II. Rotational Spectroscopy

Outline

A. Diatomic Molecules
   1. Coordinates and Hamiltonian
   2. Angular momentum operators
   3. The spherical harmonics

B. Symmetric tops
   1. Energy levels
   2. Rigid body rotations
      (a) Review of Unitary Transformations
      (b) Generators of Infinesimal Rotations
      (c) The Euler Angles
   3. Symmetric top wave functions
   4. The action of operators
   5. Selection rules and line strengths

C. Asymmetric Tops
   1. The moment of inertia tensor
   2. Symmetry classification
   3. Wavefunctions and energy levels
   4. Selection rules
   5. Centrifugal distortion
D. Experimental Methods and Applications
   1. Practical considerations
      – resolution, pressure broadening and the Stark effect
   2. Gas cells and Frequency Scans
   3. Balle-Flygare – FTMW
   4. Broadband and coherent Methods
   5. Molecular structure determination
      - Kraitchman’s rules
II. Rotational Spectroscopy

References
1. Bernath, Chapter 6


4. Walter Gordy and Robert L. Cook, Microwave Molecular Spectra, Wiley, 1984. (out of print, but a digital copy can be obtained.)
II. Rotational Spectroscopy

A. Diatomic molecules

1. Co-ordinates and Hamiltonian

(a) Center of Mass Transformation

\[ \mu = \frac{m_1 m_2}{m_1 + m_2} \]

\( m_1: \mathbf{r}_1 = (x_1, y_1, z_1) \)

\[ \mu: \mathbf{r} = (x_2 - x_1, y_2 - y_1, z_2 - z_1) \]

\[ = (x, y, z) \]  

\( m_2: \mathbf{r}_2 = (x_2, y_2, z_2) \)

\[ M: \mathbf{R} = \frac{m_1 \mathbf{r}_2 + m_2 \mathbf{r}_1}{m_1 + m_2} \]
(b) Transformation to Spherical Polar Coordinates

The Schrödinger equation is

\[ H\psi = E\psi \]  \hspace{1cm} (2)

For the rotation of a diatomic molecule, we have in Cartesian coordinates

\[ H = -\frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \]  \hspace{1cm} (3)

Transforming to spherical polar coordinates

\[ x = r \sin \theta \cos \phi \]
\[ y = r \sin \theta \sin \phi \]
\[ z = r \cos \theta \]

\[ \text{eq (4)} \]
we get for fixed $r$:

$$H = -\frac{\hbar^2}{2\mu r^2} \left[ \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]$$  \hspace{1cm} (5)$$

We then solve eq (2) for $\psi = \psi(\theta, \phi)$. 
2. Angular momentum operators

Classically, the linear momentum is specified in terms of the velocity: (Zare p. 1)

\[ \mathbf{p} = m \mathbf{v} \quad (6) \]

and the angular momentum is defined using the vector cross product as

\[ \mathbf{l} = \mathbf{r} \times \mathbf{p} \quad (7) \]

In quantum mechanics, we convert classical variables to operators using

\[ p_x = -i\hbar \frac{\partial}{\partial x} \quad p_y = -i\hbar \frac{\partial}{\partial y} \quad p_z = -i\hbar \frac{\partial}{\partial z} \quad (8) \]

which give the angular momentum operators:

\[ l_x = yp_z - zp_y = -i \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \]
\[ l_y = zp_x - xp_z = -i \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \quad (9) \]
\[ l_z = xp_y - yp_x = -i \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \]
The commutator of a pair of operators, $A$ and $B$, is

$$[ A, B ] \equiv AB - BA \quad (10)$$

If the observables corresponding to $A$ and $B$ can both have definite values at the same time, then their commutator is zero. That is, there are states that are simultaneously eigenfunctions of both operators. On the other hand $x$ and $p_x$ may not both have definite values at the same time because their measurements are subject to the uncertainty principle. Accordingly, one finds that their commutator is not zero:

$$[ x, p_x ] = i\hbar \quad [ x, p_y ] = 0 \quad \text{etc.} \quad (11)$$

At this point, I will follow Zare and adopt units with $\hbar = 1$. We then find the commutation relations for the angular momentum operators:

$$[ l_x, l_y ] = i(\hbar)l_z \quad [ l_y, l_z ] = il_x \quad [ l_z, l_x ] = il_y \quad (12)$$

These commutation relationships are considered to be so fundamental that we define a general angular momentum $\mathbf{j}$ as one whose components obey these rules:

$$[ j_x, j_y ] = i j_z \quad [ j_y, j_z ] = i j_x \quad [ j_z, j_x ] = i j_y \quad (13)$$
We define

\[ \mathbf{j}^2 = j_x^2 + j_y^2 + j_z^2 \]  

(14)

One can show that

\[ \left[ j^2, j_x \right] = \left[ j^2, j_y \right] = \left[ j^2, j_z \right] = 0 \]  

(15)

Therefore we can construct states \( |jm\rangle \) that are simultaneous eigenfunction of \( j^2 \) and one component of \( \mathbf{j} \):

\[ j^2 |jm\rangle = \lambda_j |jm\rangle \]
\[ j_z |jm\rangle = m |jm\rangle \]  

(16)

We will now proceed to find the eigenvalues \( m \) and \( \lambda_j \). Consider the action of the following operator:

\[ \left( j_x^2 + j_y^2 \right) |jm\rangle = \left( j^2 - j_z^2 \right) |jm\rangle \]
\[ = \left( \lambda_j - m^2 \right) |jm\rangle \]
Now, the eigenvalues and expectation values of a *Hermitian* operator are real, and therefore their squares are positive. That is

\[ m^2 \geq 0 \quad \text{and} \quad (\lambda_j - m^2) \geq 0 \]  

which means

\[ \lambda_j \geq 0 \quad \text{and} \quad m^2 \leq \lambda_j \]

Therefore there must be maximum and minimum values of *m* which we will call \( m_{\text{max}} \) and \( m_{\text{min}} \) respectively.

To proceed toward finding the actual eigenvalues, we define two new operators:

\[ j_+ \equiv j_x + ij_y \quad \text{and} \quad j_- \equiv j_x - ij_y \]  

From eq (13) and (15), we find

\[
\left[ j^2, j_\pm \right] = 0
\]

\[
\left[ j_z, j_\pm \right] = \pm j_\pm
\]

\[
\left[ j_+, j_- \right] = 2j_z
\]
Consider the behavior of the function \( \{ j_{\pm} | j m \} \). One finds

\[
\begin{align*}
\mathbf{j}^2 \{ j_{\pm} | j m \} &= \frac{j_{\pm} \mathbf{j}^2}{\text{commutator used}} | j m \rangle \\
&= \lambda_j \{ j_{\pm} | j m \} \quad (20)
\end{align*}
\]

and

\[
\begin{align*}
\mathbf{j}_z \{ j_{\pm} | j m \} &= (j_{\pm} \mathbf{j}_z \pm j_{\pm}) | j m \rangle \\
&= (m \pm 1) \{ j_{\pm} | j m \} \quad (21)
\end{align*}
\]

Therefore \( \{ j_{\pm} | j m \} \) is proportional to the normalized eigenfunction \( | j, m \pm 1 \rangle \):

\[
\{ j_{\pm} | j m \} = C_{\pm} | j, m \pm 1 \rangle \quad (22)
\]

where \( C_{\pm} \) is the proportionality constant.
Since $j_\pm$ changes $m$ by ±1 unit, we call these operators

raising and lowering operators, or
step-up and step-down operators, or
ladder operators, or
shift operators.

We will rely heavily on these operators throughout the course.

All of above states have the same values of $\lambda_j$. The ladder operators only change the values of $m$. 
So far we have found boundary conditions on the eigenvalues and ladder operators relating the eigenfunctions, but now we need to find the actual eigenvalues. To get a specific answer we try applying the raising operator to the top rung of the ladder and the lowering operator to the bottom rung of the ladder.

\[ j_+ |j m_{\text{max}}\rangle = 0 \]  
\[ j_- |j m_{\text{min}}\rangle = 0 \]  

(23)

Now apply \( j_- \) and \( j_+ \) to the upper and lower parts of eq (23) respectively and use the identity

\[ j_\mp j_\pm = j^2 - j_z (j_z \pm 1) \]  

(24)

This gives

\[ \lambda_j - m_{\text{max}} (m_{\text{max}} + 1) = 0 \]  
\[ \lambda_j - m_{\text{min}} (m_{\text{min}} - 1) = 0 \]  

(25)

Elinimating \( \lambda_j \) we find

\[ m_{\text{max}} = -m_{\text{min}} \]  

(26)
Since the ladder operators only change $m$ by one unit

$$m_{\text{max}} - m_{\text{min}} = 2j$$  \hspace{1cm} (27)$$

where $j$ is a positive integer or half-integer.

Combining eq (26) and (27), we find

$$m_{\text{max}} = j \quad \text{and} \quad m_{\text{min}} = -j$$  \hspace{1cm} (28)$$

Substitution of this into eq (25) gives

$$\lambda_j = j(j+1)$$  \hspace{1cm} (29)$$

It can be shown that the proportionality constant is

$$C_\pm = \left[ j(j+1) - m(m \pm 1) \right]^{\frac{1}{2}}$$  \hspace{1cm} (30)$$

In summary, the action of the ladder operators is given by

$$j_\pm |jm\rangle = \left( \hbar \right) \left[ j(j+1) - m(m \pm 1) \right]^{\frac{1}{2}} |j, m \pm 1\rangle$$  \hspace{1cm} (31)$$

and we also have

$$j^2 |jm\rangle = \left( \hbar^2 \right) j(j+1) |jm\rangle$$  \hspace{1cm} (32)$$
Just as a reminder, I've included the factors of $\hat{h}$ explicitly in eq (31) and (32).

