Group Theory in Quantum Mechanics

Lecture 26 *(5.02.17)*

Based on AMOP Lectures 14-20

Introduction to Rotational Eigenstates and Spectra II

(Int.J.Mol.Sci, 14, 714(2013) p.755-774 , QTCA Unit 7 Ch. 21-25)
(PSDS - Ch. 5, 7)

Review :

Symmetric rigid quantum rotor analysis of R(2) Hamiltonian $\mathbf{H}=B\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$

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

Asymmetric rigid quantum rotor analysis of D_2 *Hamiltonian* $\mathbf{H}=A\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$

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

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

R(3)⊃D_2 *character analysis of ℓ-level or 2ℓ+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* $\mathbf{H}=B\mathbf{J}\cdot\mathbf{J}+t_{044}\mathbf{T}^{[4]}$

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

R(3)⊂O(3)⊃O_h*⊃O character analysis of ℓ-level or 2ℓ+1-multiplet splitting in O*

SF_6 *spectral fine structure P(88)*

CF_4 *spectral fine structure P(54)*

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$R(3)\subset O(3)\supset O_h\supset O$ character analysis of ℓ-level or 2ℓ+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

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

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

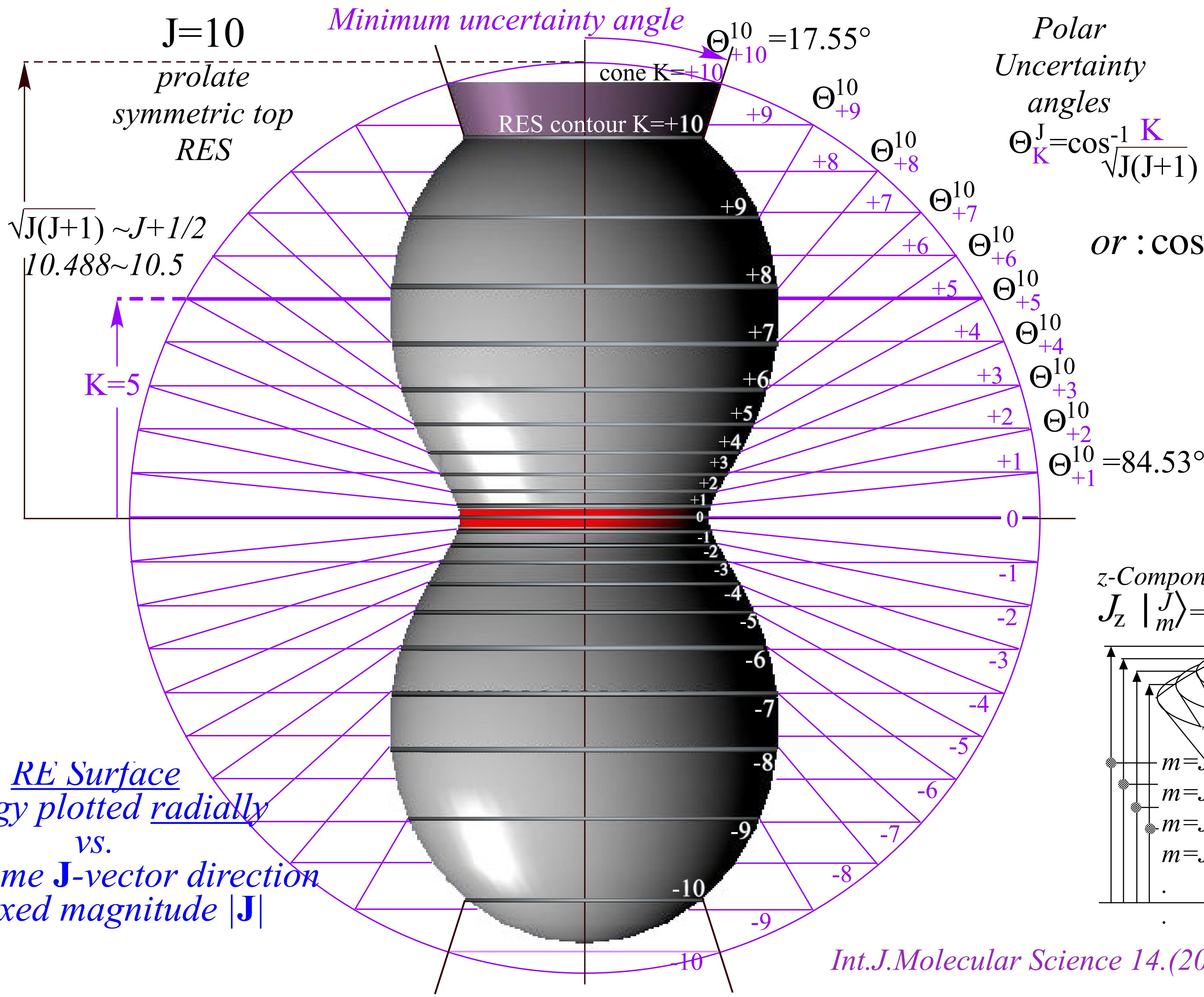
$$=BJ(J+1)+(C-B)K^2$$

(Here this gives exact quantum eigenvalues!)

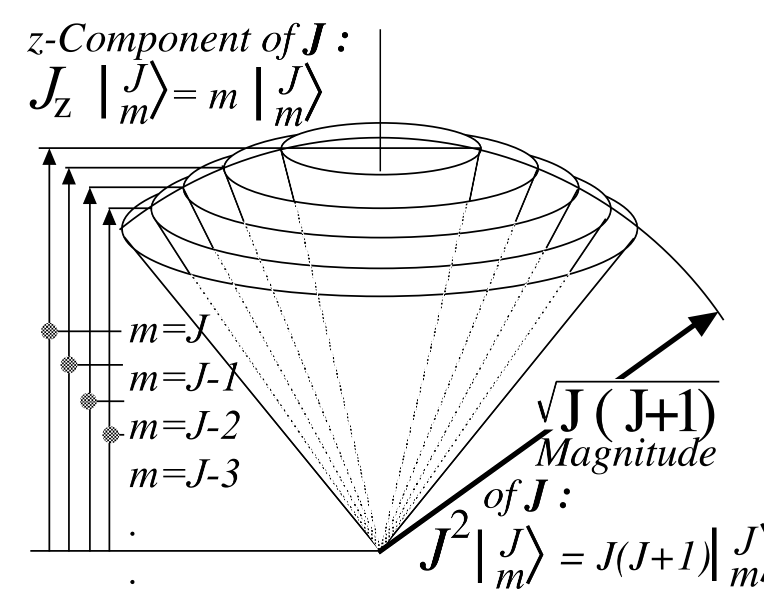
where: $\mathbf{J}_z=|\mathbf{J}|\cos\Theta=\sqrt{J(J+1)}\cos\Theta$

$\left|\begin{matrix} j \\ m,n \end{matrix}\right\rangle$ *Conventional notation:* $n=K$

LAB $m=M$ *BOD* $n=K$



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



RE Surface
Energy plotted radially
vs.
BOD frame **J***-vector direction*
for fixed magnitude |**J**|

