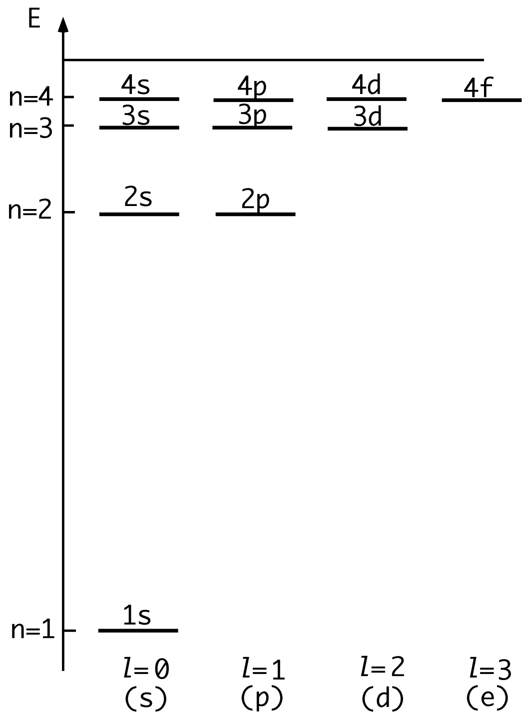
9 Angular Momentum I

So far we haven't examined QM's biggest success–atomic structure and the explanation of atomic spectra–in detail. To do this need better understanding of angular momentum. In brief: we'll find that eigenfunctions of atomic problem have structure

$$\psi(\mathbf{r}) = u_n(r) Y_{lm}(\theta, \phi) \tag{1}$$

where $u_n(r)$ is soln. to *radial* S.-eqn. we examined in Week 4, and $Y_{lm}(\theta, \phi)$ is eigenfunction of angular momentum operator $\mathbf{L}$. Degeneracy of atomic states *within a given shell* corresponding to *principal quantum number* n explained by angular momentum quantum numbers l, m.



9.1 Orbital Angular Momentum

Classical analogy, take

$$\mathbf{L} = \mathbf{r} \times \hat{\mathbf{p}} \tag{2}$$

In other words

$$\begin{aligned}
\hat{L}_x &= y\hat{p}_z - z\hat{p}_y \\
\hat{L}_y &= z\hat{p}_x - x\hat{p}_z \qquad (3)\\
\hat{L}_z &= x\hat{p}_y - y\hat{p}_x \qquad (4)
\end{aligned}$$

Note that since $[y, \hat{p}_x] = 0$, etc., antisymmetry property $\mathbf{r} \times \hat{\mathbf{p}} = -\hat{\mathbf{p}} \times \mathbf{r}$ is ok, meaning there is no ambiguity in taking the classical expression and replacing r and p by their operator forms everywhere.

Before solving H-atom, we need to derive formal properties of $\mathbf{L}$. First summarize these, then prove a few of the interesting ones. Need definition of antisymmetric "permutation symbol"

$$\epsilon_{ijk} = \begin{cases} 1 & \text{if } ijk \text{ are in "cyclic" order, e.g. } 123,\ 312\text{,etc.} \\ -1 & \text{if } ijk \text{ are in "anticyclic" order, e.g. } 321,\ 132\text{, etc.} \\ 0 & \text{if any two indices are equal} \end{cases} \tag{5}$$

So the components of $\mathbf{L}$ in this notation are

$$\hat{L}_i = \epsilon_{ijk} x_j \hat{p}_k \tag{6}$$

with implied summation convention (if I write a two repeated indices below, it means sum over them, even if I leave out the Σ).

<u>Summary of useful relations involving **L**</u>

1. $\hat{L}_i^\dagger = \hat{L}_i$ All components of $\mathbf{L}$ Hermitian.
2. $[\hat{L}_i, \hat{L}_j] = i\hbar\epsilon_{ijk}\hat{L}_k$ e.g. $[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z$
3. $[\hat{L}_i, x_j] = i\hbar\epsilon_{ijk}x_k$ e.g. $[\hat{L}_y, x] = -i\hbar z$
4. $[\hat{L}_i, \hat{p}_j] = i\hbar\epsilon_{ijk}\hat{p}_k$ e.g. $[\hat{L}_y, \hat{p}_x] = -i\hbar\hat{p}_z$
5. $[\hat{L}_i, \hat{p}^2] = 0$

6. $[\hat{L}_i, V(\mathbf{r})] = 0$

7. $[\hat{L}^2, \hat{L}_i] = 0$ where $\hat{L}^2 \equiv \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$

$\star$ Major point will be that due to 5),6),7), the eigenfctns of central force problems can be chosen as simultaneous eigenfunctions of $H = -\frac{\hbar^2}{2m}\nabla^2 + V(r)$ *and* $\hat{L}^2$ *and* any component of $\mathbf{L}$, e.g. $\hat{L}_z$.