The results that we have derived in eq (13) to (32) are general for all angular momenta so it is useful to summarize the matrix elements here:

\[
\begin{align*}
\langle jm | j^2 | j' m' \rangle &= j(j + 1) \delta_{jj'} \delta_{mm'} \\
\langle jm | j_z | j' m' \rangle &= m' \delta_{jj'} \delta_{mm'} \\
\langle jm | j_+ | j' m' \rangle &= \left[ j(j + 1) - m'(m' + 1) \right]^{\frac{1}{2}} \delta_{jj'} \delta_{m,m' + 1} \\
\langle jm | j_- | j' m' \rangle &= \left[ j(j + 1) - m'(m' - 1) \right]^{\frac{1}{2}} \delta_{jj'} \delta_{m,m' - 1} \\
\langle jm | j_x | j' m' \rangle &= \frac{1}{2} j(j + 1) - m'(m' \pm 1) \right]^{\frac{1}{2}} \delta_{jj'} \delta_{m,m' \pm 1} \\
\langle jm | j_y | j' m' \rangle &= \mp i \frac{1}{2} j(j + 1) - m'(m' \pm 1) \right]^{\frac{1}{2}} \delta_{jj'} \delta_{m,m' \pm 1}
\end{align*}
\]

In writing these matrix elements, I have used the operator relationships derived above and the orthonormalization of the eigenfunctions:

\[
\langle jm | j' m' \rangle = \delta_{jj'} \delta_{mm'}
\]
Angular Momentum Operators as Matrices

This section worksheet uses the equations in my notes "Rotational Spectroscopy - A Intro", specifically equations 16, 18, 32, and 33.

Let's find the matrices for $J := 4$

Since all of the operators, Jplus, Jminus, Jx, Jy, and Jz conserve the value of J, we can use the 2J+1 different m states as our basis states:

\[
\begin{align*}
\text{m} & := -J..J \\
\text{m} & = \begin{array}{c}
-4 \\
-3 \\
-2 \\
-1 \\
0 \\
1 \\
2 \\
3 \\
4
\end{array}
\end{align*}
\]

This means that each angular momentum operator will be represented by a $2J+1 \times 2J+1$ matrix where the rows and columns are labelled by the values of m given above.
Define the raising operator $J_{\text{plus}}$ (Eq (33) with the following routine:

$$J_{\text{plus}} := \begin{cases} n \leftarrow 2J + 1 \\ \text{for } r \in \text{ORIGIN..} n - 1 + \text{ORIGIN} \\ \text{for } s \in \text{ORIGIN..} n - 1 + \text{ORIGIN} \\ \text{if } r = s + 1 \\ \quad \text{m} \leftarrow \text{ORIGIN} - J + s \\ \quad r_{a,r,s} \leftarrow \sqrt{J \cdot (J + 1) - m \cdot (m + 1)} \\ \quad (r_{a,r,s} \leftarrow 0) \text{ otherwise} \\ \end{cases}$$

$$\begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 2.828 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 3.742 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 4.243 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 4.472 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 4.472 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 4.243 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 3.742 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 2.828 & 0 & 0 \\ \end{pmatrix} = J_{\text{plus}}$$
Other matrix operators can be constructed by matrix operations:

\[ J_{\text{minus}} := J_{\text{plus}}^T \]

\[
J_{\text{minus}} = \begin{pmatrix}
0 & 2.828 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 3.742 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 4.243 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 4.472 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 4.472 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 4.243 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 3.742 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 2.828 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0
\end{pmatrix}
\]
\[ Jx := \frac{1}{2} \cdot (J\text{plus} + J\text{minus}) \]

\[
\begin{pmatrix}
0 & 1.414 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
1.414 & 0 & 1.871 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1.871 & 0 & 2.121 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 2.121 & 0 & 2.236 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 2.236 & 0 & 2.236 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 2.236 & 0 & 2.121 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 2.121 & 0 & 1.871 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1.871 & 0 & 1.414 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 1.414 & 0
\end{pmatrix}
\]
\[
\mathbf{Jy} := \frac{1}{2 \cdot \sqrt{-1}} (\mathbf{J}_{\text{plus}} + \mathbf{J}_{\text{minus}})
\]

\[
\begin{bmatrix}
0 & -1.414i & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
1.414i & 0 & -1.871i & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1.871i & 0 & -2.121i & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 2.121i & 0 & -2.236i & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 2.236i & 0 & -2.236i & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 2.236i & 0 & -2.121i & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 2.121i & 0 & -1.871i & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1.871i & 0 & -1.414i & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 1.414i & 0 & 0
\end{bmatrix}
\]
We use another short routine to construct $J_z$:

$$J_z := \begin{cases} \overline{n} \leftarrow 2J + 1 \\ \text{for } r \in \text{ORIGIN} .. n - 1 + \text{ORIGIN} \\ \text{for } s \in \text{ORIGIN} .. n - 1 + \text{ORIGIN} \\ \text{if } r = s \\ \quad m \leftarrow \text{ORIGIN} - J + s \\ \quad ra_{r,s} \leftarrow m \\ \quad (ra_{r,s} \leftarrow 0) \quad \text{otherwise} \end{cases}$$

$$J_z = \begin{pmatrix} -4 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -3 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -2 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 2 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 3 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 4 \end{pmatrix}$$
Now, I will use $J_{sq}$ for the J-squared operator:

$$J_{sq} := J_x^2 + J_y^2 + J_z^2$$

$$J_{sq} = \begin{pmatrix}
20 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 20 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 20 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 20 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 20 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 20 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 20 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 20
\end{pmatrix}$$

Now of course, we could have written down the result for $J_{sq}$ directly because $J_{sq}$ has the eigenvalue $J(J+1)$. The above result is just $J(J+1)$ times the identity matrix.

This result, as computed above, illustrates that the matrix for a complex operator can be computed by matrix operations from the elementary angular momentum operators.
3. The spherical harmonics

Eq (31) is enough to give the energy levels when we realize that the rotational Hamiltonian for a diatomic molecule is

\[ H = \frac{\mathbf{j}^2}{2I} \]  \hspace{1cm} (34)

where \( \mathbf{j} \) is specified as the rotational angular momentum and the moment of inertia is

\[ I = \mu r^2 \]  \hspace{1cm} (35)

Therefore the eigenfunctions \( |jm\rangle \) of \( \mathbf{j}^2 \) are also eigenfunctions of \( H \), so we have

\[ H|jm\rangle = \frac{j(j+1)\hbar^2}{2\mu r^2} |jm\rangle \]  \hspace{1cm} (36)

which is the solution to the Schroedinger equation (eq (2)) and give the rotational energy levels.
The functions $|jm\rangle$ are called the spherical harmonics and are often notated $Y_{jm}(\theta, \phi)$. Note that Zare and many other authors use $l$ in place of $j$ when discussing the spherical harmonics. These functions are also the angular parts of the hydrogen atom wavefunctions and are responsible for the characteristic shapes of the $s(l=0)$, $p(l=1)$, $d(l=2)$, etc. orbitals. I have used $j$ because we are concerned with molecular rotations.
The explicit forms of the spherical harmonics are

\[ Y_{jm}(\theta, \phi) = \Theta_{jm}(\theta) \Phi_m(\phi) \]

with

\[ \Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} \exp(i m \phi) \]

and

\[ \Theta_{jm}(\theta) = (-1)^m \left[ \frac{2j + 1}{2} \frac{(j - m)!}{(j + m)!} \right]^\frac{1}{2} P^m_j(\cos \theta) \]

The associated Legendre functions are

\[ P^m_j(\cos \theta) = \sin^m \theta \left[ \frac{d}{d(\cos \theta)} \right]^m P_j(\cos \theta) \]

and are expressed in terms of the ordinary Legendre functions

\[ P_j(\cos \theta) = \frac{1}{2^j j!} \left[ \frac{d}{d(\cos \theta)} \right]^j \left( \cos^2 \theta - 1 \right)^j \]
We will rely mainly on the algebra of the angular momentum operators and seldom refer to the explicit forms of the spherical harmonics. Nonetheless, it instructive to see these expressions and have them available to use when needed.
The nature of the angular momentum states can be best understood in terms of the vector model:

\[ |j| = \sqrt{j(j+1)} \]

\[ \cos \theta = \frac{m}{\sqrt{j(j+1)}} \]
B. Symmetric tops

1. Energy levels

2. Rigid body rotations
   (a) Review of Unitary Transformations
   (b) Generators of Infinesimal Rotations
   (c) The Euler Angles

3. Symmetric top wave functions

4. The action of operators

5. Selection rules and line strengths

C. Asymmetric Tops

1. The moment of inertia tensor

2. Symmetry classification

3. Wavefunctions and energy levels

4. Selection rules
B. Symmetric tops

The principal moments of inertia are given by $I_z = \sum_i m_i \left( x_i^2 + y_i^2 \right)$, etc. where the sum is over the atoms in the molecule. A symmetric top is a body with 2 equal moments of inertia. A 3-fold or higher rotational symmetry axis is a sufficient condition.
Prolate Symmetric Top  
(stick-like)

Oblate Symmetric Top  
(frisbee-like)

\[ I_a(\equiv z) < I_b = I_c \]

\[ I_a = I_b < I_c(\equiv z) \]
1. Energy levels

The rotational Hamiltonian for a rigid body is

\[
H = \frac{J_a^2}{2I_a} + \frac{J_b^2}{2I_b} + \frac{J_c^2}{2I_c}
\]

\[
= AJ_a^2 + BJ_b^2 + CJ_c^2
\]  

(1)

For example consider a prolate top where \(B=C\). We also use the relation

\[
J^2 = J_a^2 + J_b^2 + J_c^2
\]

To rewrite the Hamiltonian

\[
H = AJ_a^2 + BJ_b^2 + BJ_c^2 + BJ_a^2 - BJ_a^2
\]

\[
= BJ^2 + (A - B)J_a^2
\]  

(2)

Now we know that \(J^2\) and \(J_a^2\) commute so we can find eigenfunctions which are simultaneous eigenfunctions of both and that are therefore also eigenfunctions of \(H\):
\[ J^2 |JK\rangle = J(J+1)(\hbar^2) |JK\rangle \]

\[ J_a |JK\rangle = K(\hbar) |JK\rangle \]

\[ H|JK\rangle = \left\{ J(J+1)(\hbar^2) B + K^2 (\hbar^2)(A - B) \right\} |JK\rangle \]

Therefore the quantity within \{\} gives the prolate symmetric rigid rotor energy levels with \( J=0,1,2,... \) and \( K=-J, -J+1, ... , +J \). Note that we use \( K \) rather than \( M \) as before because \( J_a \) represents angular momentum about the molecule-fixed \( z \) axis rather than a space-fixed axis, \( Z \).

\[ K_p = 0 \quad K_p = 1 \quad K_p = 2 \quad K_p = 3 \quad K_p = 4 \]

\[ K_o = 0 \quad K_o = 1 \quad K_o = 2 \quad K_o = 3 \]

Figure 6.29. Energy levels of a prolate and an oblate symmetric top.
2. Rigid body rotations

(a) Review of Unitary Transformations

Qualitatively, a unitary transformation is one which preserve length. Examples are reflections, inversions, and also rotations - hence the relevance here. For example, a unitary transformation might be used to go from a space-fixed coordinate system to a molecule-fixed coordinate system.

