5.61 Lecture #17 Rigid Rotor I

Read McQuarrie: Chapters E and 6.

Rigid Rotors — molecular rotation and the universal angular part of all central force problems – another exactly solved problem. The rotor is free, thus $\widehat{H} = \widehat{T} \quad (V = 0)$.

Once again, we are more interested in:

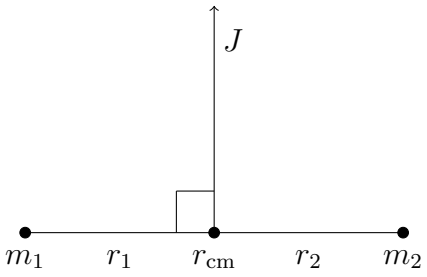
* E_J and $\left\langle \widehat{J} \right\rangle_t$
* effects of $\widehat{\mathbf{J}}^2$, $\widehat{\mathbf{J}}_z$, $\widehat{\mathbf{J}}_\pm = \widehat{\mathbf{J}}_x \pm i\widehat{\mathbf{J}}_y$ ("raising" and "lowering" or "ladder" operators)
* qualitative stuff about shape (nodal surfaces) of $\psi_{JM}(\theta, \phi)$

than we are in the actual form of $\psi_{JM}(\theta, \phi)$ and in the method for solving the rigid rotor Schrödinger Equation.

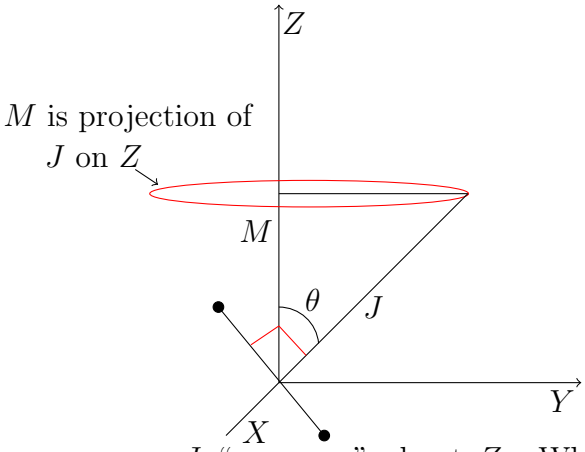
Next Lecture – no differential equation, no ψ, just:

* $[\mathbf{J}_i, \mathbf{J}_j] = i\hbar \sum_k \varepsilon_{ijk} \mathbf{J}_k$ definition of an angular momentum operator
* $\mathbf{J}^2 \psi_{JM} = \hbar^2 J(J+1)\psi_{JM}$
* $\mathbf{J}_z \psi_{JM} = \hbar M \psi_{JM}$
* $\mathbf{J}_\pm = \mathbf{J}_x \pm i\mathbf{J}_y$
* $\mathbf{J}_\pm \psi_{JM} = [J(J+1) - M(M \pm 1)]^{1/2} \psi_{JM\pm1}$

The standard problem is for the motion of a mass point constrained to the surface of a sphere. However, we are really interested in the rotational motion of a rigid diatomic molecule. *Mass point* is the same as one end of a rotor (length r_0, mass μ) with bond axis extending from the coordinate origin at the Center of Mass.



at origin,
$r_0 = r_1 + r_2$



J "precesses" about Z. Why do we say this when there is no motion in solutions to TISE?

For a molecule, there are two coordinate systems: the *body*–fixed system denoted by x, y, z and the *laboratory*-fixed system denoted by X, Y, Z.

What are we going to want to remember?

1. $E(J, M)$
2. What do J, M mean about

$$\text{NOT the same!} \left\{ \begin{array}{l} * \text{ location of } \vec{J} \\ * \text{ location of internuclear axis} \end{array} \right\} \text{distributions}$$

3. qualitative stuff about shape of $\psi_{J,M}(\theta, \phi)$

   $\left.\begin{array}{l} \#\text{ of nodes} \\ \text{locations of nodes} \end{array}\right]$ surfaces

   where is the internuclear axis?

