{B}]\hat{A}$ to obtain:

$$\begin{aligned} [\hat{J}_x^2, \hat{J}_z] &= \hat{J}_x[\hat{J}_x, \hat{J}_z] + [\hat{J}_x, \hat{J}_z]\hat{J}_x \\ &= -i\hbar(\hat{J}_x\hat{J}_y + \hat{J}_y\hat{J}_x). \end{aligned} \quad (104)$$

$$\text{Similarly, } [\hat{J}_y^2, \hat{J}_z] = +i\hbar(\hat{J}_y\hat{J}_x + \hat{J}_x\hat{J}_y), \quad (105)$$

while, finally and obviously, \hat{J}_z commutes with its own square, $[\hat{J}_z^2, \hat{J}_z] = 0$. Thus the two non-vanishing terms cancel, showing that $\hat{\mathbf{J}}^2$ indeed commutes with \hat{J}_z . Similar proofs go through for the other two components, giving finally:

$$[\hat{\mathbf{J}}^2, \hat{J}_i] = 0, \quad \text{for all } i = 1, 2, 3 \quad (106)$$

Since $\hat{\mathbf{J}}^2$ and \hat{J}_z commute they have a common eigenfunction ψ , with as yet unknown eigenvalues $\hbar^2\lambda$ and $\hbar\lambda_z$ respectively:

$$\hat{\mathbf{J}}^2\psi = \hbar^2\lambda\psi \quad (107)$$

$$\hat{J}_z\psi = \hbar\lambda_z\psi \quad (108)$$

We now proceed to show that the commutation relations alone imply the quantisation rules obtained before for orbital angular momentum, but with a bonus: half-integral angular momentum is also possible. The analysis is divided into several distinct steps:

Step 1: $|\lambda_z| \leq \sqrt{\lambda}$

Since the square of an operator has a positive expectation value we obtain,

$$\langle \hat{\mathbf{J}}^2 \rangle = \langle \hat{J}_x^2 \rangle + \langle \hat{J}_y^2 \rangle + \langle \hat{J}_z^2 \rangle \geq \langle \hat{J}_z^2 \rangle, \quad (109)$$

which translates immediately into a statement about the eigenvalues:¹⁴

$$\lambda_z^2 \leq \lambda \quad \text{or, taking the square root of these positive numbers,} \quad |\lambda_z| \leq \sqrt{\lambda}. \quad (110)$$

Notice that λ_z can have any sign, but λ is positive because it's the eigenvalue of the square of an operator. This result is not surprising when we refer to the quasi-classical Figure 10, since the projection of the angular momentum vector onto the z -axis can never be larger than the length of the vector!¹⁵

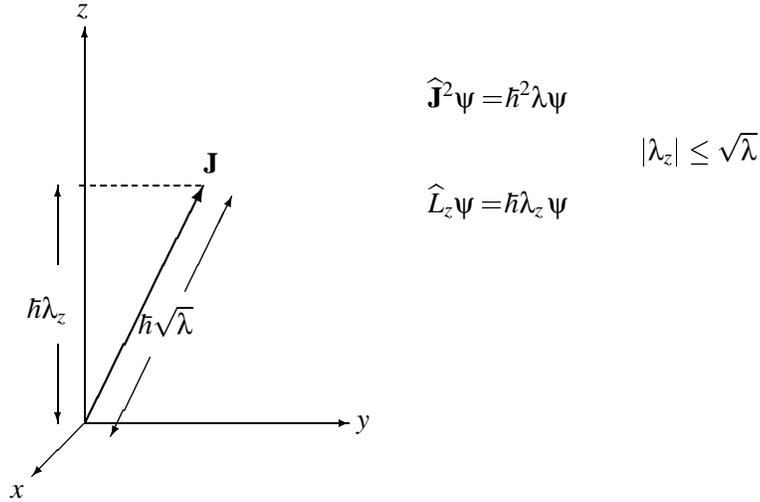


Figure 10: Picturing the inequality, $|\lambda_z| \leq \sqrt{\lambda}$ for an eigenstate of \hat{J}_z and $\hat{\mathbf{J}}^2$ with eigenvalues $\hbar\lambda_z$ and $\hbar^2\lambda$.

¹⁴Remember that the eigenvalue μ of an operator \hat{O} is just the expectation value of that operator when the system is in the corresponding eigenstate:

$$\begin{aligned} \langle \hat{O} \rangle &= \int \psi^* \hat{O} \psi dx = \mu \int \psi^* \psi dx \quad \text{for an eigenstate, } \hat{O}\psi = \mu\psi, \\ &= \mu \quad \text{for a normalised eigenstate.} \end{aligned}$$

¹⁵Deeper thought reveals that the result is more subtle: the quasi-classical picture does no more than depict the content of the eigenvalue equations. That the eigenvalues do indeed behave this way is true but not trivial to prove. In the case of spin one has to prove that the expectation value of a squared operator is positive without knowing anything about the nature of the 'coordinates' upon which the wave function depends - indeed such coordinates may not even exist for intrinsic properties like spin. However if the wave functions are dependent on the spatial variables, as in the case of *orbital* angular momentum, then it's clear why the square of a Hermitian operator has positive expectation value:

$$\begin{aligned} \langle \hat{O}^2 \rangle &= \int \psi^* \hat{O}^2 \psi dx = \int (\hat{O}\psi)^* \hat{O}\psi dx \quad \text{since } \hat{O} \text{ is Hermitian} \\ &= \int |\hat{O}\psi|^2 dx \geq 0, \quad \text{since it's the integral of a positive quantity.} \end{aligned}$$

The matrix or Dirac formalism is needed to prove this result when, as for spin angular momentum, we do not know what is the analogue of the coordinates x, y, z or r, θ, ϕ . That is the great merit of Heisenberg's matrix form of QM and why we will use it later for dealing with spin.

Step 2: Introducing raising & lowering operators, \hat{J}_\pm .

As we discovered in solving the SHO, the introduction of **raising and lowering operators** is the key to the analysis. They are simple linear combinations of \hat{J}_x and \hat{J}_y :

$$\hat{J}_\pm \equiv \hat{J}_x \pm i\hat{J}_y \quad \text{with} \quad \hat{J}_+^\dagger = \hat{J}_-. \quad (111)$$

Their properties all follow from those of the \hat{J} -operators:¹⁶

$$\hat{J}_+ \hat{J}_- = \hat{\mathbf{J}}^2 - \hat{J}_z^2 + \hbar \hat{J}_z \quad (112)$$

$$\hat{J}_- \hat{J}_+ = \hat{\mathbf{J}}^2 - \hat{J}_z^2 - \hbar \hat{J}_z \quad (113)$$

$$\text{or, more succinctly, } \hat{J}_\pm \hat{J}_\mp = \hat{\mathbf{J}}^2 - \hat{J}_z^2 \pm \hbar \hat{J}_z, \quad (114)$$

leading to:

$$[\hat{J}_\pm, \hat{J}_\mp] = \pm 2\hbar \hat{J}_z, \quad (115)$$

and

$$[\hat{J}_z, \hat{J}_\pm] = \pm \hbar \hat{J}_\pm. \quad (116)$$

Finally, and most simply, they commute with $\hat{\mathbf{J}}^2$ because \hat{J}_x and \hat{J}_y do:

$$[\hat{\mathbf{J}}^2, \hat{J}_\pm] = 0. \quad (117)$$

This has the immediate consequence that,

Step 3: $\hat{J}_\pm \psi$ are eigenstates of $\hat{\mathbf{J}}^2$ with the same eigenvalue as ψ .

To prove this we merely act on ψ with $\hat{\mathbf{J}}^2$ and \hat{J}_\pm in each order:

$$\begin{aligned} \hat{J}_\pm (\hat{\mathbf{J}}^2 \psi) &= \hat{\mathbf{J}}^2 (\hat{J}_\pm \psi) \\ &= \hbar^2 \lambda (\hat{J}_\pm \psi); \text{ using on the left that } \psi \text{ is an eigenstate of } \hat{\mathbf{J}}^2, \end{aligned} \quad (118)$$

thereby showing that $(\hat{J}_\pm \psi)$ is also an eigenfunction of $\hat{\mathbf{J}}^2$ with the *same* eigenvalue $\hbar^2 \lambda$ as ψ .

Step 4: $\hat{J}_\pm \psi$ are eigenstates of \hat{J}_z with eigenvalues $\hbar(\lambda_z \pm 1)$.

The proof shows why \hat{J}_\pm are called raising and lowering operators. We use their commutators with \hat{J}_z in the form,

$$\hat{J}_z \hat{J}_\pm = \hat{J}_\pm \hat{J}_z \pm \hbar \hat{J}_\pm, \quad (119)$$

to find

$$\begin{aligned} \hat{J}_z (\hat{J}_\pm \psi) &= \hat{J}_\pm (\hat{J}_z \psi) \pm \hbar \hat{J}_\pm \psi \quad \text{from the above commutator,} \\ &= \hbar \lambda_z (\hat{J}_\pm \psi) \pm \hbar \hat{J}_\pm \psi \quad \text{since } \hat{J}_z \psi = \hbar \lambda_z \psi. \end{aligned} \quad (120)$$

¹⁶Thus, for example,

$$\begin{aligned} \hat{J}_+ \hat{J}_- &= (\hat{J}_x + i\hat{J}_y)(\hat{J}_x - i\hat{J}_y) \\ &= \hat{J}_x^2 + \hat{J}_y^2 - i(\hat{J}_x \hat{J}_y - \hat{J}_y \hat{J}_x) \end{aligned}$$

Recognising the first two terms as $\hat{\mathbf{J}}^2 - \hat{J}_z^2$ and the bracketed combination as the commutator $[\hat{J}_x, \hat{J}_y] = i\hbar \hat{J}_z$ we obtain the result quoted. The other results all follow in a similar manner.