Suppose that $\mathbf{U}$ is a unitary operator such that

$$\lvert \psi' \rangle = \mathbf{U} \lvert \psi \rangle$$

(4)

Then we have

$$\langle \psi' \lvert \psi' \rangle = \langle \psi \lvert \mathbf{U}^\dagger \mathbf{U} \lvert \psi \rangle$$

(5)

where $\mathbf{U}^\dagger$ is the transpose conjugate of $\mathbf{U}$. For a unitary transformation, we require that

$$\langle \psi' \lvert \psi' \rangle = \langle \psi \lvert \psi \rangle$$

(6)

so that
\[ U^\dagger U = 1 \] \hspace{1cm} (7)

where \( 1 \) is the identity operation. In other words, the inverse of \( U \) is

\[ U^{-1} = U^\dagger \] \hspace{1cm} (8)

If \( Q \) is an operator corresponding to a quantum mechanical observable, then we have

\[ Q_{ij} = \langle \psi_i | Q | \psi_j \rangle \] \hspace{1cm} (9)

Using eq (7), this can be written as

\[ Q_{ij} = \langle \psi_i | U^\dagger UQU^\dagger U | \psi_j \rangle \]
\[ = \langle \psi'_i | UQU^\dagger | \psi'_j \rangle \]
\[ = Q'_{ij} \] \hspace{1cm} (10)

Therefore, the unitary transformation transforms \( Q \) into

\[ Q' = UQU^\dagger = UQU^{-1} \] \hspace{1cm} (11)
(b) Generators of Infinesimal Rotations

Suppose that a unitary transformation $U$ approaches the identity operator $I$ as some variable $\varepsilon$ approaches 0. Then $U$ may be written as

$$U = I + i\varepsilon S$$  \hspace{1cm} (12)$$

where $\varepsilon$ is an infinitesimal real quantity and $S$ is called the generator of the infinitesimal transformation. Since $U$ is unitary one can show that $S$ is Hermitian, that is $S = S^\dagger$. We can divide $U$ into $n$ even smaller transformations

$$U = [I + i\delta S]^n$$  \hspace{1cm} (13)$$

where $\delta = \varepsilon/n$. We take the limit as $n$ increases

$$U = \lim_{\delta \to 0} [I + i\delta S]^n = \lim_{\delta \to 0} [I + i\frac{\varepsilon}{n} S]^n$$

$$= I + n\left(i\frac{\varepsilon}{n} S\right) + \frac{n(n-1)}{2!}\left(i\frac{\varepsilon}{n} S\right)^2 + \frac{n(n-1)(n-2)}{3!}\left(i\frac{\varepsilon}{n} S\right)^3 + ...$$  \hspace{1cm} (14)$$

$$\approx I + \frac{1}{2!}(i\varepsilon S)^2 + \frac{1}{3!}(i\varepsilon S)^3 + ...$$

$$= \exp(i\varepsilon S)$$
The operators $U$ and $S$ commute since

$$\left[ \exp(i\varepsilon S), S \right] = 0$$

(15)

Therefore, the eigenfunctions of $S$ are also eigenfunctions of $U$, and the eigenvalues of $S$ are unchanged by the transformation $U$. Invariance of the system under the unitary transformation $U$ implies that the observable $S$ is conserved.
Let’s consider the case where $\mathbf{U}$ is a rotation about the $z$ axis by an angle $\phi$:

$$\mathbf{R}_z(\phi|\phi_0) = |\phi'\rangle$$

The transformation which takes the physical system from $\phi_0 \rightarrow \phi_0 + \phi$ is equivalent to moving the coordinate frame in the opposite direction: $\phi_0 \rightarrow \phi' = \phi_0 - \phi$.

A function $f$ transforms as $f(\phi_0) \rightarrow f(\phi_0 - \phi)$. 
Now expand $|\phi'\rangle$ as a Taylor series about the initial state:

$$
|\phi'\rangle = |\phi_0\rangle + (-\phi) \frac{\partial}{\partial \phi} |\phi_0\rangle + \frac{1}{2!} (-\phi)^2 \frac{\partial^2}{\partial \phi^2} |\phi_0\rangle + \ldots
$$

$$
= \left\{ \exp \left( -\phi \frac{\partial}{\partial \phi} \right) \right\} |\phi_0\rangle
$$

Identifying eq (17) with eq (14) with $\epsilon = -\phi$ we find

$$
S = -i \frac{\partial}{\partial \phi} = J_z
$$

that is

$$
R_z = \exp( -i \phi J_z )
$$

This result can be generalized to rotations about any axis. In general, invariance of the system to rotation about a certain axis causes the projection of the angular momentum on that axis to be conserved.
(c) The Euler Angles

Transformation from space-fixed frame $F=(X,Y,Z)$ to molecule-fixed frame $g=(x,y,z)$

\[(X,Y,Z) \rightarrow (x,y,z)\]

- First: $\phi$ about $Z$
- Second: $\theta$ about $N$
- Third: $\chi$ about $z$
(d) Rotations in 3 Dimensions

According to eq (19), we may express the series of Euler rotations as

\[
R(\phi, \theta, \chi) = \exp(-i\chi J_z) \exp(-i\theta J_N) \exp(-i\phi J_Z) \quad (20)
\]

Since these angular momenta are referenced to axes in 3 different frames, it is convenient to use successive applications of eq (11) to transform eq (20) so that all of the angular momenta refer to axes in the same frame.

\[
R(\phi, \theta, \chi) = \exp(-i\phi J_Z) \exp(-i\theta J_Y) \exp(-i\chi J_Z) \quad (21)
\]

Notice now that the operations are applied in reverse order.

See Zare section 3.4 for explicit expressions for the angular momentum operators in both the \(F=(X,Y,Z)\) and \(g=(x,y,z)\) frames.

Since \(R\) commutes with \(J^2\), an Euler rotation acting on a state will conserve the quantum number \(J\). However, the projection on the \(Z\)-axis \(M\) may not be conserved. The result then is a linear combination of \(M\) states:

\[
R(\phi, \theta, \chi)|JM\rangle = \sum_{M'} D^J_{M'M}(\phi, \theta, \chi)|JM'\rangle \quad (22)
\]

with the coefficients.
\[ D_{M'M}^J(\phi, \theta, \chi) = \langle JM' | R(\phi, \theta, \chi) | JM \rangle \]  

(23)

The coefficients for the $2J+1$ values of $M$ and $M'$ form a $(2J+1)$ by $(2J+1)$ matrix. Such matrices are called rotation matrices. The coefficients can be evaluated with the help of eq (21)

\[
D_{M'M}^J(\phi, \theta, \chi) = \langle JM' | R(\phi, \theta, \chi) | JM \rangle \\
= \langle JM' | \exp(-i\phi J_Z) \exp(-i\theta J_Y) \exp(-i\chi J_Z) | JM \rangle \\
= \langle JM' | \exp(-i\phi M') \exp(-i\theta J_Y) \exp(-i\chi M) | JM \rangle \\
= \exp(-i\phi M') \langle JM' | \exp(-i\theta J_Y) | JM \rangle \exp(-i\chi M) \\
= \exp(-i\phi M') d_{M'M}^J(\theta) \exp(-i\chi M)
\]

(24)

The $d_{M'M}^J(\theta)$ are given explicitly by Zare on p 86 and 89.
3. Symmetric top wave functions

We expect the symmetric rotor wave functions to be eigenfunctions of three operators

\[ J^2 |JKM\rangle = J(J+1) |JKM\rangle \]  
\[ J_Z |JKM\rangle = M |JKM\rangle \]  
\[ J_z |JKM\rangle = K |JKM\rangle \]

Examine the explicit forms of the rotation matrix elements with \( M=0 \).

\[ D^{J}_{M'0}(\phi, \theta, \chi) = \exp(-i\phi M') d^{J}_{M'0}(\theta) \]  

With the help of the explicit forms of the \( d^{J}_{M'0}(\theta) \) given on p 89 of Zare, we see that the rotation matrix elements of eq (25) are proportional to the spherical harmonics:

\[ Y_{JM'}(\theta, \phi) = \left( \frac{2J+1}{4\pi} \right)^{1/2} D^{J*}_{M'0}(\phi, \theta, \chi) \]

Similarly if we examine the form of the rotation matrix elements with \( M'=0 \), we find that they are also proportional to the spherical harmonics:

\[ Y_{J,-M}(\theta, \chi) = \left( \frac{2J+1}{4\pi} \right)^{1/2} D^{J}_{0M}(\phi, \theta, \chi) \]
Now eq (29) tells us that the rotation matrix elements obey eq (25) and (26) and eq (30) tells us that they obey eq (25) and (27). Therefore the symmetric rotor wavefunction are proportional to rotation matrix elements:

\[
|JKM\rangle = \left( \frac{2J+1}{8\pi^2} \right)^{\frac{1}{2}} D_{MK}^{J^*}(\phi, \theta, \chi) \quad (31)
\]

where the constant is determined by normalization. For a proof see Zare chapter 3.
4. Selection rules and line strengths

\[ \frac{\partial \mu}{\partial q_i} \]

3-fold axis

perpendicular transition moment
\[ \Delta K = \pm 1 \]
\[ \Delta J = 0, \pm 1 \]

parallel transition moment
\[ \Delta K = 0 \]
\[ \Delta J = 0, \pm 1 \text{ for } K > 0 \]
\[ \Delta J = \pm 1 \text{ only for } K = 0 \]
The selection rules are more complicated for cases with nonzero electronic spin.