   "reduced" pictures of $\psi_{J,M}(\theta, \phi)$

4. Selection rules and values of integrals of $\mathbf{J}^2$, $\mathbf{J}_Z$, $\mathbf{J}_\pm$

Rotor is free

bond length

$$V(r = r_0, \theta, \phi) = 0, \qquad V(r \neq r_0, \theta, \phi) = \infty$$

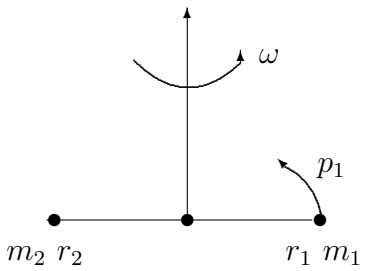
Need to keep track of only $\widehat{T}(\theta, \phi)$ because $\widehat{V} = 0$ when $r = r_0$

$$\widehat{H} = \widehat{T}$$

$$\text{for 1–D} \quad \widehat{T} = \frac{\hat{p}^2}{2\mu} \qquad \text{linear momentum}$$

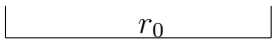
For rotor we want *angular* rather than linear momentum. From classical mechanics:

$$\vec{L} = \vec{r} \times \vec{p}$$



$r_1 \perp p_1 \quad , \quad r_2 \perp p_2$

$r_0 = r_1 + r_2$



for rotation on surface of sphere $\vec{r} \perp \vec{p}$

$$\therefore v_1 = r_1\omega, \quad |p| = m|v| = mr|\omega|$$

$$|\vec{r} \times \vec{p}| = |L| = m_1 r_1^2 \omega + m_2 r_2^2 \omega \equiv I\omega$$

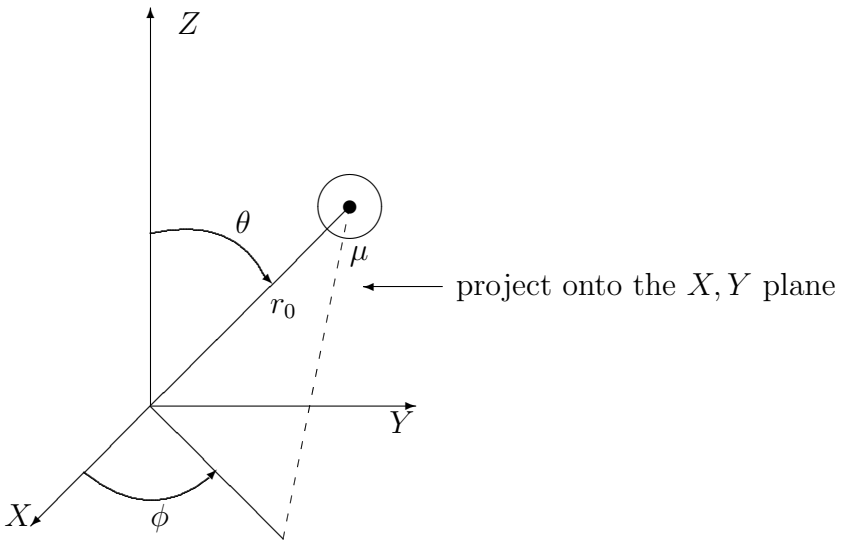
$$I = \sum_i m_i r_i^2. \quad \text{moment of inertia (for a diatomic or any linear molecule)}$$

Use $m_1 r_1 = m_2 r_2$ center of mass constraint to get $I = \mu r_0^2$

Now write $\widehat{T}$ as analogous to $\frac{p^2}{2\mu}$ $\quad \begin{matrix} p \to L \\ \mu \to I \end{matrix}$

$$\widehat{T} = \frac{\widehat{L}^2}{2I}.$$

Now we have a mass point μ (at r_0 from origin), where bond axis points at the mass point, μ



ASA: get $XYZ \rightarrow r\theta\phi$

$$\widehat{T} = -\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta}\left(\frac{\partial}{\partial\theta}\right)\left(\sin\theta\left(\frac{\partial}{\partial\theta}\right)\right) + \frac{1}{\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right)\right]$$

looks bad!

$\widehat{H}\psi = \widehat{T}\psi = E\psi$

solutions are $\psi(r_0, \theta, \phi) \equiv Y(\theta, \phi)$

Solve for θ, ϕ dependence of $Y(\theta, \phi)$

We really *do not want to do this* in detail because we have little reason to actually look at the $Y(\theta, \phi)$ eigenfunctions. THIS SHOULD BOTHER YOU!

Outline of Steps

separation of variables

$$Y(\theta, \phi) = \Theta(\theta)\Phi(\phi) \qquad \text{seen this before}$$

standard process — arrange θ stuff on LHS, ϕ stuff on RHS. Then divide both sides by $\Theta(\theta)\Phi(\phi)$.