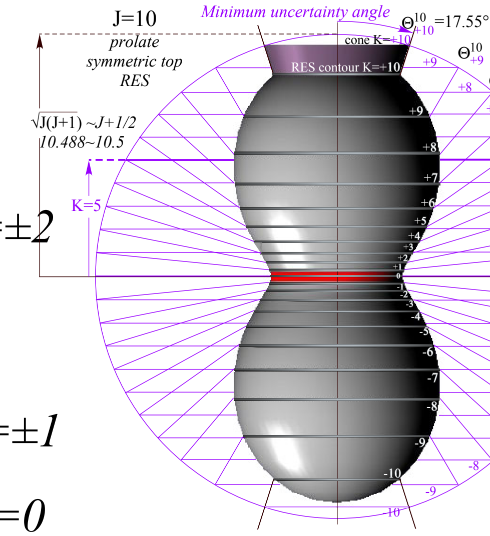
Int.J.Molecular Science 14.(2013) Fig.1 p. 730

R(3)~U(2) representations applied to molecular symmetric rotor analysis

$$\mathbf{H}_{symmetric\ top} = B\mathbf{J}_{\bar{X}}^2 + B\mathbf{J}_{\bar{Y}}^2 + B\mathbf{J}_{\bar{Z}}^2 + (A-B)\mathbf{J}_{\bar{Z}}^2 = B\mathbf{J}\bullet\mathbf{J} + (A-B)\mathbf{J}_{\bar{Z}}^2$$

Kinetic energy inertial coefficients:

$$B = \frac{1}{2I_{\bar{X}}} = C = \frac{1}{2I_{\bar{Y}}},\ A = \frac{1}{2I_{\bar{Z}}}$$



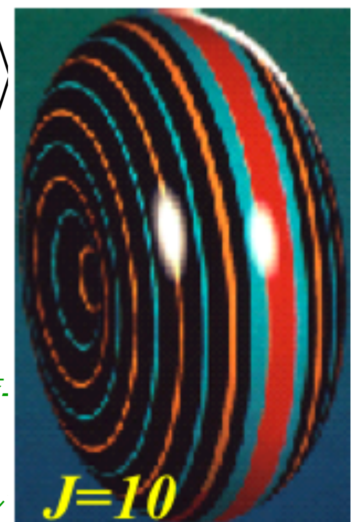
Eigensolution equations:

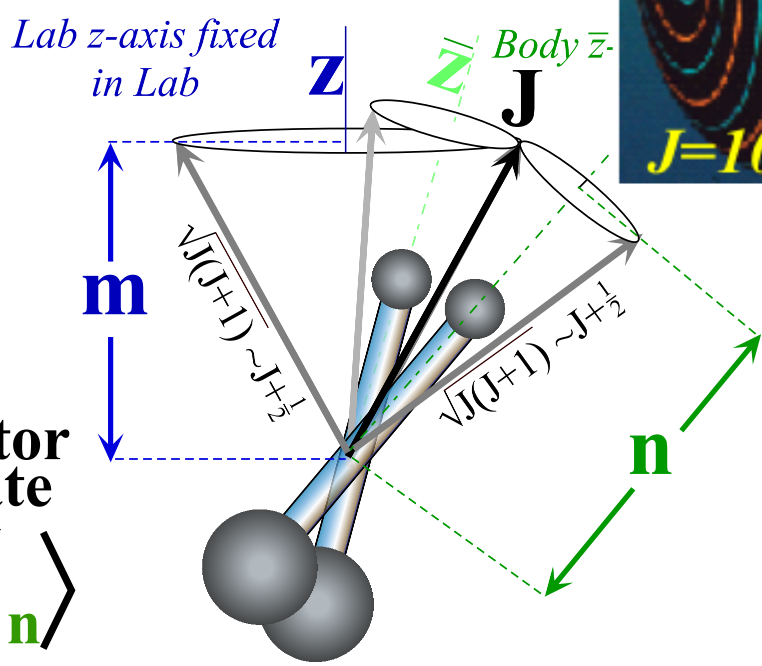
$$\mathbf{H}_{symmetric\ top}\left|\begin{matrix} j \\ m,n \end{matrix}\right\rangle$$

$$= B\mathbf{J}\bullet\mathbf{J} + (A-B)\mathbf{J}_{\bar{Z}}^2\left|\begin{matrix} j \\ m,n \end{matrix}\right\rangle$$

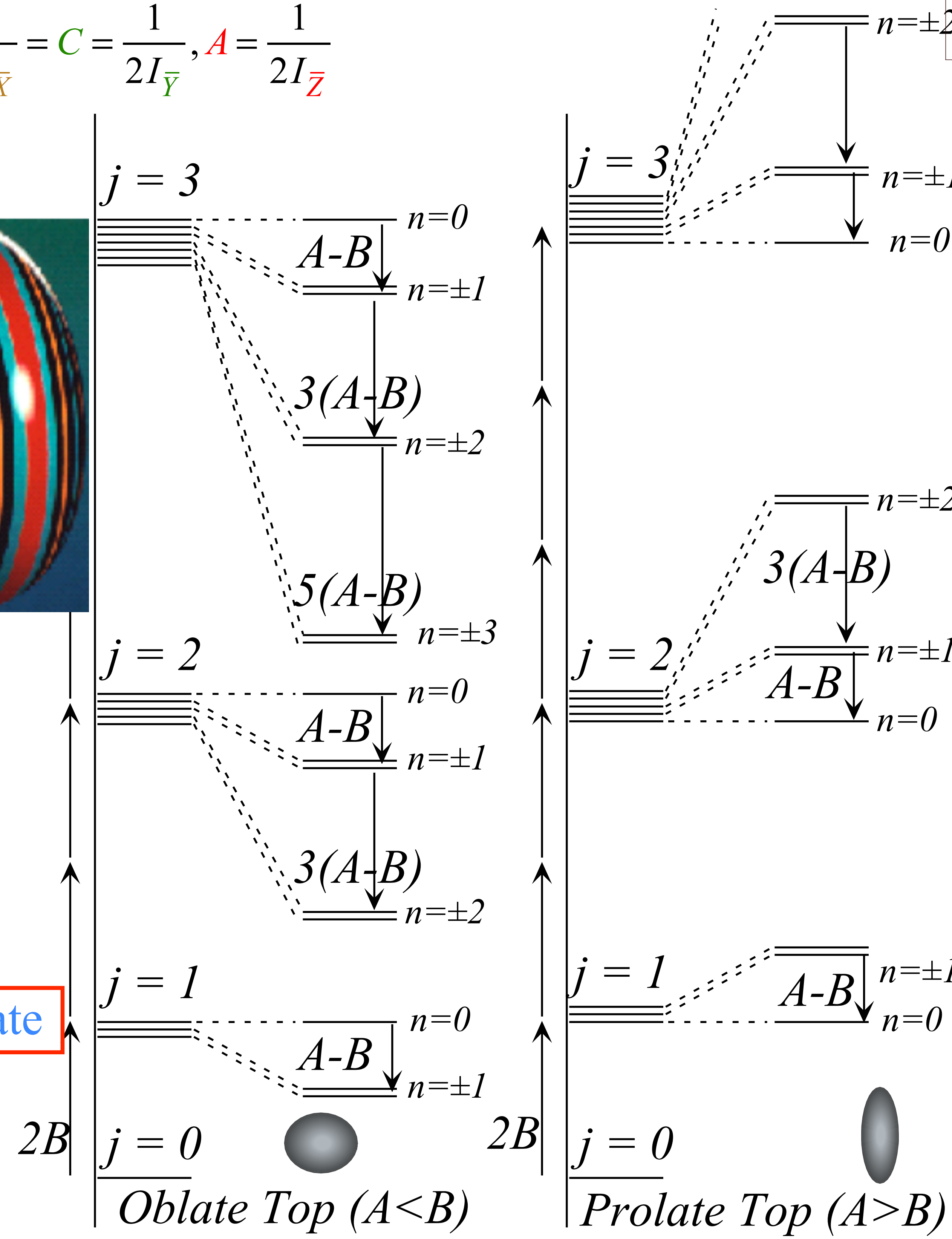
$$= \left[BJ(J+1) + (A-B)n^2\right]\left|\begin{matrix} j \\ m,n \end{matrix}\right\rangle$$