Under inversion operation \((X,Y,Z)\Rightarrow(-X,-Y,-Z)\), rotational states are classed as either “+” or “-” according to their symmetry, and we also have the selection rules

\[ + \Leftrightarrow - \quad + \Leftrightarrow + \quad - \Leftrightarrow - \]

The absorption strengths of rotational lines in vibrational bands of symmetric tops are given in Herzberg II (p 421,426) as

\[ I_{JK} \propto A_{JK} \nu g_{JK} \exp\left(\frac{-F(K,J)}{k_B T}\right) \quad (32) \]

where \(\nu\) is the transition frequency

- \(g\) is the degeneracy of the \(JK\) lower state level: \(2J+1\) for \(K\neq0\) and \(2(2J+1)\) for \(K=0\).

- \(F(K,J)\) is the energy (term value) of the lower state level, and \(A_{JK}\) is given below
For parallel bands, we have

\[ \Delta J = +1: \quad A_{JK} = \frac{(J + 1)^2 - K^2}{(J + 1)(2J + 1)} \]

\[ \Delta J = 0: \quad A_{JK} = \frac{K^2}{J(2J + 1)} \]  

\[ (33) \]

\[ \Delta J = -1: \quad A_{JK} = \frac{J^2 - K^2}{J(2J + 1)} \]

and for perpendicular bands, we have

\[ \Delta J = +1: \quad A_{JK} = \frac{(J + 2 \pm K)(J + 1 \pm K)}{(J + 1)(2J + 1)} \]

\[ \Delta J = 0: \quad A_{JK} = \frac{(J + 1 \pm K)(J \mp K)}{J(2J + 1)} \]  

\[ (34) \]

\[ \Delta J = -1: \quad A_{JK} = \frac{(J - 1 \mp K)(J \mp K)}{J(2J + 1)} \]

In eq (34) the upper sign is for \( \Delta K = +1 \) and the lower for \( \Delta K = -1 \). For \( K = 0 \rightarrow 1 \), multiply by 2.
5. Complications

As we saw above, the rotational Hamiltonian

\[
H = \frac{J_a^2}{2I_a} + \frac{J_b^2}{2I_b} + \frac{J_c^2}{2I_c}
\]

\[
= AJ_a^2 + BJ_b^2 + CJ_c^2
\]  (1)

leads, for a prolate symmetric top, to the rotational energy expression

\[
F_v(J,K) = B_v J(J+1) + \left(A_v - B_v\right)K^2
\]  (35)

The subscript \(v\) reminds us that the rotational constants \(A\) and \(B\) will be slightly different for the upper and lower states. Often the vibrational dependence of the rotational constants can be represented as

\[
B_v = B_e - \sum_i \alpha_i^B \left(v_i + \frac{d_i}{2}\right) + \ldots
\]

\[
A_v = A_e - \sum_i \alpha_i^A \left(v_i + \frac{d_i}{2}\right) + \ldots
\]  (36)

where \(i\) labels the molecular vibrations, \(d_i\) is the degeneracy of each, and \(v_i\) is the number of vibrational quanta excited in each. Frequently there is insufficient
information known to use eq (36), so one must be content with deducing just the upper and lower state constants, $A', B'$ and $A'', B''$. Of course for pure rotational transitions the upper and lower constants are the same. Otherwise the transition energies are

$$\Delta E = v_0 + F'(J', K') - F''(J'', K'')$$

(37)

where the upper and lower state quantum numbers are constrained to satisfy the selection rules.
Centrifugal Distortion

Molecules are not completely rigid and therefore may subtly change shape because of rotation. The lowest order centrifugal distortion corrections to $F(J,K)$ have the form

$$-DJ J^2 (J + 1)^2 + DJK J (J + 1) K^2 + DK K^4$$

(38)
Degenerate Vibrations and Vibrational Angular Momentum

The perpendicular vibrations are doubly degenerate and carry one unit of angular momentum

$$\pi_z |JKM v_i l_i \rangle = l_i \xi_i \hbar |JKM v_i l_i \rangle$$  (39)

with $l_i = \pm 1$ for $v_i = 1$ and $0 \leq \xi_i \leq 1$. For a general degenerate vibration one has the rotational Hamiltonian

$$H_{rot} = \frac{(J_x - \pi_x)^2}{2I_x} + \frac{(J_y - \pi_y)^2}{2I_y} + \frac{(J_z - \pi_z)^2}{2I_z}$$  (40)

For symmetric tops only $\pi_z$ is non zero, so we have for the prolate case

$$H_{rot} = B_v J^2 + (A_v - B_v) J_z^2 - 2 A_v \pi_z J_z + \pi_z^2$$  (41)

The last term is normally included in the vibrational part of the Hamiltonian so we get the rotational term values

$$F_v (J, K) = B_v J (J + 1) + (A_v - B_v) K^2 - 2 A_v \xi_i l_i K$$  (42)

The splitting between $l_i = \pm 1$ is called $l$-doubling. For more details see pp 420 ff in Herzberg II or pp 79 ff in Townes and Schawlow.
Advanced Symmetric Rotor References

   This book contains a detailed ranking of a great number of possible terms in the symmetric rotor Hamiltonian.
   QC454 .A443


C. Asymmetric Tops
   1. The moment of inertia tensor
   2. Symmetry classification
   3. Wavefunctions and energy levels
   4. Selection rules
C. Asymmetric Tops

1. The moment of inertia tensor

Assume that the molecule is a rigid body consisting of point masses. The total mass is \( M = \sum_i m_i \).
By definition, in the center of mass frame we have

\[ \sum_i m_i \mathbf{r}_i = 0 \quad (1) \]

The translation from an arbitrary origin to an origin at the center of mass is

\[ \mathbf{R} = \frac{1}{M} \sum_i m_i \bar{\mathbf{r}}_i \quad (2) \]

In the center of mass frame, the angular momentum is

\[ \mathbf{J} = \sum_i \mathbf{r}_i \times \mathbf{p}_i \]

\[ = \sum_i m_i (\mathbf{r}_i \times \mathbf{v}_i) \quad (3) \]

The linear velocity \( \mathbf{v}_i \) is given in terms of the angular velocity \( \omega \) by

\[ \mathbf{v}_i = \omega \times \mathbf{r}_i \quad (4) \]
Combining eq (3) and (4),

\[
\mathbf{J} = \sum_i m_i \left[ \mathbf{r}_i \times (\omega \times \mathbf{r}_i) \right] \\
= \sum_i m_i \left[ \omega r_i^2 - \mathbf{r}_i (\mathbf{r}_i \cdot \omega) \right]
\]

(5)

where the last line makes use of the vector identity

\[
\mathbf{A} \times (\mathbf{B} \times \mathbf{C}) = \mathbf{B}(\mathbf{A} \cdot \mathbf{C}) - \mathbf{C}(\mathbf{A} \cdot \mathbf{B})
\]

(6)

Writing out the vector components of eq (5) explicitly we have

\[
J_x = \left[ \sum_i m_i \left( r_i^2 - x_i^2 \right) \right] \omega_x - \left[ \sum_i m_i x_i y_i \right] \omega_y - \left[ \sum_i m_i x_i z_i \right] \omega_z \\
J_y = -\left[ \sum_i m_i x_i y_i \right] \omega_x + \left[ \sum_i m_i \left( r_i^2 - y_i^2 \right) \right] \omega_y - \left[ \sum_i m_i y_i z_i \right] \omega_z \\
J_z = -\left[ \sum_i m_i x_i z_i \right] \omega_x - \left[ \sum_i m_i y_i z_i \right] \omega_y + \left[ \sum_i m_i \left( r_i^2 - z_i^2 \right) \right] \omega_z
\]

(7)
In matrix notation, this is

\[ \mathbf{J} = \mathbf{I} \cdot \omega \]  \hspace{1cm} (8)

which is

\[
\begin{bmatrix}
J_x \\
J_y \\
J_z
\end{bmatrix} =
\begin{bmatrix}
I_{xx} & I_{xy} & I_{xz} \\
I_{yx} & I_{yy} & I_{yz} \\
I_{zx} & I_{zy} & I_{zz}
\end{bmatrix}
\begin{bmatrix}
\omega_x \\
\omega_y \\
\omega_z
\end{bmatrix}
\]  \hspace{1cm} (9)

where the elements of the moment of inertia tensor \( \mathbf{I} \) are given in eq (7).

Because \( \mathbf{I} \) is symmetric, it is possible to find a new set of molecule-fixed coordinate axes \((a,b,c)\) such that \( \mathbf{I} \) becomes diagonal. The elements \( I_{aa}, I_{bb}, \text{ and } I_{cc} \) of the diagonalized tensor are called the principal moments of inertia and are found by solving

\[
\begin{vmatrix}
I_{xx} - \lambda & I_{xy} & I_{xz} \\
I_{yx} & I_{yy} - \lambda & I_{yz} \\
I_{zx} & I_{zy} & I_{zz} - \lambda
\end{vmatrix} = 0  \hspace{1cm} (10)
\]
Eq (7) becomes

\[
J_a = I_{aa} \omega_a \\
J_b = I_{bb} \omega_b \\
J_c = I_{cc} \omega_c
\]  

(11)

By convention, we choose the labels \(a,b,c\) such that

\[
I_{aa} \leq I_{bb} \leq I_{cc}
\]

(12)

We can distinguish 5 possible cases:

- \(I_{aa} = 0, I_{bb} = I_{cc}\) linear
- \(I_{aa} < I_{bb} = I_{cc}\) prolate symmetric top
- \(I_{aa} = I_{bb} < I_{cc}\) oblate symmetric top
- \(I_{aa} = I_{bb} = I_{cc}\) spherical top
- \(I_{aa} < I_{bb} < I_{cc}\) asymmetric top
The classical expression for the rotational kinetic energy is

\[ T = \frac{1}{2} \sum_i m_i v_i^2 \]

\[ = \frac{1}{2} \sum_i m_i v_i \cdot (\omega \times r_i) \]

\[ = \frac{1}{2} \omega \cdot \sum_i m_i (r_i \times v_i) \]

\[ = \frac{1}{2} \omega \cdot J \]

where the vector identity \( A \cdot (B \times C) = B \cdot (C \times A) \) has been used. In the principal axis system the rotational Hamiltonian becomes

\[ H_{rot} = T = \frac{1}{2} \left( \omega_a J_a + \omega_b J_b + \omega_c J_c \right) \]

\[ = \frac{J_a^2}{2I_{aa}} + \frac{J_b^2}{2I_{bb}} + \frac{J_c^2}{2I_{cc}} \]

\[ = AJ_a^2 + BJ_b^2 + CJ_c^2 \]

where \( A \geq B \geq C \).
For right-handed coordinate systems, there are 3 ways of indentifying the principal axes with the body-fixed coordinates $x,y,z$:

<table>
<thead>
<tr>
<th>Representation</th>
<th>$I_r$</th>
<th>$II_r$</th>
<th>$III_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x$</td>
<td>$b$</td>
<td>$c$</td>
<td>$a$</td>
</tr>
<tr>
<td>$y$</td>
<td>$c$</td>
<td>$a$</td>
<td>$b$</td>
</tr>
<tr>
<td>$z$</td>
<td>$a$</td>
<td>$b$</td>
<td>$c$</td>
</tr>
</tbody>
</table>

$I_r$ is most natural for near prolate asymmetric tops which is the most common case. There are 3 corresponding representations which are left-handed; $III_l$ is frequently used for near-oblate tops.
2. Symmetry classification

Since no two of the rotational constants are equal for an asymmetric top, we can no longer use the simple shortcut to the eigenvalues that we did for the symmetric rotor. In particular, the projection of \( J \) on a molecule-fixed axis is no longer a rigorous quantum number. However, \( J \), the total angular momentum, and \( M \), its projection on a space-fixed axis are still good quantum numbers. Therefore we can write the asymmetric rotor wavefunctions as a linear combination of symmetric rotor functions:

\[
\Psi_{JM}(\phi, \theta, \chi) = \sum_K A_K |J K M\rangle
\]  

(15)

Therefore solving the Schrödinger equation \( H_{rot} \Psi = E \Psi \) is reduced to diagonalizing a \( (2J+1) \times (2J+1) \) matrix with elements

\[
H_{K',K} = \langle JK'M|H_{rot}|JKM\rangle
\]  

(16)

which are given by

\[
H_{KK} = \frac{1}{2}(B + C)\left[ J(J+1) - K^2 \right] + AK^2
\]

\[
K_{K,K \pm 2} = \frac{1}{4}(B - C)\left[ J(J+1) - K(K \pm 1) \right]^{\frac{1}{2}} \left[ J(J+1) - (K \pm 1)(K \pm 2) \right]^{\frac{1}{2}}
\]  

(17)
All of the information about the molecule is contained in the principal moments of inertia as indicated in eq (14). From the form of the diagonal moments of inertia in eq (7), one can see that these diagonal moments and remain unchanged if the principal axes are rotated by 180° about the a-axis. For this operation \( a \rightarrow a \), \( b \rightarrow -b \) and \( c \rightarrow -c \). Since in the principal axis system, only the diagonal elements of the moment of inertia tensor are non-zero, the whole Hamiltonian remains unchanged. Likewise, rotations by 180° about the b and c axes also leave the Hamiltonian invariant. These 3 operations, plus the identity operation form a group of 4 operations which commute with the Hamiltonian. Let \( C_{2a} \) be one of these operations. The Schrödinger equation \( H\Psi = E\Psi \) transforms to

\[
H(C_{2a}\Psi) = C_{2a}(H\Psi) = C_{2a}(E\Psi) = E(C_{2a}\Psi)
\]

So \( C_{2a}\Psi \) is also an eigenfunction of \( H \) with the same eigenvalue \( E \) as \( \Psi \). For nondegenerate eigenvalues, this means \( C_{2a}\Psi \propto \Psi \). This, combined with the normalization of both \( \Psi \) and \( C_{2a}\Psi \) implies that

\[
|\Psi|^2 = |C_{2a}\Psi|^2
\]

that is, that

\[
C_{2a}\Psi = \pm \Psi
\]

This means that the wavefunction transforms to plus or minus itself under each of the symmetry operations.
These results are summarized in what is called a group character table:

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Group Operations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E</td>
</tr>
<tr>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>B(_1)</td>
<td>B(_c)</td>
</tr>
<tr>
<td>B(_2)</td>
<td>B(_b)</td>
</tr>
<tr>
<td>B(_3)</td>
<td>B(_a)</td>
</tr>
</tbody>
</table>

The group is sometimes called the Viergruppe (V). In group theory, the symmetry labels refer to irreducible representations.
Since there are 4 distinct symmetries of wavefunctions, it should be possible to choose basis functions which transform according to these irreducible representations. Eq (17) gives a clue as to how to go about this. Since the off-diagonal terms relate only \( K' = K \pm 2 \), the even \( K \)'s couple only to even \( K \)'s and odd \( K \)'s only to odd \( K \)'s. This separation into even (E) and odd (O) \( K \) is the first transformation that we applied in the homework. It can be shown from the form of the symmetric rotor wavefunctions that the remaining transformation is accomplished by taking the “+” and “-” combinations of states with the same \( |K| \):

\[
|J K M s\rangle = \frac{1}{\sqrt{2}} \left[ |J K M \rangle + (-1)^s |J, -K, M\rangle \right]
\] (21)

\[
|J 0 M s\rangle = |J 0 M\rangle
\]

This is the Wang basis with \( s = 0,1 \) and now \( K \geq 0 \).

<table>
<thead>
<tr>
<th>Bloc ( k )</th>
<th>( K )</th>
<th>( s )</th>
<th>( J ) ( \text{even} )</th>
<th>( J ) ( \text{odd} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>E(^+)</td>
<td>Even</td>
<td>0</td>
<td>A</td>
<td>B(_z)</td>
</tr>
<tr>
<td>E(^-)</td>
<td>Even</td>
<td>1</td>
<td>B(_z)</td>
<td>A</td>
</tr>
<tr>
<td>O(^+)</td>
<td>Odd</td>
<td>0</td>
<td>B(_x)</td>
<td>B(_y)</td>
</tr>
<tr>
<td>O(^-)</td>
<td>Odd</td>
<td>1</td>
<td>B(_y)</td>
<td>B(_x)</td>
</tr>
</tbody>
</table>
3. Wavefunctions and energy levels

For each $J$, there are $2J+1$ asymmetric rotor functions, each of which is a linear combination of the symmetric rotor functions. We need some consistent way of labelling these. Ray’s asymmetry parameter is defined as

$$\kappa \equiv \frac{2B - A - C}{A - C}$$  \hspace{1cm} (22)

We find that for a prolate top ($B=C$), $\kappa=-1$, and for an oblate top ($A=B$), $\kappa=+1$. For asymmetric rotors, $\kappa$ lies between these limits.

The limiting $K$ as $\kappa \to -1$ is labelled $K_{-1}$; limiting $K$ as $\kappa \to +1$ is called $K_1$. Any asymmetric rotor state can be identified by $J$ and these two limiting values of $K$:

$$JK_{-1}K_1$$

An alternative labelling is $J_\tau$ where $\tau \equiv K_{-1} - K_1$. This results in values of $\tau$ ranging from $\tau=-J$, $-J+1$, ..., $+J$ which orders the asymmetric rotor states from lowest to highest energies respectively.
Figure 6.33. Prolate–oblate correlation diagram useful for labeling asymmetric top levels.

\[
K_{-1} = K_a = K_p = K_{\text{prolate}}
\]

\[
K_{+1} = K_c = K_o = K_{\text{oblate}}
\]
The symmetries are determined by whether $K_{-1}$ and $K_1$ are even ($e$) or odd ($o$) in the various combinations:

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>$K_{-1}$ $K_1$</th>
<th>E</th>
<th>$C_{2c}$</th>
<th>$C_{2b}$</th>
<th>$C_{2a}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>ee</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$B_c$</td>
<td>oe</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_b$</td>
<td>oo</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_a$</td>
<td>eo</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

Remember that $a,b,c$ can be identified with the $x,y,z$ axes in several different ways.

Notice that for $K>0$, the states become doubly degenerate in the symmetric rotor limit. The splitting of the degenerate pairs for slightly asymmetric rotors is called asymmetry splitting. The splitting is strongest for $K=1$ because these states are directly coupled by the $\Delta K=\pm2$ matrix elements. As $K$ increases, more and more stages of coupling are requires and so the asymmetry splitting decreases rapidly with $K$. From eq (17) one can see that the asymmetry splitting increases approximately linearly with $J$ and is determined by $(B-C)/2$. Since the split pair are equally intense, this produces a very characteristic pattern in molecular spectra which is a great help with assignments.
Asymmetric rotor example spectrum:

\[ \nu_6 \text{ CH stretch band of jet-cooled CF}_2\text{Cl}_2 \]
In Townes and Schawlow (pp 83-89 and 522-526), expansions are given for the energy levels relative to either symmetric rotor limit in terms of the asymmetry parameter $b=b_p$ or $b_o$:

$$b_p = \frac{C - B}{2A - B - C} = \frac{\kappa + 1}{\kappa - 3}$$

$$b_o = \frac{A - B}{2C - B - A} = \frac{\kappa - 1}{\kappa + 3}$$

These “$b$” parameters are zero in the respective symmetric top limits and increase in absolute value as one moves away from that limit. For a near-prolate asymmetric rotor the energies are given by

$$F(J, K_{-1}, K_1) = \frac{B + C}{2} J(J + 1) + \left( A - \frac{B + C}{2} \right) w$$

$$w = K_{-1}^2 + c_1 b_p + c_2 b_p^2 + c_1 b_p^3 + ...$$

where the constants $c_0, c_1, \text{etc}$, depend on $J, K_{-1}, \text{and} K_1$ and are tabulated for $J$ up to 12 in Townes and Schawlow (pp 522-526). From these constants one can see that for $K_{-1}=1$, the asymmetry splitting increases linearly in $b_p$; for $K_{-1}=2$, it increases as $b_p^2$. A similar expansion applies in the near oblate case. A general expression for the asymmetry splitting is
\[ \Delta w = \frac{b^K (J + K)!}{8^{K-1} (J - K)! [(K - 1)!]^2} \]  

(25)

where \( b \) and \( K \) have the appropriate prolate or oblate values.