A lot of algebra

$$\underbrace{\frac{\sin\theta}{\Theta(\theta)}\left(\frac{\partial}{\partial\theta}\right)\left(\sin\theta\left(\frac{\partial}{\partial\theta}\right)\right)\Theta(\theta)+\beta\sin^2\theta}_{\text{only }\theta}=\underbrace{-\frac{1}{\Phi(\phi)}\left(\frac{\partial^2}{\partial\phi^2}\right)\Phi(\phi)}_{\text{only }\phi}$$

$$\beta\equiv\frac{2IE}{\hbar^2}\text{ collecting constants}$$

both sides must equal same *constant*: call it m^2

2 separate equations:

separation constant

1. ϕ: $\dfrac{1}{\Phi(\phi)}\left(\dfrac{\partial^2}{\partial\phi^2}\right)\Phi(\phi)=-m^2$ Easy to solve
2. θ: $\dfrac{\sin\theta}{\Theta(\theta)}\left(\dfrac{\partial}{\partial\theta}\right)\left(\sin\theta\left(\dfrac{\partial}{\partial\theta}\right)\right)\Theta(\theta)+\beta\sin^2\theta=m^2$ Leads to Legendre Equation

Most of the useful insight comes from # 1!

$$\left(\frac{\partial^2\Phi}{\partial\phi^2}\right)=-m^2\Phi(\phi)$$

$\Phi(\phi)=A_me^{im\phi}$ $\quad m=0,\pm1,\pm2,\quad A_m$ is normalization constant

$\Phi(\phi)=\Phi(\phi+2m\pi)$ periodic boundary condition

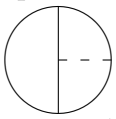
$A_m=(2\pi)^{-1/2}$ $\quad\leftarrow$ HOW DO WE GET THIS?

Notice that $e^{im\phi}$ is complex

Can convert to real functions by $2^{-1/2}[e^{im\phi}\pm e^{-im\phi}]$. Are these eigenstates?

Turns out we exchange the all-real functions of the geometric picture for a picture of the eigenstates of $\widehat{L}_z$.

nodes in XY plane



$m=1$

$$\left.\begin{aligned}\cos\phi=0\ @\ \frac{\pi}{2}&=m\phi\quad&\phi&=\frac{\pi}{2m}\\ @\ \frac{3\pi}{2}&=m\phi\quad&\phi&=3\left(\frac{\pi}{2m}\right)\end{aligned}\right\}\text{ same nodal plane if }m=1$$

m is # of nodal planes thru XY plane.

2nd differential equation for $\Theta(\theta)$ is more complicated. Legendre Equation: can look at notes. Note that the Θ DE depends on the value of m.

$*$ 2nd boundary condition — the requirement of continuity in θ gives energy quantization.

Notice that the form of $\Theta(\theta)$ eigenstates depends on *both* L, M.

Final result for energy levels of rotor is

$$E_L = \frac{\hbar^2}{2I} L(L+1) \quad L = 0, 1, 2, \ldots$$

Notation:
- L general orbital angular momentum
- ℓ angular momentum of one electron
- J angular momentum of molecular rotation

] several places where rigid rotor appears

Same equations, L, ℓ, J often used interchangeably. Also other angular momenta S, I, and N. *The beauty is that once we understand one angular momentum we understand all angular momenta.*

Pictures

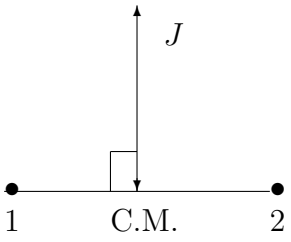
$$\psi_{LM}(\theta, \phi) = Y_L^M(\theta, \phi) \qquad \text{“spherical harmonic”}$$
$$= \underbrace{\left[\left(\frac{2L+1}{4\pi}\right)\frac{(L-|M|)!}{(L+|M|)!}\right]^{1/2}}_{\text{normalization constant}} \underbrace{P_L^{|M|}(\cos\theta)}_{\substack{\text{Legendre Polynomial} \\ \text{(solution of Legendre Equation)}}} e^{iM\phi}$$

But we want memorable pictures and intuition–guiding cartoons! See McQuarrie, page 286 for table of $Y_L^m(\theta, \phi)$ [at end of these notes].

Vector Model

- relates “body frame” (x, y, z) properties to “lab frame” (X, Y, Z) observations.

1. $\vec{J} = \vec{r} \times \vec{p}$ $\vec{J}$ is a vector $\perp$ to plane of rotation.



