Lecture #18: Rigid Rotor II

Read McQuarrrie, Chapter 6

Last time:

1.   Analogy between linear and angular momenta

Momentum =	(mass factor)	(vector velocity factor)
$\vec{p}$	m (or μ)	$\vec{v}$
$\vec{L}$ (or $\vec{J}$)	$I = \mu r_0^2$	$\vec{\omega} = \vec{v}/r_0$
	(the mass factor is more complicated for polyatomic molecules)	(ω_z means angular velocity about the laboratory z-axis)

2.   Transformation to molecular center-of-mass coordinate system permits replacement of $m_1, m_2,$ by μ.

3.   Rigid rotor is either free rotation of
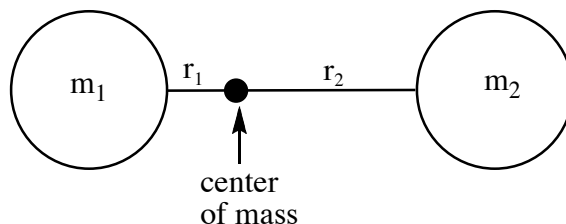
        a dumbbell about its center of mass or free motion of a mass μ particle confined to the
            surface of a sphere of radius $r_0 = R_e = r_1 + r_2$.

4.   Transform kinetic energy from Cartesian to spherical polar coordinates. Since there is no
        r-motion, the $\dfrac{\partial}{\partial r}$ derivatives are all zero and we have a θ,ϕ differential equation. The θ,ϕ
        equations may be separated following a procedure analogous to what we used to separate
        $x, y,$ and z for the 3-D box.

        The ϕ differential equation is simple, giving normalized eigenstates
        $$\Phi_M(\phi) = (2\pi)^{-1/2} e^{\pm iM\phi}$$
        $$M \text{ is an integer } -L \leq M \leq L$$

        The θ differential equation (Legendre equation) is not simple.

        Eigenfunctions are:

            Spherical Harmonics, $Y_L^M(\theta,\phi)$

$Y_L^M(\theta,\phi)$ and $P_L^{|M|}(\cos\theta)$ are differently normalized functions.

$$Y_L^M(\theta,\phi) = \left[\left(\frac{2L+1}{4\pi}\right)\frac{(L-|M|)!}{(L+|M|)!}\right]^{1/2} P_L^{|M|}(\cos\theta)e^{iM\phi}$$

Notice that the form of the θ dependence depends on the value of the ϕ quantum number, M. A consequence of the separation of variables procedure.

Today:

1. Rotational Spectra. A way to measure molecular geometry by a surprisingly *indirect* path.

   Why not just put a ruler on it?

2. Visualization of the $Y_L^M(\theta,\phi)$ functions.
   * polar plot
   * real vs. complex representations

3. A wavefunction and differential operator-free approach via $\left[\hat{L}_i,\hat{L}_j\right] = i\hbar\sum_k \varepsilon_{ijk}\hat{L}_k$

   commutation rules.
   This is how we define and work out the properties of multiple angular momenta (selection rules and matrix elements). A very powerful algebra.

$$\hat{L}^2\psi_{L,M_L} = \hbar^2 L(L+1)\psi_{L,M_L}$$

$$\hat{L}_z\psi_{L,M_L} = \hbar M_L\psi_{L,M_L}$$

$$\hat{L}_\pm \equiv \hat{L}_x \pm i\hat{L}_y \quad \text{(raising and lowering operators)}$$

$$\hat{L}_\pm\psi_{L,M_L} = \hbar\left[L(L+1) - M_L(M_L \pm 1)\right]^{1/2}\psi_{L,M_L\pm 1}$$

We are going to derive all of this from commutation rules.
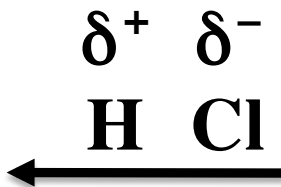
But first, spectra

$$\widehat{H}_{\text{rot}} = \hat{T}_{\text{rot}} + \overbrace{0}^{\substack{\text{free}\\\text{rotation}}} = \frac{\hat{L}^2}{2\mu r_0^2} \equiv \frac{hc\,\overbrace{B}^{\substack{\text{cm}^{-1}\\\text{units}}}}{\hbar^2}\hat{L}^2$$

