Introduction to Rotational Eigenstates and Spectra II

Review:

**Symmetric** rigid quantum rotor analysis of $R(2)$ Hamiltonian $H = B J_x^2 + B J_y^2 + C J_z^2$

Rotational Energy Surfaces (RE or RES) and $R(3) \sim U(2)$ representations

**Asymmetric** rigid quantum rotor analysis of $D_2$ Hamiltonian $H = A J_x^2 + B J_y^2 + C J_z^2$

RES and Multipole $T_q^k$ tensor expansions

Atomic or molecular $R(3)$ $\ell$-level or $2\ell+1$-multiplet splitting

$R(3) \supset D_2$ character analysis of $\ell$-level or $2\ell+1$-multiplet splitting in $D_2$

Detailed angular momentum operator analysis for $J=1-2$ for $D_2$ symmetry

Asymmetric rotor levels and RES plots for high-$J$

**Octahedral** semi-rigid quantum rotor analysis of $O_h$ Hamiltonian $H = B J \cdot J + t_{044} T^{[4]}$

Spherical rotor levels and RES plots of $O_h$ tensor eigenvalues

$R(3) \subset O(3) \supset O_h \supset O$ character analysis of $\ell$-level or $2\ell+1$-multiplet splitting in $O$

$SF_6$ spectral fine structure $P(88)$

$CF_4$ spectral fine structure $P(54)$
Review:

**Symmetric rigid quantum rotor analysis of R(2) Hamiltonian** \( H = B J_x^2 + B J_y^2 + C J_z^2 \)

Rotational Energy Surfaces (RE or RES) and \( R(3) \sim U(2) \) representations

**Asymmetric rigid quantum rotor analysis of D\(_2\) Hamiltonian** \( H = A J_x^2 + B J_y^2 + C J_z^2 \)

RES and Multipole \( T_q^k \) tensor expansions

Atomic or molecular \( R(3) \) \( \ell \)-level or \( 2\ell + 1 \)-multiplet splitting

\( R(3) \supset D_2 \) character analysis of \( \ell \)-level or \( 2\ell + 1 \)-multiplet splitting in \( D_2 \)

Detailed angular momentum operator analysis for \( J = 1-2 \) for \( D_2 \) symmetry

Asymmetric rotor levels and RES plots

**Octahedral semi-rigid quantum rotor analysis of O\(_h\) Hamiltonian** \( H = B \mathbf{J} \cdot \mathbf{J} + t_{044} \mathbf{T}^{[4]} \)

Spherical rotor levels and RES plots of \( O_h \) tensor eigenvalues

\( R(3) \supset O(3) \supset O_h \supset O \) character analysis of \( \ell \)-level or \( 2\ell + 1 \)-multiplet splitting in \( O \)

\( SF_6 \) spectral fine structure

\( CF_4 \) spectral fine structure
Rotational Energy Surfaces (RE or RES) applied to symmetric quantum rotor analysis

Plot Hamiltonian $\mathbf{H} = B \mathbf{J}^2 + (C - B) \mathbf{J}_z^2$ radially as $H(\Theta) = BJ(J + 1) + (C - B)J(J + 1)\cos^2 \Theta$

Conventional notation: $n = K$

$H(\Theta^J_K) = BJ(J + 1) + (C - B)J(J + 1)\cos^2 \Theta^J_K$

$= BJ(J + 1) + (C - B)K^2$

(Here this gives exact quantum eigenvalues!)

**Minimum uncertainty angle**

$\Theta^{10}_{+10} = 17.55^\circ$

**Polar Uncertainty angles**

$\Theta^J_K = \cos^{-1} \frac{K}{\sqrt{J(J + 1)}}$

$\Theta^J_{+10} = 84.53^\circ$

**RE Surface Energy plotted radially**

$\sqrt{J(J + 1)} \sim J + 1/2$

$10.488 \sim 10.5$

**BOD frame $\mathbf{J}$-vector direction for fixed magnitude $|\mathbf{J}|$**

**Fig. 1 p. 730**

*Int. J. Molecular Science 14 (2013)*
$R(3)\sim U(2)$ representations applied to molecular symmetric rotor analysis

$$H_{\text{symmetric top}} = BJ_X^2 + BJ_Y^2 + BJ_Z^2 + (A - B)J_Z^2 = BJ \cdot J + (A - B)J_Z^2$$

Eigensolution equations:

$$H_{\text{symmetric top}} \left| j_{m,n} \right> = BJ \cdot J + (A - B)J_Z^2 \left| j_{m,n} \right>$$

Mock-Mach-Multiplicity:

is $(2j+1)^2$ for each $j$

Even $n=0$ levels are $2j+1$-fold degenerate.
If $n$ is non-zero the degeneracy is $4j+2$. 

Kinetic energy inertial coefficients:

$$B = \frac{1}{2I_X}, C = \frac{1}{2I_Y}, A = \frac{1}{2I_Z}$$

QTforCA Unit 8. Ch. 23 Fig. 23.2.4

QTforCA Unit 8. Ch. 23 Fig. 23.1.3
Review:

**Symmetric rigid quantum rotor analysis of \( R(2) \) Hamiltonian** \( H = B J_x^2 + B J_y^2 + C J_z^2 \)

Rotational Energy Surfaces (RE or RES) and \( R(3) \sim U(2) \) representations

**Asymmetric rigid quantum rotor analysis of \( D_2 \) Hamiltonian** \( H = A J_x^2 + B J_y^2 + C J_z^2 \)

RES and Multipole \( T_q^k \) tensor expansions

Atomic or molecular \( R(3) \) \( \ell \)-level or \( 2\ell + 1 \)-multiplet splitting

\( R(3) \supset D_2 \) character analysis of \( \ell \)-level or \( 2\ell + 1 \)-multiplet splitting in \( D_2 \)

Detailed angular momentum operator analysis for \( J=1-2 \) for \( D_2 \) symmetry

Asymmetric rotor levels and RES plots

**Octahedral semi-rigid quantum rotor analysis of \( O_h \) Hamiltonian** \( H = B J \cdot J + t_{044} T^{[4]} \)

Spherical rotor levels and RES plots of \( O_h \) tensor eigenvalues

\( R(3) \subset O(3) \supset O_h \supset O \) character analysis of \( \ell \)-level or \( 2\ell + 1 \)-multiplet splitting in \( O \)

\( SF_6 \) spectral fine structure

\( CF_4 \) spectral fine structure
RES of symmetric rotor (J=10 Prolate and Oblate)...
... and related RES of asymmetric rotors

Spectra and RES of asymmetric rotors
\[ H = AJ_x^2 + BJ_y^2 + CJ_z^2 \]
for J=1,2,3,...,10 discussed below

How do you predict \( 4A_1 \oplus 3A_2 \oplus 3B_1 \oplus 3B_2 \)? See p. 22.

Note: \( A_1B_1A_2B_2 \) “monodromy”
Review:

**Symmetric rigid quantum rotor analysis of R(2) Hamiltonian** \[ H = B J_x^2 + B J_y^2 + C J_z^2 \]

Rotational Energy Surfaces (RE or RES) and R(3)~U(2) representations

**Asymmetric rigid quantum rotor analysis of D$_2$ Hamiltonian** \[ H = A J_x^2 + B J_y^2 + C J_z^2 \]

RES and Multipole $T_{q,k}$ tensor expansions

Atomic or molecular R(3) $\ell$-level or 2$\ell$+1-multiplet splitting

R(3)$\supset$D$_2$ character analysis of $\ell$-level or 2$\ell$+1-multiplet splitting in D$_2$

Detailed angular momentum operator analysis for J=1-2 for D$_2$ symmetry

Asymmetric rotor levels and RES plots

**Octahedral semi-rigid quantum rotor analysis of O$_h$ Hamiltonian** \[ H = B J \cdot J + t_{044} T^{[4]} \]

Spherical rotor levels and RES plots of O$_h$ tensor eigenvalues

R(3)$\subset$O(3)$\supset$O$_h$$\supset$O character analysis of $\ell$-level or 2$\ell$+1-multiplet splitting in O

SF$_6$ spectral fine structure

CF$_4$ spectral fine structure
RES and Multipole $T_q^k$ tensor expansions

Peeking into BLACK BOX of matrix diagonalization:

$H = \begin{pmatrix} H_{11} & H_{12} & H_{13} \\ H_{21} & H_{22} & H_{23} \\ H_{31} & H_{32} & H_{33} \\ \vdots & \vdots & \vdots \end{pmatrix}$

Plotting $2^k$-pole expansion of $H$ into Fano-Racah tensors

$H = aT_0^0 + bT_1^1 + cT_1^l + ... + dT_2^2 + eT_2^l + ... = \sum c^k_q T_q^k$

Monopole $k=0$ (even)

Dipole $k=1$ (odd)

Quadrupole $k=2$ (even)

Mixed-$k$
**RES and Multipole $\mathbf{T}_q^k$ tensor expansions**

**Momentum 101**
\[ p = m \nu \]
(linear)

**Energy 101**
\[ E = \frac{1}{2} m \nu^2 = p^2 / 2m \]
\[ E = \frac{1}{2} I \omega^2 = J^2 / 2I \]

Simple Rigid Rotor Hamiltonian...

Hamiltonian $H=E$ is energy in terms of momentum

...and its multi-pole expansion...

\[
H = A J_x^2 + B J_y^2 + C J_z^2 + \cdots
\]

\[
\begin{align*}
\left( \frac{A + B + C}{3} \right) & \left( J_x^2 + J_y^2 + J_z^2 \right) + \left( \frac{2C - A - B}{6} \right) \left( 2J_z^2 - J_x^2 - J_y^2 \right) + \left( \frac{A - B}{2} \right) \left( J_x^2 - J_y^2 \right) + \frac{2}{3} \sqrt{2} \left( T_2^{(2)} + T_{-2}^{(2)} \right) \nonumber \\
\end{align*}
\]

(Derivation in preceding Lecture 25)
RES and Multipole $T_q^k$ tensor expansions

$2^k$-pole expansion of an N-by-N matrix $\mathbf{H}$

2-by-2 case: $\mathbf{H} = \begin{pmatrix} A & B-iC \\ B+iC & D \end{pmatrix} = \frac{A+D}{2} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + B \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + C \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} + \frac{A-D}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

$\mathbf{H} = \frac{A+D}{2} \mathbf{1} + B \mathbf{\sigma}_x + C \mathbf{\sigma}_y + \frac{A-D}{2} \mathbf{\sigma}_z$

$U(2)$ generators (spin $J=1/2$)

$\mathbf{u}_+^1 = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$, $\mathbf{u}_-^1 = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$, rank-1 (vector)

$\mathbf{u}_0^0 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$, rank-0 (scalar)
RES and Multipole $T_q^k$ tensor expansions

2$^k$-pole expansion of an N-by-N matrix $H$

2-by-2 case: $H = \begin{pmatrix} A & B-iC \\ B+iC & D \end{pmatrix} = \frac{A+D}{2} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + B \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + C \begin{pmatrix} 0 & i \\ i & 0 \end{pmatrix} + \frac{A-D}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$

= $\frac{A+D}{2} \begin{pmatrix} 1 \\ \end{pmatrix} + B \sigma_x + C \sigma_y + \frac{A-D}{2} \sigma_z$

= $\frac{A+D}{2} T_0^0 + (B-iC) T_1^1 + (B+iC) T_{-1}^1 + \frac{A-D}{2} T_0^1$

= $\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}$

Generalization of U(2) spinor analysis to U(3)$\subset$U(4)$\subset$U(5)...

(Introduced in following Lecture 27)

3-by-3 case: $H = \begin{pmatrix} H_{11} & H_{12} & H_{13} \\ H_{21} & H_{22} & H_{23} \\ H_{31} & H_{32} & H_{33} \end{pmatrix} = B T_0^0 + \ldots + t_2 T_2^2 + \ldots$

U(3) generators (spin $J=1$)

$u_{+2}^2 = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}$
$u_{+1}^2 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$
$u_0^2 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$
$u_{-1}^2 = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}$
$u_{-2}^2 = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}$

$u_{+1}^1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$
$u_0^1 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$
$u_{-1}^1 = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}$

$u_0^0 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$

Mutually commuting diagonal operators
**RES and Multipole $T_q^k$ tensor expansions**

**J-Phase Paths** (Intersection(s) of RE Surface and Energy Sphere) and

**Quantum angular momentum cones**

*in body frame LEFT HAND RULE gives J-phase flow*

Clockwise around a High

Counter Clockwise around a Low

**RE Surface**

Energy plotted radially vs.