Collecting the $(\hat{J}_\pm \psi)$ terms on the right together gives the result:

$$\hat{J}_z(\hat{J}_\pm \psi) = \hbar(\lambda_z \pm 1)(\hat{J}_\pm \psi) \quad (121)$$

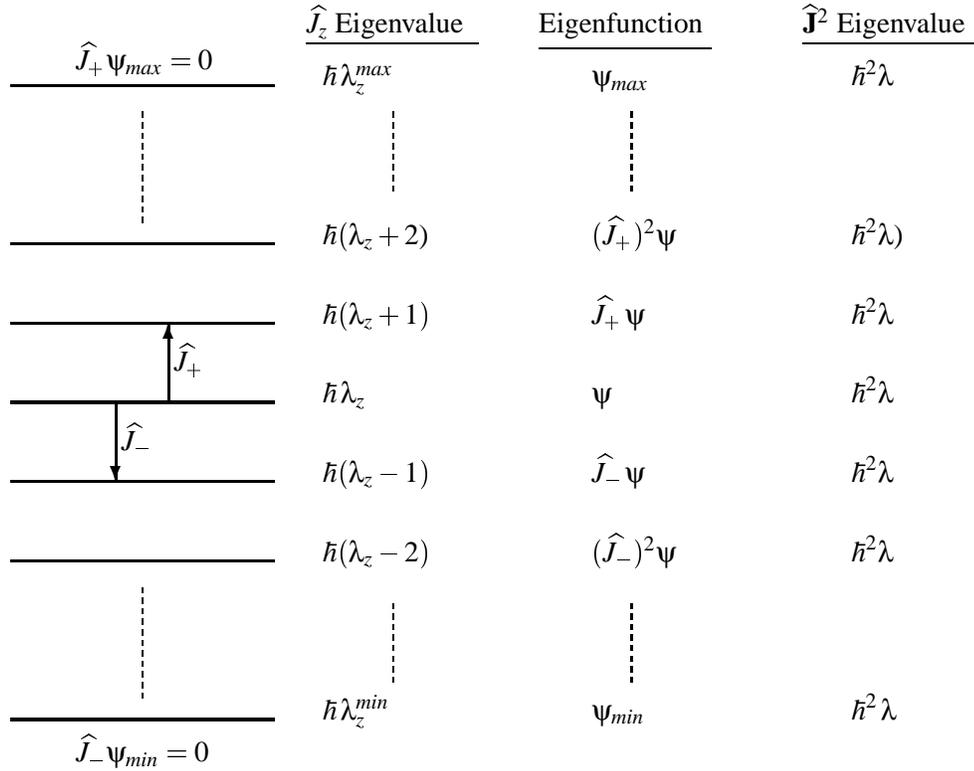


Figure 11: Illustrating the action of the raising and lowering operators on the eigenstates of \hat{J}_z and \hat{J}^2 . All are eigenstates of \hat{J}^2 with eigenvalue $\hbar^2 \lambda$.

Figure 11 depicts the action of these ladder operators: a single application of \hat{J}_+ to an eigenstate raises it up the ladder, increasing its \hat{J}_z eigenvalue by one unit of \hbar ; repeated applications simply create eigenstates progressively higher up the ladder. \hat{J}_- performs the same operations *down* the ladder, *decreasing* the eigenvalue by one unit of \hbar at each application. Can we continue the process indefinitely? No, because Step 1 showed us that the magnitude of the \hat{J}_z eigenvalue cannot exceed $\hbar\sqrt{\lambda}$.

Step 5: Hence, there must exist on the ladder both a highest eigenstate, ψ_{max} and a lowest one, ψ_{min} .

Just as for the ground state of the SHO, so these states must be annihilated by the action of the appropriate ladder operator, thereby blocking any further progress on the ladder:

$$\hat{J}_+ \psi_{max} = 0, \quad (122)$$

$$\hat{J}_- \psi_{min} = 0. \quad (123)$$

These states, being eigenstates of \hat{J}_z , have the maximum and minimum allowed eigenvalues:

$$\hat{J}_z \psi_{max} = \lambda_z^{max} \psi_{max}, \quad (124)$$

$$\hat{J}_z \psi_{min} = \lambda_z^{min} \psi_{min}. \quad (125)$$

Step 6: With $\lambda_z^{max} \equiv j$, $\lambda = j(j+1)$.

We now proceed to relate the eigenvalue $\hbar^2\lambda$ of $\hat{\mathbf{J}}^2$ to the eigenvalue $\hbar\lambda_z^{max}$ of \hat{J}_z by applying to ψ_{max} the operator identity $\hat{J}_-\hat{J}_+ = \hat{\mathbf{J}}^2 - \hat{J}_z^2 - \hbar\hat{J}_z$ obtained in Step 2. The key is to notice that this operator annihilates the state because \hat{J}_+ does so:

$$\hat{J}_-\hat{J}_+\psi_{max} = \hat{J}_-(\hat{J}_+\psi_{max}) = 0 \quad (126)$$

$$= (\hat{\mathbf{J}}^2 - \hat{J}_z^2 - \hbar\hat{J}_z)\psi_{max} \quad (127)$$

$$= \hbar^2(\lambda - (\lambda_z^{max})^2 - \lambda_z^{max})\psi_{max} \quad (128)$$

Since ψ_{max} is not zero, we conclude that $(\lambda - (\lambda_z^{max})^2 - \lambda_z^{max}) = 0$. Similarly, by applying to ψ_{min} the state annihilating operator $\hat{J}_-\hat{J}_+ = \hat{\mathbf{J}}^2 - \hat{J}_z^2 - \hbar\hat{J}_z$ we find that $(\lambda - (\lambda_z^{min})^2 + \lambda_z^{min}) = 0$. Solving both conditions for λ then yields the pair of equations,

$$\lambda = \lambda_z^{max}(\lambda_z^{max} + 1) \quad (129)$$

$$\lambda = \lambda_z^{min}(\lambda_z^{min} - 1) \quad (130)$$

which immediately imply ¹⁷

$$\lambda_z^{min} = -\lambda_z^{max} \equiv -j, \quad (131)$$

where, because of its pivotal role in the argument we introduce a more succinct notation for the maximum eigenvalue of the $\hbar\hat{J}_z$ operator,

$$\lambda_z^{max} \equiv j \quad (132)$$

so that the eigenvalue of the $\hbar\hat{\mathbf{J}}^2$ operator is:

$$\hbar^2\lambda = \hbar^2 j(j+1) \quad (133)$$

This remarkable result then leads to our final conclusion,

Step 7: $2j = \text{INTEGER}$

Our final steps begin with the lowest eigenstate ψ_{min} and climb the ladder of eigenstates by operating repeatedly on it with the raising operator \hat{J}_+ . Each step increases the eigenvalue by one unit of \hbar ; after n steps we have reached the state $(\hat{J}_+)^n\psi_{min}$ which has \hat{J}_z eigenvalue $\hbar(\lambda_z^{min} + n) = \hbar(-j + n)$. But we know that this climb must end, and that the end must be the state of maximum eigenvalue ψ_{max} because this is the defining property of ψ_{max} .¹⁸ Thus there is some n for which the resulting eigenvalue is $\hbar j$, giving

$$-j + n = j \quad \text{or,} \quad j = \frac{n}{2}, \quad n = 0, 1, 2, \dots \quad (134)$$

We therefore discover *two* possibilities, integral (for n even) and half-integral (for n odd) angular momentum (in units of \hbar), whereas for *orbital* angular momentum only integral values were possible. Writing for the eigenvalues $\lambda_z \equiv m_j$ we then have the quantisation rules for general angular momentum:

$$\text{Integral angular momentum: } j = 0, 1, 2, \dots \quad m_j = -j, -j+1, \dots, 0, \dots, j-1, j \quad (135)$$

$$\text{Half-integral angular momentum: } j = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots \quad m_j = -j, -j+1, \dots, j-1, j \quad (136)$$

¹⁷The equations actually give *two* possible solutions, $\lambda_z^{min} = -\lambda_z^{max}$ or $\lambda_z^{min} = \lambda_z^{max} + 1$, but this latter is inconsistent with the obvious fact that $\lambda_z^{min} < \lambda_z^{max}$.

¹⁸The reason is that there is *only one* function which is annihilated by \hat{J}_+ ; in other words the solution to $\hat{J}_+\psi_{max} = 0$ is *unique*.

Thus, for an eigenstate of general angular momentum we have,

$$\hat{\mathbf{J}}^2 \psi_{j,m_j} = \hbar^2 j(j+1) \psi_{j,m_j} \quad (137)$$

$$\hat{J}_z \psi_{j,m_j} = \hbar m_j \psi_{j,m_j} \quad (138)$$

The angular momentum quantum numbers j and m_j labelling an eigenstate are often loosely referred to as the angular momentum and its z -component, or azimuthal projection, although strictly the angular momentum is $\hbar j$ and $\hbar m_j$. A special case of integral angular momentum is obviously the already encountered orbital angular momentum $\hat{\mathbf{J}} = \hat{\mathbf{L}}$; we shall see later that spin angular momentum, $\hat{\mathbf{J}} = \hat{\mathbf{S}}$, which cannot be pictured classically as a microscopic spinning top, can have both integral and half-integral values.