Pf. of $\hat{L}_i^\dagger = \hat{L}_i$: e.g.,

$$\begin{aligned} \hat{L}_x^\dagger &= (y\hat{p}_z - z\hat{p}_y)^\dagger \\ &= \hat{p}_z y - \hat{p}_y z \\ &= y\hat{p}_z - z\hat{p}_y = \hat{L}_x \end{aligned} \tag{7}$$

Pf. of $[\hat{L}_i, \hat{L}_j] = i\hbar\epsilon_{ijk}\hat{L}_k$, e.g.

$$\begin{aligned} [\hat{L}_z, \hat{L}_y] &= [(x\hat{p}_y - y\hat{p}_x), (z\hat{p}_x - x\hat{p}_z)] \\ &= [x\hat{p}_y, z\hat{p}_x] - [x\hat{p}_y, x\hat{p}_z] \\ &\quad -[y\hat{p}_x, z\hat{p}_x] + [y\hat{p}_x, x\hat{p}_z] \\ &= \hat{p}_y z[x, \hat{p}_x] - 0 - 0 + y\hat{p}_z[\hat{p}_x, x] \\ &= i\hbar(\hat{p}_y z - y\hat{p}_z) = -i\hbar\hat{L}_x \end{aligned} \tag{8}$$

Does it work? Check sign $\epsilon_{321} = -1$ OK!

Pf. of $[\hat{L}_i, \hat{p}^2] = 0$: First need general relation

$$\begin{aligned} [A, BC] &= ABC - BCA \\ &= ABC - BAC + BAC - BCA \\ &= [A, B]C + B[A, C] \end{aligned} \tag{9}$$

Now evaluate using 4):

$$[L_i, \hat{p}^2] = \sum_j [L_i, \hat{p}_j^2]$$

$$
\begin{aligned}
&= \sum_j \Big([\hat{L}_i, \hat{p}_j]\hat{p}_j - \hat{p}_j[\hat{L}_i, \hat{p}_j] \Big) \\
&= -i\hbar\epsilon_{ijk}\hat{p}_k\hat{p}_j + i\hbar\epsilon_{ijk}\hat{p}_j\hat{p}_k = 0
\end{aligned} \tag{10}
$$

Pf. of $[\hat{L}^2, \hat{L}_i] = 0$. Use (9):

$$
\begin{aligned}
[\hat{L}^2, \hat{L}_i] &= -[\hat{L}_i, \hat{L}^2] = -[\hat{L}_i, \hat{L}_x^2] - [\hat{L}_i, \hat{L}_y^2] - [\hat{L}_i, \hat{L}_z^2] \\
&= -([\hat{L}_i, \hat{L}_x]\hat{L}_x + \hat{L}_x[\hat{L}_i, \hat{L}_x]) + (x \to y) + (x \to z) \\
&= -i\hbar\epsilon_{i1k}(\hat{L}_k\hat{L}_x + \hat{L}_x\hat{L}_k) + \ldots = 0
\end{aligned} \tag{11}
$$

since ϵ_{ijk} is antisymmetric.

9.2 Eigenfunctions of $\hat{L}_z$

For a central force problem, $V(\mathbf{r}) = V(r)$, $\hat{L}^2$, $\hat{L}_z$, and Π all commute with H, so we can find a complete set of eigenfctns. of all 4 ops. First construct eigenfctns of $\hat{L}_z$ in polar coordinates,

$$
\begin{aligned}
x &= r\sin\theta\cos\phi \\
y &= r\sin\theta\sin\phi \\
z &= \cos\theta.
\end{aligned}
$$

Notice that

$$
\begin{aligned}
\left.\frac{\partial\psi}{\partial\phi}\right|_{r,\theta} &= \frac{\partial\psi}{\partial x}\frac{\partial x}{\partial\phi} + \frac{\partial\psi}{\partial y}\frac{\partial y}{\partial\phi} + \frac{\partial\psi}{\partial z}\frac{\partial z}{\partial\phi} \\
&= \frac{\partial\psi}{\partial x}(-)r\sin\theta\sin\phi + \frac{\partial\psi}{\partial y}r\sin\theta\sin\phi \\
&= x\frac{\partial\psi}{\partial y} - y\frac{\partial\psi}{\partial x}
\end{aligned} \tag{12}
$$

Mutiply by $i\hbar$ to find $-i\hbar\frac{\partial\psi}{\partial\phi} = (x\hat{p}_y - y\hat{p}_x)\psi$, or

$$\boxed{L_z = -i\hbar\frac{\partial}{\partial\phi}} \quad (13)$$

Eigenfctns of $\hat{L}_z$, i.e. soln. to $\hat{L}_z\psi = \alpha\psi$ is

$$\psi \propto e^{i\alpha\phi/\hbar} \quad (14)$$

Require ψ be *single-valued* fctn. of position, i.e. when $\phi \to \phi + 2\pi$, better get same value back again. Thus we find new quantum number $\alpha = m\hbar$, or

$$\psi \propto e^{im\phi}, \quad m = 0, \pm 1, \pm 2 \ldots \quad (15)$$

Eigenvalues of $\hat{L}_z$ therefore $m\hbar$.

