14. <u>The Rotations of Gaseous Polyatomic Molecules</u>

rigid

A. Linear Polyatomic Molecules

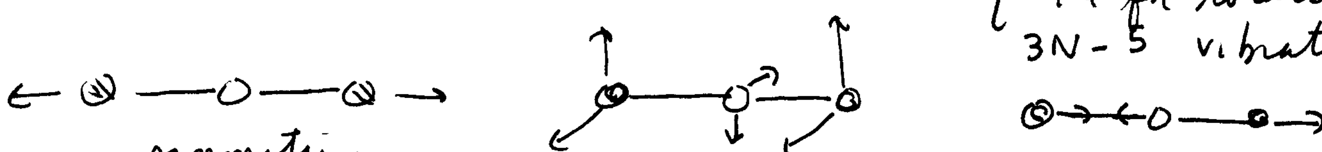
$$E_J/h = B_{\{v_i\}} J(J+1) - D J^2 (J+1)^2$$ as in diatomic

$I \neq \mu R^2$

molecules. The vibrational correction to B_e is more complex because in general there are $3N-5$ normal modes of vibration. ($3N-6$ if non-linear)

Example: triatomic  $3N-5 = 4$ modes

N nuclei $\rightarrow$ $3N$ coordinates $\left\{ \begin{array}{l} 3 \text{ for CM translation} \\ \theta, \varphi \text{ for rotation} \\ 3N-5 \text{ vibration} \end{array} \right\}$



symmetric stretch ν_1, v_1 — two bends ν_2, v_2 — asymmetric stretch ν_3, v_3

$$B_{v_1 v_2 v_3} = B_e - \alpha_1 (v_1 + 1/2) - \alpha_3 (v_3 + 1/2) - \alpha_2 (v_2' + 1/2 + v_2'' + 1/2)$$

Ground st te: 000 $\quad -\alpha_2 (v_2+1)$

$\mu \neq 0$ for strong rotational spectrum

B. (Symmetric) Tops (rigid motion)

The classical expression for rotational energy (kinetic) of a non-linear system can be expressed as

$$E_{rot} = \frac{1}{2} (I_a \omega_a^2 + I_b \omega_b^2 + I_c \omega_c^2)$$

or, using angular momenta $J_i = I_i \omega_i$

$$E_{rot} = \frac{1}{2} \left(J_a^2/I_a + J_b^2/I_b + J_c^2/I_c \right)$$

where a, b, c are the so-called principal axes, based in the molecule. Origin = center of mass

<u>Determination of Principal Axes</u>

1. Define an axis system x, y, z in the molecule.
2. Determine the center of mass $X_{cm} Y_{cm} Z_{cm}$
   $M = \sum m_i \qquad M X_{cm} = \sum m_i x_i$ etc. (discrete)
3. Determine the components of the moment of inertia tensor in the x, y, z system. (around c. of mass)

$$I_{xx} \; (I_x) = \sum_i m_i \left\{ (y_i - Y_{cm})^2 + (z_i - Z_{cm})^2 \right\}$$

$$I_{yy} \; (I_y) = \sum_i m_i \left\{ (x_i - X_{cm})^2 + (z_i - Z_{cm})^2 \right\}$$

$$I_{zz} \; (I_z) = \sum_i m_i \left\{ (x_i - X_{cm})^2 + (y_i - Y_{cm})^2 \right\}$$

+ products of inertia:

$$I_{xy} = - \sum_i m_i (x_i - X_{cm})(y_i - Y_{cm}) \text{ etc.}$$

4. Write the I tensor as a matrix and diagonalize it so that there are no cross-terms; e.g.

$$\begin{vmatrix} I_{xx} - I & I_{xy} & I_{xz} \\ I_{xy} & I_{yy} - I & I_{yz} \\ I_{xz} & I_{yz} & I_{zz} - I \end{vmatrix} = 0$$

which yields 3 roots known as the components of the moment of inertia in the principal axis system (as well as the principal axes themselves). These are designated I_a, I_b, I_c.

Normal convention $I_a \leq I_b \leq I_c$

<u>spherical top</u> (rare) $I_a = I_b = I_c$ $\mu = 0$

<u>symmetric top</u> $I_a < I_b = I_c$ prolate top

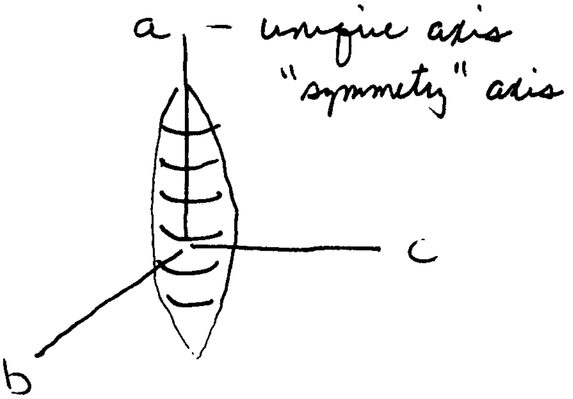
$I_a = I_b < I_c$ oblate top

common; requires only a three-fold symmetry axis.