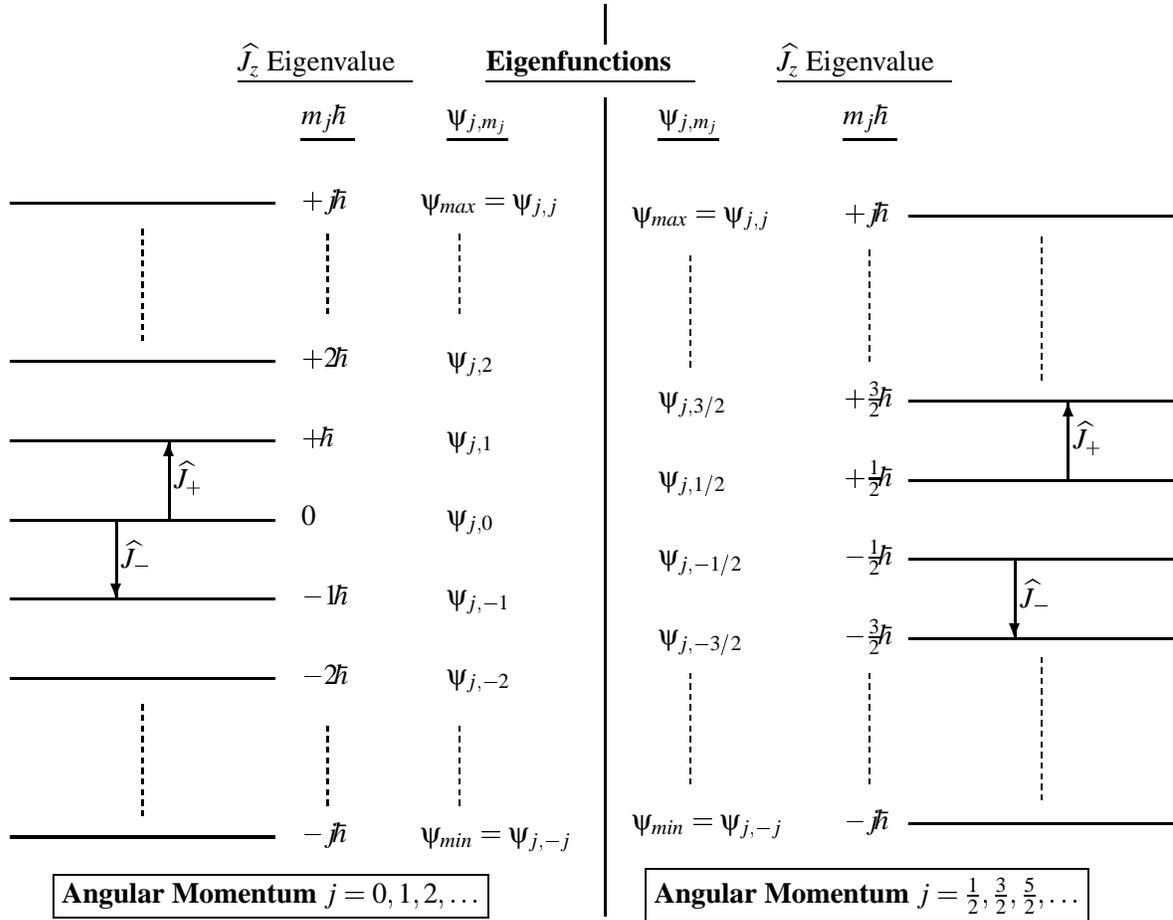


Figure 12: The angular momentum spectrum. All are eigenstates of $\hat{\mathbf{J}}^2$ with eigenvalue $\hbar^2 j(j+1)$. On the left is shown the case of integral j , which allows $m_j = 0$. Orbital angular momentum always gives such a spectrum, with $\hat{\mathbf{J}} = \hat{\mathbf{L}}$, $j = \ell$ and $m_j = m_\ell = m$; so does integral spin (eg. the photon has spin $s=1$) with $\hat{\mathbf{J}} = \hat{\mathbf{S}}$, $j = s$ and $m_j = m_s$. On the right is shown half-integral angular momentum (eg. the electron and proton have spin $s = 1/2$), which forbids $m_j = 0$.

5. SUMMARY.

5.1 ORBITAL ANGULAR MOMENTUM $\hat{\mathbf{L}}$ & ITS COMMUTATORS.

The QM Orbital Angular Momentum Operator is:

$$\hat{\mathbf{L}} = \mathbf{r} \times \hat{\mathbf{p}} = -i\hbar \mathbf{r} \times \nabla, \quad (139)$$

or, in cartesian components,

$$\hat{L}_x = y\hat{p}_z - z\hat{p}_y = -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right), \quad (140)$$

$$\hat{L}_y = z\hat{p}_x - x\hat{p}_z = -i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right), \quad (141)$$

$$\hat{L}_z = x\hat{p}_y - y\hat{p}_x = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right). \quad (142)$$

First we note that, as befits an observable dynamical variable, $\hat{\mathbf{L}}$ is a Hermitian operator because both \mathbf{r} and $\hat{\mathbf{p}}$ are Hermitian,

$$\hat{L}_i^\dagger = \hat{L}_i, \quad i = 1, 2, 3 \quad (143)$$

These components do not commute, but obey the angular momentum algebra. This can be expressed succinctly as:

$$\hat{\mathbf{L}} \times \hat{\mathbf{L}} = i\hbar \hat{\mathbf{L}} \quad \text{or, in fully explicit form,} \quad \begin{cases} [\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z, \\ [\hat{L}_z, \hat{L}_x] = i\hbar \hat{L}_y, \\ [\hat{L}_y, \hat{L}_z] = i\hbar \hat{L}_x. \end{cases} \quad (144)$$

Hence, by the generalised Heisenberg uncertainty relation, only one component, conventionally taken to be \hat{L}_z , can be measured with perfect precision ($\Delta L_z = 0$). Once this measurement has been performed, we cannot determine the other two components precisely ($\Delta L_x \neq 0$ and $\Delta L_y \neq 0$)¹⁹ because the operator \hat{L}_z commutes with neither \hat{L}_x nor \hat{L}_y . Formally we can say that an eigenstate of \hat{L}_z cannot also be an eigenstate of either \hat{L}_x or \hat{L}_y .

However, there is a further twist to the story: the *length* of the angular momentum vector *can also* be measured with perfect precision along with its *z*-component because the *square* of the angular momentum, $\hat{\mathbf{L}}^2$,

$$\hat{\mathbf{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2. \quad (145)$$

commutes with \hat{L}_z :

$$[\hat{\mathbf{L}}^2, \hat{L}_i] = 0, \quad \text{for all } i = 1, 2, 3 \quad (146)$$

Figure 1 illustrates succinctly the physical consequences of these results: the length and the *z*-component of the angular momentum can be measured exactly, but the angular momentum vector can lie at any orientation on the cone indicated by the circle. In terms of eigenstates it means that eigenstates of \hat{L}_z are

¹⁹The precise expressions are quite easy to obtain: for a simultaneous eigenstate of $\hat{\mathbf{L}}^2$ and \hat{L}_z , we can show that

$$\langle \hat{L}_x \rangle = \langle \hat{L}_y \rangle = 0$$

and that

$$\langle \hat{L}_x^2 \rangle = \langle \hat{L}_y^2 \rangle = \frac{\hbar^2}{2} \{ \ell(\ell+1) - m^2 \}$$

so that the uncertainties are

$$\Delta L_x = \Delta L_y = \frac{\hbar}{\sqrt{2}} \sqrt{\ell(\ell+1) - m^2}$$

These are consistent with Heisenberg's generalised uncertainty relation. The proof uses the raising and lowering operators $\hat{L}_\pm = (\hat{L}_x \pm i\hat{L}_y)/2$ and the orthonormality of the eigenstates.

also eigenstates of $\widehat{\mathbf{L}}^2$, but not of either \widehat{L}_x or \widehat{L}_y .

5.2 REPRESENTING $\widehat{\mathbf{L}}$ IN SPHERICAL POLARS.

In spherical polars we write the unit vectors in the orthogonal (r, θ, φ) directions as $(\mathbf{e}_r, \mathbf{e}_\theta, \mathbf{e}_\varphi)$; these are the analogues of the cartesian unit vectors $(\mathbf{e}_x, \mathbf{e}_y, \mathbf{e}_z) = (\mathbf{i}, \mathbf{j}, \mathbf{k})$. See Figures 2, 3 & 4 for the notation. Then since orbital angular momentum is always perpendicular to the \mathbf{r} -vector, it has no component along \mathbf{r} ,

$$\widehat{\mathbf{L}} = (\mathbf{e}_r r) \times (\mathbf{e}_r \widehat{p}_r + \mathbf{e}_\theta \widehat{p}_\theta + \mathbf{e}_\varphi \widehat{p}_\varphi) \quad (147)$$

$$= r(\mathbf{e}_\varphi \widehat{p}_\theta - \mathbf{e}_\theta \widehat{p}_\varphi) \quad (148)$$

$$= -i\hbar \left(\mathbf{e}_\varphi \frac{\partial}{\partial \theta} - \mathbf{e}_\theta \frac{1}{\sin \theta} \frac{\partial}{\partial \varphi} \right), \quad (149)$$

I quote this result to show explicitly that $\widehat{\mathbf{L}}$ only acts on the angles, not on r . This should not surprise us since angular momentum is concerned with rotation, ie. changing angles, not changing radial coordinate r . The immediate consequence is that any function of r , such as a central potential $V(r)$, commutes with $\widehat{\mathbf{L}}^2$ and all the components of $\widehat{\mathbf{L}}$:

$$[V(r), \widehat{\mathbf{L}}] = 0 \quad \text{and} \quad [V(r), \widehat{\mathbf{L}}^2] = 0 \quad (150)$$

Also, since the kinetic energy term in the Hamiltonian,²⁰

$$\widehat{KE} = \frac{\widehat{\mathbf{p}}^2}{2m} \quad (152)$$

$$= \frac{\widehat{p}_r^2}{2m} - i\hbar \frac{\widehat{p}_r}{mr} + \frac{\widehat{\mathbf{L}}^2}{2mr^2} \quad (153)$$

$$= -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{\widehat{\mathbf{L}}^2}{2mr^2} \quad (154)$$

$$= -\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{\widehat{\mathbf{L}}^2}{2mr^2} \quad (155)$$

depends only on r and $\widehat{\mathbf{L}}^2$, it too commutes with the angular momentum and its square:

$$[\widehat{H}, \widehat{L}_i] = 0 \quad i = 1, 2, 3 \quad (156)$$

For a Central Potential

$$[\widehat{H}, \widehat{\mathbf{L}}^2] = 0 \quad (157)$$

which imply that **eigenstates of energy are also eigenstates of \widehat{L}_z and $\widehat{\mathbf{L}}^2$** . Recall that once we have chosen to make our energy eigenstates also eigenfunctions of \widehat{L}_z they cannot also be made eigenfunctions of \widehat{L}_x and \widehat{L}_y because these don't commute with \widehat{L}_z .