Asymmetry splittings as represented in Fig. 4-2 on p 87 of Townes and Schawlow
4. Selection rules

The transition moment $\mu$ is resolved along the 3 principal axes, $a, b, \text{ and } c$. For pure rotational (microwave) spectroscopy, $\mu$ is the permanent dipole moment; for infrared spectroscopy, $\mu$ is the derivative of the dipole moment relative to a vibrational coordinate; for electronic spectroscopy, $\mu$ is the change in the dipole moment on electronic excitation.

$G$ represents one of the space-fixed axes $X, Y, \text{ or } Z$ along which the exciting light might be polarized.
The rotational part of the transition moment is a matrix element of the direction cosines and has the form

$$\langle \mu_a \rangle = \langle J'' K''_1 K''_1 M'' | \cos (aG) | J' K'_{-1} K'_{1} M' \rangle$$  \hspace{1cm} (26)$$

Remember that the asymmetric rotor functions $| J K_{-1} K_1 M \rangle$ are linear combinations of the symmetric rotor functions and in general must be determined by numerical diagonalization of the rotational Hamiltonian. Since there are 3 principal axes $a,b,c$ and 3 space-fixed axes $X,Y,Z$, there are 9 angles between various pairs of these axes. The cosines of these angles are called direction cosines.

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} c \phi c \theta c \chi - s \phi s \chi & c \phi c \theta s \chi - s \phi c \chi & c \phi s \theta \\ s \phi c \theta c \chi + c \phi s \chi & s \phi c \theta s \chi + c \phi c \chi & s \phi s \theta \\ - s \theta c \chi & s \theta s \chi & c \theta \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$  \hspace{1cm} (27)$$

Here $c = \cos$ and $s = \sin$ and $\{x,y,z\}$ are identified with $\{a,b,c\}$ according to one of the 6 possible representations.
Eq (26) gives the selection rules:

<table>
<thead>
<tr>
<th>Transition Dipole</th>
<th>Selection Rules</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_a$</td>
<td>$ee \Leftrightarrow eo$</td>
</tr>
<tr>
<td></td>
<td>$oo \Leftrightarrow oe$</td>
</tr>
<tr>
<td>$\mu_b$</td>
<td>$ee \Leftrightarrow oo$</td>
</tr>
<tr>
<td></td>
<td>$eo \Leftrightarrow oe$</td>
</tr>
<tr>
<td>$\mu_c$</td>
<td>$ee \Leftrightarrow oe$</td>
</tr>
<tr>
<td></td>
<td>$oo \Leftrightarrow eo$</td>
</tr>
</tbody>
</table>

For bands with more than one transition dipole component, the selection rules for all non-zero dipole components apply; the result is a *hybrid* band.

Line strengths are tabulated in Appendix V of Townes and Schawlow.
For molecules which are near-symmetric rotors, the selection rules and line strengths are approximately those of the symmetric rotor.

<table>
<thead>
<tr>
<th>“Symmetric Rotor” Subbranches</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>a and c subbranches</strong></td>
<td></td>
</tr>
<tr>
<td>Prolate and Oblate</td>
<td></td>
</tr>
<tr>
<td>( cQ_{1,0} )</td>
<td>( cQ_{-1,0} )</td>
</tr>
<tr>
<td>( cR_{1,0} )</td>
<td>( cP_{-1,0} )</td>
</tr>
<tr>
<td>Prolate only (c)</td>
<td>Oblate only (a)</td>
</tr>
<tr>
<td>( cQ_{1,2} )</td>
<td>( cQ_{1,-2} )</td>
</tr>
<tr>
<td>( cR_{1,2} )</td>
<td>( cP_{1,-2} )</td>
</tr>
<tr>
<td><strong>b subbranches</strong></td>
<td></td>
</tr>
<tr>
<td>Prolate only</td>
<td>Oblate only</td>
</tr>
<tr>
<td>( bQ_{-1,1} )</td>
<td>( bQ_{1,-1} )</td>
</tr>
<tr>
<td>( bR_{1,1} )</td>
<td>( bP_{-1,1} )</td>
</tr>
</tbody>
</table>

Key:

- superscript = type of branch
  - P, Q, R ⇒ ΔJ= -1, 0, +1
- 1\(^{\text{st}}\) subscript = ΔK\(_{-1}\)
- 2\(^{\text{nd}}\) subscript = ΔK\(_{1}\)

This table appears in Townes and Schawlow p 100, but the **bold-faced** \(b\)-type entries are printed incorrectly there.
C.22

First-order Forbidden Subbranches

<table>
<thead>
<tr>
<th>$a$ and $c$ subbranches</th>
<th>$aQ_{2,-3}$</th>
<th>$aQ_{-2,3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$cQ_{-3,2}$</td>
<td>$cQ_{3,-2}$</td>
<td>$aQ_{2,-3}$</td>
</tr>
<tr>
<td>$cQ_{-3,4}$</td>
<td>$cQ_{3,-4}$</td>
<td>$aQ_{4,-3}$</td>
</tr>
<tr>
<td>$cR_{3,-2}$</td>
<td>$cP_{-3,2}$</td>
<td>$aR_{-2,3}$</td>
</tr>
<tr>
<td>$cR_{-3,4}$</td>
<td>$cP_{3,-4}$</td>
<td>$aR_{4,-3}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$b$ subbranches</th>
<th>$bQ_{3,-3}$</th>
<th>$bQ_{-3,3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$bQ_{-3,3}$</td>
<td>$bQ_{3,-3}$</td>
<td>$bQ_{3,-3}$</td>
</tr>
<tr>
<td>$bR_{-3,3}$</td>
<td>$bP_{-3,3}$</td>
<td>$bP_{-3,3}$</td>
</tr>
<tr>
<td>$bR_{-3,5}$</td>
<td>$bP_{3,-5}$</td>
<td>$bR_{5,-3}$</td>
</tr>
<tr>
<td></td>
<td>$bP_{-5,3}$</td>
<td></td>
</tr>
</tbody>
</table>

There are also 2\textsuperscript{nd} and higher order forbidden subbranches which will be correspondingly weaker for near-symmetric tops. This table was just copied from Townes and Schawlow p 100 so beware of possible mistakes! A comprehensive list of transitions and their intensities is given in Appendix V of Townes and Schawlow and I have not yet found any mistakes there.
C5. Centrifugal Distortion

A. Introduction

There are two famous treatments of centrifugal distortion in asymmetric rotors. The first by E. Bright Wilson\textsuperscript{1} was plagued by initially unsuspected redundancies in the centrifugal constants. Watson\textsuperscript{2} showed how such redundancies arose and how the rotational Hamiltonian could be reduced to contain fewer centrifugal distortion coefficients which were then uniquely determinable.

The Wilson Hamiltonian has been extensively used in the literature, but now the Watson Hamiltonian is now more common. The Wilson Hamiltonian uses quartric centrifugal constants notated in the form $\tau_{\alpha\beta\gamma\delta}$. There are 6 such quartic constants of which one is redundant. Likewise in the Watson Hamiltonian there are 6 quartic constants which are reduced to 5 by the $A$-reduction ("A" for asymmetric) or the $S$-reduction ("S" for symmetric). Remember that we still need to keep track of the representation $I_r \ldots III_l$ depending on how $(a,b,c)$ are identified with $(x,y,z)$. There are many notations and subtle variations in the Hamiltonian in the literature; however, these are some of the most significant distinctions to be recognized. Sadly enough, it is sometimes easier to refit the experimental transition frequencies than it is to reproduce a calculation a published Hamiltonian.


Watson begins with a treatment of rigid asymmetric rotors that is very similar to the one in Zare’s book. He uses angular momenta referenced to the molecule-fixed frame and notes the anomalous commutation relationships. The matrix elements of $J_\pm$ given in his eq (4) are the same as eq 3.49 of Zare.
Physically, centrifugal distortion arises from the distortion of the shape of a molecule by its rotational motion. When there are soft large amplitude vibrations, such as a low-barrier torsions, these motions must be treated together with rotation. The result is a very complicated Hamiltonian such as for methanol where the Hamiltonian includes expansions in the Fourier terms in the torsional potential and the torsional angular momentum, as well as in the rotational angular momenta. For the water dimer, large basis set quantum calculations are necessary to find the rovibrational eigenstates.

For molecules where the non-rigid behavior is not too severe, the Hamiltonian can be written as an expansion in the angular momentum operators. A general power series expansion contains terms like

\[ J_x J_z J_x J_y \]  

where there may be any number of \( J \)'s and the \( x,y,z \)'s may be in any combination and in any order.

With the aid of the commutation relationships, the Hamiltonian may be rearranged into a standard form

\[ H_{rot} = \sum_{pqr} h_{pqr} \left( J_x^p J_y^q J_z^r + J_z^r J_y^q J_x^p \right) \]

where \( p,q,r \) are integers and the coefficients may be real or complex.
Now $H_{rot}$ must be Hermitian

$$H_{rot} = H_{rot}^\dagger$$  \hspace{1cm} (3)

and it must be invariant under time reversal, $T$,

$$H_{rot} = T H_{rot} T^{-1}$$  \hspace{1cm} (4)

Using

$$J_\dagger = J$$

$$T J T^{-1} = -J$$  \hspace{1cm} (5)

$$h_{pqr}^\dagger = Th_{pqr} T^{-1} = h_{pqr}^*$$

one finds that the terms in eq (2) with $p+q+r=$odd change sign with the combined effects of Hermitian conjugation and time reversal. Therefore coefficients of the odd powers of $J$ must be zero. Either eq (3) or (4) is enough to show that the coefficients in the remaining terms are real.
The allowed terms in the Hamiltonian can be categorized into orders which are the even powers of \( J \). There are 6 second order terms which have coefficients \( 1/2I_{xy} \) given by the 6 elements of the moment of inertia tensor. We have already seen that these can be reduced to the 3 principal moments of inertia by a suitable transformation. There are as well 15 fourth order terms and 28 terms of sixth degree. These will form the quartic and sextic centrifugal distortion constants.