$$\widehat{H}_{\text{rot}}\psi_{L,M_L} = \frac{hcB}{\hbar^2}\hbar^2 L(L+1)\psi_{L,M_L}$$

$$E/hc = BL(L+1)$$

A rotational spectrum requires that a molecule has a permanent electric dipole moment, μ. This dipole moment is the "handle" torqued by the electric field of the photon.
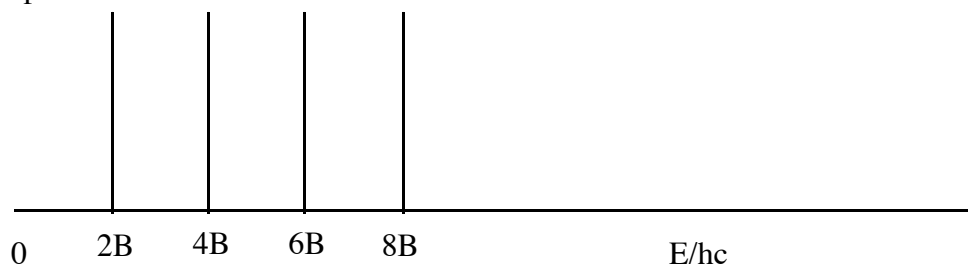
For example:

$$\delta^+ \quad \delta^-$$
$$\text{H} \quad \text{Cl}$$

Selection rule for rotational transitions is $\Delta L = \pm 1$, $\Delta M_L = 0, \pm 1$ (*ad hoc*, Sorry!)

$$E_L/hc = BL(L + 1)$$

Transition	$\Delta E/hc$	
$1 \leftrightarrow 0$	2B	$(2 - 0)B$
		2B
$2 \leftrightarrow 1$	4B	$(6 - 2)B$
		2B
$3 \leftrightarrow 2$	6B	$(12 - 6)B$

$$(L + 1) \leftrightarrow L \quad 2(L + 1)B \quad [(L + 1)(L + 2) - L(L + 1)]$$

Spectrum:

0   2B   4B   6B   8B   E/hc

"Assignment" – seems to be trivial but is not, because typical microwave oscillators cover only a $\nu, \nu + 0.3\nu$ 30% band.

Typically, for light molecules, only one rotational line per molecule appears in the spectrum! What can we do to put rotational quantum number assignments onto the spectral lines?

Isotope shift (light and heavy isotopes of atom #1) $\mu_L = \dfrac{m_1^L m_2}{m_1^L + m_2}$ $\mu_H = \dfrac{m_1^H m_2}{m_1^H + m_2}$

$H^{35}Cl$ $\mu_L = \dfrac{35}{36} = 0.9722$

$$H^{37}Cl \qquad \mu_H = \frac{37}{38} = 0.9737 \qquad \frac{\mu_L}{\mu_H} = 0.9985$$

Not too small! Very high precision in spectrum, typically better than 1 part in 10^5!

$B_H = B_L \dfrac{\mu_L}{\mu_H}$, know masses, natural abundance. Assign L, L + 1 transition to determine

B. Get r_0 from B.

What is wrong with this argument? (Depends on seeing a pattern when the observed spectrum contains only one transition.) What additional information can we bring to this problem?

Visualization of $Y_L^M(\theta,\phi)$.

You already know polar plots of *s, p, d, f* atomic orbitals from 5.111, 5.112. Same thing. But what are they really and how do they ENCODE L, M_L and the direction that $\vec{L}$ is pointing in the laboratory frame?

Polar plot: (r, θ,ϕ) is a point in 3D spherical polar coordinates.

The trick is that we plot, for each θ,ϕ

$$r = \frac{1}{2}\left[\psi_{L,M_L}(\theta,\phi) \pm \psi_{L-M_L}(\theta,\phi) \right]$$

Top sign makes the thing we plot a real number even though ψ_{L,M_L} has a complex $e^{iM_L\phi}$ phase factor. What does the bottom sign give?

We plot a point located at (r,θ,ϕ) where r is the magnitude of ψ in the θ,ϕ direction.

The things we plot are not eigenfunctions of $\hat{L}_z$ (why not?), but they are eigenfunctions of $\widehat{H}$ and $\hat{L}^2$.