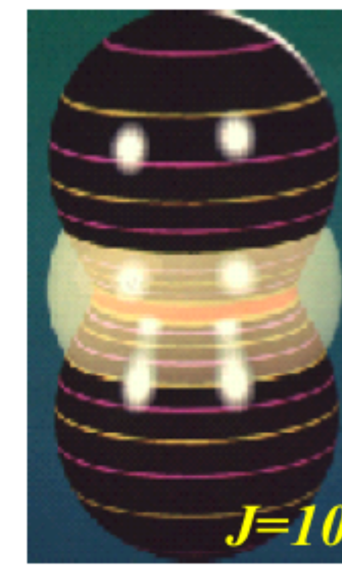
Mock-Mach-Multiplicity
is $(2j+1)^2$ for each j





Rotor state $\left|\begin{matrix} \mathbf{J} \\ \mathbf{m}\ \mathbf{n} \end{matrix}\right\rangle$





Even $n=0$ levels are $2j+1$-fold degenerate

If n is non-zero the degeneracy is $4j+2$.

QTforCA Unit 8. Ch. 23 Fig. 23.2.4

QTforCA Unit 8. Ch. 23 Fig. 23.1.3

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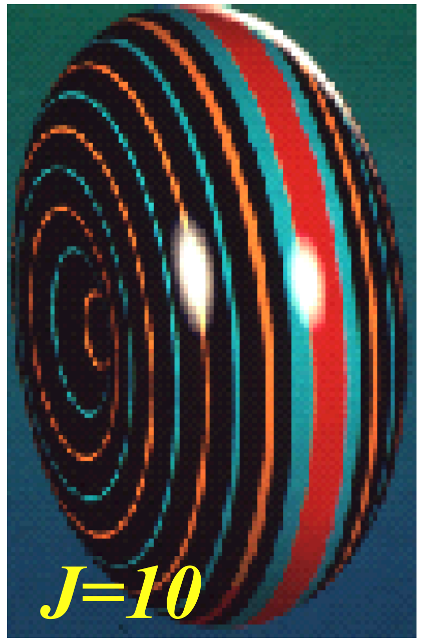
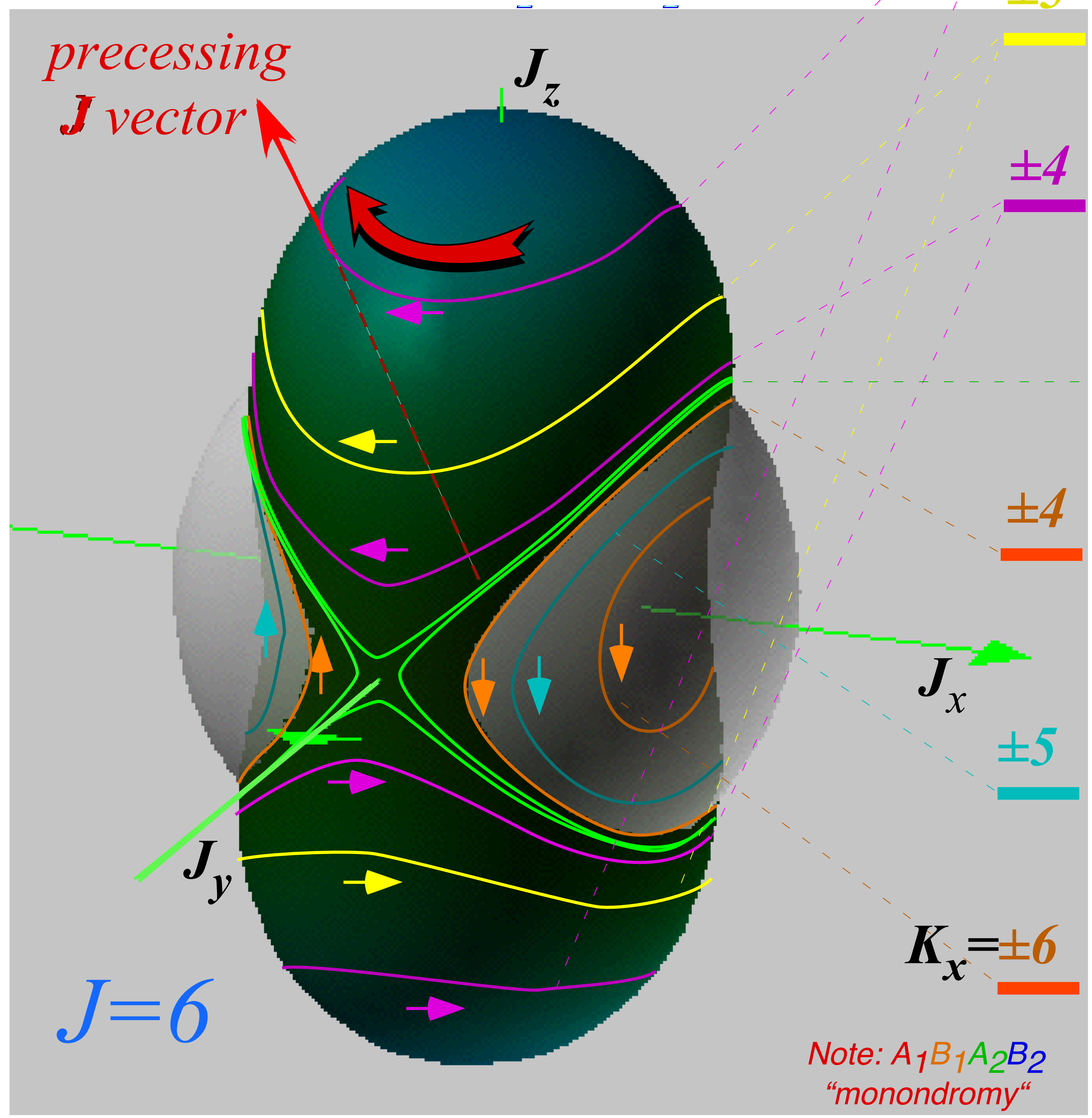
RES of symmetric rotor (J=10 Prolate and Oblate)...
... and related RES of asymmetric rotors