BOD frame $J$-vector direction for fixed magnitude $|J|$
\[ J^2 |J_K\rangle = J(J+1) |J_K\rangle \]
\[ J_z |J_K\rangle = K |J_K\rangle \]

*Interpreted “Literally” is:*
\[ \sqrt{J(J+1)} \approx J+1/2 \]

**Quantum Angular Cone Uncertainty Angles**

\[
\cos \Theta_J^K = \frac{K}{\sqrt{J(J+1)}}
\]

For \( J = 3 \),

- \( |J=3\ K=+3\rangle \) \( \Theta_3^3 = 30^\circ \)
- \( |J=3\ K=+2\rangle \) \( \Theta_3^3 = 54.7^\circ \)
- \( |J=3\ K=+1\rangle \) \( \Theta_3^3 = 73.2^\circ \)
- \( |J=3\ K=0\rangle \) \( \Theta_0^3 = 90^\circ \)

\[ \sqrt{J(J+1)} = \sqrt{3}(4) \text{ for } J=3 \]
(S) Semiclassical J-Phase Paths for 
(J=3) Prolate Symmetric Rotor

(J=3) Oblate Symmetric Rotor
Review:

Symmetric rigid quantum rotor analysis of R(2) Hamiltonian $H = BJ_x^2 + BJ_y^2 + CJ_z^2$

Rotational Energy Surfaces (RE or RES) and R(3) ~ U(2) representations

Asymmetric rigid quantum rotor analysis of D₂ Hamiltonian $H = AJ_x^2 + BJ_y^2 + CJ_z^2$

RES and Multipole $T_{q^k}$ tensor expansions

Atomic or molecular R(3) $\ell$-level or 2$\ell$+1-multiplet splitting (Review of D₃)

R(3) ⊆ D₂ character analysis of $\ell$-level or 2$\ell$+1-multiplet splitting in D₂

Detailed angular momentum operator analysis for J=1-2 for D₂ symmetry

Asymmetric rotor levels and RES plots for high-J

Octahedral semi-rigid quantum rotor analysis of Oₜ Hamiltonian $H = BJ \cdot J + t_{044} T^{[4]}$

Spherical rotor levels and RES plots of Oₜ tensor eigenvalues

R(3) ⊆ O(3) ⊆ Oₜ ⊆ O character analysis of $\ell$-level or 2$\ell$+1-multiplet splitting in O

SF₆ spectral fine structure

CF₄ spectral fine structure
Atomic $\ell$-level or $2\ell+1$-multiplet splitting in $D_3$

See p.47-68 of Lect.16 on $D_3$ level splitting

Example: ($\ell=4$)

$$f^{(b)} = \frac{1}{\text{D}_3} \sum_{\kappa \in \text{D}_3} \kappa \chi_k^{(b)} \chi_k^{(\ell)}$$

$\chi^{(\ell)}(2\pi n) = \sin(2\ell+1)n \pi$ is $\ell$-orbital dimension

$\chi^\ell(\Theta) = \sin(\ell + \frac{1}{2})\Theta \sin \frac{\pi}{2}$

$\chi^{A_1}(g) = \begin{cases} 1 & r^1, r^2 \end{cases}$

$\chi^{A_2}(g) = \begin{cases} 1 & i_1, i_2, i_3 \end{cases}$

$\chi^{E_1}(g) = \begin{cases} 2 & -1 \end{cases}$

$\chi^{A_1}(g) = 1 \ 1 \ 1$

$0 \chi^{A_2}(g) = 0 \ 0 \ 0$

$2 \chi^{E_1}(g) = 4 \ -2 \ 0$

$\ell=0$, s-singlet

$2\ell+1=1$

$\ell=1$, p-triplet

$2\ell+1=3$

$\ell=2$, d-quintet

$2\ell+1=5$

$\ell=3$, f-septet

$2\ell+1=7$

$\ell=4$, g-nonet

$2\ell+1=9$

$\ell=5$, h-(11)-let

$2\ell+1=11$

...and $D_3$ character table from p. 24:

$$\mathbf{g} = \{ 1 \}, \{ r^1, r^2 \}, \{ i_1, i_2, i_3 \}$$

$\chi^\mathbf{A_1}(g) = \begin{cases} 1 & 1 \end{cases}$

$\chi^\mathbf{A_2}(g) = \begin{cases} 1 & 1 \end{cases}$

$\chi^\mathbf{E_1}(g) = \begin{cases} 5 & -1 \end{cases}$

$\mathbf{g}^\mathbf{A_1} = 1 \ A_1$

$0 A_1 \oplus A_2 \oplus E_1$

$1 A_1 \oplus 2 E_1$

$\text{trial&error??}$
Review:

Symmetric rigid quantum rotor analysis of $R(2)$ Hamiltonian $H = B J_x^2 + B J_y^2 + C J_z^2$
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Atomic or molecular $R(3)$ $\ell$-level or $2\ell + 1$-multiplet splitting (Review of $D_3$)
$R(3) \supset D_2$ character analysis of $\ell$-level or $2\ell + 1$-multiplet splitting in $D_2$
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$SF_6$ spectral fine structure
$CF_4$ spectral fine structure
Atomic $\ell$-level or $2\ell+1$-multiplet splitting in $D_2$
Here we apply that to $D_2$ level splitting

Example: ($\ell=1$) \[ f^{(b)} = \frac{1}{\sum_{\text{classes}} \kappa_k \chi_k^{(b)} \chi_k^{(\ell)}} = \frac{1}{4} \sum_{g \in D_2} \chi_k^{(b)} \chi_k^{(\ell)} \]

\[ \chi^\ell(\Theta) = \frac{\sin(2\ell+1)\pi}{n} \]

$\ell=0$, s-singlet
$2\ell+1=1$

$\ell=1$, p-triplet
$2\ell+1=3$

$\ell=2$, d-quintet
$2\ell+1=5$

$\ell=3$, f-septet
$2\ell+1=7$

$\ell=4$, g-nonet
$2\ell+1=9$

$\ell=5$, h-(11)-let
$2\ell+1=11$

$\ell=2$ (absent)

$\Omega$ or $R_2$ symmetry

$2\ell+1$ is $\ell$-orbital dimension

$U(2)$ characters
from Lecture 12.6 p.134:

<table>
<thead>
<tr>
<th>$\ell$</th>
<th>$\Theta = 0$</th>
<th>$R_x\pi$</th>
<th>$R_y\pi$</th>
<th>$R_z\pi$</th>
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Atomic $\ell$-level or $2\ell+1$-multiplet splitting in $D_2$

Here we apply that to $D_2$ level splitting

Example: ($\ell=1$)

$$f^{(b)} = \frac{1}{\pi} \sum_{\kappa_k \in D_2} \kappa_k \chi_k^{(b)*} \chi_k^{(\ell)} = \frac{1}{4} \sum_{g \in D_2} \chi_k^{(b)*} \chi_k^{(\ell)}$$

$U(2)$ characters

from Lecture 12.6 p.134:

<table>
<thead>
<tr>
<th>$\chi^{\ell}(\Theta)$</th>
<th>$\Theta = 0$</th>
<th>$R_x \pi$</th>
<th>$R_y \pi$</th>
<th>$R_z \pi$</th>
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</tbody>
</table>

$R(3)$ character

where: $2\ell + 1$ is $\ell$-orbital dimension

$$\chi^{\ell}(\frac{2\pi}{n}) = \frac{\sin((2\ell+1)\pi)}{\sin \frac{n\pi}{n}}$$

$D_2$ characters:

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<th>$D_2$</th>
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<th>$R_y$</th>
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</tr>
<tr>
<td>$B_1$</td>
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<td>1</td>
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<td>-1</td>
</tr>
<tr>
<td>$B_2$</td>
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<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

$\ell = 0$, s-singlet
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$\ell = 5$, h-(11)-let
$2\ell+1 = 11$

...and Lect.13 p.79
Atomic $\ell$-level or $2\ell+1$-multiplet splitting in $D_2$

Here we apply that to $D_2$ level splitting

Example: ($\ell=1$)  \[ f^{(b)} = \frac{1}{\mathcal{O}_{D_2}} \sum_{\kappa_k \in \mathcal{O}_{D_2}} \kappa_k \chi_k^{(b)^*} \chi_k^{(\ell)} = \frac{1}{4} \sum_{g \in D_2} \chi_k^{(b)^*} \chi_k^{(\ell)} \]

$U(2)$ characters
from Lecture 12.6 p.134:

<table>
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<tr>
<th>$\ell$</th>
<th>$\chi^{\ell}(\Theta)$</th>
</tr>
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<td>$\Theta = 0$ $R_x \pi$ $R_y \pi$ $R_z \pi$</td>
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<td>5 1 1 1 1</td>
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<td>3</td>
<td>7 -1 -1 -1</td>
</tr>
<tr>
<td>4</td>
<td>9 1 1 1</td>
</tr>
<tr>
<td>5</td>
<td>11 -1 -1 -1</td>
</tr>
<tr>
<td>6</td>
<td>13 1 1 1</td>
</tr>
<tr>
<td>7</td>
<td>15 -1 -1 -1</td>
</tr>
<tr>
<td>8</td>
<td>17 1 1 1</td>
</tr>
</tbody>
</table>

$R(3)$ character
where: $2\ell+1$

is $\ell$-orbital dimension

<table>
<thead>
<tr>
<th>$\ell$</th>
<th>$f^{(\alpha)}(\ell)$</th>
<th>$f^{A_1}$</th>
<th>$f^{A_2}$</th>
<th>$f^{B_1}$</th>
<th>$f^{B_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td>$1A_1$</td>
</tr>
<tr>
<td>1</td>
<td>$\cdot$</td>
<td>1 1 1 1 1 1</td>
<td>$0A_1 \oplus A_2 \oplus B_1 \oplus B_2$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$D_2$ characters:

<table>
<thead>
<tr>
<th>$\chi^{\ell}(\Theta)$</th>
<th>$\Theta = 0$ $R_x \pi$ $R_y \pi$ $R_z \pi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1 1 1 1</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1 -1 1 -1</td>
</tr>
<tr>
<td>$B_1$</td>
<td>1 1 -1 -1</td>
</tr>
<tr>
<td>$B_2$</td>
<td>1 -1 -1 1</td>
</tr>
</tbody>
</table>

...and Lect.13 p.79

$\chi^{A_1}(g) = 1 1 1 1$
$\chi^{A_2}(g) = 1 -1 1 -1$
$\chi^{B_1}(g) = 1 1 -1 -1$
$\chi^{B_2}(g) = 1 -1 -1 1$

trial&error??
Atomic $\ell$-level or $2\ell+1$-multiplet splitting in $D_2$

Here we apply that to $D_2$ level splitting

Example: ($\ell=1$)

$$f^{(b)} = \frac{1}{oD_2} \sum_{\kappa_k \in D_2 \text{ classes}} \kappa_k \chi_k^{(b)*} \chi_k^{(\ell)} = \frac{1}{4} \sum_{g \in D_2} \chi_k^{(b)*} \chi_k^{(\ell)}$$

and: ($\ell=2$)

$$\ell=0, \text{ s-singlet}$$
$$2\ell+1=1$$
$$\ell=1, \text{ p-triplet}$$
$$2\ell+1=3$$
$$\ell=2, \text{ d-quintet}$$
$$2\ell+1=5$$
$$\ell=3, \text{ f-septet}$$
$$2\ell+1=7$$
$$\ell=4, \text{ g-nonet}$$
$$2\ell+1=9$$
$$\ell=5, \text{ h-(11)-let}$$
$$2\ell+1=11$$

**$U(2)$ characters**

from Lecture 12.6 p.134:

<table>
<thead>
<tr>
<th>$\ell$</th>
<th>$\Theta=0$</th>
<th>$R_x\pi$</th>
<th>$R_y\pi$</th>
<th>$R_z\pi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>4</td>
<td>9</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>11</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>6</td>
<td>13</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>7</td>
<td>15</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>8</td>
<td>17</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

**$R(3)$ character**

where: $2\ell+1$

is $\ell$-orbital dimension

<table>
<thead>
<tr>
<th>$f^{(\alpha)}(\ell)$</th>
<th>$f^{A_1}$</th>
<th>$f^{A_2}$</th>
<th>$f^{B_1}$</th>
<th>$f^{B_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\ell=0$</td>
<td>1</td>
<td>.</td>
<td>.</td>
<td>1 $A_1$</td>
</tr>
<tr>
<td>1</td>
<td>.</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

...and Lect.13 p.79

$D_2$ characters:

<table>
<thead>
<tr>
<th>$D_2$</th>
<th>1</th>
<th>$R_x$</th>
<th>$R_y$</th>
<th>$R_z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_1$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_2$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

| $2\chi^{A_1}(g)$= | 2 | 2 | 2 | 2 |
| $1\chi^{A_2}(g)$= | 1 | -1 | 1 | -1 |
| $1\chi^{B_1}(g)$= | 1 | 1 | -1 | -1 |
| $1\chi^{B_2}(g)$= | 1 | -1 | -1 | 1 |

trial&error??
**Atomic \(l\)-level or \(2l+1\)-multiplet splitting in \(D_2\)**

Here we apply that to \(D_2\) level splitting

**Example:** \((l=1)\)

\[
f^{(b)} = \frac{1}{\text{number of classes}} \sum_{\kappa \in D_2} \chi_{\kappa}^{(b)} \chi_{\kappa}^{(l)} = \frac{1}{4} \sum_{g \in D_2} \chi_{g}^{(b)} \chi_{g}^{(l)}
\]

and: \((l=2)\)

\[
f^{(b)} = \frac{1}{\text{number of classes}} \sum_{\kappa \in D_2} \chi_{\kappa}^{(b)} \chi_{\kappa}^{(l)} = \frac{1}{4} \sum_{g \in D_2} \chi_{g}^{(b)} \chi_{g}^{(l)}
\]

**U(2) characters**

from Lecture 12.6 p.134:

| \(\ell\) | \(\chi^{\ell}(\Theta)\) | \(\Theta = 0\) | \(R_x\) | \(R_y\) | \(R_z\)
|---|---|---|---|---|---|
| 0 | \(\chi^{0}(\Theta)\) | 1 | 1 | 1 | 1
| 1 | \(\chi^{1}(\Theta)\) | 3 | -1 | -1 | -1
| 2 | \(\chi^{2}(\Theta)\) | 5 | 1 | 1 | 1
| 3 | \(\chi^{3}(\Theta)\) | 7 | -1 | -1 | -1
| 4 | \(\chi^{4}(\Theta)\) | 9 | 1 | 1 | 1
| 5 | \(\chi^{5}(\Theta)\) | 11 | -1 | -1 | -1
| 6 | \(\chi^{6}(\Theta)\) | 13 | 1 | 1 | 1
| 7 | \(\chi^{7}(\Theta)\) | 15 | -1 | -1 | -1
| 8 | \(\chi^{8}(\Theta)\) | 17 | 1 | 1 | 1