Nodes remain!   L = 0   zero   angular nodes

              1   one

              2   two

If angular momentum is about the laboratory z-axis, $M_L = \pm L$ and the maximum amplitude of ψ
is mostly in the plane $\perp$ to z-axis.

$\psi(\theta,\phi)$ is the probability amplitude of what? $\vec{L}$ or the internuclear axis?

Be careful! Primary amplitude of ψ is NOT along the angular momentum vector, $\vec{L}$. It is in the
plane $\perp$ to $\vec{L}$. We could have plotted $\psi^*_{L,M_L}\psi_{L,M_L}$, but this loses the phases, which are
important for understanding Quantum Mechanical interference effects. It does preserve
nodal surfaces, and you know that the phase reverses on opposite sides of a nodal surface.

Commutation Rule Algebra — the general definition of angular momenta.

$L = \vec{r} \times \vec{p}$ is the classical mechanical definition of orbital angular momentum.

However, there is no spatial coordinate associated with electron and nuclear (NMR!) "spins".
But we want to think of them as angular momenta.

$$\left.\begin{array}{c} \vec{J} = \vec{L} + \vec{S} \\ \vec{F} = \vec{J} + \vec{I} \end{array}\right)$$ This coupling of different types of angular momenta is
observable in many kinds of spectra

So we adopt a formal, *general* approach.

Any angular momentum must obey this general commutation rule. Use $\vec{L}$ for illustration.

$$\left[\hat{L}_i,\hat{L}_j\right] = i\hbar\sum_k \varepsilon_{ijk}L_k$$

ε_{ijk} "Levi-Civita" symbol (i, j, k are Cartesian axis labels)

$\varepsilon_{ijk} = +1$ if x, y, z are in standard cyclic order
                    xyz, yzx, zxy

$\varepsilon_{ijk} = -1$ if   anti-cyclic order
$\varepsilon_{ijk} = \;0$ if   two indices are identical, e.g. *xxy*

We want to derive all of the properties of all angular momentum operators, operating on angular
momentum eigenstates without ever looking at the differential operator form of the

operators or the functional form of the eigenfunctions. We always start with the
fundamental equation

$$\left[\hat{L}_i,\hat{L}_j\right] = i\hbar\sum_k \varepsilon_{ijk}\hat{L}_k .$$

First we need to derive some commutation rule results using the general commutation rule above.

$$
\begin{aligned}
\left[\hat{L}^2,\hat{L}_z\right] &= \left[\hat{L}_x^2,\hat{L}_z\right]+\left[\hat{L}_y^2,\hat{L}_z\right]+\left[\overbrace{\hat{L}_z^2,\hat{L}_z}^{=0}\right]\\
&= \hat{L}_x\left[\hat{L}_x,\hat{L}_z\right]+\left[\hat{L}_x,\hat{L}_z\right]\hat{L}_x + \hat{L}_y\left[\hat{L}_y,\hat{L}_z\right]+\left[\hat{L}_y,\hat{L}_z\right]\hat{L}_y\\
&= \hat{L}_x\left(-i\hbar\hat{L}_y\right)+\left(-i\hbar\hat{L}_y\hat{L}_x\right)+ \hat{L}_y\left(i\hbar\hat{L}_x\right)+\left(i\hbar\hat{L}_x\right)\hat{L}_y\\
&= 0.
\end{aligned}
$$

[This nicely illustrates the power of ε_{ijk} algebra!]

Generalize

$$\left[\hat{L}^2,\vec{\hat{L}}\right] = 0 \quad \text{(for all 3 components of } \vec{\hat{L}}\text{)}.$$

But the one we really care about is

$$\left[\hat{L}^2,\hat{L}_z\right] = 0$$

because this means we can have simultaneous eigenstates of $\hat{L}^2$ and $\hat{L}_z$.

We need to work out one other commutation rule result:

$$
\begin{aligned}
\hat{L}_\pm &\equiv \hat{L}_x \pm i\hat{L}_y\\
\left[\hat{L}_z,\hat{L}_\pm\right] &= \left[\hat{L}_z,\hat{L}_x\right]\pm i\left[\hat{L}_z,\hat{L}_y\right]\\
&= i\hbar\hat{L}_y \pm i\left(-i\hbar\hat{L}_x\right)\\
&= \pm\hbar\left(\hat{L}_x \pm i\hat{L}_y\right) = \pm\hbar\hat{L}_\pm .
\end{aligned}
$$

Also, by inspection

$$\left[\hat{L}^2,\hat{L}_\pm\right] = 0 .$$

We are going to derive the eigenvalues of $\hat{L}^2,\hat{L}_z$, and the effects of $\hat{L}_\pm$ without ever looking at a
wavefunction or a differential operator.