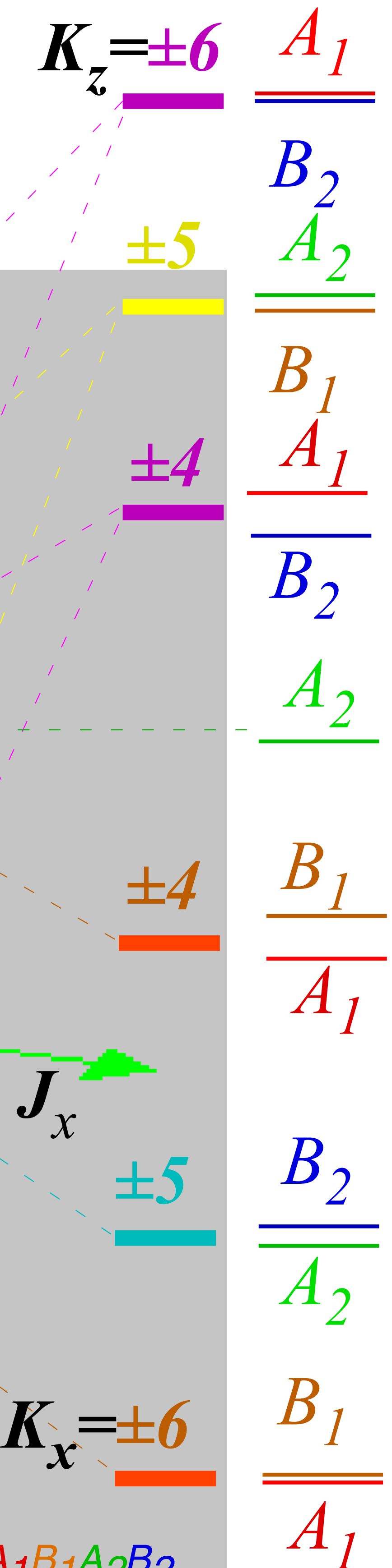


Spectra and RES of asymmetric rotors

$\mathbf{H}=A\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$

for J=1,2,3,...,10 discussed below





after QTforCA Unit 8. Ch. 25 Fig. 25.4.1

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

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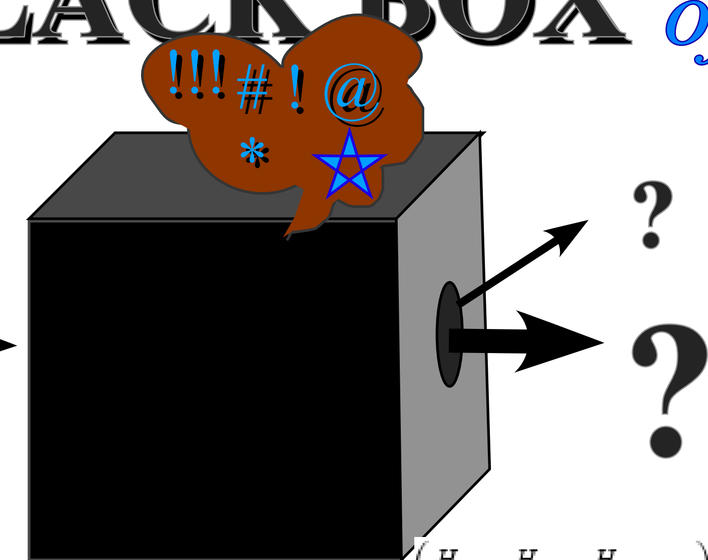
RES and Multipole $\mathbf{T}_q^k$ tensor expansions

Peeking into BLACK BOX of matrix diagonalization:

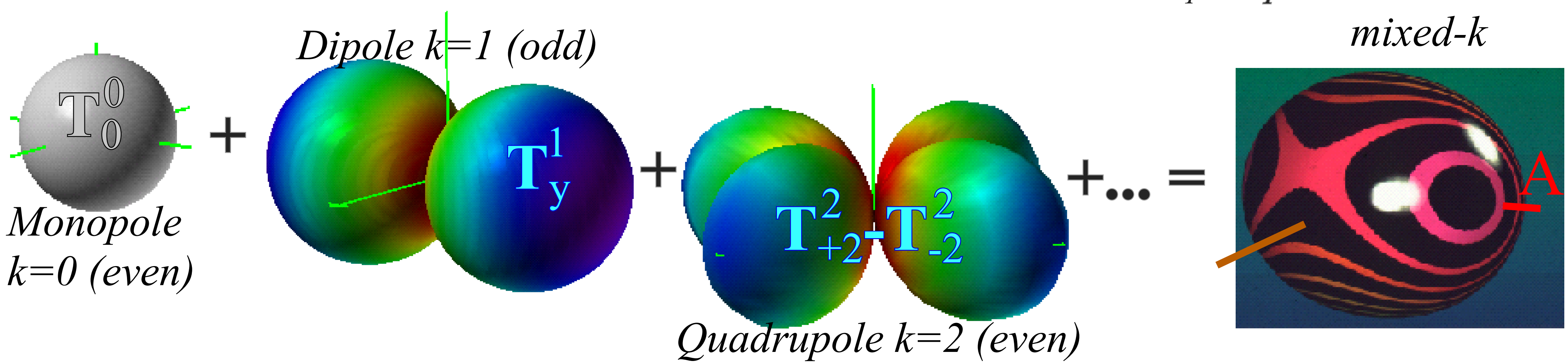
$$\mathbf{H}=\begin{pmatrix} H_{11} & H_{12} & H_{13} & \cdots \\ H_{21} & H_{22} & H_{23} & \cdots \\ H_{31} & H_{32} & H_{33} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \rightarrow$$



Plotting 2^k-pole expansion of $\begin{pmatrix} H_{11} & H_{12} & H_{13} & \cdots \\ H_{21} & H_{22} & H_{23} & \cdots \\ H_{31} & H_{32} & H_{33} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}$ into Fano-Racah tensors

scalar+ *+ vector+* *+ 2^2-tensor +...* *+ 2^k-tensor +..*

$$\mathbf{H}= a\mathbf{T}^0_0+b\mathbf{T}^1_0+c\mathbf{T}^1_1+\ldots+d\mathbf{T}^2_0+e\mathbf{T}^2_1+\ldots=\Sigma c^k_q\mathbf{T}^k_q$$



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

Momentum 101 $p = m\,v$ *(linear)* $J = L = I\,\omega$ *(rotation)* BANG!