**R(3) character**

where: \(2\ell+1\)

is \(\ell\)-orbital dimension

**D\(_2\) characters**:

\[
\begin{array}{c|cccc}
D_2 & \text{1} & \text{R}_x & \text{R}_y & \text{R}_z \\
\hline
A_1 & 1 & 1 & 1 & 1 \\
A_2 & 1 & -1 & 1 & -1 \\
B_1 & 1 & 1 & -1 & -1 \\
B_2 & 1 & -1 & -1 & 1 \\
\end{array}
\]

**f-formula better than trial&error**

\[
\begin{array}{cccc}
\frac{1}{4} & 1 & 1 & 1 \\
\frac{1}{4} & 5 & 1 & 1 \\
\end{array} = \frac{5+1+1+1}{4} = 2
\]

\[
\begin{array}{cccc}
\frac{1}{4} & 1 & -1 & 1 \\
\frac{1}{4} & 5 & 1 & 1 \\
\end{array} = \frac{5-1+1-1}{4} = 1
\]

\(\ell=0\), \(s\)-singlet
\(2\ell+1=1\)
\(\ell=1\), \(p\)-triplet
\(2\ell+1=3\)
\(\ell=2\), \(d\)-quintet
\(2\ell+1=5\)
\(\ell=3\), \(f\)-septet
\(2\ell+1=7\)
\(\ell=4\), \(g\)-nonet
\(2\ell+1=9\)
\(\ell=5\), \(h\)-(11)-let
\(2\ell+1=11\)

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\(D_2\) characters:

\[
\begin{array}{c|cccc}
D_2 & \text{1} & \text{R}_x & \text{R}_y & \text{R}_z \\
\hline
A_1 & 1 & 1 & 1 & 1 \\
A_2 & 1 & -1 & 1 & -1 \\
B_1 & 1 & 1 & -1 & -1 \\
B_2 & 1 & -1 & -1 & 1 \\
\end{array}
\]

\(f^{(\alpha)}(\ell)\) | \(f^{A_1}\) | \(f^{A_2}\) | \(f^{B_1}\) | \(f^{B_2}\)
---|---|---|---|---
\(\ell=0\) | 1 | -1 | -1 | -1 | 1
\(\ell=1\) | 1 | 1 | 1 | 1 | 0
\(\ell=2\) | 2 | 1 | 1 | 1 | 2
Atomic $\ell$-level or $2\ell+1$-multiplet splitting in $D_2$

Here we apply that to $D_2$ level splitting

Example: ($\ell=1$)

$$f^{(b)} = \frac{1}{\circ D_2} \sum_{\kappa_k \in D_2} \kappa_k \chi_k^{(b)*} \chi_k^{(\ell)} = \frac{1}{4} \sum \chi_k^{(b)*} \chi_k^{(\ell)}$$

and: ($\ell=2$)

and: ($\ell=3$)

\[\begin{array}{cccc}
\ell=0 & \ell=1 & \ell=2 & \ell=3 \\
1 & 1 & 1 & 1 \\
3 & -1 & -1 & -1 \\
9 & 1 & 1 & 1 \\
11 & -1 & -1 & -1 \\
13 & 1 & 1 & 1 \\
15 & -1 & -1 & -1 \\
17 & 1 & 1 & 1 \\
\end{array}\]

\[\begin{array}{cccc}
1 & 1 & 1 & 1 \\
1 & -1 & 1 & -1 \\
1 & 1 & -1 & -1 \\
1 & -1 & -1 & 1 \\
\end{array}\]

$U(2)$ characters from Lecture 12.6 p.134:

$$\chi^\ell(\Theta) = \frac{\sin(2\ell+1)\pi}{\frac{n}{\sin\frac{\pi}{n}} \frac{2\pi}{\Theta}}$$

where: $2\ell+1$ is $\ell$-orbital dimension

$R(3)$ character

is $\ell$-orbital dimension

\[\begin{array}{c|cccc}
\ell=0 & f^{A_1} & f^{A_2} & f^{B_1} & f^{B_2} \\
1 & 1 & 1 & 1 & 1 \\
2 & 2 & 1 & 1 & 1 \\
3 & 1 & 2 & 2 & 1 \\
4 & 1 & 2 & 2 & 1 \\
5 & 1 & 2 & 2 & 1 \\
6 & 1 & 2 & 2 & 1 \\
\end{array}\]

$f$-formula better than trial&error

\[\begin{array}{cccc}
\frac{1}{4} & 1 & 1 & 1 \\
\frac{7}{4} & -1 & -1 & -1 \\
\frac{1}{4} & 1 & -1 & -1 \\
\frac{7}{4} & -1 & -1 & -1 \\
\end{array}= \frac{7-1-1-1}{4} = 1 \]

\[\frac{1}{4} & 1 & 1 & 1 \\
\frac{7}{4} & -1 & -1 & -1 \\
\frac{1}{4} & 1 & -1 & -1 \\
\frac{7}{4} & -1 & -1 & -1 \\
\end{array}= \frac{7+1-1+1}{4} = 2 \]
Atomic $\ell$-level or $2\ell+1$-multiplet splitting in $D_2$
Here we apply that to $D_2$ level splitting

Example: $(\ell=1)$
\[ f^{(b)} = \frac{1}{\circ_{D_2} \chi_k(b)} \sum_{\kappa \in D_2} \chi_k^{(b)*} \chi_k^{(\ell)} = \frac{1}{4} \sum_{g \in D_2} \chi_k^{(b)*} \chi_k^{(\ell)} \]

and: $(\ell=2)$
\[ f^{(b)} = \frac{1}{\circ_{D_2} \chi_k(b)} \sum_{\kappa \in D_2} \chi_k^{(b)*} \chi_k^{(\ell)} = \frac{1}{4} \sum_{g \in D_2} \chi_k^{(b)*} \chi_k^{(\ell)} \]

and: $(\ell=3)$ etc.

$U(2)$ characters
from Lecture 12.6 p.134:

<table>
<thead>
<tr>
<th>$\chi(\Theta)$</th>
<th>$\Theta = 0$</th>
<th>$R_x \pi$</th>
<th>$R_y \pi$</th>
<th>$R_z \pi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\ell = 0$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>4</td>
<td>9</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>11</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>6</td>
<td>13</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>7</td>
<td>15</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>8</td>
<td>17</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

$R(3)$ character
where: $2\ell+1$ is $\ell$-orbital dimension

\[ \chi^{(2\pi n)}(\Theta) = \frac{\sin((2\ell+1)\pi n)}{n} \]

\[ \chi^{(\ell)}(\Theta) = \frac{\sin((\ell+\frac{1}{2})\Theta)}{\Theta} \]

...and Lect.13 p.79

$D_2$ characters:

<table>
<thead>
<tr>
<th>$D_2$</th>
<th>1</th>
<th>$R_x$</th>
<th>$R_y$</th>
<th>$R_z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_1$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_2$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

\[ f^{(a)}(\ell) \]

\[ f^{A_1} f^{A_2} f^{B_1} f^{B_2} \]

\[ \ell=0, s\text{-singlet} \]
\[ 2\ell+1=1 \]
\[ \ell=1, p\text{-triplet} \]
\[ 2\ell+1=3 \]
\[ \ell=2, d\text{-quintet} \]
\[ 2\ell+1=5 \]
\[ \ell=3, f\text{-septet} \]
\[ 2\ell+1=7 \]
\[ \ell=4, g\text{-nonet} \]
\[ 2\ell+1=9 \]
\[ \ell=5, h\text{-}(11)\text{-let} \]
\[ 2\ell+1=11 \]

...and Lect.13 p.79
Review:

Symmetric rigid quantum rotor analysis of $R(2)$ Hamiltonian $H = B J_x^2 + B J_y^2 + C J_z^2$
Rotational Energy Surfaces (RE or RES) and $R(3) \sim U(2)$ representations

Asymmetric rigid quantum rotor analysis of $D_2$ Hamiltonian $H = A J_x^2 + B J_y^2 + C J_z^2$
RES and Multipole $T_q^k$ tensor expansions
Atomic or molecular $R(3) \ell$-level or $2\ell+1$-multiplet splitting (Review of $D_3$)
$R(3) \supset D_2$ character analysis of $\ell$-level or $2\ell+1$-multiplet splitting in $D_2$
Detailed angular momentum operator analysis for $J=1-2$ for $D_2$ symmetry
Asymmetric rotor levels and RES plots for high-$J$

Octahedral semi-rigid quantum rotor analysis of $O_h$ Hamiltonian $H = B J \cdot J + t_{044} T^{[4]}$
Spherical rotor levels and RES plots of $O_h$ tensor eigenvalues
$R(3) \subset O(3) \supset O_h \supset O$ character analysis of $\ell$-level or $2\ell+1$-multiplet splitting in $O$
$SF_6$ spectral fine structure
$CF_4$ spectral fine structure
Detailed angular momentum operator analysis for $j=1-2$ for $D_2$ symmetry

Formulas for momentum operator matrix elements:

\[ n_{\uparrow} = j + m \quad , \quad n_{\downarrow} = j - m \]

\[
| \frac{j}{m} \rangle = \frac{(a_{\uparrow}^{\dagger})^{j+m} (a_{\downarrow}^{\dagger})^{j-m}}{\sqrt{(j+m)! \sqrt{(j-m)!}}} |0,0\rangle = \frac{|n_{\uparrow}, n_{\downarrow}\rangle}{\sqrt{(n_{\uparrow})! \sqrt{(n_{\downarrow})!}}}
\]

\[ a_{\uparrow}^{\dagger} a_{\downarrow} = J_+ = J_X + iJ_Y \]

\[ a_{\downarrow}^\dagger a_{\uparrow} = J_- = J_X - iJ_Y = J_+^\dagger \]

\[ J_X = \frac{1}{2} [J_+ + J_-] \]

\[ J_Y = -\frac{i}{2} [J_+ - J_-] \]

\[ (\text{From Lecture 24 p. 36}) \]

\[ a_{\uparrow}^\dagger a_{\downarrow} | n_{\uparrow}, n_{\downarrow} \rangle = \sqrt{n_{\uparrow}+1} \sqrt{n_{\downarrow}+1} n_{\uparrow} n_{\downarrow} - 1 \Rightarrow J_+ | j_m \rangle = \sqrt{j+m+1} \sqrt{j-m} \left| \frac{j}{m+1} \right\rangle \]

\[ a_{\downarrow}^\dagger a_{\uparrow} | n_{\uparrow}, n_{\downarrow} \rangle = \sqrt{n_{\uparrow}+1} \sqrt{n_{\downarrow}+1} n_{\uparrow} n_{\downarrow} + 1 \Rightarrow J_- | j_m \rangle = \sqrt{j+m} \sqrt{j-m+1} \left| \frac{j}{m-1} \right\rangle \]
**Detailed angular momentum operator analysis for j=1-2 for D₂ symmetry**

\( j,m,n \) formulas for momentum operator matrix elements:

\[
\langle j, m | n \rangle = \frac{(a^\dagger)^{j+m}(a^\dagger)^{j-m}}{\sqrt{(j+m)! \sqrt{(j-m)!}}} |0,0\rangle = \frac{|n^\uparrow, n^\downarrow\rangle}{\sqrt{(n^\uparrow)! \sqrt{(n^\downarrow)!}}}
\]

\[
a^\dagger \downarrow a^\downarrow = J_+ = J_X + i J_Y
\]

\[
a^\uparrow \downarrow a^\dagger = J_- = J_X - i J_Y = J_+^\dagger
\]

\[
J_X = \frac{1}{2} [J_+ + J_-]
\]

\[
J_Y = -\frac{i}{2} [J_+ - J_-]
\]

LAB matrix elements use the usual atomic formula:

\[
\langle j^m, n^m', n | J, J_X \rangle = D_{m', m}^J \delta_{n', n}
\]

\[
\langle j^m, n^m, n' | J, J_Y \rangle = D_{m', m}^J (i) \delta_{n', n}
\]

\[
\langle j^m, n^m, n' | J, J_Z \rangle = D_{m', m}^J \delta_{n', n}
\]

(From Lecture 24 p. 36)
Detailed angular momentum operator analysis for \( j=1-2 \) for \( D_2 \) symmetry

\( j,m,n \) formulas for momentum operator matrix elements:  
\[
\frac{\langle j \mid m \rangle}{\sqrt{(j+m)!(j-m)!}} = \frac{\langle n_\uparrow, n_\downarrow \rangle}{\sqrt{(n_\uparrow)!\sqrt{(n_\downarrow)!}} \]
\[
\langle j \mid m \rangle = \sqrt{n_\uparrow + 1 \sqrt{n_\downarrow + 1 \ n_\downarrow - 1 \ n_\uparrow + 1}} \]
\[
\langle j \mid m \rangle = \sqrt{n_\uparrow \ n_\uparrow + 1 \ n_\downarrow - 1 \ n_\uparrow + 1} \]
\[
\langle j \mid m \rangle = \sqrt{n_\uparrow \ n_\downarrow + 1 \ n_\uparrow - 1 \ n_\downarrow + 1} \]
\[
\langle j \mid m \rangle = \sqrt{n_\uparrow \ n_\downarrow + 1 \ n_\downarrow - 1 \ n_\uparrow + 1} \]

