Lecture #22: Rotation of Polyatomic Molecules I

A diatomic molecule is very limited in how it can rotate and vibrate.

* \( \vec{R} \) is \( \perp \) to internuclear axis
* only one kind of vibration

A polyatomic molecule can have \( \vec{R} \) oriented along any body fixed direction — symmetric and asymmetric tops\(^\dagger\).

A polyatomic molecule can stretch any bond or bend any bond pair — Normal modes of vibration

A lot of very complicated classical mechanics.

TODAY: Derive \( \hat{H}^{\text{ROT}} = \frac{\vec{R}_x^2}{2I_x} + \frac{\vec{R}_y^2}{2I_y} + \frac{\vec{R}_z^2}{2I_z} \) and evaluate matrix elements in \(|KJM\rangle\) basis set, where \( I_x, I_y, \) and \( I_z \) are called principal components (i.e. eigenvalues) of the \( 3 \times 3 \) moment of inertia tensor, \( \mathbf{I} \), and are analogous to \( \mu R_{AB}^2 \) in an AB diatomic.

1. Center of mass.
2. rigid body rotation
   \( \hat{T}^{\text{ROT}} \) in terms of \( \vec{\omega} \) (angular velocity), \( m_i, (x_i, y_i, z_i) \)
   (positions of atom \( i \) in center of mass body frame)
   \[
   \frac{1}{2} \vec{\omega} \cdot \mathbf{I} \vec{\omega} = \begin{pmatrix} I_a & 0 & 0 \\ 0 & I_b & 0 \\ 0 & 0 & I_c \end{pmatrix}
   \]
3. \( \hat{H}^{\text{ROT}} \) and matrix elements in \(|KJM\rangle\) basis.
4. Symmetric tops - prolate and oblate energy level formulas.

Consider a rigid N-body system. Each atom has mass \( m \), and body-fixed coordinate \( \vec{q} \) (defined relative to an arbitrary body-fixed origin).

Our first task is to locate the center of mass, because we expect to separate the \( 3N \) degrees of freedom into 3 center of mass translations, 3 rotations about the center of mass, and \( 3N - 6 \) vibrations.

Center of Mass: 3 Cartesian component equations.

\[
0 = \sum_{i=1}^{3N} m_i (\vec{q}_i - \vec{q}_{CM})
\]

\(^\dagger\) In fact, the definition of body fixed axis system is not even obvious for vibrating molecule.
Example:

\[ \text{NH}_3 \] (projected onto xy plane)

Take advantage of symmetry whenever possible!

pick \( C_3 \) (3-fold rotation axis) axis as z axis
locate origin at N atom (a convenient way to start)
locate \( H_1 \) at \( \phi = 0 \) (i.e. in xz plane)

\[ \begin{aligned}
\mathbf{q}_{H_1} &= (r, \theta, \phi) = (R, \theta, 0) \Rightarrow (x_1, y_1, z_1) = (R \sin \theta, 0, R \cos \theta) \\
\mathbf{q}_{H_2} &= (R, \theta, \frac{2\pi}{3}) \Rightarrow (x_2, y_2, z_2) = \left(-\frac{1}{2}R \sin \theta, \frac{\sqrt{3}}{2}R \sin \theta, R \cos \theta\right) \\
\mathbf{q}_{H_3} &= (R, \theta, \frac{4\pi}{3}) \Rightarrow (x_3, y_3, z_3) = \left(-\frac{1}{2}R \sin \theta, -\frac{\sqrt{3}}{2}R \sin \theta, R \cos \theta\right) \\
\mathbf{q}_N &= (0, 0, 0)
\end{aligned} \]

Now solve for center of mass.

\( x_{\text{CM}} = y_{\text{CM}} = 0 \) are trivial

\[ z_{\text{CM}} = \frac{3m_H R \cos \theta}{3m_H + m_N} \]

So we have coordinates of all atoms relative to new origin now at center of mass, expressed in terms of 2 unknown bond coordinates, \( R \) and \( \theta \).
Next we need to write out $H^{\text{ROT}}$ and put it into a convenient form.

$$
\hat{H}^{\text{ROT}} = \hat{T}^{\text{ROT}} + V^{\text{ROT}}
$$

free rotor, thus $V^{\text{ROT}} = 0$

$$
\hat{T}^{\text{ROT}} = \frac{1}{2} \sum_i m_i v_i^2
$$

Want to re-express all $v_i$'s in terms of $\vec{q}_i$ and $\vec{\omega}$ where $\vec{\omega}$ specifies the direction and magnitude of the angular velocity of the rigid body rotations. (All atoms experience the same $\vec{\omega}$.)