Suppose *f* is an eigenfunction of $\hat{L}^2$ with eigenvalue λ and of $\hat{L}_z$ with eigenvalue μ, as stated
here.

$$\hat{L}^2 f = \lambda f$$
$$\hat{L}_z f = \mu f.$$

1. Show that $\left(\hat{L}_\pm f\right)$ is eigenfunction of both $\hat{L}^2$ and $\hat{L}_z$. $\hat{L}^2$, $\hat{L}_\pm$ commute, thus

$$\hat{L}^2\left(\hat{L}_\pm f\right) = \hat{L}_\pm\left(\hat{L}^2 f\right) = \lambda\left(\hat{L}_\pm f\right)$$

>   Thus $\hat{L}_\pm f$ is eigenfunction of $\hat{L}^2$ with eigenvalue λ (same as that of f). Operation by $\hat{L}_\pm$ does not affect the value of λ.

2. Now, use $\left[\hat{L}_z, \hat{L}_\pm\right] = \pm\hbar\hat{L}_\pm$.

$$\hat{L}_z\hat{L}_\pm - \hat{L}_\pm\hat{L}_z = \pm\hbar\hat{L}_\pm$$
$$\hat{L}_z\left(\hat{L}_\pm f\right) - \hat{L}_\pm\left(\underbrace{\hat{L}_z f}_{\mu f}\right) = \pm\hbar\left(\hat{L}_\pm f\right)$$
$$\hat{L}_z\left(\hat{L}_\pm f\right) = \hat{L}_\pm\left(\mu f\right) \pm \hbar\left(\hat{L}_\pm f\right)$$
$$= \left(\mu \pm \hbar\right)\left(\hat{L}_\pm f\right).$$

Thus, $\hat{L}_\pm f$ is eigenfunction of $\hat{L}_z$ belonging to eigenvalue $\mu \pm\hbar$.

We have a ladder of states increasing in μ by steps of $\hbar$: $\mu, \mu + \hbar, \mu + 2\hbar, \ldots$. The ladder must be finite because a projection of $\hat{L}$ cannot be larger than $\left|\vec{L}\right|$.

3. Use fact that there must exist a maximum value of μ (which is initially unknown to us).

$$\hat{L}_+ f_{\max\mu} = 0$$
$$\hat{L}_z f_{\max\mu} = \hbar\ell f_{\max\mu} \qquad \text{(we really do not know yet that } \ell \text{ is an integer or half-integer or anything, nor what its relationship to } \lambda \text{ is)}$$

4.   We need to derive another important operator equation.

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

rearranging

$$\boxed{\hat{L}^2 = \hat{L}_z^2 \mp \hbar\hat{L}_z + \hat{L}_{\pm}\hat{L}_{\mp}}\ .$$

5.   Use this boxed equation to find the value of λ for the top rung of the ladder:

$$\hat{L}^2 f_{\max\mu} = \hat{L}_{\pm}\hat{L}_{\mp}f_{\max\mu} + \hat{L}_z^2 f_{\max\mu} \mp \hbar\hat{L}_z f_{\max\mu}$$

use lower sign

$$= 0 + (\hbar\ell)^2 f_{\max\mu} + \hbar^2 \ell f_{\max\mu}$$
$$= \hbar^2(\ell^2 + \ell)f_{\max\mu}.$$

Thus λ, an eigenvalue of $\hat{L}^2$, is $\lambda = \hbar^2\ell(\ell+1)$.