²⁰This is easy to remember because it is so similar to the *classical Kinetic energy*

$$(KE)_{cl} = \frac{\mathbf{p}^2}{2m} = \frac{(p_r + \mathbf{p}_\perp)^2}{2m} = \frac{\mathbf{p}_r^2}{2m} + \frac{\mathbf{L}_{cl}^2}{2mr^2} \quad (151)$$

The only difference is the additional quantum correction due to non-commuting operators:

$$-i\hbar \widehat{p}_r / mr = -\frac{\hbar^2}{2m} (2/r) \partial / \partial r$$

Finally we note the following expressions for the cartesian components:

$$\hat{L}_x = i\hbar \left(\sin \varphi \frac{\partial}{\partial \theta} + \cot \theta \cos \varphi \frac{\partial}{\partial \varphi} \right) \quad (158)$$

$$\hat{L}_y = -i\hbar \left(\cos \varphi \frac{\partial}{\partial \theta} - \cot \theta \sin \varphi \frac{\partial}{\partial \varphi} \right) \quad (159)$$

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \varphi} \quad (160)$$

$$\hat{\mathbf{L}}^2 = -\hbar^2 \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right\}. \quad (161)$$

Note particularly the very simple form taken by \hat{L}_z , which is a consequence of the fact that rotation about the z -axis corresponds to rotation in the $x - y$ plane which is described only by a varying φ -angle.

5.3 QUANTISING ORBITAL ANGULAR MOMENTUM.

5.3.1 SIMULTANEOUS EIGENSTATES OF $\widehat{\mathbf{L}}^2$ and \widehat{L}_z .

Since the commuting operators $\widehat{\mathbf{L}}^2$ and \widehat{L}_z only act on the angles, their simultaneous eigenstates, $Y_{\ell m}(\theta, \varphi)$ are only functions of these angles. Their eigenvalues are expressible in terms of two quantum numbers ℓ and m which are only allowed discrete integer values:

$$\begin{aligned} \ell &= 0, 1, 2, \dots & \text{and for each } \ell, m \text{ is allowed any of } (2\ell + 1) \text{ values,} \\ m &= -\ell, -\ell + 1, \dots, 0, \dots, \ell - 1, \ell. \end{aligned} \quad (162)$$

The fact that these quantum numbers are integers comes from the *physical* requirement that the wave functions be finite and single-valued. The eigenfunctions $Y_{\ell m}(\theta, \varphi)$, known as *Spherical Harmonics*, are eigenfunctions of both the $\widehat{\mathbf{L}}^2$ operator,

$$\widehat{\mathbf{L}}^2 Y_{\ell m}(\theta, \varphi) = \hbar^2 \ell(\ell + 1) Y_{\ell m}(\theta, \varphi) \quad (163)$$

and the \widehat{L}_z operator,

$$\widehat{L}_z Y_{\ell m}(\theta, \varphi) = \hbar m Y_{\ell m}(\theta, \varphi) \quad (164)$$

The form of the normalised eigenfunctions is

$$Y_{\ell m}(\theta, \varphi) \equiv N_{\ell m} P_{\ell}^{|m|}(\cos \theta) e^{im\varphi}, \quad (165)$$

(the $N_{\ell m}$ are normalisation constants, see footnote¹¹) where the *associated Legendre Function*, $P_{\ell}^{|m|}(\cos \theta)$, are well-studied functions of $\cos \theta$. As expected for eigenfunctions of Hermitian operators the spherical harmonics are orthonormal:

$$\int Y_{\ell' m'}^*(\theta, \varphi) Y_{\ell m}(\theta, \varphi) d\Omega = \delta_{\ell' \ell} \delta_{m' m} \quad (166)$$

where we use the solid angle notation as a convenient shorthand for the angular integration variable, $d\Omega \equiv \sin \theta d\theta d\varphi$, with the accompanying shorthand for the integration itself:

$$\int d\Omega \equiv \int_0^{2\pi} d\varphi \int_0^{\pi} \sin \theta d\theta \quad (167)$$

$$\int |Y_{\ell m}(\theta, \varphi)|^2 d\Omega = 1, \quad (168)$$

Finally note that the expansion theorem allows us to write the most general wave function for a particle whose magnitude of orbital angular momentum is $\hbar\sqrt{\ell(\ell + 1)}$, ie. orbital angular momentum quantum number ℓ , as a linear combination of eigenstates with definite projections along the z -axis:

$$Y_{(\ell)}(\theta, \varphi) = \sum_{m=-\ell}^{+\ell} c_m Y_{\ell m}(\theta, \varphi), \quad \text{where} \quad \sum_{m=-\ell}^{+\ell} |c_m|^2 = 1, \quad (169)$$

For a system in this normalised state the outcome of a measurement of $\widehat{\mathbf{L}}^2$ will certainly yield $\hbar^2 \ell(\ell + 1)$; but a measurement of \widehat{L}_z will yield one of its eigenvalues, $\hbar m$, $m \equiv m_{\ell} = -\ell, -\ell + 1, \dots, \ell - 1, \ell$, with probability $|c_m|^2$; if the outcome is $\hbar m$ then immediately after the measurement the wave function will be $Y_{\ell m}(\theta, \varphi)$.

The angular momentum vector, in units of \hbar , is a vector of length $\sqrt{\ell(\ell + 1)}$; the only permissible orientations of the vector being those for which its projection onto the z -axis have the values $m = -\ell, -\ell + 1, \dots, \ell$. Thus for $\ell = 1$ there are 3 allowed m -values, $m = -1, 0, 1$; for $\ell = 2$ there are 5 allowed values, $m = -2, -1, 0, 1, 2$. Figure 6 illustrates these rules and emphasises the fact that \widehat{L}_x and \widehat{L}_y are indeterminate by showing the angular momentum vector as having any orientation corresponding

to rotations about the z -axis.

5.3.2 QUANTISATION FROM THE PHYSICS OF ANGULAR MOMENTUM IN A CENTRAL POTENTIAL.

Since in a central potential, eigenstates of $\hat{\mathbf{L}}^2$ and \hat{L}_z are also eigenstates of energy, we therefore see that a particle such as an electron in a state of definite energy will also be in an eigenstate of $\hat{\mathbf{L}}^2$ and \hat{L}_z :

$$\text{If } \hat{H}\psi_E(\mathbf{r}) = E\psi_E(\mathbf{r}), \quad (170)$$

$$\text{then } \hat{\mathbf{L}}^2\psi_E(\mathbf{r}) = \hbar^2\ell(\ell+1)\psi_E(\mathbf{r}) \quad \ell = 0, 1, 2, \dots, \quad (171)$$

$$\text{and } \hat{L}_z\psi_E(\mathbf{r}) = \hbar m\psi_E(\mathbf{r}) \quad m = -\ell, -\ell+1, \dots, 0, \dots, \ell-1, \ell. \quad (172)$$

That the eigenvalues of $\hat{\mathbf{L}}^2$ and \hat{L}_z are quantised as above is shown by writing down the TISE for a central potential,

$$\hat{H}(r, \theta, \varphi) \psi_E(r, \theta, \varphi) = E \psi_E(r, \theta, \varphi), \quad (173)$$

which we can write more explicitly as,

$$\left\{ -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{\hat{\mathbf{L}}^2}{2mr^2} + V(r) \right\} \psi_E(r, \theta, \varphi) = E \psi_E(r, \theta, \varphi) \quad (174)$$

or in its full glory,

$$\left\{ -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) - \frac{\hbar^2}{2mr^2} \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\varphi^2} \right] + V(r) \right\} \psi_E = E \psi_E \quad (175)$$

This equation is solved by *separation of variables*, writing the wave function as a product:

$$\psi_E(r, \theta, \varphi) = R(r)Y(\theta, \varphi) \quad (176)$$

Thus we obtain the **radial equation** whose solution depends on the precise form of the potential,

$$-\frac{\hbar^2}{2m} \left(\frac{d^2R(r)}{dr^2} + \frac{2}{r} \frac{dR(r)}{dr} \right) + \left(V(r) + \frac{\hbar^2\ell(\ell+1)}{2mr^2} \right) R(r) = ER(r), \quad (177)$$

and the angular equation *which is independent of the potential*:

$$-\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial Y(\theta, \varphi)}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2 Y(\theta, \varphi)}{\partial\varphi^2} \right] Y(\theta, \varphi) = \hbar^2\ell(\ell+1)Y(\theta, \varphi). \quad (178)$$

which we recognise as the equation for the eigenfunctions and eigenvalues of the $\hat{\mathbf{L}}^2$ operator,

$$\hat{\mathbf{L}}^2 Y(\theta, \varphi) = \hbar^2\ell(\ell+1)Y(\theta, \varphi) \quad (179)$$