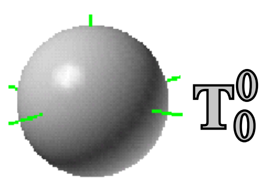
Energy 101 $E = \frac{1}{2} m\,v^2 = p^2/2m$ $E = \frac{1}{2} I\,\omega^2 = J^2/2I$ $BUCKS$

Simple Rigid Rotor Hamiltonian... (Hamiltonian H=E is $BUCKS$ energy in terms of BANG! momentum)

$$\mathbf{H} = A\mathbf{J}_x^2 + B\mathbf{J}_y^2 + C\mathbf{J}_z^2 + \cdots$$

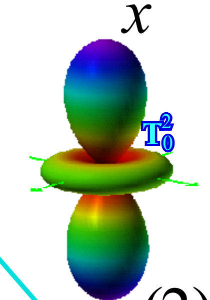
...and its multi-pole expansion...

$$\left(\frac{A+B+C}{3}\right)\left(\mathbf{J}_x^2 + \mathbf{J}_y^2 + \mathbf{J}_z^2\right) + \left(\frac{2C-A-B}{6}\right)\left(2\mathbf{J}_z^2 - \mathbf{J}_x^2 - \mathbf{J}_y^2\right) + \left(\frac{A-B}{2}\right)\left(\mathbf{J}_x^2 - \mathbf{J}_y^2\right)$$



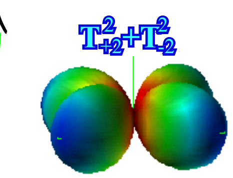
Spherical Top
(A=B=C)
$\mathbf{H} = B\,\mathbf{J}^2$

$$\mathbf{T}_0^{(0)} = \mathbf{J}^2$$



Symmetric Top
(A=B≠C)
$\mathbf{H} = B\,\mathbf{J}^2 + (C - B)(2/3)\mathbf{T}_0^{(2)}$

$$2\mathbf{T}_0^{(2)}$$



$$\sqrt{\frac{2}{3}}\left(\mathbf{T}_2^{(2)} + \mathbf{T}_{-2}^{(2)}\right)$$

Asymmetric Top
(A≠B≠C)

$$\mathbf{H} = B\,\mathbf{J}^2 + (2C - A - B)/3\;\mathbf{T}_0^{(2)} + (A - B)/\sqrt{6}\left(\mathbf{T}_2^{(2)} + \mathbf{T}_{-2}^{(2)}\right)$$

(Derivation in preceding Lecture 25)

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

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

2-by-2 case:

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

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

$$= \frac{A+D}{2}\,\mathbf{T}^0_0 + (B-iC)\,\mathbf{T}^1_1 + (B+iC)\,\mathbf{T}^1_{-1} + \frac{A-D}{2}\,\mathbf{T}^1_0$$

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

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

$$\mathbf{u}^1_{+1}=\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \quad \mathbf{u}^1_0=\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\frac{1}{\sqrt{2}} \quad \mathbf{u}^1_{-1}=\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

rank-1 (vector)

$$\mathbf{u}^0_0=\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\frac{1}{\sqrt{2}}$$

rank-0 (scalar)

RES and Multipole $\mathbf{T}^k_q$ tensor expansions

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

2-by-2 case:

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

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

$$=\frac{A+D}{2}\,\mathbf{T}^0_0+(B-iC)\,\mathbf{T}^1_1+(B+iC)\,\mathbf{T}^1_{-1}+\frac{A-D}{2}\,\mathbf{T}^1_0$$

$$\mathbf{T}^1_1:\begin{pmatrix}0&1\\0&0\end{pmatrix}\qquad \mathbf{T}^1_{-1}:\begin{pmatrix}0&0\\1&0\end{pmatrix}$$

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rank-1 (vector)

$$\mathbf{u}^0_0=\begin{pmatrix}1&0\\0&1\end{pmatrix}\frac{1}{\sqrt2}$$

rank-0 (scalar)

Generalization of U(2) spinor analysis to U(3)⊂U(4)⊂U(5)... (Introduced in following Lecture 27)

3-by-3 case:

$$\mathbf{H}=\begin{pmatrix}H_{11}&H_{12}&H_{13}\\H_{21}&H_{22}&H_{23}\\H_{31}&H_{32}&H_{33}\end{pmatrix}=B\,\mathbf{T}^0_0+\ldots+t_2\,\mathbf{T}^2_2+\ldots$$

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

$$\mathbf{u}^2_{+2}=\begin{pmatrix}0&0&1\\0&0&0\\0&0&0\end{pmatrix}\quad \mathbf{u}^2_{+1}=\begin{pmatrix}0&1&0\\0&0&1\\0&0&0\end{pmatrix}\frac{1}{\sqrt2}\quad \mathbf{u}^2_0=\begin{pmatrix}1&0&0\\0&-2&0\\0&0&1\end{pmatrix}\frac{1}{\sqrt6}\quad \mathbf{u}^2_{-1}=\begin{pmatrix}0&0&0\\1&0&0\\0&1&0\end{pmatrix}\frac{1}{\sqrt2}\quad \mathbf{u}^2_{-2}=\begin{pmatrix}0&0&0\\0&0&0\\1&0&0\end{pmatrix}$$

rank-2 (tensor)

$$\mathbf{u}^1_{+1}=\begin{pmatrix}0&1&0\\0&0&1\\0&0&0\end{pmatrix}\frac{1}{\sqrt2}\quad \mathbf{u}^1_0=\begin{pmatrix}1&0&0\\0&0&0\\0&0&-1\end{pmatrix}\frac{1}{\sqrt2}\quad \mathbf{u}^1_{-1}=\begin{pmatrix}0&0&0\\1&0&0\\0&1&0\end{pmatrix}\frac{1}{\sqrt2}$$

rank-1 (vector)

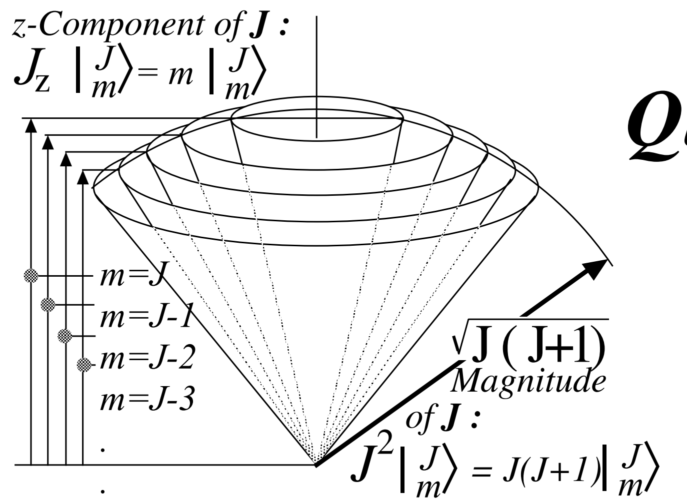
$$\mathbf{u}^0_0=\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}\frac{1}{\sqrt3}$$