\[\vec{\omega}\]

\[
\vec{q}_i = \frac{\vec{q}_i \cdot \vec{\omega}}{||\vec{\omega}||} = \frac{q_i ||\omega|| \cos \theta}{||\omega||}
\]

need velocities for $T^{\text{ROT}}$ parallel to $\frac{\vec{\omega}}{||\omega||}$ unit vector

\[v_i = -\vec{q}_i \times \vec{\omega} \quad \text{(right hand rule requires minus sign)}\]

\[|v_i| = |q_i| \ |\omega| \sin \theta_i \quad q_i, \omega \text{ known. Must solve for } \sin \theta_i.\]

\[
\sin \theta_i = \frac{q_i \cdot q_{i\perp}}{q_i} = \frac{q_{i\perp}^2 - \left(\frac{q_i \cdot \omega}{||\omega||}\right)^2}{q_i}
\]

so

\[v_i^2 = q_i^2 \omega^2 \sin^2 \theta_i = \left[q_i^2 \omega^2 - (q_i \cdot \omega)^2\right] \quad \text{(sin}^2 \theta_i = 1 - \cos^2 \theta_i)\]

\[\hat{H}^{\text{ROT}} = \frac{1}{2} \sum_i m_i \left[q_i^2 \omega^2 - (q_i \cdot \omega)^2\right]\]

Go to Cartesian coordinates (always safe for setting up quantum mechanical Hamiltonian operator).
\[
\mathbf{H}^{\text{rot}} = \frac{1}{2} \sum_i m_i \left[ (x_i^2 + y_i^2 + z_i^2) \left( \omega_x^2 + \omega_y^2 + \omega_z^2 \right) - \left( x_i \omega_x + y_i \omega_y + z_i \omega_z \right)^2 \right]
\]

a bit of algebra

\[
= \frac{1}{2} \sum_i m_i \left[ (x_i^2 + y_i^2) \omega_z^2 + (x_i^2 + z_i^2) \omega_y^2 + (y_i^2 + z_i^2) \omega_x^2 - 2 x_i y_i \omega_x \omega_y - 2 x_i z_i \omega_x \omega_z - 2 y_i z_i \omega_y \omega_z \right]
\]

Reformulate as matrix diagonalization problem!

\[
I_{xx} \equiv \sum_i m_i \left( y_i^2 + z_i^2 \right) \quad \text{etc. perpendicular distance squared from x axis}
\]

Define

\[
I_{xy} = - \sum_i m_i \left( x_i y_i \right) = I_{yx} \quad \text{etc.}
\]

\[
\mathbf{H}^{\text{rot}} = \frac{1}{2} \mathbf{\omega}^T \mathbf{I} \mathbf{\omega}
\]

This is a compact form for messy equation above!

\[
\mathbf{\omega} = \begin{pmatrix} \omega_x \\ \omega_y \\ \omega_z \end{pmatrix}, \quad \mathbf{I} = \begin{pmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} \end{pmatrix}, \quad \mathbf{\omega}' = \begin{pmatrix} \omega_x \\ \omega_y \\ \omega_z \end{pmatrix}
\]

"moment of inertia tensor"

\[\mathbf{I}\] is a real, symmetric matrix.

It can be diagonalized (by a coordinate transformation, a rotation about center of mass) to give

\[
\mathbf{T}^T \mathbf{I} \mathbf{T} = \begin{pmatrix} I_a & 0 & 0 \\ 0 & I_b & 0 \\ 0 & 0 & I_c \end{pmatrix}
\]

\[I_a \leq I_b \leq I_c\] by definition and are called the “principal moments of inertia”.

\[
\mathbf{T}^T = \mathbf{1} \quad \mathbf{H}^{\text{rot}} = \frac{1}{2} \mathbf{\omega}^T \mathbf{I} \mathbf{\omega} = \frac{1}{2} (\mathbf{\omega}' \mathbf{T})(\mathbf{T}^T \mathbf{I} \mathbf{T})(\mathbf{T}' \mathbf{\omega})
\]
\[
\begin{pmatrix}
\omega_x \\
\omega_y \\
\omega_z
\end{pmatrix}
\begin{pmatrix}
T' \\
x \\
y \\
z
\end{pmatrix}
= 
\begin{pmatrix}
\omega_a \\
\omega_b \\
\omega_c
\end{pmatrix}
\]

We find a special body fixed coordinate system with origin at the center of mass which causes \( I \) to be diagonal.

Usually possible to find principal axes by inspection.

1. One axis is axis of highest order rotational symmetry, called \( z \) by convention.
2. Another axis is \( \perp \) to \( C_n \) and \( \perp \) to a \( \sigma_v \) plane. E.g. if \( \sigma(xz) \) exists, then
   \[
   \sum_i m_i x_i y_i = \sum_i m_i y_i z_i = 0 \text{ because there is always an identical nucleus at } (x, +y, z) \text{ and at } (x, -y, z).
   \]
   (What happens when there is no \( \sigma_z \) plane? e.g. \( S_1 \) acetylene.)
3. 3rd is \( \perp \) to first 2 axes.