\( a_\uparrow a_\downarrow = J_+ = J_X + iJ_Y \)
\( a_\downarrow a_\uparrow = J_- = J_X - iJ_Y = J_+^* \)

\( J_X = \frac{1}{2} [J_+ + J_-] \)
\( J_Y = -\frac{i}{2} [J_+ - J_-] \)

LAB matrix elements use the usual atomic formula:

\[
\langle j' \mid m' \mid J_X \mid j \rangle = D_{m',m}^J (J_X) \delta_{n'n'} = \frac{1}{2} \left[ \delta_{m'm+1} \sqrt{(j-m)(j+m+1)} + \delta_{m'm-1} \sqrt{(j+m)(j-m+1)} \right] \delta_{n'n'}
\]
\[
\langle j' \mid m' \mid J_Y \mid j \rangle = D_{m',m}^J (J_Y) \delta_{n'n'} = \frac{-i}{2} \left[ \delta_{m'm+1} \sqrt{(j-m)(j+m+1)} - \delta_{m'm-1} \sqrt{(j+m)(j-m+1)} \right] \delta_{n'n'}
\]
\[
\langle j' \mid m' \mid J_Z \mid j \rangle = D_{m',m}^J (J_Z) \delta_{n'n'} = \delta_{m'm} \delta_{n'n'}
\]

BOD matrix elements are the same after switching \( m \)'s into \( n \)'s and changing sign of \( J_Y \) matrix (*-conjugation)

\[
\langle j' \mid m' \mid J_X \mid j \rangle = \delta_{m'm} D_{n',n}^J (J_X) = \frac{1}{2} \delta_{m'm} \left[ \sqrt{(j-n)(j+n+1)} \delta_{n'n+1} + \sqrt{(j+n)(j-n+1)} \delta_{n'n-1} \right]
\]
\[
\langle j' \mid m' \mid J_Y \mid j \rangle = \delta_{m'm} D_{n',n}^J (J_Y) = \frac{-i}{2} \delta_{m'm} \left[ \sqrt{(j-n)(j+n+1)} \delta_{n'n+1} - \sqrt{(j+n)(j-n+1)} \delta_{n'n-1} \right]
\]
\[
\langle j' \mid m' \mid J_Z \mid j \rangle = \delta_{m'm} D_{n',n}^J (J_Z) = \delta_{m'm} \delta_{n'n}
\]
Hamiltonian matrices for asymmetric rotor Hamiltonian

\[ H = \frac{1}{2} \left( \frac{J^2_x}{I_x} + \frac{J^2_y}{I_y} + \frac{J^2_z}{I_z} \right) = A J^2_x + B J^2_y + C J^2_z \]

First are matrix formulas for BOD $J^2$ components.

\[
\begin{align*}
J^2_x \left| J_{m,n} \right> &= \frac{1}{2} \sqrt{(j-n)(j+n+1)} J \left| J_{m,n+1} \right> \\
&+ \frac{1}{2} \sqrt{(j+n)(j-n+1)} J \left| J_{m,n-1} \right>

&= \frac{1}{4} \sqrt{(j-n)(j+n+1)(j-n-1)(j+n+2)} J \left| J_{m,n+2} \right> \\
&+ \frac{1}{4} \sqrt{(j+n)(j-n+1)(j-n-1)(j+n+2)} J \left| J_{m,n-2} \right>

J^2_y \left| J_{m,n} \right> &= \frac{i}{2} \sqrt{(j-n)(j+n+1)} J \left| J_{m,n+1} \right> \\
&- \frac{i}{2} \sqrt{(j+n)(j-n+1)} J \left| J_{m,n-1} \right>

&= \frac{-1}{4} \sqrt{(j-n)(j+n+1)(j-n-1)(j+n+2)} J \left| J_{m,n+2} \right> \\
&- \frac{1}{4} \sqrt{(j+n)(j-n+1)(j-n-1)(j+n+2)} J \left| J_{m,n-2} \right>

J^2_z \left| J_{m,n} \right> &= n^2 J \left| J_{m,n} \right>

&= \frac{-i}{4} \sqrt{(j-n)(j-n-1)(j+n+1)(j+n+2)} J \left| J_{m,n+2} \right> \\
&+ \frac{i}{4} \sqrt{(j+n)(j+n-1)(j-n+1)(j-n+2)} J \left| J_{m,n-2} \right>

&= (A-B) \left[ \frac{(j+n)(j+n-1)(j+n+1)(j+n+2)}{4} \right] J \left| J_{m,n+2} \right> \\
&+ \left[ (A+B) \frac{j(j+1)-n^2}{2} + Cn^2 \right] J \left| J_{m,n} \right> \\
&+ (A-B) \frac{j(j+n)(j-n+1)(j-n+2)}{4} J \left| J_{m,n-2} \right>
\end{align*}
\]

This gives the rigid asymmetric-top matrix formula for general $A$, $B$, $C$ and $J,n$:

\[
(A J^2_x + B J^2_y + C J^2_z) \left| J_{m,n} \right> = \]

\[
= (A-B) \left[ \frac{(j+n)(j+n-1)(j+n+1)(j+n+2)}{4} \right] J \left| J_{m,n+2} \right> \\
+ \left[ (A+B) \frac{j(j+1)-n^2}{2} + Cn^2 \right] J \left| J_{m,n} \right> \\
+ (A-B) \frac{j(j+n)(j-n+1)(j-n+2)}{4} J \left| J_{m,n-2} \right>
\]
Review:

**Symmetric rigid quantum rotor analysis of** $R(2)$ **Hamiltonian**

\[ H = B J_x^2 + B J_y^2 + C J_z^2 \]

**Rotational Energy Surfaces (RE or RES) and R(3)~U(2) representations**

**Asymmetric rigid quantum rotor analysis of** $D_2$ **Hamiltonian**

\[ H = A J_x^2 + B J_y^2 + C J_z^2 \]

**RES and Multipole $T_q^k$ tensor expansions**

**Atomic or molecular** $R(3)$ **$\ell$-level or** $2\ell+1$-**multiplet splitting (Review of D$_3$)**

**R(3)$\supseteq$D_2$ character analysis of $\ell$-level or $2\ell+1$-**multiplet splitting in $D_2$**

**Detailed angular momentum operator analysis for** $J=1$-$2$ **for** $D_2$ **symmetry**

**Asymmetric rotor levels and RES plots for high-J**

**Octahedral semi-rigid quantum rotor analysis of** $O_h$ **Hamiltonian**

\[ H = B J \cdot J + t_{044} T^{[4]} \]

**Spherical rotor levels and RES plots of** $O_h$ **tensor eigenvalues**

**R(3)$\subset O(3)$\supseteq O_h$\supset O$ **character analysis of $\ell$-level or $2\ell+1$-**multiplet splitting in** $O$

**SF$_6$ spectral fine structure**

**CF$_4$ spectral fine structure**
\((J=1)\)-Matrix for \(A=1, B=2, C=3\).

\[
\begin{align*}
\langle \frac{1}{m,n'} | \mathbf{J}_X | \frac{1}{m,n} \rangle &= \begin{pmatrix}
\cdot & \frac{\sqrt{2}}{2} & \cdot \\
\frac{\sqrt{2}}{2} & \cdot & \frac{\sqrt{2}}{2} \\
\cdot & \frac{\sqrt{2}}{2} & \cdot 
\end{pmatrix}, &
\langle \frac{1}{m,n'} | \mathbf{J}_Y | \frac{1}{m,n} \rangle &= \begin{pmatrix}
\cdot & i\frac{\sqrt{2}}{2} & \cdot \\
-i\frac{\sqrt{2}}{2} & \cdot & i\frac{\sqrt{2}}{2} \\
\cdot & -i\frac{\sqrt{2}}{2} & \cdot 
\end{pmatrix}, &
\langle \frac{1}{m,n'} | \mathbf{J}_Z | \frac{1}{m,n} \rangle &= \begin{pmatrix}
+1 & \cdot & \cdot \\
\cdot & 0 & \cdot \\
\cdot & \cdot & -1 
\end{pmatrix} \\
\langle \frac{1}{m,n'} | \mathbf{J}^2_X | \frac{1}{m,n} \rangle &= \begin{pmatrix}
\frac{1}{2} & \cdot & \frac{1}{2} \\
\cdot & 1 & \cdot \\
\frac{1}{2} & \cdot & \frac{1}{2}
\end{pmatrix}, &
\langle \frac{1}{m,n'} | \mathbf{J}_Y^2 | \frac{1}{m,n} \rangle &= \begin{pmatrix}
\frac{1}{2} & \cdot & -\frac{1}{2} \\
\cdot & 1 & \cdot \\
-\frac{1}{2} & \cdot & \frac{1}{2}
\end{pmatrix}, &
\langle \frac{1}{m,n'} | \mathbf{J}_Z^2 | \frac{1}{m,n} \rangle &= \begin{pmatrix}
+1 & \cdot & \cdot \\
\cdot & 0 & \cdot \\
\cdot & \cdot & +1 
\end{pmatrix}.
\end{align*}
\]
\((J=1)\)-Matrix for \(A=1, B=2, C=3\).

\[
\langle \frac{1}{m,n'} | \mathbf{J} \times_1 | \frac{1}{m,n} \rangle = \begin{pmatrix}
\frac{\sqrt{2}}{2} & \cdot & \frac{\sqrt{2}}{2} \\
\frac{\sqrt{2}}{2} & \cdot & \frac{\sqrt{2}}{2} \\
\frac{\sqrt{2}}{2} & \cdot & \frac{\sqrt{2}}{2}
\end{pmatrix}, \quad \langle \frac{1}{m,n'} | \mathbf{J} \cdot_1 | \frac{1}{m,n} \rangle = \begin{pmatrix}
\cdot & i\frac{\sqrt{2}}{2} & \cdot \\
-i\frac{\sqrt{2}}{2} & \cdot & i\frac{\sqrt{2}}{2} \\
\cdot & -i\frac{\sqrt{2}}{2} & \cdot
\end{pmatrix}, \quad \langle \frac{1}{m,n'} | \mathbf{J} \cdot_1 | \frac{1}{m,n} \rangle = \begin{pmatrix}
+1 & \cdot & \cdot \\
\cdot & 0 & \cdot \\
\cdot & \cdot & -1
\end{pmatrix}
\]

\[
\langle \frac{1}{m,n'} | \mathbf{J}^2 \times_1 | \frac{1}{m,n} \rangle = \begin{pmatrix}
\frac{1}{2} & \cdot & \frac{1}{2} \\
\cdot & 1 & \cdot \\
\frac{1}{2} & \cdot & \frac{1}{2}
\end{pmatrix}, \quad \langle \frac{1}{m,n'} | \mathbf{J}^2 \cdot_1 | \frac{1}{m,n} \rangle = \begin{pmatrix}
\frac{1}{2} & \cdot & -\frac{1}{2} \\
\cdot & 1 & \cdot \\
-\frac{1}{2} & \cdot & \frac{1}{2}
\end{pmatrix}, \quad \langle \frac{1}{m,n'} | \mathbf{J}^2 \cdot_1 | \frac{1}{m,n} \rangle = \begin{pmatrix}
+1 & \cdot & \cdot \\
\cdot & 0 & \cdot \\
\cdot & \cdot & +1
\end{pmatrix}
\]

\[
\left( AJ^2 \times_1 + BJ^2 \cdot_1 + CJ^2 \cdot_1 \right)^{J=1} = \begin{pmatrix}
\frac{A}{2} + \frac{B}{2} + C & \cdot & \frac{A}{2} - \frac{B}{2} \\
\cdot & A + B & \cdot \\
\frac{A}{2} - \frac{B}{2} & \cdot & \frac{A}{2} + B + C
\end{pmatrix} = \begin{pmatrix}
\frac{1}{2} + \frac{2}{2} + 3 & \cdot & \frac{1}{2} - \frac{2}{2} \\
\cdot & 1 + 2 & \cdot \\
\frac{1}{2} - \frac{2}{2} & \cdot & \frac{1}{2} + \frac{2}{2} + 3
\end{pmatrix} = \begin{pmatrix}
\frac{9}{2} & \cdot & -\frac{1}{2} \\
\cdot & 3 & \cdot \\
-\frac{1}{2} & \cdot & \frac{9}{2}
\end{pmatrix}
\]

\[\begin{array}{c|cccc}
\ell & f^{(\alpha)}(\ell) & f^A & f^B & f^C \\
\hline
\ell = 0 & 1 & \cdot & \cdot & 1A_1 \\
1 & \cdot & 1 & 1 & 1 \quad 0A_1 \oplus A_2 \oplus B_1 \oplus B_2
\end{array}\]
(J=1)-Matrix for A=1, B=2, C=3.