9.3 L as generator of rotations

Q: How does wave fctn. $\psi(\mathbf{r})$ change when we rotate coordinate system to new coordinates $\mathbf{r}'$? Define rotation to be around axis $\hat{\mathbf{n}}$, through angle θ.

A:

$$\psi' = e^{-i\theta\hat{\mathbf{n}}\cdot\mathbf{L}/\hbar}\psi \quad (16)$$

where $U = e^{-i\theta\hat{\mathbf{n}}\cdot\mathbf{L}/\hbar}$ is an operator to be understood in terms of its Taylor expansion, $U = 1 - i\theta\hat{\mathbf{n}}\cdot\mathbf{L}/\hbar + \frac{1}{2}(i\theta\hat{\mathbf{n}}\cdot\mathbf{L}/\hbar)^2 + \cdots$. Note $\theta\hat{\mathbf{n}}\cdot\mathbf{L}$ is a Hermitian operator, so U is *unitary*, $U^\dagger U = 1$. The operator $\mathbf{L}$ is referred to as the generator of intfinesimal rotations, see below.

Check in special case: rotate around $\hat{z}$, 1st by infinitesimal angle $\delta\phi$:

$$\begin{aligned} \psi'(r,\theta,\phi) &= \psi(r,\theta,\phi-\delta\phi) \\ &\simeq \psi(r,\theta,\phi) - \delta\phi\frac{\partial}{\partial\phi}\psi(r,\theta,\phi) \end{aligned} \quad (17)$$

Now use representation of $\hat{L}_z$ we just worked out:

$$\psi' = (1 - \delta\phi\frac{\partial}{\partial\phi})\psi \quad (18)$$

$$= (1 - i\delta\phi\hat{L}_z/\hbar)\psi \quad (19)$$

Now rotate by finite angle ϕ_0: apply above tranformation $n \gg 1$ times for small ϕ_0/n:

$$\psi' = (1 - \frac{i\phi_0\hat{L}_z}{n\hbar})^n\psi \quad (20)$$

Recall

$$\lim_{n\to\infty}(1 + x/n)^n = e^x \quad (21)$$

$$\Longrightarrow \psi' = e^{-i\phi_0\hat{L}_z/\hbar} \quad (22)$$

Generalize to infinitesimal rotation $\delta\phi$ around $\hat{n}$ to get Eq. (16)

9.4 Eigenvalues of $\hat{L}^2$

Program is to find complete set of eigenfunctions of both $\hat{L}_z$ and $\hat{L}^2$. (Could pick any component of $\mathbf{L}$, $\hat{L}_z$ is conventional):

$$\hat{L}^2\psi = a\psi \quad (23)$$

$$\hat{L}_z\psi = b\psi. \quad (24)$$

First note

$$(\psi, \hat{L}^2\psi) = (\psi, \hat{L}_x^2\psi) + (\psi, \hat{L}_y^2\psi) + (\psi, \hat{L}_z^2\psi) \quad (25)$$

$$\geq 0 \quad (26)$$

since each term $(\psi, \hat{L}_i^2\psi) = (\hat{L}_i\psi, \hat{L}_i\psi) = \int dx|\hat{L}_i\psi|^2$. Now can figure out something about a and b:

$$\begin{array}{ccccccc} (\psi, L^2\psi) & = & (\psi, L_x^2\psi) & + & (\psi, L_y^2\psi) & + & (\psi, L_z^2\psi) \\ \downarrow & & \downarrow & & \downarrow & & \downarrow \\ a(\psi,\psi) & & \geq 0 & & \geq 0 & & b^2(\psi,\psi) \end{array} \quad (27)$$

So we see $a \geq b^2$.

Ladder operators for angular momentum

Define

$$\hat{L}_+ = \hat{L}_x + i\hat{L}_y \quad (28)$$
$$\hat{L}_- = \hat{L}_x - i\hat{L}_y \quad (29)$$

Note $\hat{L}_+^\dagger = \hat{L}_-$, etc. Since $[\hat{L}^2, \hat{L}_i] = 0$ and $[\hat{L}_i, \hat{L}_j] = i\hbar\epsilon_{ijk}\hat{L}_k$, find (check!)

$$[L^2, L_\pm] = 0 \quad (30)$$
$$[\hat{L}_z, \hat{L}_\pm] = \pm\hbar\hat{L}_\pm \quad . \quad (31)$$