6.   Similar argument (top signs) for λ of lowest rung of ladder.

$$\hat{L}^2 f_{\min\mu} = \underbrace{\hat{L}_+\hat{L}_- f_{\min\mu}}_{=0} + \hat{L}_z^2 f_{\min\mu} - \hbar\hat{L}_z f_{\min\mu}$$

$$\text{Let } \hat{L}_z f_{\min\mu} = \hbar\,\overline{\ell}\,f_{\min\mu}$$

we do not know what this $\overline{\ell}$ is, no assumption is being made here.

$$\hat{L}^2 f_{\min\mu} = 0 + \hbar^2 \overline{\ell}^2 f_{\min\mu} - \hbar^2 \overline{\ell} f_{\min\mu}$$

$$\lambda f_{\min\mu} = \hbar^2 \left(\overline{\ell}^2 - \overline{\ell} \right) f_{\min\mu}$$

so $\lambda = \hbar^2 \overline{\ell}(\overline{\ell} - 1)$. This is a second constraint on the value of λ.

7.   Putting it all together:

we saw previously $\lambda = \hbar^2 \ell(\ell + 1)$, now we also require $\lambda = \hbar^2 \overline{\ell}(\overline{\ell} - 1)$, thus

$$\ell(\ell + 1) = \overline{\ell}(\overline{\ell} - 1)$$
$$\ell^2 + \ell = \overline{\ell}^2 - \overline{\ell}$$

so we have 2 possibilities

$$\ell = -\overline{\ell}$$

OR

$$\overline{\ell} = \ell + 1$$

This second possibility cannot be correct
because we know that L_- lowers μ.

Thus we are left with the following results:

$$\ell = -\overline{\ell}$$
$$\mu_{\min\mu} = -\mu_{\max\mu}$$
$$\lambda = \hbar^2 \ell(\ell + 1)$$
$$\mu = (\ell, \ell - 1, \ldots - \ell).$$

8.   We are not quite done. 2 possibilities.

ℓ can be an integer a or half-integer. Cannot get, in steps of 1, from $+\ell$ to $-\ell$ if ℓ is neither an integer nor a half-integer.

This is not a defect! We can have half-integer angular momenta, like electron spin $S = \frac{1}{2}$ or some nuclear spins $I = 1/2, 3/2, 5/2$ (as in $H, Cl, {}^{17}O$). Our formalism deals with both integer and half-integer angular momenta!

9.   What about the effect of $\hat{L}_\pm$ on ψ_{L,M_L}? We are now going to prove that

$$\hat{L}_\pm \psi_{L,M_L} = \hbar \left[L(L + 1) - M_L(M_L \pm 1) \right]^{1/2} \psi_{L,M_L \pm 1}.$$

Use

$$\hat{L}^2 = \hat{L}_z^2 \mp \hbar \hat{L}_z + \hat{L}_\pm \hat{L}_\mp \text{ (boxed equation on page 8)},$$

rearrange

$$\hat{L}_\pm \hat{L}_\mp \Psi_{L,M_L} = \left(\hat{L}^2 - \hat{L}_z^2 \pm \hbar \hat{L}_z \right) \Psi_{L,M_L}$$

$$= \left(\hbar^2 L(L+1) - \hbar^2 M_L^2 \pm \hbar^2 M_L \right) \Psi_{L,M_L}$$

$$= \hbar^2 \left[L(L+1) - M_L (M_L \mp 1) \right] \Psi_{L,M_L},$$

multiply on left by ψ_{L,M_L}^* and integrate ($d\tau$ means all coordinates):

$$\text{RHS} = \hbar^2 \left[L(L+1) - M_L (M_L \mp 1) \right]$$

Now use property of complex conjugation:

$$\left(\hat{L}_\mp \psi_{L,M_L} \right)^* = \psi_{L,M_L}^* \hat{L}_\pm = X^*$$

$$\text{LHS} = \int X^* X d\tau = \int |X|^2 d\tau = \int \left| c_\mp \psi_{L,M_L \mp 1} \right|^2 d\tau = \left| c_\mp \right|^2$$

$$\hat{L}_\mp \psi_{L,M_L} \equiv \left| c_\mp \right| \psi_{L,M_L \mp 1}$$

thus

$$\left| c_\mp \right| = \hbar \left[L(L+1) - M_L (M_L \mp 1) \right]^{1/2}$$

and this gives us the last of our results. Note that the sign of

$L_\pm \psi_{L,M_L} = (\text{sign}) \hbar \left[L(L+1) - M_L (M_L + 1) \right]^{1/2} \psi_{L,M_L \pm 1}$ is undetermined. One must make a phase choice and stick to it because we have no actual wavefunctions or differential operators to check for internal phase consistency. This is a minor (but not ignorable) cost of using this elegant operator algebra.

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