Lecture #22: Asymmetric Top

R = Iω

\[ H^{\text{ROT}} = \frac{1}{2} T^T \begin{bmatrix} I_a & 0 & 0 \\ 0 & I_b & 0 \\ 0 & 0 & I_c \end{bmatrix} T \]

J = R + L + S + \ell

\[ H^{\text{ROT}} = \frac{1}{2}(J - L - S - \ell) \begin{bmatrix} I_a^{-1} & 0 & 0 \\ 0 & I_b^{-1} & 0 \\ 0 & 0 & I_c^{-1} \end{bmatrix}(J - L - S - \ell) \]

inverse inertial matrix


forget about L, S, \ell for now

\[ H^{\text{ROT}} = AJ_a^2 + BJ_b^2 + CJ_c^2 \]

a-axis is “light”

c-axis is “heavy”

A ≥ B ≥ C

\[ A / \text{cm}^{-1} = \frac{h}{c} \sum_i \left( b_i^2 + c_i^2 \right) \]

perpendicular distance from named axis

prolate top

I_b = I_c

\[ E_p^{\text{ROT}} (J, K) = BJ(J + 1) + (A - B)K^2 \]

oblate top

I_a = I_b

\[ E_o^{\text{ROT}} (J, K) = BJ(J + 1) + (C - B)K^2 \]

TODAY: Asymmetric Top

1. Correlation Diagram

   qualitative pattern for Energy levels

   notation \( J_{K_a K_c} \) and \( J_t \)

2. \( H^{\text{ROT}} \) in \( |JKLM\) basis set

   \( \Delta K = 0 \) and \( \Delta K = \pm 2 \) matrix elements

3. Perturbation theory and \( \kappa = \frac{2B - A - C}{A - C} \) asymmetry parameter

4. Wang factorization: 4 symmetry species

5. Townes and Schawlow Tables for Asymmetric Top Levels

What do we expect energy levels for an asymmetric top to look like? Intermediate between prolate and oblate limits. Correlation diagram is based on non-crossing rule. Imagine a continuous transformation of a molecule from prolate to oblate limit. Levels belonging to different values of a rigorously good quantum number can cross, all others cannot. \( J \) is good, \( K \) is not good.
Levels within a J can’t cross. K > 0 are doubly degenerate and the degeneracy is lifted as soon as top becomes asymmetric. Near the corresponding limit, high K has small “asymmetry splitting” and low K has large splitting.

Vertical lines give a good sense of level pattern at any point between prolate and oblate limits.

Two notation schemes:

- \( J^K_p K_p \): projection on a-axis
- \( J^K_0 K_0 \): projection on c-axis

Two notation schemes:

- \( J \): eigenvalues rank
- \( -J \leq \tau \leq +J \)

\( K_p + K_0 = J \) or \( J + 1 \) asymmetry doublet
Near prolate limit \( K_p + K_o = J \) is the higher energy member of the doublet, near oblate limit \( K_p + K_o = J \) is the lower member.

OK. Now we know what to expect qualitatively, and how to label the levels, but how do we compute accurate energy levels and wavefunctions?

Set up \( \hat{H}^{\text{ROT}} \) in symmetric top basis set \( |JKM\rangle \). Initially, we do not even have to worry about whether to select a, b, or c axis as the quantization axis.

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

\[
\hat{J}_z |JKM\rangle = \hbar^2 K^2 |JKM\rangle
\]

\[
\hat{J}^2 |JKM\rangle = \hbar^2 J(J+1) |JKM\rangle
\]

\[
J_z = J_x \pm iJ_y
\]

\[
\hat{J}_z = |JKM\rangle = \hbar [J(J+1) - K(K+1)]^{1/2} |JK \mp 1M\rangle \quad (\hat{J}_+ \text{ is lowering operator})
\]

\[
J_x = \frac{1}{2}(J_+ + J_-)
\]

\[
J_y = -\frac{i}{2}(J_+ - J_-)
\]

So

\[
\hat{J}_x^2 = \frac{J_x^2 + J_y^2}{4} + \frac{J^2 - J_z^2}{2}
\]

both have same diagonal part

\[
\hat{J}_y^2 = \frac{J_x^2 - J_y^2}{4} + \frac{J^2 - J_z^2}{2}
\]

both have same off-diagonal magnitude but opposite sign

\[
\Delta \hat{K} = \pm 2 \quad \Delta \hat{K} = 0
\]

\[
\hat{H}^{\text{ROT}} = \left\{ \frac{\hat{J}_x^2 - \hat{J}_z^2}{2} \left[ \frac{1}{2I_x} + \frac{1}{2I_y} \right] + \frac{\hat{J}_z^2}{2I_z} \right\} + \left\{ \frac{J_x^2 + J_y^2}{4} \left[ \frac{1}{2I_x} - \frac{1}{2I_y} \right] \right\}
\]