Now proceed à la harmonic oscillator case—apply $\hat{L}_+$ to Eq.(23):

$$\hat{L}_+(\hat{L}^2)\psi = a\hat{L}_+\psi = \hat{L}^2(\hat{L}_+\psi) \quad (32)$$

so $\hat{L}_+\psi$ is an eigenfctn. of $\hat{L}^2$ with eigenvalue a. Now apply to Eq.(24):

$$\hat{L}_+\hat{L}_z\psi = b(\hat{L}_+\psi) \quad (33)$$
$$\downarrow \quad (34)$$
$$[\hat{L}_+, \hat{L}_z]\psi + \hat{L}_z(\hat{L}_+\psi) = -\hbar\hat{L}_+\psi + \hat{L}_z(\hat{L}_+\psi) \quad (35)$$

Rearrange to get

$$\hat{L}_z(\hat{L}_+\psi) = (b + \hbar)(\hat{L}_+\psi), \quad (36)$$

which $\Longrightarrow$ $\hat{L}_+\psi$ is eigenfctn of $\hat{L}_z$ with eigenvalue $b + \hbar$. Label simult. e'fctns of $\hat{L}^2$ and $\hat{L}_z$ by ψ_{ab}, then

$$\hat{L}_+\psi_{ab} = \psi_{a,b+\hbar} \quad (37)$$
$$\hat{L}_-\psi_{ab} = \psi_{a,b-\hbar} \quad (38)$$

in general.

$\star$ So we begin to get the picture—$\hat{L}_\pm$ move us up and down the ladder of $\hat{L}_z$ quantum numbers. Recalling the SHO, need to find out where the top and bottom of the ladder are!

Know $b^2 \leq a$ from above, so sequence $b, b\pm\hbar, b\pm 2\hbar \cdots$ must terminate above and below, i.e. there exist b_{max} and b_{min} for each choice of a:

$$\hat{L}_+\psi_{a,b_{max}} = 0 \quad , \quad \hat{L}_z\psi_{a,b_{max}} = b_{max}\psi_{a,b_{max}} \tag{39}$$

$$\hat{L}_-\psi_{a,b_{min}} = 0 \quad , \quad \hat{L}_z\psi_{a,b_{min}} = b_{min}\psi_{a,b_{min}} \tag{40}$$

Now apply $\hat{L}^2$ to $\psi_{a,b_{max}}$ to find a. Convenient to have form

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 = \hat{L}_-\hat{L}_+ + i[\hat{L}_y, \hat{L}_x] + L_z^2 \tag{41}$$

$$\implies \boxed{\hat{L}^2 = \hat{L}_-\hat{L}_+ + \hat{L}_z^2 + \hbar\hat{L}_z} \tag{42}$$

and similarly

$$\boxed{\hat{L}^2 = \hat{L}_+\hat{L}_- + \hat{L}_z^2 - \hbar\hat{L}_z} \tag{43}$$

Therefore using (42)

$$\hat{L}^2\psi_{a,b_{max}} = a\psi_{a,b_{max}} = (b_{max}^2 + \hbar b_{max})\psi_{a,b_{max}} \tag{44}$$

and same argument applied to $\psi_{a,b_{min}}$ using (43) gives

$$\hat{L}^2\psi_{a,b_{min}} = a\psi_{a,b_{min}} = (b_{min}^2 - \hbar b_{min})\psi_{a,b_{min}} \tag{45}$$

Summarize:

$$a = b_{max}^2 + \hbar b_{max} \tag{46}$$

$$a = b_{min}^2 - \hbar b_{min} \tag{47}$$

Difference of (46) and (47) is

$$0 = (b_{max} - b_{min})(b_{max} + b_{min}) + \hbar(b_{max} + b_{min}) \tag{48}$$

which has soln. only when $b_{max} = -b_{min}$.

Now recall b is eigenvalue of $\hat{L}_z$, showed $b = m\hbar$, $m = 0, \pm 1, \pm 2 \cdots$ so must have

$$b_{max} - b_{min} = n\hbar \tag{49}$$

for some integer $n > 0$. (48) and (49) together now say

$$b_{max} = \frac{n\hbar}{2} \equiv \ell\hbar \tag{50}$$

where I've defined 2ℓ to be the integer n in (49). In terms of this ℓ, plug back into (46) and find

$$a = \hbar^2 \ell(\ell + 1). \tag{51}$$

Allowed values of quantum numbers which follow from commutation relations:

$$\hat{L}^2 \;:\; \hbar^2 \ell(\ell+1),\; \ell = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \cdots \tag{52}$$

$$\hat{L}_z \;:\; m\hbar, m = -\ell,\; m = -\ell, -\ell + 1, \cdots \ell - 1, \ell \tag{53}$$

But note for *orbital* angular momentum specifically we showed $m =$ integer, so only integer values of ℓ are allowed. Half-integer values will be encountered when we discuss spin.