\[ \langle 1_{m,n'} | J_{X}^{2} | 1_{m,n} \rangle = \begin{pmatrix} \cdot & \frac{\sqrt{2}}{2} & \cdot \\ \frac{\sqrt{2}}{2} & \cdot & \frac{\sqrt{2}}{2} \\ \cdot & \frac{\sqrt{2}}{2} & \cdot \end{pmatrix}, \quad \langle 1_{m,n'} | J_{Y}^{2} | 1_{m,n} \rangle = \begin{pmatrix} \cdot & i\frac{\sqrt{2}}{2} & \cdot \\ -i\frac{\sqrt{2}}{2} & \cdot & i\frac{\sqrt{2}}{2} \\ \cdot & -i\frac{\sqrt{2}}{2} & \cdot \end{pmatrix}, \quad \langle 1_{m,n'} | J_{Z}^{2} | 1_{m,n} \rangle = \begin{pmatrix} 1 & \cdot & \cdot \\ \cdot & 0 & \cdot \\ \cdot & \cdot & -1 \end{pmatrix} \]

\[ \langle 1_{m,n'} | J_{X} | 1_{m,n} \rangle = \begin{pmatrix} \frac{1}{2} & \cdot & \frac{1}{2} \\ \cdot & 1 & \cdot \\ \frac{1}{2} & \cdot & \frac{1}{2} \end{pmatrix}, \quad \langle 1_{m,n'} | J_{Y} | 1_{m,n} \rangle = \begin{pmatrix} \frac{1}{2} & \cdot & -\frac{1}{2} \\ \cdot & 1 & \cdot \\ -\frac{1}{2} & \cdot & \frac{1}{2} \end{pmatrix}, \quad \langle 1_{m,n'} | J_{Z} | 1_{m,n} \rangle = \begin{pmatrix} 1 & \cdot & \cdot \\ \cdot & 0 & \cdot \\ \cdot & \cdot & 1 \end{pmatrix} \]

\[ \left( A J_{X}^{2} + B J_{Y}^{2} + C J_{Z}^{2} \right)_{J=1} = \begin{pmatrix} \frac{A+B}{2} + C & \cdot & \frac{A-B}{2} \\ \cdot & A+B & \cdot \\ \frac{A-B}{2} & \cdot & \frac{A+B}{2} + C \end{pmatrix} = \begin{pmatrix} \frac{1}{2} + \frac{3}{2} + 3 & \cdot & \frac{1}{2} - \frac{2}{2} \\ \cdot & 1 + 2 & \cdot \\ \frac{1}{2} - \frac{2}{2} & \cdot & \frac{1}{2} + \frac{3}{2} + 3 \end{pmatrix} = \begin{pmatrix} \frac{9}{2} & \cdot & -\frac{1}{2} \\ \cdot & 3 & \cdot \\ -\frac{1}{2} & \cdot & \frac{9}{2} \end{pmatrix} \]

eigen-values: \quad (B + C = 5, \quad A + B = 3, \quad A + C = 4)

eigen-vectors: \quad \begin{pmatrix} 1/\sqrt{2} & 0 & 1/\sqrt{2} \\ 0 & 1 & 0 \\ -1/\sqrt{2} & 0 & +1/\sqrt{2} \end{pmatrix} \]

\begin{array}{c|cccc}
\ell = 0 & f & A_1 & f & A_2 & f & B_1 & f & B_2 \\
\hline
f^{(\alpha)}(\ell) & 1 & \cdot & \cdot & 1 & \cdot & 1 & 1 & 1 \\
0 & A_1 & \oplus & A_2 & \oplus & B_1 & \oplus & B_2
\end{array}
\((J=1)\)-Matrix for \(A=1, B=2, C=3\).

\[
\begin{pmatrix}
\frac{1}{m,n'} & | & J & | & \frac{1}{m,n} \\
\end{pmatrix} = \begin{pmatrix}
\frac{\sqrt{2}}{2} & \cdot & \frac{\sqrt{2}}{2} \\
\cdot & \frac{\sqrt{2}}{2} & \cdot \\
\cdot & \cdot & \frac{\sqrt{2}}{2} \\
\end{pmatrix}, \quad \begin{pmatrix}
\frac{1}{m,n'} & | & J & | & \frac{1}{m,n} \\
\end{pmatrix} = \begin{pmatrix}
\frac{i\sqrt{2}}{2} & \cdot & \frac{i\sqrt{2}}{2} \\
\cdot & \frac{i\sqrt{2}}{2} & \cdot \\
\cdot & \cdot & \frac{i\sqrt{2}}{2} \\
\end{pmatrix}, \quad \begin{pmatrix}
\frac{1}{m,n'} & | & J & | & \frac{1}{m,n} \\
\end{pmatrix} = \begin{pmatrix}
1 & \cdot & 0 \\
\cdot & \cdot & -1 \\
\end{pmatrix}.
\]

\[
\begin{pmatrix}
\frac{1}{m,n'} & | & J^2 & | & \frac{1}{m,n} \\
\end{pmatrix} = \begin{pmatrix}
\frac{1}{2} & \cdot & \frac{1}{2} \\
\cdot & \frac{1}{2} & \cdot \\
\frac{1}{2} & \cdot & \frac{1}{2} \\
\end{pmatrix}, \quad \begin{pmatrix}
\frac{1}{m,n'} & | & J^2 & | & \frac{1}{m,n} \\
\end{pmatrix} = \begin{pmatrix}
\frac{1}{2} & \cdot & -\frac{1}{2} \\
\cdot & 1 & \cdot \\
-\frac{1}{2} & \cdot & \frac{1}{2} \\
\end{pmatrix}, \quad \begin{pmatrix}
\frac{1}{m,n'} & | & J^2 & | & \frac{1}{m,n} \\
\end{pmatrix} = \begin{pmatrix}
1 & \cdot & 0 \\
\cdot & \cdot & 1 \\
\cdot & \cdot & +1 \\
\end{pmatrix}.
\]

\[
\begin{pmatrix}
A & B \\
\frac{A}{2} & \frac{B}{2} + C \\
\frac{A}{2} & \frac{B}{2} + C \\
\frac{A}{2} & \frac{B}{2} + C \\
\end{pmatrix} = \begin{pmatrix}
\frac{A}{2} + \frac{B}{2} & \frac{A}{2} - \frac{B}{2} \\
\frac{A}{2} + \frac{B}{2} & \frac{A}{2} - \frac{B}{2} \\
\frac{A}{2} + \frac{B}{2} & \frac{A}{2} - \frac{B}{2} \\
\frac{A}{2} + \frac{B}{2} & \frac{A}{2} - \frac{B}{2} \\
\end{pmatrix} = \begin{pmatrix}
\frac{9}{2} & -\frac{1}{2} \\
\frac{9}{2} & -\frac{1}{2} \\
\frac{9}{2} & -\frac{1}{2} \\
\frac{9}{2} & -\frac{1}{2} \\
\end{pmatrix}.
\]

**eigen-values:** \((B + C = 5, \ A + B = 3, \ A + C = 4)\)

\[
\begin{pmatrix}
1 & \sqrt{2} & 0 & 1 & \sqrt{2} \\
0 & 1 & 0 & 0 & 1 & \sqrt{2} \\
-1 & \sqrt{2} & 0 & +1 & \sqrt{2} \\
\end{pmatrix}
\]

**eigen-vectors:**

<table>
<thead>
<tr>
<th>(D_2)</th>
<th>(1)</th>
<th>(R_x)</th>
<th>(R_y)</th>
<th>(R_z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A_1)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>(A_2)</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>(B_1)</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>(B_2)</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(f^{(\alpha)}(\ell))</th>
<th>(f^{A_1})</th>
<th>(f^{A_2})</th>
<th>(f^{B_1})</th>
<th>(f^{B_2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\ell = 0)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

\(1A_1\) \(0A_1 \oplus A_2 \oplus B_1 \oplus B_2\)
\((J=1)\)-Matrix for \(A=1, B=2, C=3\).

\[
\begin{pmatrix}
\frac{\sqrt{2}}{2} & \frac{\sqrt{2}}{2} \\
\frac{\sqrt{2}}{2} & \frac{\sqrt{2}}{2} \\
\frac{\sqrt{2}}{2} & \frac{\sqrt{2}}{2} \\
\end{pmatrix}
\]

\[
\begin{pmatrix}
\frac{i\sqrt{2}}{2} & \frac{\sqrt{2}}{2} \\
-\frac{\sqrt{2}}{2} & \frac{i\sqrt{2}}{2} \\
\frac{\sqrt{2}}{2} & -\frac{\sqrt{2}}{2} \\
\end{pmatrix}
\]

\[
\begin{pmatrix}
+1 & \cdot & \cdot \\
\cdot & 0 & \cdot \\
\cdot & \cdot & -1 \\
\end{pmatrix}
\]

\[
\begin{pmatrix}
\frac{A+B}{2} + C & \cdot & \frac{A-B}{2} \\
\cdot & A+B & \cdot \\
\frac{A-B}{2} & \cdot & \frac{A+B}{2} + C \\
\end{pmatrix}
\]

\[
\begin{pmatrix}
\frac{1}{2} + \frac{3}{2} & \cdot & \frac{1}{2} - \frac{2}{2} \\
\cdot & 1 + 2 & \cdot \\
\frac{1}{2} - \frac{2}{2} & \cdot & \frac{1}{2} + \frac{2}{2} + 3 \\
\end{pmatrix}
\]

\[
\begin{pmatrix}
\frac{9}{2} & \cdot & -\frac{1}{2} \\
\cdot & 3 & \cdot \\
-\frac{1}{2} & \cdot & \frac{9}{2} \\
\end{pmatrix}
\]

eigen-values: \(B+C = 5, \ A+B = 3, \ A+C = 4\)

eigen-vectors:

\[
\begin{pmatrix}
1/\sqrt{2} & 0 & 1/\sqrt{2} \\
0 & 1 & 0 \\
-1/\sqrt{2} & 0 & +1/\sqrt{2} \\
\end{pmatrix}
\]

\(\Psi_z = D_l z_0\)

\(\Psi_y = D_l y_0\)

\(\Psi_x = D_l x_0\)

Body-based \(J=1\)

vector-like eigenfunctions
Review:

Symmetric rigid quantum rotor analysis of $R(2)$ Hamiltonian $H = B J_x^2 + B J_y^2 + C J_z^2$

Rotational Energy Surfaces (RE or RES) and $R(3) \sim U(2)$ representations

Asymmetric rigid quantum rotor analysis of $D_2$ Hamiltonian $H = A J_x^2 + B J_y^2 + C J_z^2$

RES and Multipole $T^k_q$ tensor expansions

Atomic or molecular $R(3)$ $\ell$-level or $2\ell+1$-multiplet splitting (Review of $D_3$

$R(3) \supset D_2$ character analysis of $\ell$-level or $2\ell+1$-multiplet splitting in $D_2$

Detailed angular momentum operator analysis for $J=1$-$2$ for $D_2$ symmetry

Asymmetric rotor levels and RES plots for high-$J$

Octahedral semi-rigid quantum rotor analysis of $O_h$ Hamiltonian $H = B J \cdot J + t_{044} T^{[4]}$

Spherical rotor levels and RES plots of $O_h$ tensor eigenvalues

$R(3) \subset O(3) \supset O_h \supset O$ character analysis of $\ell$-level or $2\ell+1$-multiplet splitting in $O$

$SF_6$ spectral fine structure

$CF_4$ spectral fine structure
\[ (J=2)-\text{Matrix for } A=1, B=2, C=3. \]

\[
\begin{pmatrix}
  (A + B) + 4C & \frac{\sqrt{6}}{2} (A - B) & \cdot & \cdot & \cdot \\
  \cdot & \frac{5}{2} (A + B) + C & \cdot & \frac{3}{2} (A - B) & \cdot \\
  \frac{\sqrt{6}}{2} (A - B) & \cdot & 3(A + B) & \cdot & \frac{\sqrt{6}}{2} (A - B) \\
  \cdot & \frac{3}{2} (A - B) & \cdot & \frac{5}{2} (A + B) + C & \cdot \\
  \cdot & \cdot & \frac{\sqrt{6}}{2} (A - B) & \cdot & (A + B) + 4C
\end{pmatrix}^{J=2} = \begin{pmatrix}
  15 & -\frac{\sqrt{6}}{2} & \cdot & \cdot & \cdot \\
  15 & 2 & -\frac{3}{2} & \cdot & \cdot \\
  -\frac{\sqrt{6}}{2} & 6 & -\frac{\sqrt{6}}{2} & \cdot & \cdot \\
  -3 & \frac{15}{2} & \cdot & \cdot & \cdot \\
  -\frac{\sqrt{6}}{2} & 15 & \cdot & \cdot & \cdot 
\end{pmatrix}
\]

\[ j = 2 \quad \text{Standing } d\text{-Waves} \]

\[
\begin{align*}
  f^{(\alpha)}(\ell) & \quad f^{A_1} & f^{A_2} & f^{B_1} & f^{B_2} \\
  \ell = 0 & & 1 & \cdot & \cdot \\
  1 & & \cdot & 1 & 1 & 1 \\
  2 & & 2 & 1 & 1 & 1 \\
  3 & & 1 & 2 & 2 & 2 \\
  4 & & 3 & 2 & 2 & 2 \\
  5 & & 2 & 3 & 3 & 3 \\
  6 & & 4 & 3 & 3 & 3 \\
  7 & & 3 & 4 & 4 & 4
\end{align*}
\]
\[(J=2)\text{-Matrix for } A=1, B=2, C=3.\]

\[
\begin{pmatrix}
(A + B) + 4C & \sqrt{6} (A - B) & \cdot & \cdot & \cdot \\
\cdot & \frac{5}{2} (A + B) + C & \cdot & \frac{3}{2} (A - B) & \cdot \\
\sqrt{6} (A - B) & \cdot & 3 (A + B) & \cdot & \sqrt{6} (A - B) \\
\cdot & \frac{3}{2} (A - B) & \cdot & \frac{5}{2} (A + B) + C & \cdot \\
\cdot & \cdot & \sqrt{6} (A - B) & \cdot & (A + B) + 4C
\end{pmatrix}^{J=2} = 
\begin{pmatrix}
15 & \frac{-\sqrt{6}}{2} \\
\frac{15}{2} & \frac{-3}{2} \\
\frac{-\sqrt{6}}{2} & 6 & \frac{-\sqrt{6}}{2} \\
\frac{-3}{2} & \frac{15}{2} \\
\frac{-\sqrt{6}}{2} & 15
\end{pmatrix}
\]