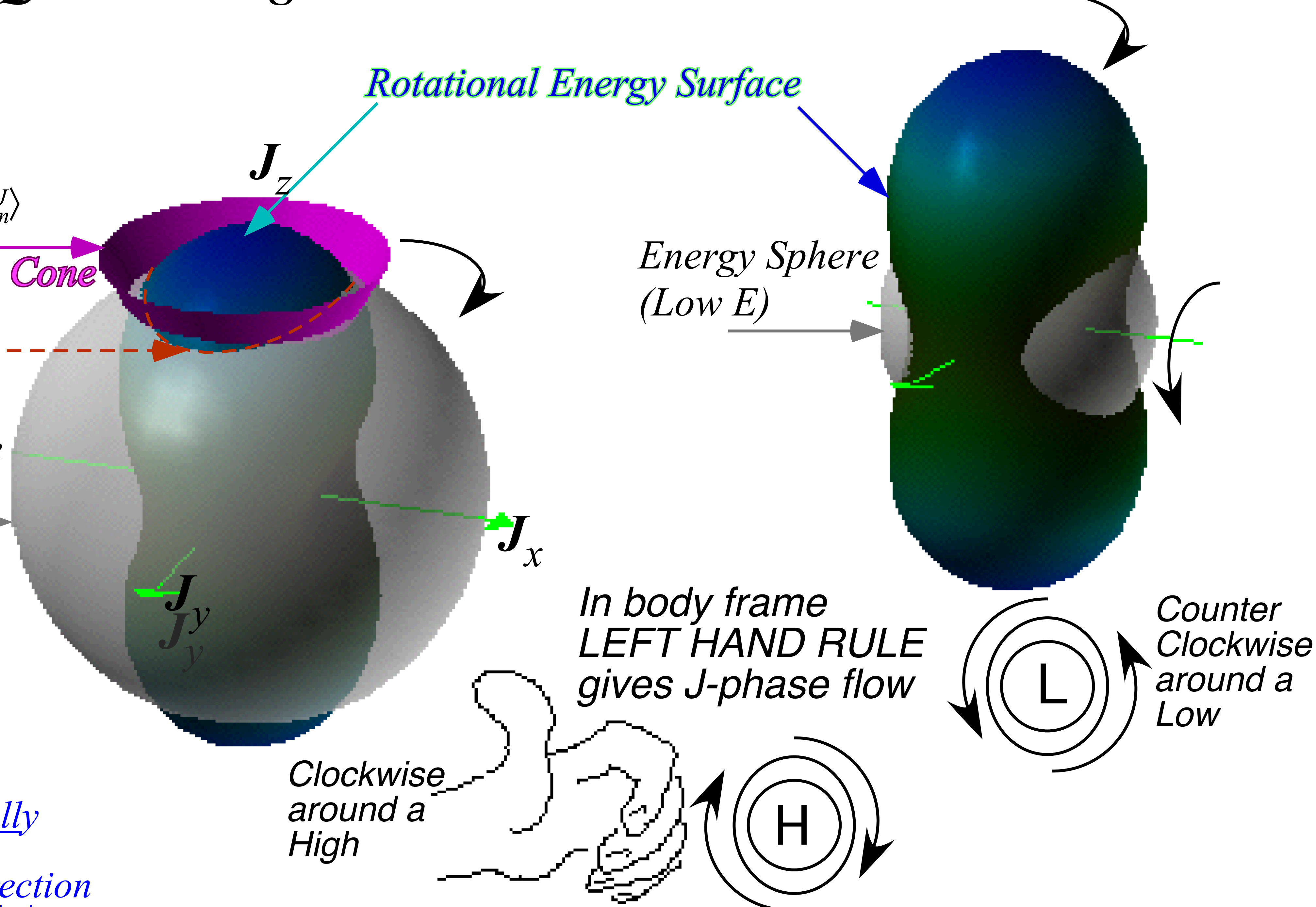
rank-0 (scalar)

Mutually commuting diagonal operators

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

J-Phase Paths *(Intersection(s) of RE Surface and Energy Sphere)*
and
Quantum angular momentum cones



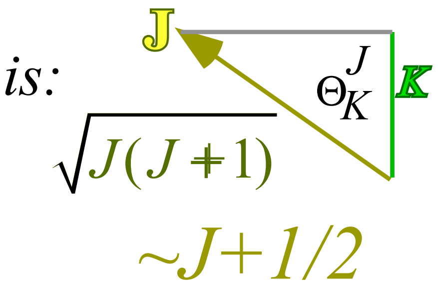


RE Surface
Energy plotted radially
vs.
*BOD frame **J**-vector direction*
*for fixed magnitude |**J**|*

$$\mathbf{J}^2 \left| \begin{matrix} J \\ K \end{matrix} \right\rangle = J(J+1) \left| \begin{matrix} J \\ K \end{matrix} \right\rangle$$

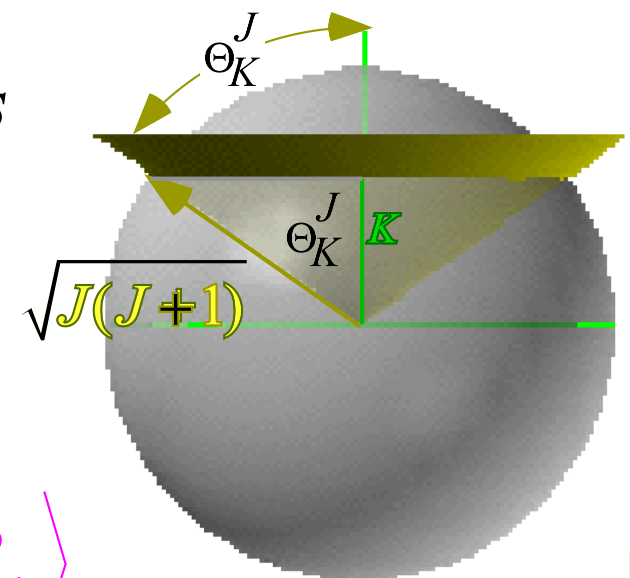
$$\mathbf{J}_z \left| \begin{matrix} J \\ K \end{matrix} \right\rangle = K \left| \begin{matrix} J \\ K \end{matrix} \right\rangle$$

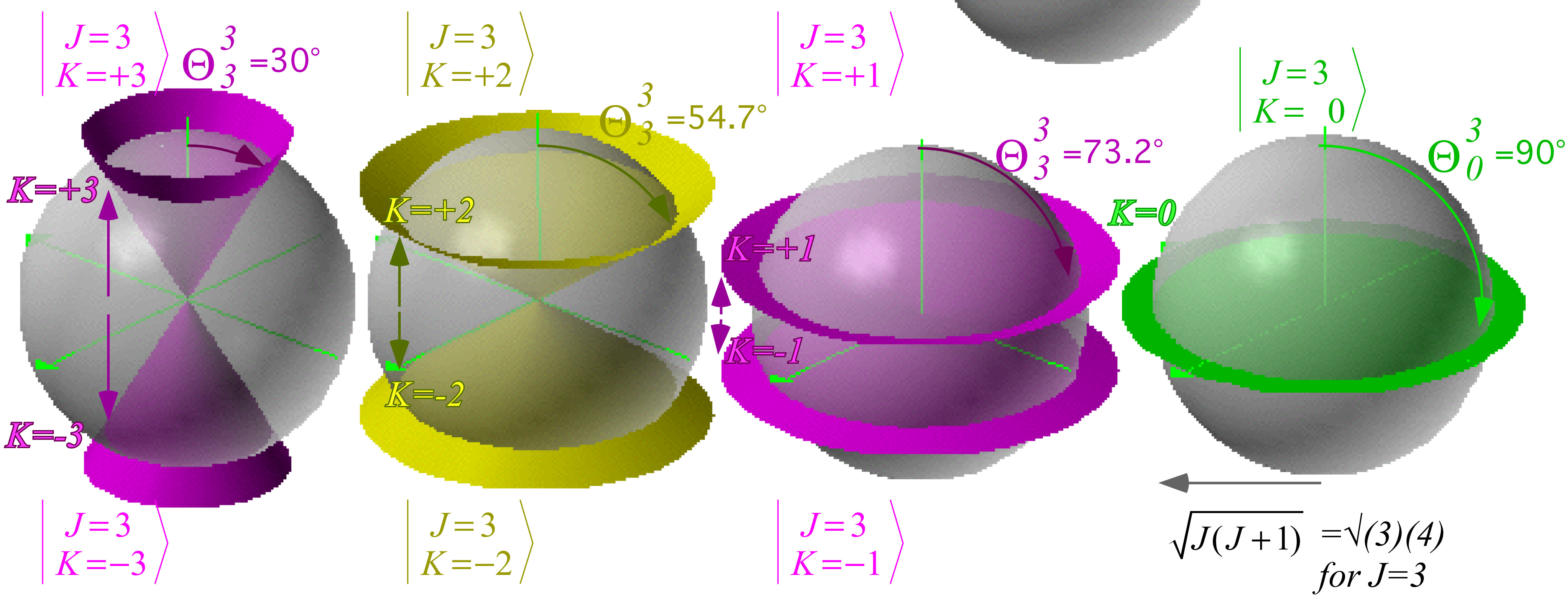
Interpreted "Literally" is:



Quantum Angular Cone Uncertainty Angles

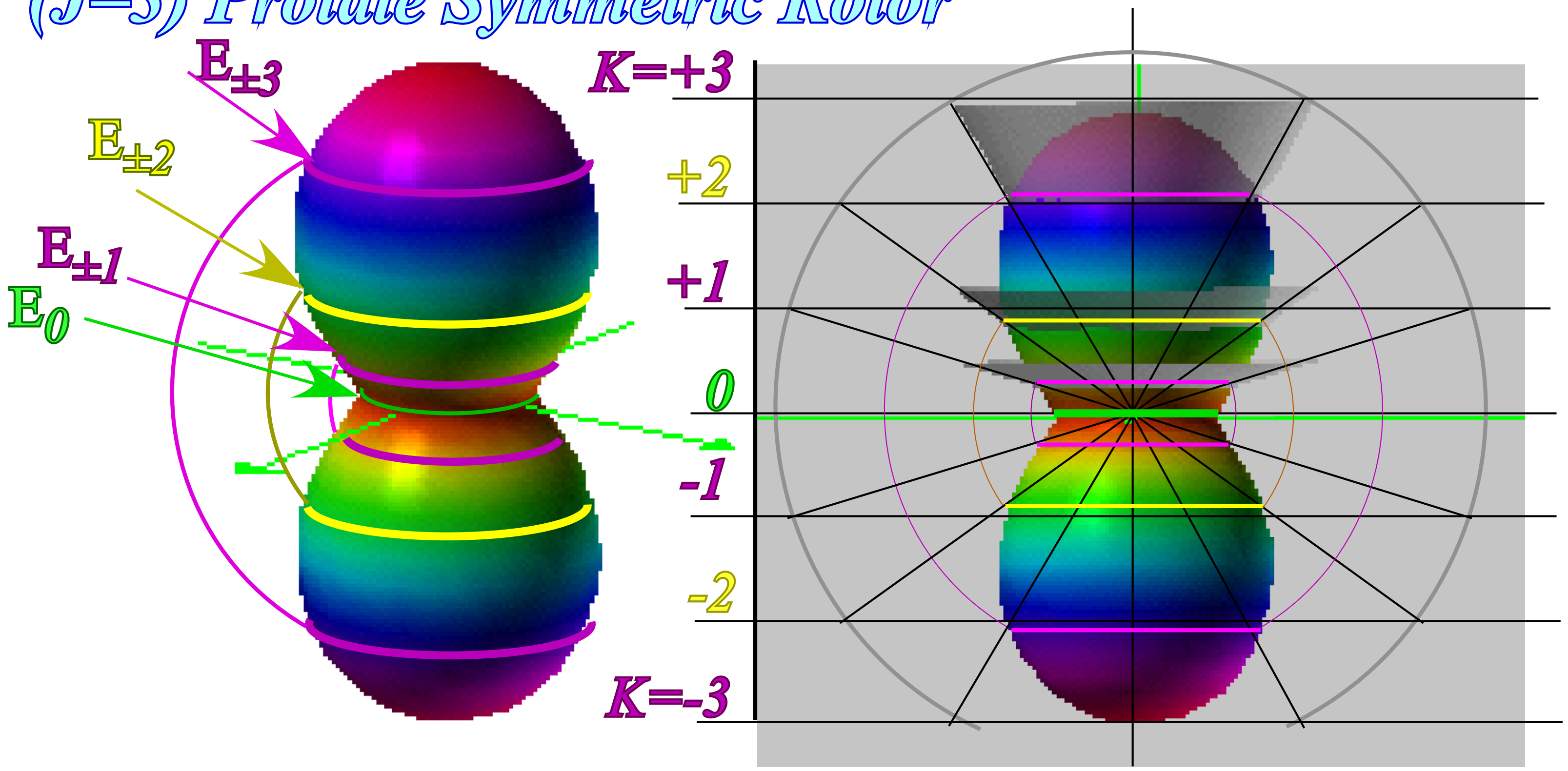
$$\cos\Theta_K^J = \frac{K}{\sqrt{J(J+1)}}$$