At this stage the eigenvalue $-\hbar^2\ell(\ell+1)$ is an unknown separation constant: we only know that it has the dimensions of \hbar^2 ; but its value comes from solving this equation. This is accomplished by another step of variable separation,

$$Y(\theta, \varphi) = \Theta(\theta)\Phi(\varphi). \quad (180)$$

leading to the very simple φ equation,

$$\frac{d^2\Phi(\varphi)}{d\varphi^2} = -m^2\Phi(\varphi). \quad (181)$$

where m is a second unknown separation constant. This equation is nothing but \widehat{L}_z acting on the eigenvalue equation for \widehat{L}_z ,

$$\widehat{L}_z \Phi(\varphi) = \hbar m \Phi(\varphi) \quad (182)$$

The solutions are of the general form

$$\Phi(\varphi) = e^{im\varphi}, \quad (183)$$

and the *physical* assumption that the wave function be single-valued in φ , ie. that $\Phi(\varphi + 2n\pi) = \Phi(\varphi)$, yields the eigenvalues

$$m = 0, \pm 1, \pm 2, \pm 3 \dots \quad (184)$$

The θ equation is altogether more complicated,

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta(\theta)}{d\theta} \right) + \left[\ell(\ell + 1) - \frac{m^2}{\sin^2 \theta} \right] \Theta(\theta) = 0, \quad (185)$$

This is the **associated Legendre equation** whose *finite* solutions, known as the **associated Legendre functions**, are well-studied and are labelled by the values of the two constants ℓ and m :

$$\Theta(\theta) = P_\ell^{|m|}(\cos \theta). \quad (186)$$

The requirement that the solutions be finite imposes a relationship between ℓ and m ,

$$\begin{aligned} \ell &= 0, 1, 2, \dots & \text{and for each } \ell, m \text{ has } (2\ell + 1) \text{ allowed values,} \\ m &= -\ell, -\ell + 1, \dots, 0, \dots, \ell - 1, \ell. \end{aligned} \quad (187)$$

5.3.3 ORTHONORMALITY OF ANGULAR MOMENTUM EIGENSTATES:

We have now shown that the wave function depends on the energy and on the quantum numbers ℓ, m ; in fact if we look at the equations satisfied by $R(r)$ and $Y(\theta, \varphi)$ we see that the former depends only on E and ℓ , $R(r) = R_{E\ell}(r)$, while the latter does not involve E at all, but *does* depend on both ℓ and m , $Y(\theta, \varphi) = Y_{\ell m}(\theta, \varphi)$. Thus we should write the energy eigenstates as:

$$\Psi_E(\mathbf{r}) \equiv \Psi_{E\ell m}(\mathbf{r}) = R_{E\ell}(r) Y_{\ell m}(\theta, \varphi). \quad (188)$$

The angular momentum eigenfunctions, known as **spherical harmonics**,

$$Y_{\ell m}(\theta, \varphi) \equiv N_{\ell m} P_\ell^{|m|}(\cos \theta) e^{im\varphi}, \quad (189)$$

(the $N_{\ell m}$ are normalisation constants, see footnote¹¹) are orthonormal, as expected for eigenfunctions of Hermitian operators:

$$\int Y_{\ell' m'}^*(\theta, \varphi) Y_{\ell m}(\theta, \varphi) d\Omega = \delta_{\ell' \ell} \delta_{m' m} \quad (190)$$

where we use the solid angle notation as a convenient shorthand for the angular integration variable, $d\Omega \equiv \sin \theta d\theta d\varphi$, with the accompanying shorthand for the integration itself:

$$\int d\Omega \equiv \int_0^{2\pi} d\varphi \int_0^\pi \sin \theta d\theta \quad (191)$$

$$\int |Y_{\ell m}(\theta, \varphi)|^2 d\Omega = 1, \quad (192)$$

Hence, to normalise the wave function $\Psi_{E\ell m}(\mathbf{r})$ the radial wave function $R_{E\ell}(r)$ is normalised only when multiplied by r^2 :²¹

$$\int_0^\infty |R_{E\ell}(r)|^2 r^2 dr = 1. \quad (193)$$

5.3.2 GENERAL ANGULAR MOMENTUM OPERATORS $\hat{\mathbf{J}}$: QUANTISATION . USING ONLY ABSTRACT COMMUTATION RELATIONS.

The foregoing discussion showed that the eigenfunctions of orbital angular momentum, the spherical harmonics $Y_{\ell m}(\theta, \varphi)$, do not depend on the detailed form of the potential: the eigenvalue equations and the quantisation do not involve the potential. This suggests that all their properties are a consequence only of the fact that they are eigenstates of the angular momentum operators, whose properties are in turn entirely encapsulated in the commutation relations. This is the point of view we take here. The consequence will be the discovery that there is more to angular momentum in quantum mechanics than just orbital angular momentum: there is in addition spin angular momentum. Reserving the symbol $\hat{\mathbf{L}}$ for *orbital* angular momentum, we shall use the notation $\hat{\mathbf{J}}$ for angular momentum *in general*. We now *postulate* that *in general* these abstract angular momentum operators obey the same commutation relations as those of orbital angular momentum, and are defined through their commutation relations:

$$\hat{\mathbf{J}} \times \hat{\mathbf{J}} = i\hbar \hat{\mathbf{J}} \quad \left\{ \begin{array}{l} [\hat{J}_x, \hat{J}_y] = i\hbar \hat{J}_z, \\ [\hat{J}_z, \hat{J}_x] = i\hbar \hat{J}_y, \\ [\hat{J}_y, \hat{J}_z] = i\hbar \hat{J}_x. \end{array} \right. \quad (194)$$

From these equations we can deduce that $\hat{\mathbf{J}}^2$ commutes with all the components of $\hat{\mathbf{J}}$. The proof follows exactly the sequence eqs. (15) to (20) which used only the commutation relations and not the explicit representation of orbital angular momentum. Defining

$$\hat{\mathbf{J}}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2. \quad (195)$$

the angular momentum commutation relations can be used to show that

$$[\hat{\mathbf{J}}^2, \hat{J}_i] = 0, \quad \text{for all } i = 1, 2, 3 \quad (196)$$

Since $\hat{\mathbf{J}}^2$ and \hat{J}_z commute they have a common eigenfunction Ψ_{j, m_j} , with as yet unknown quantum numbers j and m_j respectively (see Figure 10):

$$\hat{\mathbf{J}}^2 \Psi_{j, m_j} = \hbar^2 j(j+1) \Psi_{j, m_j} \quad (197)$$

$$\hat{J}_z \Psi_{j, m_j} = \hbar m_j \Psi_{j, m_j} \quad (198)$$

The proof of quantisation utilises the raising and lowering operators,

$$\hat{J}_\pm \equiv \hat{J}_x \pm i\hat{J}_y \quad \text{with} \quad \hat{J}_\pm^\dagger = \hat{J}_\mp. \quad (199)$$

which are shown to have properties analogous to the raising and lowering operators of the SHO, \hat{a}^\dagger and \hat{a} : they move us up and down the ladder of eigenstates,

$$\hat{J}_\pm \Psi_{j, m_j} = c \Psi_{j, m_j \pm 1} \quad (200)$$

²¹This is important for the physical interpretation of plots of the radial wave function: one normally plots $|rR_{E\ell}(r)|^2$ because this represents the physical probability density at a distance r from the origin. Of course we must remember that this is then modulated by the direction-dependent angular wave function $|Y_{\ell m}(\theta, \varphi)|^2$ factor to give the full spatial dependence of the probability density. See Table 1 and Figures 8a,b.

where c is a constant, $c = \hbar\{j(j+1) - m(m \pm 1)\}^{1/2}$. It is then possible to show that there is a lowest eigenstate (as for the SHO) and also a highest eigenstate (unlike the SHO where the ladder of eigenstates goes on forever); see Figure 11. Because the raising and lowering operators change the quantum number m_j by one unit this immediately leads to the identification of $m_j^{max} = j$, $m_j^{min} = -j$. Thus if we start from the lowest eigenstate, $m_j = -j$ and repeatedly apply the raising operator we must eventually reach the highest state, $m_j = j$, and be able to go no further. If n is the the number of times the raising operator must be applied to reach the highest state, then we have

$$-j + n = m_j^{max} = j \quad \text{or,} \quad j = \frac{n}{2}, \quad n = 0, 1, 2, \dots \quad (201)$$

$$\text{ie.,} \quad \boxed{2j = \text{INTEGER}}$$

We therefore discover *two* possibilities: integral and half-integral angular momentum (in units of \hbar), whereas for *orbital* angular momentum only integral values were possible. We then have the quantisation rules for general angular momentum:

$$\text{Integral angular momentum: } j = 0, 1, 2, \dots \quad m_j = -j, -j+1 \dots 0 \dots, j-1, j \quad (202)$$

$$\text{Half-integral angular momentum: } j = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots \quad m_j = -j, -j+1 \dots, j-1, j \quad (203)$$

Note the absence of the $m_j = 0$ state for half-integral j . Thus, for an eigenstate of general angular momentum we have,

$$\hat{\mathbf{J}}^2 \psi_{j,m_j} = \hbar^2 j(j+1) \psi_{j,m_j} \quad (204)$$

$$\hat{J}_z \psi_{j,m_j} = \hbar m_j \psi_{j,m_j} \quad (205)$$

The angular momentum quantum numbers j and m_j labelling an eigenstate are often referred to as the angular momentum and its z -component, or azimuthal projection, although strictly the angular momentum is $\hbar j$ and $\hbar m_j$. Figure 12 illustrates the properties of the ladder of angular momentum eigenstates. A special case of integral angular momentum is obviously the already encountered orbital angular momentum $\hat{\mathbf{J}} = \hat{\mathbf{L}}$; we shall see later that spin angular momentum, $\hat{\mathbf{J}} = \hat{\mathbf{S}}$, which cannot be pictured classically as microscopic spinning top, can have both integral and half-integral values.