Diagonal part of \( \hat{H}^{\text{ROT}} \)

\[
\langle JK | \hat{H}^{\text{ROT}} | JK \rangle = \frac{\hbar^2}{2} \left[ \frac{1}{2I_x} + \frac{1}{2I_y} \right] J(J+1) + \frac{\hbar^2}{2} \left[ \frac{1}{2I_z} - \frac{1}{2I_x} - \frac{1}{2I_y} \right] K^2
\]

<table>
<thead>
<tr>
<th>( z = a )</th>
<th>near prolate</th>
<th>( \equiv B )</th>
<th>( A - B )</th>
<th>( &gt; 0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( z = c )</td>
<td>near oblate</td>
<td>( \frac{B + C}{2} \equiv B )</td>
<td>( C - B )</td>
<td>( &lt; 0 )</td>
</tr>
<tr>
<td>( z = b )</td>
<td>midway (basis for perturbation theory treatment of either limit)</td>
<td>( \frac{A + C}{2} \equiv B - \frac{A + C}{2} )</td>
<td>?</td>
<td></td>
</tr>
</tbody>
</table>
Off-Diagonal part of $H^{\text{ROT}}$

$$\langle JK \pm 2 | H^{\text{ROT}} | JK \rangle = \frac{\hbar^2}{2} \left[ \frac{1}{2I_x} - \frac{1}{2I_y} \right] \left[ J(J+1) - K(K \pm 1) \right]^{1/2} \left[ J(J+1) - (K \pm 1)(K \pm 2) \right]^{1/2}$$

Coefficient for $\Delta K = \pm 2$ matrix elements

| $(z = a)$ | near prolate | $BC$ | $\Delta K = \pm 2$ matrix elements would be $0$ if $B = C$ or $A = B$ (i.e. symmetric top limit) |
| $(z = c)$ | near oblate | $AB$ | |
| $(z = b)$ | midway (basis for perturbation theory treatment of either limit) | $AC$ | |

Since the only off-diagonal matrix elements are $\Delta J = 0$, $\Delta K = \pm 2$, $H^{\text{ROT}}$ factors into even-$K$ and odd-$K$ sub-blocks.

Use perturbation theory to get an idea about $H'_{\Delta E^o}$. Use b-axis as quantization axis, because this is midway between prolate and oblate limits.

$$\frac{H'_{ij}}{E_{ij}^o} = \frac{H^{\text{ROT}}_{K,K \pm 2}}{E_{JK}^o - E_{JK \pm 2}^o} = m \left[ \frac{J^2(J+1)^2}{(K \pm 1)^2} + K(K \pm 2) - 2J(J+1) \right]^{1/2} \frac{A - C}{2B - A - C}$$

(result of some algebra)

$$\kappa \equiv \frac{2B - A - C}{A - C}$$

is called “asymmetry parameter”.

| prolate | $B = C$ | $\kappa = -1$ |
| oblate | $A = B$ | $\kappa = +1$ |

most asymmetric (also spherical top) possible. $B = \frac{A + C}{2}$, $K = 0$

Rule out $A = B = C$ (spherical top).

Use $\kappa^{-1}$ as order-sorting parameter for perturbation theory.

Perturbation Theory (using b-axis for quantization) will give bad approximation when $\frac{1}{2} \frac{H'}{E^o} \gtrsim 1$.

This occurs when:

1. $\kappa \to 0$
2. $\kappa \ll J$, $J \gg 0$ because then $\left[ \right]^{1/2}$ gets large. We already saw with correlation diagram that asymmetry splittings are largest for $K \ll J$. 

\[ \begin{align*} \\end{align*} \]
The only time perturbation theory can work (with b-axis quantization) is if \( J \approx K \) and \( J \) small. Otherwise we must diagonalize a matrix.

Factor \( H^{\text{ROT}} \).

1. No \( \Delta J \neq 0 \) matrix elements. Each \( J \)-block has \( 2J + 1 \) eigenvalues.

2. Within each \( J \)-block, only \( \Delta K = \pm 2, 0 \) matrix elements.
   So factor into even \( K \) (\( J \) or \( J + 1 \) eigenvalues)
   and odd \( K \) (\( J + 1 \) or \( J \) eigenvalues).