Matrix is nearly diagonalized in standing-wave \(D_2\)-symmetry basis

\[
\begin{align*}
|A_1^+\rangle &= \frac{1}{\sqrt{2}} |2^+\rangle + \frac{1}{\sqrt{2}} |2^-\rangle, \\
|B_1^+\rangle &= \frac{1}{\sqrt{2}} |2^+\rangle + \frac{1}{\sqrt{2}} |2^-\rangle, \\
|A_1^0\rangle &= |2^0\rangle, \\
|B_2^-\rangle &= \frac{1}{\sqrt{2}} |2^+\rangle - \frac{1}{\sqrt{2}} |2^-\rangle, \\
|A_2^-\rangle &= \frac{1}{\sqrt{2}} |2^+\rangle - \frac{1}{\sqrt{2}} |2^-\rangle
\end{align*}
\]
For $J=2$, let $\Sigma = A + B$ and $\Delta = A - B$ to shorten expressions. The following basis transformation “almost diagonalizes” $\langle H \rangle^{J=2}$ by reducing it to block form.

\[
\begin{pmatrix}
\langle A \rangle^2 + B \langle J \rangle^2 + C \langle J \rangle^3
\end{pmatrix}^{J=2} =
\begin{pmatrix}
(A + B) + 4C & \sqrt{6} (A - B) & \cdot & \cdot & \cdot \\
\cdot & \frac{5}{2} (A + B) + C & \cdot & \frac{3}{2} (A - B) & \cdot \\
\cdot & \cdot & 3(A + B) & \cdot & \sqrt{6} (A - B) \\
\cdot & \cdot & \cdot & \frac{3}{2} (A - B) & \cdot \\
\cdot & \cdot & \cdot & \cdot & \sqrt{6} (A - B) \\
\end{pmatrix}
= \begin{pmatrix}
15 & -\sqrt{6} & \frac{15}{2} & \frac{-3}{2} \\
\end{pmatrix}
\]

Matrix is nearly diagonalized in standing-wave $D_2$-symmetry basis:

- $| A_1 \rangle^2^+ = \frac{1}{\sqrt{2}} | 2 \rangle^+ + \frac{1}{\sqrt{2}} | 2 \rangle^-$,
- $| B_1 \rangle^1^+ = \frac{1}{\sqrt{2}} | 2 \rangle^+ + \frac{1}{\sqrt{2}} | 2 \rangle^-$,
- $| A_1 \rangle^0 = | 0 \rangle$

- $| B_2 \rangle^2^- = \frac{1}{\sqrt{2}} | 2 \rangle^+ - \frac{1}{\sqrt{2}} | 2 \rangle^-$,
- $| A_2 \rangle^1^- = \frac{1}{\sqrt{2}} | 2 \rangle^+ - \frac{1}{\sqrt{2}} | 2 \rangle^-$

The following basis transformation “almost diagonalizes” $\langle H \rangle^{J=2}$ by reducing it to block form.

Let $\Sigma = A + B$ and $\Delta = A - B$ to shorten expressions.

\[
\begin{pmatrix}
1 & \cdot & \cdot & \cdot & 1 \\
1 & \cdot & \cdot & \cdot & 1 \\
1 & \cdot & \cdot & \cdot & 1 \\
\cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot \\
\end{pmatrix}
\begin{pmatrix}
4C - \Sigma & \cdot & \sqrt{6} \Delta & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot \\
\end{pmatrix}
\begin{pmatrix}
1 & 1 & \cdot & \cdot & \cdot \\
\cdot & 1 & 1 & \cdot & \cdot \\
\cdot & \cdot & 1 & \cdot & 1 \\
\cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot \\
\end{pmatrix}
\begin{pmatrix}
1 & 1 & \cdot & \cdot & \cdot \\
\cdot & 1 & 1 & \cdot & \cdot \\
\cdot & \cdot & 1 & \cdot & 1 \\
\cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot \\
\end{pmatrix}
= \begin{pmatrix}
15 & -\sqrt{6} & \frac{15}{2} & \frac{-3}{2} \\
\end{pmatrix}
\]

New $D_2$ basis:

- $| A_1 \rangle^2^+ = \frac{1}{\sqrt{2}} | 2 \rangle^+ + \frac{1}{\sqrt{2}} | 2 \rangle^-$
- $| B_2 \rangle^2^- = \frac{1}{\sqrt{2}} | 2 \rangle^+ - \frac{1}{\sqrt{2}} | 2 \rangle^-$
- $| A_1 \rangle^0 = | 0 \rangle$
- $| B_1 \rangle^1^+ = \frac{1}{\sqrt{2}} | 2 \rangle^+ + \frac{1}{\sqrt{2}} | 2 \rangle^-$
- $| A_2 \rangle^1^- = \frac{1}{\sqrt{2}} | 2 \rangle^+ - \frac{1}{\sqrt{2}} | 2 \rangle^-$
- $| A_1 \rangle^0 = | 0 \rangle$
Completing diagonalization from new $D_2$ basis:

$$
\begin{bmatrix}
4C + A + B & \cdot & \cdot & \cdot & \sqrt{3}(A - B) \\
\cdot & 4C + A + B & \cdot & \cdot & \cdot \\
\cdot & \cdot & C + 4A + B & \cdot & \cdot \\
\cdot & \cdot & \cdot & C + A + 4B & \cdot \\
\sqrt{3}(A - B) & \cdot & \cdot & \cdot & 3A + 3B
\end{bmatrix}
$$

<table>
<thead>
<tr>
<th>$D_2$</th>
<th>$I$</th>
<th>$R_x$</th>
<th>$R_y$</th>
<th>$R_z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_1$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_2$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

$$
C_x^I \times C_y^I = \begin{bmatrix}
+ & + \\
- & -
\end{bmatrix} \times \begin{bmatrix}
+ & + \\
+ & -
\end{bmatrix}
$$

$$
D_2 = \begin{bmatrix}
+ & + & A_1 & 1 & 1 & 1 & 1 \\
- & - & A_2 & 1 & -1 & 1 & -1 \\
+ & - & B_1 & 1 & 1 & -1 & -1 \\
- & + & B_2 & 1 & -1 & -1 & 1
\end{bmatrix}
$$

$|A_1\rangle = \begin{bmatrix} 1 \\ 2 \\ 2 \\ -2 \end{bmatrix}$

$|B_2\rangle = \begin{bmatrix} 1 \\ 2 \\ -2 \\ -2 \end{bmatrix}$

$|B_1\rangle = \begin{bmatrix} 1 \\ 2 \\ 2 \\ -1 \end{bmatrix}$

$|A_2\rangle = \begin{bmatrix} 1 \\ 2 \\ 1 \\ -2 \end{bmatrix}$

$|A_0\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix}$
Completing diagonalization from new $D_2$ basis:

$$\begin{pmatrix}
4C + A + B & \cdot & \cdot & \sqrt{3}(A - B) \\
\cdot & 4C + A + B & \cdot & \cdot \\
\cdot & \cdot & C + 4A + B & \cdot \\
\sqrt{3}(A - B) & \cdot & \cdot & 3A + 3B
\end{pmatrix}$$

<table>
<thead>
<tr>
<th>$D_2$</th>
<th>$I$</th>
<th>$R_x$</th>
<th>$R_y$</th>
<th>$R_z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_1$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_2$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

Need only diagonalize the two $A_1$'s:

(It is $n=0$ versus $n=2^+$)

$$\begin{pmatrix} 4C + A + B & \sqrt{3}(A - B) \end{pmatrix}$$

$$\begin{pmatrix} A_1^{2^+} = \frac{1}{\sqrt{2}} \begin{pmatrix} 2 \\ +2 \end{pmatrix} + \frac{1}{\sqrt{2}} \begin{pmatrix} 2 \\ -2 \end{pmatrix} \\
B_2^{-2} = \frac{1}{\sqrt{2}} \begin{pmatrix} 2 \\ +2 \end{pmatrix} - \frac{1}{\sqrt{2}} \begin{pmatrix} 2 \\ -2 \end{pmatrix} \\
B_1^{2^+} = \frac{1}{\sqrt{2}} \begin{pmatrix} 2 \\ +1 \end{pmatrix} + \frac{1}{\sqrt{2}} \begin{pmatrix} 2 \\ -1 \end{pmatrix} \\
A_2^{-2} = \frac{1}{\sqrt{2}} \begin{pmatrix} 2 \\ +1 \end{pmatrix} - \frac{1}{\sqrt{2}} \begin{pmatrix} 2 \\ -1 \end{pmatrix} \\
A_1^{0} = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \end{pmatrix}$$

$X_{xy}$

$X_{x^2-y^2}$

$X_{2z^2-x^2-y^2}$

$j = 2$

Standing $d$-Waves

$(180°)$
Completing diagonalization from new \( D_2 \) basis:

\[
\begin{pmatrix}
4C + A + B & . & . & \sqrt{3}(A - B) \\
. & 4C + A + B & . & . \\
. & . & C + 4A + B & . \\
\sqrt{3}(A - B) & . & . & 3A + 3B
\end{pmatrix}
\]

Need only diagonalize the two \( A_1 \)'s:

\[
\begin{pmatrix}
4C + A + B & \sqrt{3}(A - B)
\end{pmatrix}
\begin{pmatrix}
A_1^{2+}
\end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 2 \\ 1 \end{pmatrix} + \frac{1}{\sqrt{2}} \begin{pmatrix} 2 \\ -1 \end{pmatrix}
\]

\[
\begin{pmatrix}
\sqrt{3}(A - B) & 3A + 3B
\end{pmatrix}
\begin{pmatrix}
A_1^{0}
\end{pmatrix} = \begin{pmatrix} 2 \\ 0 \end{pmatrix}
\]

\[
= (2C + 2A + 2B) \cdot \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix}
\]

\[
= \begin{pmatrix} 2C - A - B \\ \sqrt{3}(A - B) \\ -(2C - A - B) \end{pmatrix}
\]

\[
\begin{pmatrix}
A_2
\end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}
\]

\[
\begin{pmatrix}
B_2
\end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}
\]

\[
\begin{pmatrix}
B_1
\end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}
\]

\[
\begin{pmatrix}
A_1
\end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}
\]

\[
\begin{pmatrix}
B_1
\end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}
\]

\[
\begin{pmatrix}
A_2
\end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}
\]

\[
\begin{pmatrix}
B_2
\end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}
\]

\[
\begin{pmatrix}
A_1
\end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}
\]

\[
\begin{pmatrix}
B_1
\end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}
\]

\[
\begin{pmatrix}
A_2
\end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}
\]

\[
\begin{pmatrix}
B_2
\end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}
\]

\[
\begin{pmatrix}
A_1
\end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}
\]

\[
\begin{pmatrix}
B_1
\end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}
\]

\[
\begin{pmatrix}
A_2
\end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}
\]

\[
\begin{pmatrix}
B_2
\end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}
\]

\[
\begin{pmatrix}
A_1
\end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}
\]

\[
\begin{pmatrix}
B_1
\end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}
\]

\[
\begin{pmatrix}
A_2
\end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}
\]

\[
\begin{pmatrix}
B_2
\end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}
\]

\[
\begin{pmatrix}
A_1
\end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}
\]

\[
\begin{pmatrix}
B_1
\end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}
\]

\[
\begin{pmatrix}
A_2
\end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}
\]

\[
\begin{pmatrix}
B_2
\end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}
\]

\[
\begin{pmatrix}
A_1
\end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}
\]

\[
\begin{pmatrix}
B_1
\end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}
\]

\[
\begin{pmatrix}
A_2
\end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}
\]

\[
\begin{pmatrix}
B_2
\end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}
\]

\[
\begin{pmatrix}
A_1
\end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}
\]

\[
\begin{pmatrix}
B_1
\end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix}
\]

\[
\begin{pmatrix}
A_2
\end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}
\]

\[
\begin{pmatrix}
B_2
\end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{pmatrix}
\]
Completing diagonalization from new $D_2$ basis:

\[
\begin{pmatrix}
4C + A + B & . & . & \sqrt{3}(A - B) \\
. & 4C + A + B & . & . \\
. & . & C + 4A + B & . \\
. & . & . & C + A + 4B \\
\sqrt{3}(A - B) & . & . & 3A + 3B
\end{pmatrix}
\]

\[
\begin{align*}
|2^+ \rangle &= \frac{1}{\sqrt{2}} |2\rangle + \frac{1}{\sqrt{2}} |\frac{3}{2}\rangle \\
|2^- \rangle &= \frac{1}{\sqrt{2}} |\frac{3}{2}\rangle - \frac{1}{\sqrt{2}} |2\rangle \\
|1^+ \rangle &= \frac{1}{\sqrt{2}} |\frac{3}{2}\rangle + \frac{1}{\sqrt{2}} |\frac{1}{2}\rangle \\
|1^- \rangle &= \frac{1}{\sqrt{2}} |\frac{1}{2}\rangle - \frac{1}{\sqrt{2}} |\frac{3}{2}\rangle \\
|0 \rangle &= \begin{pmatrix} \frac{1}{2} \\ 0 \end{pmatrix}
\end{align*}
\]