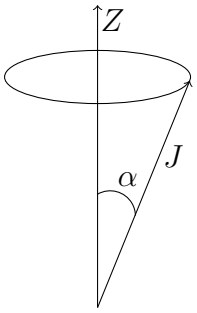
2. θ, ϕ are the lab frame coordinates of a fictitious particle of mass μ moving on the surface of a sphere of radius r_0. They are also the coordinates of one end of the rotor axis where the rotation is about the center of mass along this axis.

3. Key questions:

   a. Where does $\vec{J}$ point in lab?

   b. How long is $\vec{J}$?

   c. Where does internuclear axis, r, point in lab? ($J \perp r$)



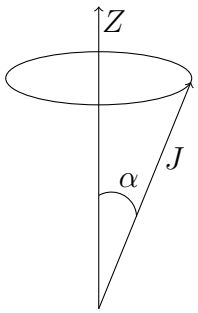
$\vec{J}$ precesses about laboratory Z at constant α.

$$\mathbf{J}_Z Y_J^M = \underbrace{\hbar M}_{\text{length of projection of } \vec{J} \text{ on } Z} Y_J^M$$

* Length of $\vec{J}$

$$|\mathbf{J}| = [\mathbf{J} \cdot \mathbf{J}]^{1/2} = \left\langle \vec{\mathbf{J}}^2 \right\rangle^{1/2}$$
$$\mathbf{J}^2 Y_J^M = \hbar^2 J(J+1) Y_J^M$$
$$|\mathbf{J}| = \hbar[J(J+1)]^{1/2} \approx \hbar(J + 1/2)$$

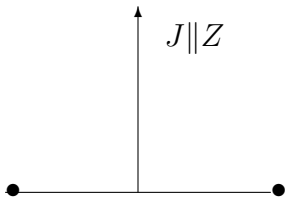
* What is $\langle \cos\alpha \rangle$?



$$\langle \cos\alpha \rangle = \frac{\hbar M}{\hbar[J(J+1)]^{1/2}} \approx \frac{M}{J}$$ CRUCIAL INSIGHT

Where is the internuclear axis in lab for a specified tilt of $\vec{J}$ from laboratory Z axis?

If $J = M$, $\vec{J}$ is almost exactly along lab Z. (Why "almost"?)



molecular internuclear axis is rotating in XY plane

If $M = 0$, $\vec{J}$ is precessing exactly in the XY plane:

for $M = 0$ {
- when $\vec{J}$ is along X, molecular axis is in YZ plane
- when $\vec{J}$ is along Y, molecular axis is in XZ plane
- so molecular axis is maximally (but not exclusively) along Z.

Molecular Beam in Z direction

$M = \pm J$

molecular axis is in XY plane

molec. axis is more along Z

different kinds of collisions

Polar Plots

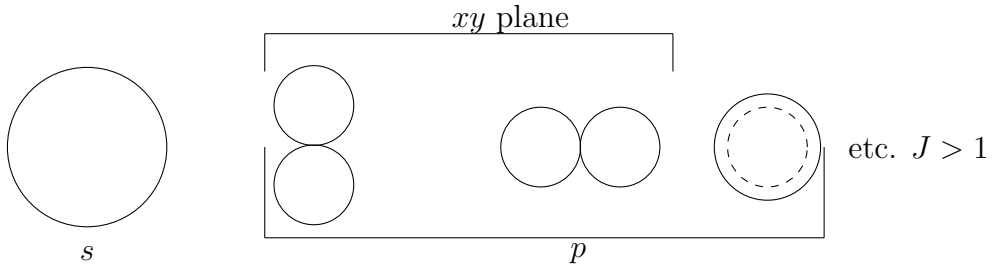
Shown without explanation in most introductory texts (for atomic orbitals)

distance of plotted point from origin

$$r(\theta,\phi) = \frac{1}{2}\left[Y_J^M(\theta,\phi) + Y_J^{-M}(\theta,\phi)\right]$$

real function of θ, ϕ

These are *not* the solutions of the (r, θ, ϕ) full 3D Schrödinger Equation. They are a way of representing a 3D object in 2D.



spherical 3 dumbbells with axis along X, Y, and Z

Notice that # of nodal surfaces is L (or J).

L	# surfaces
0(s)	0
1(p)	1
2(d)	2

Number of nodal lines in XY plane is $|M|$.

Now you should be able to

- recognize J, M_J (or L, M_L) from the number and placement of nodes
- know how $\vec{J}$ is located in a laboratory frame
- know how internuclear axis is located in a laboratory frame.

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