So when \( I \) is diagonal

\[
\hat{H}^{\text{ROT}} = \frac{1}{2} \left( I_a \omega_a^2 + I_b \omega_b^2 + I_c \omega_c^2 \right)
\]

the nuclear rotational angular momentum is defined as

\[
\hat{J} = I \omega
\]

should actually use notation of \( R \) or \( N \)

\[
\hat{H}^{\text{ROT}} = \frac{1}{2} \hat{J}^\dagger I^{-1} \hat{J} = \frac{J^2}{2I_a} + \frac{J^2}{2I_b} + \frac{J^2}{2I_c}
\]

like \( \frac{p^2}{2m} \rightarrow \frac{J^2}{2I} \)

(The reciprocal or inverse of a diagonal matrix is trivial.)
We can now define three rotational constants

\[
A = \frac{h}{c} \frac{1}{8\pi^2 I_a} \text{ cm}^{-1} (E/\hbar c)
\]

\[
B = \frac{h}{c} \frac{1}{8\pi^2 I_b} \text{ cm}^{-1}
\]

\[
C = \frac{h}{c} \frac{1}{8\pi^2 I_c} \text{ cm}^{-1}
\]

A \geq B \geq C

(again, by definition)

Note that we will sample “rotational constants” with I\(^{-1}\) averaged over specific vibrational state, not at the equilibrium geometry. Want equilibrium geometry, get strange average. Note that we are eventually going to want to compute derivatives of I\(^{-1}\) \equiv \mu with respect to each of the 3N – 6 normal coordinate displacements.

One obtains A, B, C by picking bond lengths and angles, specifying atomic masses, and diagonalizing I. For each change in masses (isotopic substitution) or iterative change in geometry, I must be rediagonalized.

Example: Principal Moments for NH\(_3\) (refer to table on page 2)

C\(_3\) axis must be one principal axis

\[
\text{so } I_z = R^2 \sin^2 \theta \left[ m_{H_1} + \left( \frac{x^2}{4} + \frac{3}{4} \right) m_{H_2} + \left( \frac{1}{4} + \frac{3}{4} \right) m_{H_3} \right]
\]

\[
= 3m_{H_1} R^2 \sin^2 \theta
\]

(the \(\perp\) distance\(^2\) of each atom from axis specified)

existence of reflection plane

\[
\sigma_v (xz) \implies I_y = R^2 \cos^2 \theta \left( \frac{3m_{H_2} m_{H_1}}{M} \right) + R^2 \sin^2 \theta \left( \frac{3m_{H_2}}{2} \right)
\]

principal component \(\perp\) to the xz plane. You show that I\(_x\) = I\(_y\) (for any symmetric top).

[General rule, every molecule with n \(\geq\) 3 C\(_3\) rotation axis has two equal moments of inertia!]

Special case of D\(_{2d}\) \(\rightarrow\) S\(_4\) axis: cyclooctatetraene and allene

allene
\( \hat{H} \text{_{\text{ROT}}} \) for symmetric top.

By convention, \( I_x = I_y, I_z \) is unique (for all sym. tops).

\[
\hat{H} \text{_{\text{ROT}}} = \frac{\hat{J}_x^2}{2I_x} + \frac{\hat{J}_y^2}{2I_y} + \frac{\hat{J}_z^2}{2I_z}
\]

manipulate this into a form convenient for \( |\text{JKM}\rangle \) basis set.

\[
I_x = I_y \quad \hat{J}^2 - \hat{J}_z^2 = \hat{J}_x^2 + \hat{J}_y^2 \quad \text{key step!}
\]

\[
\hat{H} \text{_{\text{ROT}}} = \frac{1}{2I_x} \left[ \hat{J}_x^2 + \hat{J}_y^2 \right] + \frac{\hat{J}_z^2}{2I_z} = \frac{1}{2I_x} \left( \hat{J}_x^2 - \hat{J}_z^2 \right) + \frac{\hat{J}_z^2}{2I_z}
\]

\[
\hat{H} \text{_{\text{ROT}}} = \frac{1}{2I_x} \hat{J}_x^2 + \left[ \frac{1}{2I_z} - \frac{1}{2I_x} \right] \hat{J}_z^2
\]

remember this!!

Use \( |\text{JKM}\rangle \) symmetric top basis functions which are just like \( |\text{J\Omega M}\rangle \) functions for a diatomic molecule.

So

\[
E \text{_{\text{ROT}}} = \frac{\hbar^2}{2I_x} J(J + 1) + \left[ \frac{\hbar^2}{2I_z} - \frac{\hbar^2}{2I_x} \right] K^2
\]

like a diatomic molecule

projection of \( \hat{J} \) onto unique (i.e. symmetry) axis of body (like \( \Omega \))

2 types of symmetric top:

1. \( I_z \equiv I_a \) is unique, \( I_b = I_c > I_a \), prolate top, like a cigar. Coefficient of \( K^2 \) is > 0 because \( A > B \) by definition.

\[
\frac{E \text{_{\text{prolate}}}}{\hbar c} = BJ(J + 1) + (A - B)K^2
\]

2. \( I_z \equiv I_c \) is unique. \( I_a = I_b < I_c \), oblate top, like a frisbee. Coefficient of \( K^2 \) is < 0.

\[
\frac{E \text{_{\text{oblate}}}}{\hbar c} = BJ(J + 1) - (B - C)K^2
\]
J = 0, 1, 2, …  
K = 0, ±1, … ±J  
denote as (J,K) or J_K

possible levels