3. Within each odd or even subset, we can form \( 2^{-1/2} \left[ |JK\rangle \pm |J-K\rangle \right] \) linear combinations.

This corresponds to constructing eigenfunctions of \( \sigma_v \) (zx or zy) as for a diatomic molecule.

Wang Symmetrizing Transformation constricts

\[
\begin{bmatrix}
|JOM\rangle \\
2^{-1/2} \left[ |J \ | K \ | M\rangle \pm |J-\ | K \ | M\rangle \right]
\end{bmatrix}
\]

basis functions

works because

\( H_{JK,JK} = H_{J-K,J-K} \) and \( H_{JK,JK+2} = H_{JK+2,JK} = H_{J-K,J-K-2} = H_{J-K-2,J-K} \)

Wang Transformation

\[
X^{-1} = X = 2^{-1/2}
\]

\[
\begin{bmatrix}
-1 & 1 & 1 & 1 \\
O & N & & \\
-1 & 1 & 2^{1/2} & \\
N & O & & \\
1 & 1 & & \\
\end{bmatrix}
\]

\[
K = \begin{bmatrix}
J & J-1 & 0 & -J
\end{bmatrix}
\]

\( X_{\text{Wang}}^{-1} = X = 2^{-1/2} \)
\[ X^{-1} H_{\text{ROT}} (J, \text{all } K) X \]

\[ H(J) = \]

Get 4 types of sub-blocks after rearrangement of \( X^{-1} H X \)

\[
\begin{array}{|c|c|}
\hline
(K_a, K_c) & e,e \\
\hline
(K_b, K_c) & e,o \\
\hline
o,o & (\text{Group Theory later}) \\
o,e & \\
\hline
\end{array}
\]

These are 4 distinct symmetry species

exact Asymmetric Top Energy Levels

<table>
<thead>
<tr>
<th>J = 0</th>
<th>is</th>
<th>( 1 \times 1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>is</td>
<td>( 3 \ \ 1 \times 1 )</td>
</tr>
<tr>
<td>2</td>
<td>is</td>
<td>( 3 \ \ 1 \times 1 ) and ( 1 \ \ 2 \times 2 )</td>
</tr>
<tr>
<td>3</td>
<td>is</td>
<td>( 1 \ \ 1 \times 1 ) and ( 3 \ \ 2 \times 2 )</td>
</tr>
<tr>
<td>4</td>
<td>is</td>
<td>( 3 \ \ 2 \times 2 ) and ( 1 \ \ 3 \times 3 )</td>
</tr>
<tr>
<td>5</td>
<td>is</td>
<td>( 1 \ \ 2 \times 2 ) and ( 3 \ \ 3 \times 3 )</td>
</tr>
</tbody>
</table>

| 6 |

| 7 |

\( \text{J even} \quad \frac{J}{2}, \frac{J}{2}, \frac{J}{2}, \frac{J}{2} + 1 \)

\( \text{J odd} \quad \frac{J-1}{2}, \frac{J+1}{2}, \frac{J+1}{2}, \frac{J+1}{2} \)

Trivial to set up and diagonalize \( H_{\text{ROT}} \).
Guide to tables from T & S (not needed with computers, except for checking programs).

1. pages 522-526  Asymmetric top energies for near-symmetric tops given as power series in

$$b_p = \frac{C - B}{2A - B - C} \quad \text{near prolate}$$

or

$$b_o = \frac{A - B}{2C - B - A} \quad \text{near oblate}$$

$$E = B\left(J(J+1) + \frac{1}{2}(A - C)E_{\tau}\right)$$

where $$E_{\tau}$$ is tabulated.

$$\omega \equiv K^2 + C_1b + C_2b^2 + \ldots C_nb^n$$

2. pages 527-555  explicit eigenvalues for $$H^{\text{ROT}}$$ for J = 0 – 12 and $$|\kappa| = 0 \rightarrow 1$$ in steps of 0.01.

Listed as $$E = \frac{1}{2}(A + C)J(J + 1) + \frac{1}{2}(A - C)E_{\tau}$$ where $$E_{\tau}$$ is tabulated.

Levels labeled by $$J_{K_sK_z}$$ and $$J_{\tau}$$:

$$\begin{bmatrix}
\tau = -J & E_{\min} \\
\tau = +J & E_{\max}
\end{bmatrix}$$

Next time, intensities and selection rules for pure rotation transitions of symmetric and asymmetric tops.