Need only diagonalize the two $A_1$'s: (It is $n=0$ versus $n=2^+$)

\[
\begin{pmatrix}
4C + A + B & \sqrt{3}(A - B) \\
\sqrt{3}(A - B) & 3A + 3B
\end{pmatrix}
\begin{pmatrix}
|2^+ \rangle \\
|0 \rangle
\end{pmatrix} = \begin{pmatrix}
\frac{1}{\sqrt{2}} |2\rangle + \frac{1}{\sqrt{2}} |\frac{3}{2}\rangle \\
\frac{1}{\sqrt{2}} |\frac{3}{2}\rangle - \frac{1}{\sqrt{2}} |2\rangle
\end{pmatrix}
\]

\[
= (2C + 2A + 2B) \cdot 1 + \begin{pmatrix}
2C - A - B \\
\sqrt{3}(A - B)
\end{pmatrix}
\begin{pmatrix}
\frac{1}{\sqrt{2}} \\
0
\end{pmatrix}
\]

with eigenvalues:

\[
\lambda_{\pm} = 2C + 2A + 2B \pm \sqrt{(2C - A - B)^2 + 3(A - B)^2}
\]

\[
= 2(A + B + C) \pm 2\sqrt{2C - (A + B)C + A^2 - AB + B^2}
\]

\[
= 2C + 4B \pm 2(C - B) = \begin{cases}
4C + 2B \\
6B
\end{cases}
\]

if $A = B$

$\lambda_{\pm}$ for $A = B$ prolate case: $(A=2=B=2, C=3)$

$B(J(J+1) + (C-B)n^2 = 2B + 4C = 4 + 12 = 16$ \((n=\pm 2)\)

$5B + C = 10 + 3 = 13$ \((n=\pm 1)\), $6B = 12$ \((n=0)\)

$A=B$ prolate case: $(A=2=B=2, C=3)$

$B(J(J+1) + (C-B)n^2 = 2B + 4C = 4 + 12 = 16$ \((n=\pm 2)\)

$5B + C = 10 + 3 = 13$ \((n=\pm 1)\), $6B = 12$ \((n=0)\)

$B=C$ oblate case: $(A=1, B=2= C=2)$

$B(J(J+1) + (A-B)n^2 = 2B + 4A = 4 + 4 = 8$ \((n=\pm 2)\)

$5B + A = 10 + 1 = 11$ \((n=\pm 1)\), $6B = 12$ \((n=0)\)

$A=B$ oblate case: $(A=1, B=2= C=2)$

$B(J(J+1) + (A-B)n^2 = 2B + 4A = 4 + 4 = 8$ \((n=\pm 2)\)

$5B + A = 10 + 1 = 11$ \((n=\pm 1)\), $6B = 12$ \((n=0)\)
Completing diagonalization from new $D_2$ basis:

\[
\begin{pmatrix}
4C + A + B & \cdot & \cdot & \sqrt{3}(A - B) \\
\cdot & 4C + A + B & \cdot & \cdot \\
\cdot & \cdot & C + 4A + B & \cdot \\
\sqrt{3}(A - B) & \cdot & \cdot & 3A + 3B
\end{pmatrix}
\]

\[
A_{2}^{2-} = \frac{1}{\sqrt{2}} \begin{pmatrix} 2 \\ 0 \end{pmatrix}
\]

\[
B_{1}^{2-} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ i \end{pmatrix}
\]

\[
B_{1}^{1+} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -i \end{pmatrix}
\]

\[
A_{2}^{1-} = \frac{1}{\sqrt{2}} \begin{pmatrix} 2 \\ 1 \end{pmatrix}
\]

\[
A_{0} = \begin{pmatrix} 2 \\ 0 \end{pmatrix}
\]

Need only diagonalize the two $A_1$’s:

\[
\begin{pmatrix}
4C + A + B & \sqrt{3}(A - B) \\
\sqrt{3}(A - B) & 3A + 3B
\end{pmatrix}
\]

\[
A_{1}^{2+} = \frac{1}{\sqrt{2}} \begin{pmatrix} 2 \\ 0 \end{pmatrix}
\]

\[
A_{1}^{1+} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}
\]

\[
A_{1}^{0} = \begin{pmatrix} 2 \\ 0 \end{pmatrix}
\]

with eigenvalues:

\[
\lambda_{\pm} = 10 + 2B \pm \sqrt{(4 - B)^2 + 3(2 - B)^2}
\]

\[
= 2(5 + B) \pm 2\sqrt{7 - 5B + B^2}
\]

\[
= 14 \pm 2\sqrt{13} \text{ if } A = B = 2 \text{ and } C = 3
\]

\[
A = B \text{ prolate case: } (A = 2, B = 2, C = 3)
\]

\[
B (J + 1) + (C - B) n^2 = 2B + 4C = 4 + 12 = 16 \quad (n = \pm 2)
\]

\[
5B + C = 10 + 3 = 13 \quad (n = \pm 1), \quad 6B = 12 \quad (n = 0)
\]

\[
B = C \text{ oblate case: } (A = 1, B = 2, C = 2)
\]

\[
B (J + 1) + (A - B) n^2 = 2B + 4A = 4 + 4 = 8 \quad (n = \pm 2)
\]

\[
5B + A = 10 + 1 = 11 \quad (n = \pm 1), \quad 6B = 12 \quad (n = 0)
\]
Symmetric rigid quantum rotor analysis of $R(2)$ Hamiltonian $H = B J_x^2 + B J_y^2 + C J_z^2$

Rotational Energy Surfaces (RE or RES) and $R(3) \sim U(2)$ representations

Asymmetric rigid quantum rotor analysis of $D_2$ Hamiltonian $H = A J_x^2 + B J_y^2 + C J_z^2$

RES and Multipole $T_q^k$ tensor expansions

Atomic or molecular $R(3)$ $\ell$-level or $2\ell + 1$-multiplet splitting (Review of $D_3$)

$R(3) \supset D_2$ character analysis of $\ell$-level or $2\ell + 1$-multiplet splitting in $D_2$

Detailed angular momentum operator analysis for $J=1-2$ for $D_2$ symmetry

Asymmetric rotor levels and RES plots for high-$J$

Octahedral semi-rigid quantum rotor analysis of $O_h$ Hamiltonian $H = B J \cdot J + t_{044} T^{[4]}$

Spherical rotor levels and RES plots of $O_h$ tensor eigenvalues

$R(3) \subset O(3) \supset O_h \supset O$ character analysis of $\ell$-level or $2\ell + 1$-multiplet splitting in $O$

$S F_6$ spectral fine structure

$C F_4$ spectral fine structure
Examples of Group $\supset$ Sub-group correlation $D_2 \supset C_2(x)$  $D_2 \supset C_2(y)$  $D_2 \supset C_2(z)$

Springet Handbook of Atomic, Molecular, and Optical Physics (2005)
Fig.32.2 and 32.3 p. 495-497

after QTforCA Unit 8. Ch. 25 Fig. 25.4.2
Examples of Group Sub-group correlation

<table>
<thead>
<tr>
<th>$D_2$</th>
<th>$C_2(x)$</th>
<th>$C_2(y)$</th>
<th>$C_2(z)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_2$</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_1$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_2$</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Original color mixing scheme gives:
- yellow $I_2 = (A_2B_1)$
- purple $I_2 = (A_1B_2)$
- orange $I_2 = (A_1B_1)$
- cyan $I_2 = (A_2B_2)$

for $z$-prolate axis

for $x$-oblate axis

Review: Asymmetric vs Symmetric rotor levels

Fig. 25.4.3 Correlations between the asymmetric top symmetry $D_2$ and subgroups $C_2(x)$, $C_2(y)$, and $C_2(z)$. 
Fig. 25.4.2 $J = 10$ asymmetric top energy levels and related RE surface paths ($A = 0.2$, $B = 0.4$, $C = 0.6$). Clustered pairs of levels are indicated in magnifying circles that show superfine splittings.
Fig. 32.1 $J = 10$ eigenvalue plot for symmetric rigid rotors ($A = 0.2, C = 0.6 \text{ cm}^{-1}$, $A < B < C$). Prolate and oblate energy surfaces are shown.

Fig. 32.2 $J = 10$ rotational energy surface and related level spectrum for an asymmetric rigid rotator ($A = 0.2, B = 0.4, C = 0.6 \text{ cm}^{-1}$).
Separatrix circle pair dihedral angle

\[ \theta_{sep} = \arctan \left( \frac{A-B}{B-C} \right) \]
Revised color mixing scheme gives

- **Orange** \(0_2 = (A_1 A_2)\) cyan \(1_2 = (B_1 B_2)\) for y-prolate axis
- **Purple** \(0_2 = (A_1 B_1)\) yellow \(1_2 = (A_2 B_2)\) for x-oblate axis
Review:
Symmetric rigid quantum rotor analysis of $R(2)$ Hamiltonian $H = BJ_x^2 + BJ_y^2 + CJ_z^2$
Rotational Energy Surfaces (RE or RES) and $R(3) \sim U(2)$ representations

Asymmetric rigid quantum rotor analysis of $D_2$ Hamiltonian $H = AJ_x^2 + BJ_y^2 + CJ_z^2$
RES and Multipole $T_q^k$ tensor expansions
Atomic or molecular $R(3)$ $\ell$-level or $2\ell+1$-multiplet splitting (Review of $D_3$)
$R(3) \supset D_2$ character analysis of $\ell$-level or $2\ell+1$-multiplet splitting in $D_2$
Detailed angular momentum operator analysis for $J=1-2$ for $D_2$ symmetry
Asymmetric rotor levels and RES plots for high-$J$

Octahedral semi-rigid quantum rotor analysis of $O_h$ Hamiltonian $H = BJ \cdot J + t_{044} T^{[4]}$
Spherical rotor levels and RES plots of $O_h$ tensor eigenvalues
$R(3) \subset O(3) \supset O_h \supset O$ character analysis of $\ell$-level or $2\ell+1$-multiplet splitting in $O$
Visualizing $J=30$ quantum levels of cubic, octahedral, and tetrahedral molecules
SF$_6$ spectral fine structure $P(88)$
$CF_4$ spectral fine structure $P(54)$

$R(3) \subset O(3) \supset O_h \supset O$ analysis of $\ell$-level starts on p. 10 of Lecture 27
**Semi Rigid Rotor Hamiltonian:** Centrifugal and Coriolis terms...

\[ H = AJ_x^2 + BJ_y^2 + CJ_z^2 + t_{xxx} J_x^4 + t_{xyy} J_x^2 J_y^2 + \cdots \]

**Semi Rigid \( O_h \) or \( T_d \) Spherical Top:** (Hecht Hamiltonian 1960)

\[ H = B\left(J_x^2 + J_y^2 + J_z^2\right) + t_{440} \left(J_x^4 + J_y^4 + J_z^4 - \frac{3}{5} J^4\right) + \cdots \]

\[ = BJ_x^2 \quad + t_{440} \left(T_0^4 + \sqrt{\frac{5}{14}} \left[T_4^4 + T_{-4}^4\right]\right) + \cdots \]

\[ K_4 = 88 \quad = 87 \quad = 86 \quad \text{etc.} \]

\[ J = 88 \]

\[ J = 30 \]

\[ 35.3^\circ \]

\[ 19.5^\circ \]

after QTforCA Unit 8. Ch. 25 Fig. 25.4.5
Review:

Symmetric rigid quantum rotor analysis of $R(2)$ Hamiltonian $H = B J_x^2 + B J_y^2 + C J_z^2$

Rotational Energy Surfaces (RE or RES) and $R(3) \sim U(2)$ representations

Asymmetric rigid quantum rotor analysis of $D_2$ Hamiltonian $H = A J_x^2 + B J_y^2 + C J_z^2$

RES and Multipole $T_{q^k}$ tensor expansions

Atomic or molecular $R(3)$ $\ell$-level or $2\ell + 1$-multiplet splitting (Review of $D_3$)

$R(3) \supset D_2$ character analysis of $\ell$-level or $2\ell + 1$-multiplet splitting in $D_2$

Detailed angular momentum operator analysis for $J=1-2$ for $D_2$ symmetry

Asymmetric rotor levels and RES plots for high-$J$

Octahedral semi-rigid quantum rotor analysis of $O_h$ Hamiltonian $H = B J \cdot J + t_{044} T^{[4]}$

Spherical rotor levels and RES plots of $O_h$ tensor eigenvalues

$R(3) \subset O(3) \supset O_h \supset O$ character analysis of $\ell$-level or $2\ell + 1$-multiplet splitting in $O$

Visualizing $J=30$ quantum levels of cubic, octahedral, and tetrahedral molecules

$SF_6$ spectral fine structure $P(88)$

$CF_4$ spectral fine structure $P(54)$
$R(3) \subset O(3) \subset O_h \supset O$ character analysis (From *Principles of Symmetry Dynamics & Spectroscopy* Ch.5 p.384)

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$$\chi^\ell(\Theta) = \frac{\sin(\ell + \frac{1}{2}) \Theta}{\sin \frac{\Theta}{2}}$$

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### Single Electron Orbital Spectroscopic Labeling

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$R(3) \subset O(3) \supset O_h \supset O$ character analysis (From *Principles of Symmetry Dynamics & Spectroscopy* Ch.5 p.390)

Frequency of $O$ Irreps

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$A_{1g}$

$T_{1u}$

$E_g + T_{2g}$

$A_{2u} + T_{1u} + T_{2u}$

$A_{1g} + E_g + T_{1g} + T_{2g}$

Figure 5.6.3 Detailed sketch of octahedral splitting of a $d$ orbital. The wave functions $\langle \psi_2 \rangle$ and $\langle \psi_3 \rangle$ are sketched inside the equipotential contour $x^4 + y^4 = \text{constant}$ ($z = 0$).
R(3) ⊂ O(3) ⊃ O_h ⊃ O character analysis (From Principles of Symmetry Dynamics & Spectroscopy Ch.5 p.403)

\[(A_1 \ T_1 \ E)_{04} \ (T_2 \ T_1)_{34} \ (E \ T_2 \ A_2)_{24} \ (T_2 \ T_1)_{14}\ldots (A_2 \ T_2 \ T_1 \ A_1)_{03} \ (T_1 \ E \ T_2)_{13} \ (T_1 \ E \ T_2)_{23} \ldots\]

(a) Even J

(b) Odd J

Figure 5.6.9 Mnemonic wheels for octahedral-O orbital. Splitting of J levels for (a) even J and (b) odd J.
R(3) ⊂ O(3) ⊂ Oₜ ⊂ O character analysis (From Principles of Symmetry Dynamics & Spectroscopy Ch.5 p.403)

ROTATIONAL LEVEL SPLITTING INFINITE SYMMETRY

(A₁ T₁ E)₀₄ (T₂ T₁)₃₄ (E T₂ A₂)₂₄ (T₂ T₁)₁₄ ...(A₂ T₂ T₁ A₁)₀₅ (T₁ E T₂)₁₃ (T₁ E T₂)₂₃ ...