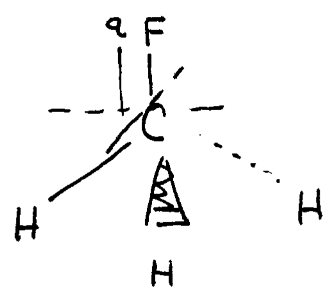
<u>asymmetric top</u> $I_a < I_b < I_c$ most common (complex)

a. <u>Prolate Tops</u>

continuous (cigar)



discrete

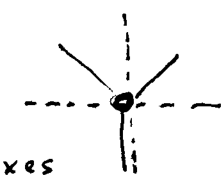


side view

(show pen)

$I_b = I_c$; $I_{bc} = 0$

I_a : less mass off axis

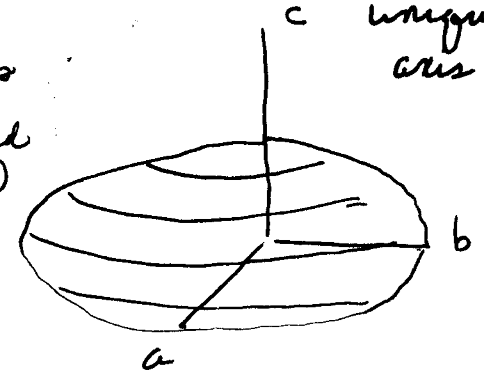


top view

b, c axes
no cross terms

b. <u>Oblate tops</u>

continuous (flattened sphere)



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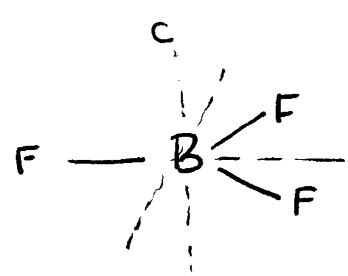
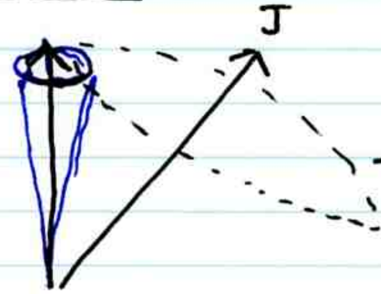


(planar)

(show coaster) planar $\Rightarrow$ $I_c = I_a + I_b$

Classical Motion



Top spins around symmetry axis with conserved angular momentum component J_a or J_c.

– symmetry axis precesses around J

which suggests that, in quantum mechanics, the following operators commute

$$\mathcal{H}_{rot},\ J^2,\ J_{a(c)},\ J_Z$$

J_Z: space-fixed

Quantum Mechanics

$$E_{rot} \rightarrow \hat{\mathcal{H}}_{rot} = \frac{1}{2}\left(\frac{\hat{J}_a^2}{I_a} + \frac{\hat{J}_b^2}{I_b} + \frac{\hat{J}_c^2}{I_c}\right)$$

$$\hat{J}^2 = \hat{J}_a^2 + \hat{J}_b^2 + \hat{J}_c^2$$

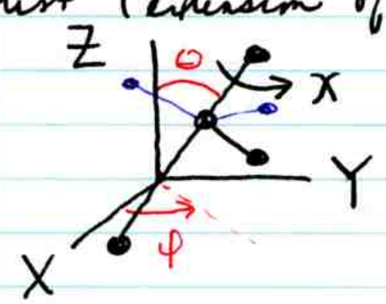
Let's consider a prolate symmetric top first.

$$I_b = I_c \qquad \hat{\mathcal{H}}_{rot} = \frac{1}{2}\left(\frac{\hat{J}_a^2}{I_a} + \frac{\hat{J}^2 - \hat{J}_a^2}{I_b}\right)$$

What are the eigenvalues and eigenfunctions of $\hat{J}^2$ & $\hat{J}_a$?

Need 3 rotational coordinates, not 2. These are known as the Euler angles, of which there are several definitions. (relate XYZ and abc)

Diplot (extension of spherical polar coordinates).



$$\hat{J}^2 \Psi(\theta, \varphi, \chi) = J(J+1)\hbar^2 \Psi(\theta, \varphi, \chi)$$

$$J = 0, 1, 2, 3 \ldots$$

$$\hat{J}_a \Psi = K_a \hbar \Psi \qquad -J \le K_a \le J$$

$$\hat{J}_Z \Psi = M_J \hbar \Psi \qquad -J \le M_J \le J$$