APPENDIX A: SPHERICAL POLAR COORDINATES.

The spherical polar coordinate system is depicted in Figures 2, 3 and the first diagram of Figure 4: the unit vectors \mathbf{e}_r , \mathbf{e}_θ and \mathbf{e}_φ corresponding to the three chosen orthogonal directions are always mutually perpendicular but vary in orientation with the vector \mathbf{r} . This is why care must be taken when working in non-cartesian coordinates. The most elementary way to see this is to just look at Figures 2, 3 (or the first diagram of Figure 4), noting that as the vector \mathbf{r} changes direction, so does the set of unit vectors attached rigidly to it. More formally, we can express these unit vectors in terms of the fixed ones, \mathbf{i} , \mathbf{j} , \mathbf{k} of the cartesian system:

$$\mathbf{e}_r = \mathbf{i} \sin \theta \cos \varphi + \mathbf{j} \sin \theta \sin \varphi + \mathbf{k} \cos \theta \quad (206)$$

$$\mathbf{e}_\varphi = -\mathbf{i} \sin \varphi + \mathbf{j} \cos \varphi. \quad (207)$$

$$\mathbf{e}_\theta = \mathbf{i} \cos \theta \cos \varphi + \mathbf{j} \cos \theta \sin \varphi - \mathbf{k} \sin \theta. \quad (208)$$

To prove this we need to find the projections of the unit vectors \mathbf{e}_r , \mathbf{e}_θ and \mathbf{e}_φ onto the x -, y -, and z -axes. This is not as difficult as it may seem. First refer to Figure 2 or 3 (the first diagram of Figure 4 may also help your 3-dimensional visualisation) and notice that the two unit vectors \mathbf{e}_r and \mathbf{e}_θ lie in the plane of the triangle OPQ ; but \mathbf{e}_φ is perpendicular to it, so also perpendicular to the line OQ and parallel to the $x-y$ plane, ie. \mathbf{e}_φ is perpendicular to the z -axis. The following proofs are illustrated graphically in Figure 4. (i) Take the unit vector \mathbf{e}_r : it lies along the direction of the vector \mathbf{r} , so that its projection in the z -direction is just $1 \times \cos \theta$; along the x - and y -axes we first project down onto the $x-y$ plane, giving a vector of length $1 \times \sin \theta$ pointing along OQ at an angle φ with the x -axis; then we see that *its* projections onto the x - and y -axes are simply $\sin \theta \cos \varphi$ and $\sin \theta \sin \varphi$ respectively. This can be summarised in the vector equation:

$$\mathbf{e}_r = \mathbf{i} \sin \theta \cos \varphi + \mathbf{j} \sin \theta \sin \varphi + \mathbf{k} \cos \theta. \quad (209)$$

Another way you may know this result is that the vector \mathbf{r} has cartesian components,

$$\mathbf{r} = (x, y, z) = (r \sin \theta \cos \varphi, r \sin \theta \sin \varphi, r \cos \theta), \quad (210)$$

and dividing by r gives the unit vector along the vector \mathbf{r} , which is \mathbf{e}_r .

$$\mathbf{e}_r \equiv \frac{\mathbf{r}}{r} = (\sin \theta \cos \varphi, \sin \theta \sin \varphi, \cos \theta), \quad (211)$$

(ii) \mathbf{e}_φ is rather special because it is perpendicular to the z -axis and it also lies parallel to the $x-y$ plane; therefore, when projected down onto that plane it still has unit length and lies perpendicular to the line OQ which is at an angle φ with the x -axis. Projection onto the x - and y -axes now gives $-\sin \varphi$ and $\cos \varphi$ respectively,

$$\mathbf{e}_\varphi = -\mathbf{i} \sin \varphi + \mathbf{j} \cos \varphi. \quad (212)$$

(iii) The most difficult one is \mathbf{e}_θ . Since it is perpendicular to \mathbf{r} its projection on the z -axis is just $-\sin \theta$ and it's projection down onto the $x-y$ plane is $\cos \theta$. The latter projection points along OQ since the original vector \mathbf{e}_θ is in the plane of the triangle OPQ . Hence the projection onto the x - and y -axes are $\cos \theta \cos \varphi$ and $\cos \theta \sin \varphi$ respectively,

$$\mathbf{e}_\theta = \mathbf{i} \cos \theta \cos \varphi + \mathbf{j} \cos \theta \sin \varphi - \mathbf{k} \sin \theta. \quad (213)$$

²²The notation \times denotes simple multiplication in this section and in Figure 13. It has nothing to do with the vector cross product; its only purpose is to emphasize that we are projecting *unit* vectors of length 1.

These equations allow us to discover how the unit vectors change with the angles by differentiating them, remembering that the *cartesian* unit vectors $\mathbf{i}, \mathbf{j}, \mathbf{k}$ are constant:

$$\begin{aligned}\frac{\partial}{\partial\theta}\mathbf{e}_\theta &= -\mathbf{i}\sin\theta\cos\varphi - \mathbf{j}\sin\theta\sin\varphi - \mathbf{k}\cos\theta \\ &= -\mathbf{e}_r\end{aligned}\quad (214)$$

$$\begin{aligned}\frac{\partial}{\partial\varphi}\mathbf{e}_\theta &= -\mathbf{i}\cos\theta\sin\varphi + \mathbf{j}\cos\theta\cos\varphi \\ &= \mathbf{e}_\varphi\cos\theta\end{aligned}\quad (215)$$

$$\frac{\partial}{\partial\theta}\mathbf{e}_\varphi = 0\quad (216)$$

$$\begin{aligned}\frac{\partial}{\partial\varphi}\mathbf{e}_\varphi &= -\mathbf{i}\cos\varphi - \mathbf{j}\sin\varphi \\ &= -\mathbf{e}_\theta\cos\theta - \mathbf{e}_r\sin\theta\end{aligned}\quad (217)$$

$$\begin{aligned}\frac{\partial}{\partial\theta}\mathbf{e}_r &= \mathbf{i}\cos\theta\cos\varphi + \mathbf{j}\cos\theta\sin\varphi - \mathbf{k}\sin\theta \\ &= \mathbf{e}_\theta\end{aligned}\quad (218)$$

$$\begin{aligned}\frac{\partial}{\partial\varphi}\mathbf{e}_r &= -\mathbf{i}\sin\theta\sin\varphi + \mathbf{j}\sin\theta\cos\varphi \\ &= \mathbf{e}_\varphi\sin\theta.\end{aligned}\quad (219)$$

Incidentally, since the unit vectors do not depend on the length r of the vector \mathbf{r} , $\partial\mathbf{e}_i/\partial r = 0$: increasing the length r does not change any unit vector's direction.

We can also get these geometrically by the sequences illustrated in Figure 13. The simplest is the variation of \mathbf{e}_r with θ . As shown in Figure 13a, we ask how \mathbf{e}_r changes when θ is increased by $d\theta$: (i) increasing θ by $d\theta$ rotates \mathbf{e}_r by $d\theta$ to the new unit vector \mathbf{e}'_r . The change, $d\mathbf{e}_r = \mathbf{e}'_r - \mathbf{e}_r$, as given by the triangle of unit vectors illustrated, is in the direction of $+\mathbf{e}_\theta$ by an amount $d\mathbf{e}_r = (\text{the length of } \mathbf{e}_r) \times d\theta = 1 \times d\theta$; remember that both \mathbf{e}_r and \mathbf{e}'_r are unit vectors, it's only the *direction* which has changed. (iii) a similar argument holds for an increase $d\varphi$, but now the change requires projection from the $x-y$ plane up to the \mathbf{e}_r direction, giving an extra factor of $\sin\theta$, Figure 13b.

APPENDIX B: AN EXPRESSION FOR THE HAMILTONIAN .