(a) Even J

(b) Odd J

Bands or “Clusters”
of levels maintain order
but change spacing as
they adapt to varying
local symmetries by
crossing separatrices
in their phase space
(see p. 73-77)

D₆ wheel

Ch.5 p.402 (A₁ E₁ E₂ B₁)₀₂ (B₂ E₂ E₁ A₂)₁₂ ...(A₂ A₁)₀₆ (E₁)₁₆ (E₂)₂₆ (B₁ B₂)₃₆ (E₂)₄₆ (E₁)₅₆...

(a) Even J

(b) Odd J

(see p. 68-72 of Lect. 18
where “band” and “gap”
spaceing varies with energy)
$D_6$ Band structure and related induced representations (Mac OS-9)

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- $A_2 \oplus E_2 \oplus E_1 \oplus B_2$
- $A_1 \oplus E_1 \oplus E_2 \oplus B_1$

Odd Band or Cluster

Even Band or Cluster

(p. 68 of Lect. 18)
$D_6$ Band structure and related induced representations (Mac OS-9)

Symmetric $P_{11}^E$ (radial) on Global $i_3$ axis

Antisymmetric $P_{22}^E$ (angular) on Local $i_1$ axis

Symmetric $P_{11}^E$ (radial) on Global $i_3$ axis

Antisymmetric $P_{22}^E$ (angular) on Local $i_1$ axis

Local $k_0 = 1.5 \text{ N/m}$

Local $k_1 = 0.05 \text{ N/m}$

Local $k_2 = 0 \text{ N/m}$

$p. 69$ of Lect. $18$
U(12)-Supersymmetry: When $D_6$ Band structure approaches single 12-fold degeneracy
Setting mutually orthogonal external $k_0$ connection springs (and tiny $k_1, k_2, ..$ coupling)

Even moderate $k_1$ coupling lifts a band of single-doublet-doublet-singlet above 6-fold degenerate sextet

Local symmetry-asymmetry is well broken as strictly radial or angular paths are avoided by masses off x-axis

(p. 72 of Lect. 18)
Symmetric rigid quantum rotor analysis of $R(2)$ Hamiltonian $H = BJ_x^2 + BJ_y^2 + CJ_z^2$

Rotational Energy Surfaces (RE or RES) and $R(3) \sim U(2)$ representations

Asymmetric rigid quantum rotor analysis of $D_2$ Hamiltonian $H = AJ_x^2 + BJ_y^2 + CJ_z^2$

RES and Multipole $T_q^k$ tensor expansions

Atomic or molecular $R(3)$ $\ell$-level or $2\ell + 1$-multiplet splitting (Review of $D_3$)

$R(3) \supset D_2$ character analysis of $\ell$-level or $2\ell + 1$-multiplet splitting in $D_2$

Detailed angular momentum operator analysis for $J = 1 - 2$ for $D_2$ symmetry

Asymmetric rotor levels and RES plots for high-$J$

Octahedral semi-rigid quantum rotor analysis of $O_h$ Hamiltonian $H = BJ \cdot J + t_{044} T^{[4]}$

Spherical rotor levels and RES plots of $O_h$ tensor eigenvalues

$R(3) \subset O(3) \supset O_h \supset O$ character analysis of $\ell$-level or $2\ell + 1$-multiplet splitting in $O$

Visualizing $J = 30$ quantum levels of cubic, octahedral, and tetrahedral molecules

$SF_6$ spectral fine structure $P(88)$

$CF_4$ spectral fine structure $P(54)$
**Semi Rigid Rotor Hamiltonian:** Centrifugal and Coriolis terms...

\[
H = AJ_x^2 + BJ_y^2 + CJ_z^2 + t_{xxx} J_x^4 + t_{xxy} J_x^2 J_y^2 + \cdots
\]

**Semi Rigid \(O_h\) or \(T_d\) Spherical Top:** (Hecht Hamiltonian 1960)

\[
H = B \left( J_x^2 + J_y^2 + J_z^2 \right) + t_{440} \left( J_x^4 + J_y^4 + J_z^4 - \frac{3}{5} J^4 \right) + \cdots
\]

\[
= BJ^2 + t_{440} \left( T_0^4 + \sqrt{\frac{5}{14}} \left[ T_4^4 + T_{-4}^4 \right] \right) + \cdots
\]

*precessing \(J\) vector*

\(K_4 = 30\)

\(K_4 = 88\)

\(J = 30\)

\(J = 88\)

*after QTforCA Unit 8, Ch. 25 Fig. 25.4.5*
Finding Hamiltonian Eigensolutions by Geometry

Uncertainty Cone Angles

\[ \cos \Theta_K^J = \frac{K}{\sqrt{J(J+1)}} \]

\( O_h \) or \( T_d \) Spherical Top: (Hecht Ro-vib Hamiltonian 1960)

\[ H = B \left( J_x^2 + J_y^2 + J_z^2 \right) + t_{440} \left( J_x^4 + J_y^4 + J_z^4 - \frac{3}{5} J^4 \right) + \cdots \]

\[ = BJ^2 + t_{440} \left( T_0^4 + \sqrt{\frac{5}{14}} \left[ T_4^4 + T_{-4}^4 \right] \right) + \cdots \]

\( J \) cone intersects \( J=88 \) RE surface to give approx. \( K=J, J-1, J-2 \ldots \) energy levels

RE Surface topo-lines track precessing semi-classical \( J \) vector

Borderline Cases of Statistically Matching Figures: (K3, K4)

Block Angle: 35.3°

Page 75 shows slice
VISUALIZING THE J = 30
LEVELS OF A
SPHERICAL TOP

\[ \vec{J}, \vec{K}, \vec{J}_x, \vec{J}_y, \vec{J}_z \]

Separatrix Region

\[ 1.0 \times 10^6 \text{ cm}^{-1}, 8.1 \times 10^6 \text{ cm}^{-1} \]

\[ 9.2 \times 10^6 \text{ cm}^{-1}, 3.8 \times 10^9 \text{ cm}^{-1}, 1.6 \times 10^{10} \text{ cm}^{-1}, 4.8 \text{ Hz} \]

\[ 1.8 \times 10^2 \text{ cm}^{-1}, 5.3 \text{ MHz} \]

\[ K_4 \approx 29, K_4 \approx 28 \]

Relative Units of $10^4 \text{ cm}^{-1} = 3.0 \text{ MHz}$
VISUALIZING THE J = 30 LEVELS OF A SPHERICAL TOP

Angular Momentum Cones for J=30

θ = arc cos [ K/√(J+1) ]

Separatrix Region

C₃ Clusters

C₄ Clusters

84.70719 cm⁻¹ Relative Units of 10⁴ cm⁻¹ = 3.0 MHz
Two molecular examples: SiF₄ and C₈H₈
Two molecular examples: SiF$_4$ and C$_8$H$_8$
**Fig. 25.4.7** Different choices of rotation axes for octahedral rotor corresponding to local symmetry $C_3$, $C_2$, and $C_4$. Tables correlate global octahedral symmetry species with the local ones.

**Fig. 25.4.9** Infrared spectra showing fine structure clusters. Tetrafluorosilane ($SiF_4$) spectrum from a v$_1$ R(30) transition. [After C. W. Patterson, R. S. McDowell, N. G. Nereson, B. J. Krohn, J. S. Wells, and F. R. Peterson, J. Mol. Spectrosc. 91, 416 (1982).]

**Review:**

**Symmetric rigid quantum rotor analysis of R(2) Hamiltonian** \( H = B J_x^2 + B J_y^2 + C J_z^2 \)

*Rotational Energy Surfaces (RE or RES) and R(3)~U(2) representations*

**Asymmetric rigid quantum rotor analysis of D_2 Hamiltonian** \( H = A J_x^2 + B J_y^2 + C J_z^2 \)

*RES and Multipole \( T_{q}^{k} \) tensor expansions*

*Atomic or molecular R(3) \( \ell \)-level or \( 2\ell+1 \)-multiplet splitting (Review of D_3)*

*R(3)\( \supset \)D_2 character analysis of \( \ell \)-level or \( 2\ell+1 \)-multiplet splitting in D_2*

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*Spherical rotor levels and RES plots of O_h tensor eigenvalues*

*R(3)\( \subset \)O(3)\( \supset \)O_h\( \supset \)O character analysis of \( \ell \)-level or \( 2\ell+1 \)-multiplet splitting in O*

*Visualizing J=30 quantum levels of cubic, octahedral, and tetrahedral molecules*

*SF_6 spectral fine structure P(88)*

*CF_4 spectral fine structure P(54)*
(a) $\text{SF}_6 \nu_4$ Rotational Structure

F.T. IR and Laser Diode Spectra
K.C. Kim, W.B. Person, D. Setz, and B.J. Krohn
Primary AET species mixing increases with distance from “separatrix.”
Primary AET species mixing increases with distance from "separatrix"

CASE 1 Unmixed
Primary AET species mixing increases with distance from "separatrix".

CASE 1 - Unmixed primary $A_1 T_1 E T_2 A_2$ species

CASE 2 - Extreme mixing in tight $C_4$-CLUSTERS

CASE 2 - Major mixing in lowest two $C_3$-CLUSTERS

(Next page: approximate theory)
IR Spectra of SF6 $\nu_4 P(88)$
SF$_6$ Spectra of O$_h$ Ro-vibronic Hamiltonian described by RE Tensor Topography

\[ H = B \left( \mathbf{J}_x^2 + \mathbf{J}_y^2 + \mathbf{J}_z^2 \right) + t_{440} \left( \mathbf{J}_x^4 + \mathbf{J}_y^4 + \mathbf{J}_z^4 - \frac{3}{5} \mathbf{J}^4 \right) + \cdots \]

\[ = BJ^2 + t_{440} \left( T_0^4 + \sqrt{\frac{5}{14}} \left[ T_4^4 + T_{-4}^4 \right] \right) + \cdots \]

Rovibronic Energy (RE)
Tensor Surface

\[ \Theta_m^J = \arccos \left( \frac{K}{\sqrt{J(J+1)}} \right) \]

SF$_6$ mu4 rovib FT spectra ~ 615 cm$^{-1}$
McDowell et al. Los Alamos

2-Fold Axis

Saddle Point

Herzberg rules still apply near separatrices or saddle points
SF\textsubscript{6} \( \nu_4 \) rovib FT spectra \( \sim \) 615 cm\(^{-1} \)

McDowell et al. LosAlamos

Saddle Point

Herzberg rules still apply near separatrices or saddle points
Primary AET species mixing increases with distance from "separatrix".

**Observed repeating sequence(s):**...A₁T₁E₁T₂T₁ET₂A₂T₂T₁A₁...

Local correlations explain clustering... ... but what about spacing and ordering?...
...and physical consequences?
**SF$_6$ spectral fine structure in P(88)**

Note that ordering of symmetry species listed on the O-wheel is maintained as they morph from C$_4$ hill-clusters to C$_3$ valley-clusters on the low side of the C$_2$ separatrix.

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**Figure 5.6.9** Mnemonic wheels for octahedral-O orbital. Splitting of $J$ levels for (a) even $J$ and (b) odd $J$. 
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$SF_6$ spectral fine structure $P(88)$
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Example of frequency hierarchy for 16 µm spectra of CF₄ (Freon-14)

W.G. Harter
Ch. 31
Atomic, Molecular, & Optical Physics Handbook
Am. Int. of Physics
Gordon Drake Editor
(1996)
Example of frequency hierarchy for 16μm spectra of CF$_4$ (Freon-14)
W.G. Harter
Fig. 32.7
Springer Handbook of Atomic, Molecular, & Optical Physics
Gordon Drake Editor (2005)
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(Apps are being upgraded as time permits)

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Harter-Soft Web Apps - Quick Reference - Testing; URL is "http://www.uark.edu/ua/modphys/testing/markup/JerkItWeb.html"
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Pendulum - Testing; URL is "http://www.uark.edu/ua/modphys/testing/markup/PendulumWeb.html"
QuantIt - Testing; URL is "http://www.uark.edu/ua/modphys/testing/markup/QuantItWeb.html"
Trebuchet Testing; URL is "http://www.uark.edu/ua/modphys/testing/markup/TrebuchetWeb.html"

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