In addition, the Hamiltonian must be totally symmetric in the point group of the molecule. The irreducible representations (symmetry species) of the components of angular momentum \( J \) are tabulated in standard group character tables. The species of the higher powers of \( J \) are generally not tabulated but can be worked out by standard group theoretical methods.
Watson proceeds by first finding the species of the even powers of $J$ in the full rotation-reflection group, $K_h$:

\[
\begin{align*}
\left[ \Gamma(J^2) \right]_{sym} &= S_g + D_g \\
\left[ \Gamma(J^4) \right]_{sym} &= S_g + D_g + G_g \\
\left[ \Gamma(J^6) \right]_{sym} &= S_g + D_g + G_g + I_g
\end{align*}
\]

Even if you have never heard of the rotation reflection group before, these symmetry labels should be familiar as certain of the atomic term symbols. The total angular momentum $J=0,1,2,3,4,5,6,...$ is denoted $S,P,D,F,G,H,I,...$ respectively. The symmetry under inversion in a molecule-fixed frame is denoted $g$ (gerade or even) and $u$ (ungerade or uneven). Don’t confuse $g/u$ with +/- which refers to the symmetry under parity which is inversion relative to a space-fixed axis. Notice that angular momentum labels are symmetry labels.
The rotation-reflection group is the point group of a sphere. All other point groups are subgroups of $K_h$ and the species of $K_h$ can be correlated with the species of particular subgroups. The most complete correlation tables are found in an appendix to Herzberg’s volume III. For example for $C_{3v}$ we have:

<table>
<thead>
<tr>
<th>$K_h$</th>
<th>$C_{3v}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_g$</td>
<td>$A_1$</td>
</tr>
<tr>
<td>$D_g$</td>
<td>$A_1+2E$</td>
</tr>
<tr>
<td>$G_g$</td>
<td>$2A_1+A_2+3E$</td>
</tr>
<tr>
<td>$I_g$</td>
<td>$3A_1+2A_2+4E$</td>
</tr>
</tbody>
</table>

where $A_1$ is the totally symmetric species in $C_{3v}$. Therefore the number of totally symmetric second-order ($J^2$) terms in $C_{3v}$ is two, one from $S_g$, and on from $D_g$. These are the $BJ(J+1)$ term and the $[A-(B+C)/2]K^2$ terms in the rotational energy reexpression for a prolate symmetric rotor such as propyne.

The combinations of angular momentum operators which transform as a particular irreducible representation can be generated mechanically. Michael Tinkham (*Group Theory and Quantum Mechanics*, McGraw-Hill (1964)) calls this procedure the “basis function generating machine”.

C5.7
B. Linear Molecules

For the nondegenerate vibrational states of linear molecules, \( J_z = 0 \) which means that \( H_{rot} \) contains only \( J_x \) and \( J_y \). The species of \((J_x, J_y)\) in \( D_{\infty h} \) is \( \Pi_g \) and the even powers are

\[
\left[ \left( \Pi_g \right)^2 \right]_{sym} = \Sigma_g^+ + \Delta_g \\
\left[ \left( \Pi_g \right)^4 \right]_{sym} = \Sigma_g^+ + \Delta_g + \Gamma_g \\
\left[ \left( \Pi_g \right)^6 \right]_{sym} = \Sigma_g^+ + \Delta_g + \Gamma_g + \Pi_g
\]

In each case the totally symmetric species \( \Sigma_g^+ \) occurs only once, so that there is only a single independent term of each degree. The rotational Hamiltonian becomes

\[
H_{rot} = B_v \left( J_x^2 + J_y^2 \right) + D_v \left( J_x^2 + J_y^2 \right)^2 + H_v \left( J_x^2 + J_y^2 \right)^3 + ... \quad (8)
\]

Just as for \( B_v \), the values of the centrifugal distortion constants \( D_v \) and \( H_v \) depend on the vibrational or vibronic state. Since \( J_z = 0 \) for linear molecules, \( J^2 = J_x^2 + J_y^2 \) and the term values become

\[
F_{rot}(J) = B_v J(J+1) + D_v J^2 (J+1)^2 + H_v J^3 (J+1)^3 + ... \quad (9)
\]
C. Symmetric Tops

Since all of the symmetric top groups are subgroups of $D_{\infty h}$, it is convenient to classify the powers of $\mathbf{J}$ in terms of the species of $D_{\infty h}$. We can use eq (6) and the correlation between $K_h$ and $D_{\infty h}$:

$$
\begin{align*}
\left[ \Gamma(\mathbf{J}^2) \right]_{sym} &= 2 \Sigma_g^+ + \Pi_g + \Delta_g \\
\left[ \Gamma(\mathbf{J}^4) \right]_{sym} &= 3 \Sigma_g^+ + 2 \Pi_g + 2 \Delta_g + \Phi_g + \Gamma_g \\
\left[ \Gamma(\mathbf{J}^6) \right]_{sym} &= 4 \Sigma_g^+ + 3 \Pi_g + 3 \Delta_g + 2 \Phi_g + 2 \Gamma_g + H_g + I_g
\end{align*}
$$

(10)

The $\Sigma_g^+$ species is nondegenerate and resolves into the totally symmetric species in all of the subgroups of $D_{\infty h}$, the minimum number of totally symmetric terms is 2, 3, and 4 for $\mathbf{J}^2$, $\mathbf{J}^4$, and $\mathbf{J}^6$, respectively.
\[ H_{\text{rot}} = B' J^2 + (A' - B') J_z^2 \]
\[ + D' \left( J^2 \right)^2 + D'_{JK} J^2 J_z^2 + D'_{K} J_z^4 \\ + H' \left( J^2 \right)^3 + H'_{JK} \left( J^2 \right)^2 J_z^2 + H'_{K} J^2 J_z^4 + H'_{K} J_z^6 \]
\[ + H_{\text{split}} \]

(11)

Here \( H_{\text{split}} \) comes from terms other than \( \Sigma_g^+ \) in eq (10) that might correlate to totally symmetric species in a particular symmetric top group.
For example, in the groups $C_{3v}$ and $D_3$, $H_{\text{split}}$ becomes

$$H_{\text{split}} = \varepsilon \left[ \left( J_+^3 + J_-^3 \right) J_z + J_z \left( J_+^3 + J_-^3 \right) \right]$$

$$+ \varepsilon_J J^3 \left[ \left( J_+^3 + J_-^3 \right) J_z + J_z \left( J_+^3 + J_-^3 \right) \right]$$

$$+ \varepsilon_K \left[ \left( J_+^3 + J_-^3 \right) J_3^3 + J_z \left( J_+^3 + J_-^3 \right) \right]$$

$$+ h_3' \left( J_+^6 + J_-^6 \right)$$

(12)

Of these 4 terms, all except the last can be removed by a suitable unitary transformation. This procedure will be discussed in more detail in connection with asymmetric rotors. The results of the transformation are

(i) the terms in $\varepsilon$, $\varepsilon_J$, and $\varepsilon_K$ are eliminated, and

(ii) the term in $h_3'$ and all terms in eq (11) remain but the values of the coefficients will be different.

For this reason, the coefficients that survive are shown with primes ('') in eq (11) and (12). The effective coefficients, which will pertain after the transformation, will be unprimed.
D. Asymmetric Tops

1. The Orthorhombic Hamiltonian \((D_{2h})\)

Since all of the asymmetric top groups are subgroups of \(D_{2h}\), it is convenient to classify the powers of \(J\) in terms of the species of \(D_{2h}\). We can use eq (6) and the correlation between \(K_h\) and \(D_{2h}\):

\[
\left[ \Gamma(J^2) \right]_{sym} = 3A_g + B_1g + B_2g + B_3g
\]

\[
\left[ \Gamma(J^4) \right]_{sym} = 6A_g + 3B_1g + 3B_2g + 3B_3g \quad (13)
\]

\[
\left[ \Gamma(J^6) \right]_{sym} = 10A_g + 6B_1g + 6B_2g + 6B_3g
\]

Thus a \(D_{2h}\) molecule has 6 centrifugal terms of fourth degree and 10 of sixth degree. The three terms of second degree are the rigid rotor Hamiltonian that we are used to. These numbers apply in general to the orthorhombic point groups \((C_{2v}, D_2, D_{2h})\). For point groups of lower symmetry, additional terms are allowed, but these can be eliminated by a unitary transformation. Therefore this preliminary reduction to 6 and 10 terms of fourth and sixth order applies to all asymmetric top molecules.
The usual group theoretical procedures can be used to show that powers of the operators \((p, q, \text{ and } r \text{ in eq (2)})\) are all even and \(H_{rot}\) becomes

\[
H_{rot} = B_{200}J^2 + B_{020}J_z^2 + B_{002}\left(J_+^2 + J_-^2\right) \\
+ T_{400}\left(J^2\right)^2 + T_{220}J^2J_z^2 + T_{040}J_z^4 \\
+ \frac{1}{2}\left[T_{202}J^2 + T_{022}J_z^2, J_+^2 + J_-^2\right]_+ + T_{004}\left(J_+^4 + J_-^4\right) \\
+ \Phi_{600}\left(J^2\right)^3 + \Phi_{420}\left(J^2\right)^2J_z^2 + \Phi_{240}J^2J_z^4 + \Phi_{060}J_z^6 \\
+ \frac{1}{2}\left[\Phi_{402}\left(J^2\right)^2 + \Phi_{222}J^2J_z^2 + \Phi_{042}J_z^4, J_+^2 + J_-^2\right]_+ \\
+ \frac{1}{2}\left[\Phi_{204}J^2 + \Phi_{024}J_z^2, J_+^4 + J_-^4\right]_+ + \Phi_{006}\left(J_+^6 + J_-^6\right)
\] (14)

This style in terms of \(J^2, J_z^2\), and \((J_+^2 + J_-^2)\) is called cylindrical tensor notation and the subscripts on the coefficients indicate the powers of the respective operators. There are a variety of notations in the literature and Watson notes some of the differences. The anticommutator \([A,B]_+\) is defined as \(AB+BA\).
2. The Concept of Reduction

In high resolution spectroscopy, the observables are transition frequencies which give information about the rotational energy levels of the molecule. One postulates a Hamiltonian, such as eq (2) or eq (14) and attempts to fit it to the observed energies in order to find the coefficients in that Hamiltonian. Unfortunately one cannot determine these coefficients directly, but we can only compare the eigenvalues of the Hamiltonian to the observed energies. Determination of the Hamiltonian parameters from the eigenvalues is an example of an inverse secular problem. Such problems tend to be indeterminate because the eigenvalues depend only on certain combinations of the parameters in the Hamiltonian. The practical symptom of such an indeterminacy is highly correlated fitted parameters with very large standard errors.