In the text we saw that the kinetic energy term in the *classical* Hamiltonian is:

$$(KE)_{cl} = \frac{\mathbf{p}^2}{2m} = \frac{(\mathbf{p}_r + \mathbf{p}_\perp)^2}{2m} = \frac{\mathbf{p}_r^2}{2m} + \frac{\mathbf{L}_{cl}^2}{2mr^2}\quad (220)$$

We now seek the quantum mechanical version of this, \widehat{KE} , which we will find to have an additional term $2(\mathbf{r}\cdot\widehat{\mathbf{p}})/r^2$ due to the fact that \mathbf{p}_r and \mathbf{p}_\perp do not commute. The most elegant method I know of finding the appropriate form for the quantum mechanical $\widehat{\mathbf{p}}^2$ is motivated by looking at the classical KE and noticing that it involves a term \mathbf{L}_{cl}^2 . This suggests that we may be able to get somewhere by evaluating the quantum mechanical $\widehat{\mathbf{L}}^2$ and trying to turn it into something containing $\widehat{\mathbf{p}}^2$. Since

$$\widehat{\mathbf{L}}^2 = \widehat{L}_x^2 + \widehat{L}_y^2 + \widehat{L}_z^2,\quad (221)$$

let us work out each term in the sum using the commutation relations:

$$[x_i, \widehat{p}_j] = i\hbar\delta_{ij}, \quad [x_i, x_j] = 0, \quad \text{and} \quad [\widehat{p}_i, \widehat{p}_j] = 0\quad (222)$$

My plan is to get all the x, y, z factors to the left and all the momentum operators to the right:

$$\begin{aligned}\widehat{L}_x^2 &= (y\widehat{p}_z - z\widehat{p}_y)(y\widehat{p}_z - z\widehat{p}_y) \\ &= (y\widehat{p}_z)(y\widehat{p}_z) - (y\widehat{p}_z)(z\widehat{p}_y) - (z\widehat{p}_y)(y\widehat{p}_z) + (z\widehat{p}_y)(z\widehat{p}_y)\end{aligned}$$

In the first and last terms all factors commute and so can be placed in any order; in the second and third terms there are two factors which don't commute, but which can be interchanged by using the known commutation relations. For the second term they are $\widehat{p}_z z = z\widehat{p}_z - i\hbar$; for the last, $\widehat{p}_y y = y\widehat{p}_y - i\hbar$. The terms can therefore be written with all momentum operators to the right and then rearranged into a suggestive form:

$$\begin{aligned}\widehat{L}_x^2 &= y^2\widehat{p}_z^2 - y(z\widehat{p}_z - i\hbar)\widehat{p}_y - z(y\widehat{p}_y - i\hbar)\widehat{p}_z + z^2\widehat{p}_y^2 \\ &= y^2\widehat{p}_z^2 + z^2\widehat{p}_y^2 - 2yz\widehat{p}_z\widehat{p}_y + i\hbar(y\widehat{p}_y + z\widehat{p}_z)\end{aligned}\quad (223)$$

Notice how I have rearranged the commuting factors at my convenience. Now the rest of the calculation is simple because \widehat{L}_y^2 and \widehat{L}_z^2 have the same structure as \widehat{L}_x^2 with an appropriate permutation of the labels x, y, z . Thus to get \widehat{L}_y^2 we make the following replacements in our equation for \widehat{L}_x^2 : $y \rightarrow z, z \rightarrow x$, giving

$$\begin{aligned}\widehat{L}_y^2 &= (z\widehat{p}_x - x\widehat{p}_z)(z\widehat{p}_x - x\widehat{p}_z) \\ &= z^2\widehat{p}_x^2 + x^2\widehat{p}_z^2 - 2zx\widehat{p}_x\widehat{p}_z + i\hbar(z\widehat{p}_z + x\widehat{p}_x)\end{aligned}\quad (224)$$

and to get \widehat{L}_z^2 we make the following replacements in our equation for \widehat{L}_x^2 : $y \rightarrow x, z \rightarrow y$, giving

$$\begin{aligned}\widehat{L}_z^2 &= (z\widehat{p}_y - y\widehat{p}_x)(z\widehat{p}_y - y\widehat{p}_x) \\ &= x^2\widehat{p}_y^2 + y^2\widehat{p}_x^2 - 2xy\widehat{p}_y\widehat{p}_x + i\hbar(x\widehat{p}_x + y\widehat{p}_y)\end{aligned}\quad (225)$$

By adding these expressions and collecting terms together we find

$$\begin{aligned}\widehat{\mathbf{L}}^2 &= (y^2 + z^2)\widehat{p}_x^2 + (x^2 + z^2)\widehat{p}_y^2 + (x^2 + y^2)\widehat{p}_z^2 \\ &\quad - 2(xy\widehat{p}_x\widehat{p}_y + xz\widehat{p}_x\widehat{p}_z + yz\widehat{p}_y\widehat{p}_z) \\ &\quad + 2i\hbar(x\widehat{p}_x + y\widehat{p}_y + y\widehat{p}_y) \\ &= (x^2 + y^2 + z^2)(\widehat{p}_x^2 + \widehat{p}_y^2 + \widehat{p}_z^2) \\ &\quad - (x^2\widehat{p}_x^2 + y^2\widehat{p}_y^2 + z^2\widehat{p}_z^2) \\ &\quad - 2(xy\widehat{p}_x\widehat{p}_y + xz\widehat{p}_x\widehat{p}_z + yz\widehat{p}_y\widehat{p}_z) \\ &\quad + 2i\hbar(x\widehat{p}_x + y\widehat{p}_y + y\widehat{p}_y) \\ &= r^2\widehat{\mathbf{p}}^2 \\ &\quad - (x^2\widehat{p}_x^2 + y^2\widehat{p}_y^2 + z^2\widehat{p}_z^2) \\ &\quad - 2(xy\widehat{p}_x\widehat{p}_y + xz\widehat{p}_x\widehat{p}_z + yz\widehat{p}_y\widehat{p}_z) \\ &\quad + 2i\hbar(\mathbf{r}\cdot\widehat{\mathbf{p}})\end{aligned}\quad (226)$$

where we have added and subtracted terms in the first line to make an $r^2 = x^2 + y^2 + z^2$ factor. Notice also that the cross terms xy , etc contain all possible pairs. The fact that the second term contains *some* of the terms that would occur in $(\mathbf{r}\cdot\widehat{\mathbf{p}})^2$ suggests we look at this operator and see what it is; the calculation is rather similar to what we have already done:

$$\begin{aligned}(\mathbf{r}\cdot\widehat{\mathbf{p}})^2 &= (x\widehat{p}_x + y\widehat{p}_y + z\widehat{p}_z)(x\widehat{p}_x + y\widehat{p}_y + z\widehat{p}_z) \\ &= x\widehat{p}_x x\widehat{p}_x + y\widehat{p}_y y\widehat{p}_y + z\widehat{p}_z z\widehat{p}_z\end{aligned}$$

$$\begin{aligned}
& +2(xy\hat{p}_x\hat{p}_y + xz\hat{p}_x\hat{p}_z + yz\hat{p}_y\hat{p}_z) \\
= & x(x\hat{p}_x - i\hbar)\hat{p}_x + y(y\hat{p}_y - i\hbar)\hat{p}_y + z(z\hat{p}_z - i\hbar)\hat{p}_z \\
& +2(xy\hat{p}_x\hat{p}_y + xz\hat{p}_x\hat{p}_z + yz\hat{p}_y\hat{p}_z) \\
= & (x^2\hat{p}_x^2 + y^2\hat{p}_y^2 + z^2\hat{p}_z^2) \\
& +2(xy\hat{p}_x\hat{p}_y + xz\hat{p}_x\hat{p}_z + yz\hat{p}_y\hat{p}_z) \\
& -i\hbar(\mathbf{r}\cdot\hat{\mathbf{p}}) \\
& +2(xy\hat{p}_x\hat{p}_y + xz\hat{p}_x\hat{p}_z + yz\hat{p}_y\hat{p}_z) \\
& -i\hbar(\mathbf{r}\cdot\hat{\mathbf{p}})
\end{aligned} \tag{227}$$

In the first three terms we have reordered non-commuting factors using the commutation relations as before, while the factors in the cross terms xy etc could be reordered because they all commute. This is very nearly the negative of the terms we found in our expression for $\hat{\mathbf{L}}^2$, except that the $-i\hbar$ term lacks a factor of 2; the result is therefore:

$$\hat{\mathbf{L}}^2 = r^2\hat{\mathbf{p}}^2 - (\mathbf{r}\cdot\hat{\mathbf{p}})^2 + i\hbar(\mathbf{r}\cdot\hat{\mathbf{p}}) \tag{228}$$

which can be solved for $\hat{\mathbf{p}}^2$ to give the quantum kinetic energy operator:

$$\widehat{KE} = \frac{\hat{\mathbf{p}}^2}{2m} = \frac{(\mathbf{r}\cdot\hat{\mathbf{p}})^2}{2mr^2} - i\hbar\frac{(\mathbf{r}\cdot\hat{\mathbf{p}})}{2mr^2} + \frac{\hat{\mathbf{L}}^2}{2mr^2} \tag{229}$$

$$= \frac{\hat{p}_r^2}{2m} - i\hbar\frac{\hat{p}_r}{mr} + \frac{\hat{\mathbf{L}}^2}{2mr^2} \tag{230}$$

The last step above is trickier than might appear: we have used the fact that $\mathbf{r}\hat{\mathbf{p}} = r\hat{p}_r$, but we also had to be very careful of the non-commuting factors in the first term:²³

$$\begin{aligned}
(\mathbf{r}\cdot\hat{\mathbf{p}})^2 &= (\mathbf{r}\cdot\hat{\mathbf{p}})(\mathbf{r}\cdot\hat{\mathbf{p}}) \\
&= (r\hat{p}_r)(r\hat{p}_r) = r(\hat{p}_r r)\hat{p}_r \\
&= r(r\hat{p}_r - i\hbar)\hat{p}_r \quad \text{using } [r, p_r] = -i\hbar[r, \frac{\partial}{\partial r}] = i\hbar \\
&= r^2\hat{p}_r^2 - i\hbar(\mathbf{r}\cdot\hat{\mathbf{p}})
\end{aligned} \tag{231}$$

The additional term coming from the non-classical non-commuting operators is the one with an explicit factor of $-i\hbar$, a clear indication of its quantum origins. You can now see why we didn't spot it at the classical level: the classical limit corresponds to replacing quantum operators by classical variables and taking the limit $\hbar \rightarrow 0$, which gives the correct expression for the classical kinetic energy; but going

²³In $(\mathbf{r}\cdot\hat{\mathbf{p}})^2$ there is an r to the *right* of the momentum operator:

$$(\mathbf{r}\cdot\hat{\mathbf{p}})^2 = (r\hat{p}_r)^2 = r\hat{p}_r(r\hat{p}_r) \neq r^2\hat{p}_r^2$$

and \hat{p}_r does not commute with r . This is quite different from the term $r^2\hat{\mathbf{p}}^2$ occurring in eq. (228) where r^2 is to the *left* of the momentum operators. Notice also that $\hat{\mathbf{p}}^2$ and \hat{p}_r^2 are very different as we see by comparing eqs. (229) and (230). If you are unconvinced, just compare

$$\hat{p}_r^2 \psi = (-i\hbar)^2 \frac{\partial^2 \psi}{\partial r^2}$$

with the horribly complicated

$$\hat{\mathbf{p}}^2 \psi = (-i\hbar)^2 \left\{ \frac{\partial^2 \psi}{\partial r^2} + \mathbf{e}_\theta \cdot \frac{\partial}{\partial \theta} \left(\mathbf{e}_\theta \frac{\partial \psi}{\partial \theta} \right) + \mathbf{e}_\phi \cdot \frac{\partial}{\partial \phi} \left(\mathbf{e}_\phi \frac{\partial \psi}{\partial \phi} \right) \right\},$$

where the angular derivatives also act on the unit vectors to their right giving nontrivial additional terms. Here we have found a way to avoid getting entangled in such calculations; but we cannot do so in Appendix C, where you can see some of the hard calculations which would be required.

the other way, from the classical to the quantum expression we have to take great care: it's not a simple matter of merely replacing variables by operators, as we saw in the subtle manipulations in this appendix.

Finally, in spherical polar coordinates we can use the representation $\hat{p} = -i\hbar\partial/\partial r$ to obtain

$$\widehat{KE} = \frac{\widehat{\mathbf{p}}^2}{2m} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{\widehat{\mathbf{L}}^2}{2mr^2} \quad (232)$$

$$= -\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{\widehat{\mathbf{L}}^2}{2mr^2} \quad (233)$$

APPENDIX C: AN EXPRESSION FOR $\widehat{\mathbf{L}}^2$ IN SPHERICAL POLARS.

We begin with the angular momentum operator in spherical polar coordinates,

$$\widehat{\mathbf{L}} = -i\hbar \left(\mathbf{e}_\varphi \frac{\partial}{\partial \theta} - \mathbf{e}_\theta \frac{1}{\sin \theta} \frac{\partial}{\partial \varphi} \right) \quad (234)$$

In squaring this we must remember that the unit vectors \mathbf{e}_θ and \mathbf{e}_φ are not constants, and that the operator should always be thought of as operating on some function $\psi(r, \theta, \varphi)$. Thus,

$$\begin{aligned} & \frac{1}{(-i\hbar)^2} \widehat{\mathbf{L}}^2 \\ &= \left(\mathbf{e}_\varphi \frac{\partial}{\partial \theta} - \mathbf{e}_\theta \frac{1}{\sin \theta} \frac{\partial}{\partial \varphi} \right) \cdot \left(\mathbf{e}_\varphi \frac{\partial \psi}{\partial \theta} - \mathbf{e}_\theta \frac{1}{\sin \theta} \frac{\partial \psi}{\partial \varphi} \right) \\ &= \mathbf{e}_\varphi \cdot \frac{\partial}{\partial \theta} \left(\mathbf{e}_\varphi \frac{\partial \psi}{\partial \theta} \right) - \mathbf{e}_\varphi \cdot \frac{\partial}{\partial \theta} \left(\mathbf{e}_\theta \frac{1}{\sin \theta} \frac{\partial \psi}{\partial \varphi} \right) \\ &\quad - \mathbf{e}_\theta \cdot \frac{1}{\sin \theta} \frac{\partial}{\partial \varphi} \left(\mathbf{e}_\varphi \frac{\partial \psi}{\partial \theta} \right) + \mathbf{e}_\theta \cdot \frac{1}{\sin \theta} \frac{\partial}{\partial \varphi} \left(\mathbf{e}_\theta \frac{1}{\sin \theta} \frac{\partial \psi}{\partial \varphi} \right) \\ &= (\mathbf{e}_\varphi \cdot \mathbf{e}_\varphi) \frac{\partial^2 \psi}{\partial \theta^2} + \left(\mathbf{e}_\varphi \cdot \frac{\partial \mathbf{e}_\varphi}{\partial \theta} \right) \frac{\partial \psi}{\partial \theta} - (\mathbf{e}_\varphi \cdot \mathbf{e}_\theta) \frac{\partial}{\partial \theta} \left(\frac{1}{\sin \theta} \frac{\partial \psi}{\partial \varphi} \right) - \left(\mathbf{e}_\varphi \cdot \frac{\partial \mathbf{e}_\theta}{\partial \theta} \right) \frac{1}{\sin \theta} \frac{\partial \psi}{\partial \varphi} \\ &\quad - (\mathbf{e}_\theta \cdot \mathbf{e}_\varphi) \frac{1}{\sin \theta} \frac{\partial^2 \psi}{\partial \varphi \partial \theta} - \left(\mathbf{e}_\theta \cdot \frac{\partial \mathbf{e}_\varphi}{\partial \varphi} \right) \frac{1}{\sin \theta} \frac{\partial \psi}{\partial \theta} + (\mathbf{e}_\theta \cdot \mathbf{e}_\theta) \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \varphi^2} + \left(\mathbf{e}_\theta \cdot \frac{\partial \mathbf{e}_\theta}{\partial \varphi} \right) \frac{1}{\sin^2 \theta} \frac{\partial \psi}{\partial \varphi} \\ &= \frac{\partial^2 \psi}{\partial \theta^2} + \frac{\cos \theta}{\sin \theta} \frac{\partial \psi}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \varphi^2} \end{aligned} \quad (235)$$

where we have used the results obtained in Appendix A together with orthogonality of the unit vectors to evaluate the dot products. We can combine the θ derivatives into one term to obtain the standard form:

$$\widehat{\mathbf{L}}^2 = -\hbar^2 \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right\}. \quad (236)$$

A final comment: by combining the results in Appendix B and C we see that we have computed the del-squared operator in polar coordinates. Using our expression for $\widehat{\mathbf{p}}^2$ from Appendix B and the expression above for $\widehat{\mathbf{L}}^2$, we have:

$$\begin{aligned} (-i\hbar)^2 \nabla^2 &= \widehat{\mathbf{p}}^2 \\ &= \frac{\widehat{p}_r^2}{r^2} - 2i\hbar \frac{\widehat{p}_r}{r} + \frac{\widehat{\mathbf{L}}^2}{r^2} \\ &= -\hbar^2 \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{\widehat{\mathbf{L}}^2}{r^2} \\ &= -\hbar^2 \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \right) \\ \text{ie. } \nabla^2 &= \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} \end{aligned} \quad (237)$$

which is the usual expression quoted in mathematics books. That the angle-dependent terms are simply related to the square of the orbital angular momentum operator cannot of course be deduced from these texts.

Figure 6. The vector model of angular momentum, depicting the quasi-classical orbital angular momentum vector as having length $\hbar\sqrt{\ell(\ell+1)}$ for an eigenstate of angular momentum, and its $2\ell+1$ allowed projections on the z -axis. The vector's length is the square root of the eigenvalue of $\hat{\mathbf{J}}^2$ and the projections are the (quantised) eigenvalues, $\hbar m$, of \hat{J}_z with $m = -\ell, \ell+1, \dots, \ell$. These are the only possible outcomes of a measurement of these variables for an *eigenstate*. In other words, for an eigenstate $\psi_{E\ell m}(\mathbf{r}) = R_{E\ell}(r)Y_{\ell m}(\theta, \varphi)$, an ensemble measurement would yield the expectation values $\sqrt{\langle \hat{\mathbf{J}}^2 \rangle} = \sqrt{\hbar^2 \ell(\ell+1)}$, and $\langle \hat{J}_z \rangle = \hbar m$ with zero uncertainty, $\Delta \mathbf{J}^2 = 0$ and $\Delta J_z = 0$. The diagrams show various ways of illustrating the quantum mechanics of orbital angular momentum, emphasising the fact that the x - and y -components are not determined.

Figure 8a. Polar plots of the the first few spherical harmonics. Here we show projections of the probability distributions

$$|Y_{\ell m}(\theta, \varphi)|^2 = (2\pi)^{-1} |\Theta_{\ell m}(\varphi)|^2 = N_{\ell m}^2 |P_\ell^{|m|}(\cos \theta)|^2$$

onto the $z-y$ plane for $\ell = 0, 1, 2, 3$. The distance from the origin of points on the curve represents this probability as indicated in the $\ell = 0$ plot. Since the probability density is independent of the azimuthal angle φ , the *actual* distribution is obtained by rotating the plots about the z -axis. Figure 8b shows the resulting 3-dimensional shapes (actually, their square root, $|Y_{\ell m}|$) for $\ell = 0, 1, 2$ obtained by rotating the plots of Figure 8a about the z -axis.

Figure 8b. The square root of the probability distributions, $|Y_{\ell m}(\theta, \varphi)|$ for $\ell = 0, 1, 2$. The distance from the origin of a point on the 3-dimensional surface represents $|Y_{\ell m}(\theta, \varphi)|$, where (θ, φ) represents the direction of the vector drawn from the origin to that point.

Figure 8.

Figure 8.

Figure 8.

Figure 8.

(238)

(239)

(240)