Therefore, we are well advised to focus only on those combinations of parameters that are determinable from rotationally resolved spectra. A Hamiltonian that contains only determinable combinations of parameters is called a reduced Hamiltonian.

The eigenvalues are not changed by a unitary transformation:

\[ \tilde{H}_{\text{rot}} = U^{-1} H_{\text{rot}} U \]  

We can choose \( U \) to eliminate the largest possible number of parameters in the Hamiltonian. An example of such a transformation is the transformation from an arbitrary center-of-mass coordinate system to the principal axis system for the rigid rotor. This eliminates the three
products of inertia and reduces the number of parameters in the rigid rotor Hamiltonian from 6 to 3.
To construct a suitable unitary operator, we can use

$$U = \exp(iS)$$  \hspace{1cm} (16)$$

where $S$ is a hermitian operator called the generator of the transformation. In an analogous way to eq (2), we can construct $S$ as a power series in the components of $\mathbf{J}$.

$$S = \sum_{p+q+r \text{ odd}} s_{pqr} (J_x^p J_y^q J_z^r + J_z^r J_y^q J_x^p)$$  \hspace{1cm} (17)$$

Under time reversal, we want $H$ and therefore $U$ to be invariant which implies that $S$ must change sign. This condition restricts the sum in eq (17) to odd powers of $\mathbf{J}$.

Nonzero terms in eq (17) will be totally symmetric in the point group of the molecule. In the rotation-reflection group $K_h$, the symmetries of the odd powers of $\mathbf{J}$ are

$$\left[ \Gamma(\mathbf{J}) \right] = P_g$$

$$\left[ \Gamma(\mathbf{J}^3) \right]_{\text{sym}} = P_g + F_g$$  \hspace{1cm} (18)$$

$$\left[ \Gamma(\mathbf{J}^5) \right]_{\text{sym}} = P_g + F_g + H_g$$

The number of totally symmetric terms obtained by resolving these into the point group of the molecule gives the number of degrees of freedom we have in selecting $S$ and therefore
the number of terms of the corresponding order in the rotational Hamiltonian which can be eliminated.

In general, each $J^{n-1}$ term in eq (18) allows the elimination of one $J^n$ term in the rotational Hamiltonian. The linear terms (first line of eq (18)) correspond to a simple rotation of the axis system to the principal axis system with the resulting elimination of the products of inertia. Henceforth we assume that this transformation has already been carried out.

If we group terms according to the powers of $J$,

$$H_{rot} = H_2 + H_4 + H_6 + ... \quad (20)$$
$$S = S_3 + S_5 + ... \quad (21)$$

then the transformed Hamiltonian is

$$\tilde{H}_{rot} = \tilde{H}'_2 + \tilde{H}'_4 + \tilde{H}'_6 + ...$$

with

$$\tilde{H}'_2 = H_2$$
$$\tilde{H}'_4 = H_4 + i[H_2, S_3] \quad (22)$$
$$\tilde{H}'_6 = H_6 + i[H_4, S_3] - \frac{1}{2}[H_2, S_3]S_3 + i[H_2, S_5]$$

The commutators will introduce some terms of lower order, but the terms of the same degree can be collected together again.
\[ \tilde{H}_{rot} = \tilde{H}_2 + \tilde{H}_4 + \tilde{H}_6 + ... \]
Asymmetric Rotor Hamiltonian

\(^a\) All terms in eq (13) become totally symmetric in \(C_1\).
\(^b\) \(A_g\) species in eq (13).

In \(D_{2h}\), eq (18) becomes

\[
\begin{align*}
\left[ \Gamma(J) \right] &= B_{1g} + B_{2g} + B_{3g} \\
\left[ \Gamma(J^3) \right]_{\text{sym}} &= A_g + 3B_{1g} + 3B_{2g} + 3B_{3g} \\
\left[ \Gamma(J^5) \right]_{\text{sym}} &= 3A_g + 6B_{1g} + 6B_{2g} + 6B_{3g}
\end{align*}
\] (24)

Note that the number of each of the “B” symmetries is just the same as in eq (13).

\[
\begin{align*}
\left[ \Gamma(J^2) \right]_{\text{sym}} &= 3A_g + B_{1g} + B_{2g} + B_{3g} \\
\left[ \Gamma(J^4) \right]_{\text{sym}} &= 6A_g + 3B_{1g} + 3B_{2g} + 3B_{3g} \\
\left[ \Gamma(J^6) \right]_{\text{sym}} &= 10A_g + 6B_{1g} + 6B_{2g} + 6B_{3g}
\end{align*}
\] (13)
Therefore even if one or more of the “B” species in eq (13) correlates to a totally symmetric species in some less symmetric point group, there is always a corresponding term in eq (24) that can be used to eliminate it.

In eq (24) the linear term gives no $A_g$ species so the $3 \ J^2$ terns in eq (13) cannot be further reduced. However there is one occurrence of $A_g$ in the cubic term so the 6 quartic terms in eq (13) may be reduced to 5. Similarly the three occurrences of $A_g$ in the quintic term may be used to reduce the number of sextic terms in eq (13) from 10 to 7. That is, a total of 4 parameters can be eliminated from the orthorhombic Hamiltonian to achieve a fully reduced form.

The transformation is accomplished by an appropriate choice of 4 coefficients in eq (17). The coefficients in question are $s_{111}, s_{311}, s_{131}, s_{113}$. There are many possible ways of choosing these coefficients to eliminate four of the centrifugal distortion constants in Eq (14), one quartic and three sextic. Below, we will discuss two of the ways, which are commonly referred to as the Watson A reduction and the Watson S reduction.
3. The Asymmetric Top (A) Reduction

Here we choose to eliminate the 4 terms in eq (14) (constants in Table 1) that involve \(|\Delta K| > 2\), that is

\[
\tilde{T}_{004} = \tilde{\Phi}_{204} = \tilde{\Phi}_{024} = \tilde{\Phi}_{006} = 0
\]  

(25)

The advantages of the A reduction are simple tridiagonal matrices and relatively simple expressions for the coefficients. The disadvantage is that it blows up in the symmetric top limit.

The A-reduction Hamiltonian is

\[
\tilde{H}_{rot}^{(A)} = B_x^{(A)} J_x^2 + B_y^{(A)} J_y^2 + B_z^{(A)} J_z^2
\]

\[
-\Delta J \left( J^2 \right)^2 - \Delta K J^2 J_z^2 - \Delta K J_z^4
\]

\[
-\frac{1}{2} \left[ \delta J J^2 + \delta K J_z^2, J_+^2 + J_-^2 \right]_+
\]

\[
+\Phi J \left( J^2 \right)^3 + \Phi_{JK} \left( J^2 \right)^2 J_z^2 + \Phi_{KJ} J^2 J_z^4 + \Phi_K J_z^6
\]

\[
+\frac{1}{2} \left[ \phi J \left( J^2 \right)^2 + \phi_{JK} J^2 J_z^2 + \phi_K J_z^4, J_+^2 + J_-^2 \right]_+
\]

(26)
4. The Symmetric Top (S) Reduction

The S-reduction is accomplished by setting all of the \( J_z \)-dependent terms with \(|\Delta K| > 0 \) equal to zero, that is,

\[
\tilde{T}_{022} = \tilde{\Phi}_{222} = \tilde{\Phi}_{042} = \tilde{\Phi}_{024} = 0
\]  

(27)

The S-reduction can be used for any non-spherical-top molecule; no singularity problem occurs for symmetric tops. It has also been shown that there is less correlation among the centrifugal constants. These benefits come at the expense of more complicated algebraic expressions and more nonzero elements in the Hamiltonian.

The S-reduced Hamiltonian is

\[
\tilde{H}_{\text{rot}}^{(S)} = B_x^{(S)} J_x^2 + B_y^{(S)} J_y^2 + B_z^{(S)} J_z^2 - D_J J^2 - D_{JK} J_z^2 J^2 - D_K J_z^4 - d_1 J^2 (J_+^2 + J_-^2) - d_2 (J_+^4 + J_-^4) + H_J J^2 + H_{JK} J_z^2 J^2 + J_z^4 - KJ J_z^4 + H_K J_z^6 + h_1 (J^2)^2 (J_+^2 + J_-^2) + h_2 J^2 (J_+^4 + J_-^4) + h_3 (J_+^6 + J_-^6)
\]  

(28)
5. Calculations and Applications

For either reduction, the Hamiltonian factors into the same four blocks as for a rigid rotor. The apparently similar constants have different meanings in the A- and S-reductions. See Table 8.16 on p 335 of Gordy and Cook for some relationships between the constants in the two reductions.

There are numerous approximate formulae, sum rules, and perturbation treatments in the literature. Some of these are summarized in Watson’s article. However, with modern computing power, it is usually preferable to diagonalize the full (block-diagonalized) Hamiltonian. Nonetheless, sum rules and approximate expressions can provide a way of checking a calculation. They can also give qualitative relationships that aid in understanding a particular problem. Particularly useful are relationships that apply in the case of a planar molecule (Gordy & Cook, p 368, Table 8.30).

Generally, centrifugal distortion has a minor effect on the pattern of energy levels, but it can sometimes cause certain energy levels to cross causing ambiguities in labelling the resulting states.

For research purposes, it is generally wise to read the literature (or ask colleagues) to find out who has written the best program for a particular type of problem. Herb Pickett’s SPFIT/SPCAT program (http://spec.jpl.nasa.gov/ftp/pub/calpgm/) has a great deal of flexibility for pure rotational spectra, but it requires a significant learning curve. To write a generally usable program and validate its output is a substantial undertaking. Often, several authors have contributed to the writing of existing programs over a period of several years.
In any case, be sure to validate any program you get with a known data set before attempting to analyze a new spectrum.

See also the web resources listed in the syllabus for this course.