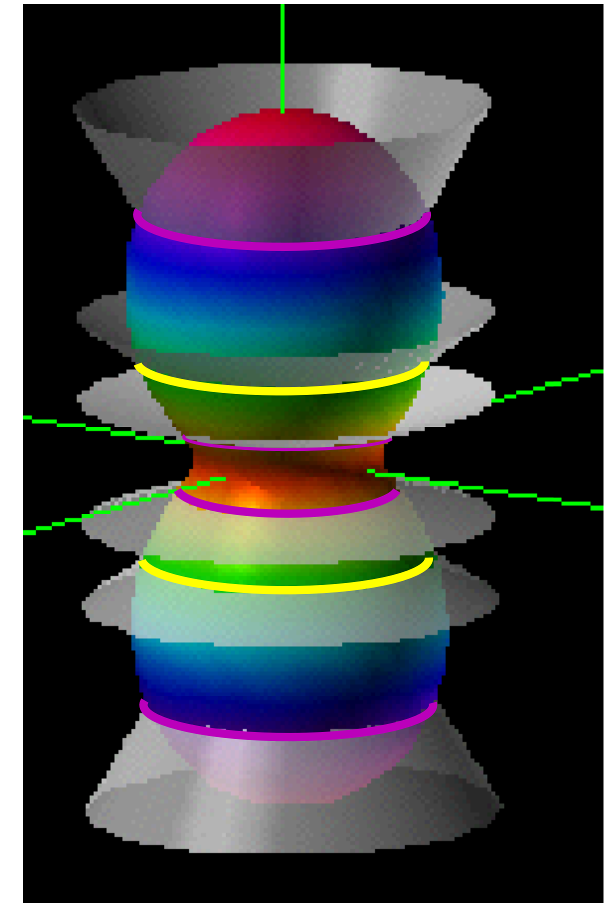




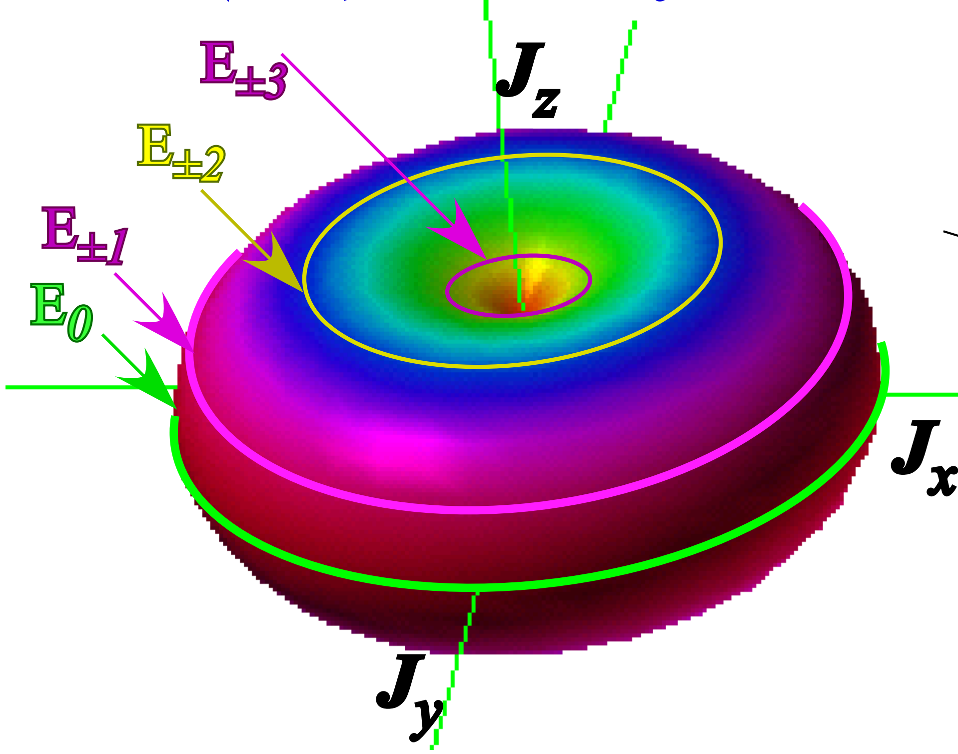
(S) Semiclassical J-Phase Paths for

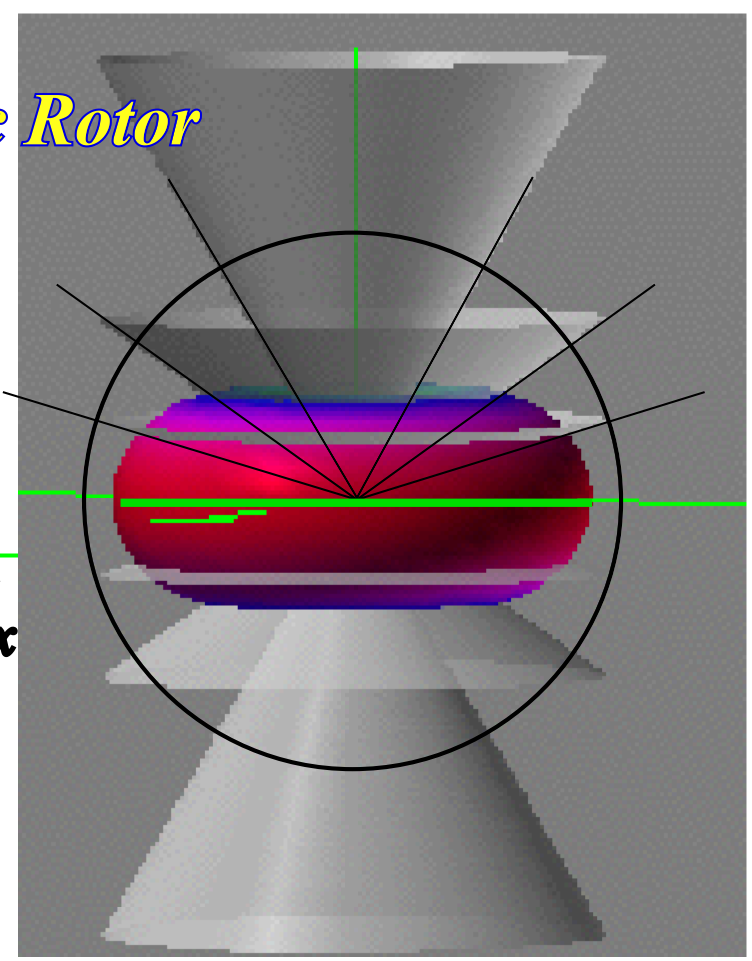
(J=3) Prolate Symmetric Rotor

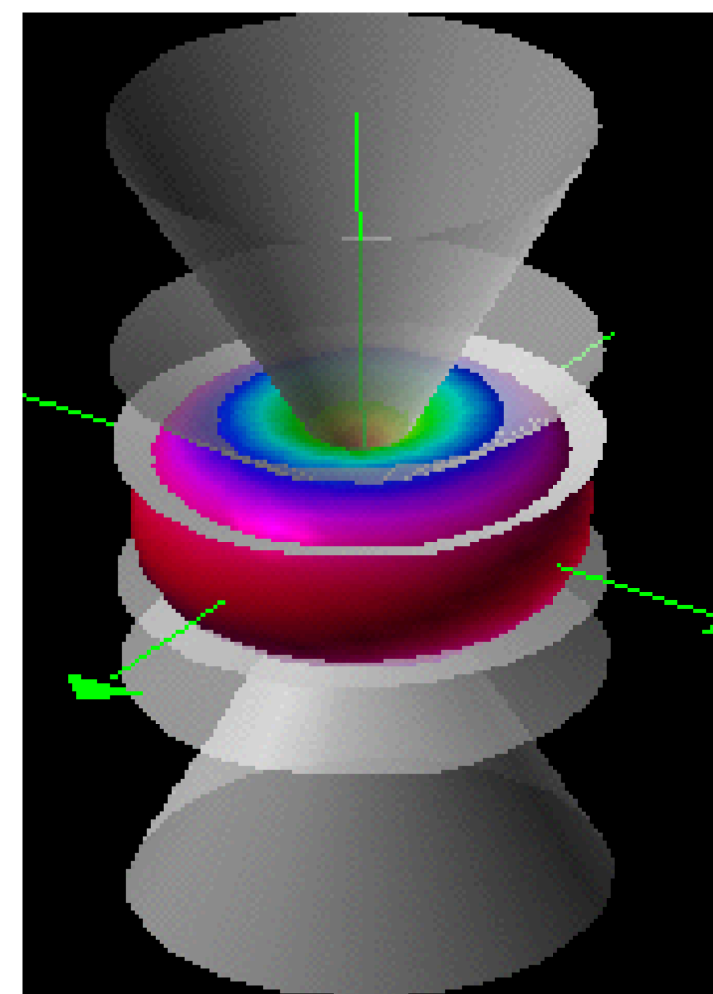




(J=3) Oblate Symmetric Rotor







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Asymmetric rotor levels and RES plots for high-J

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Spherical rotor levels and RES plots of O_h tensor eigenvalues

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SF_6 spectral fine structure

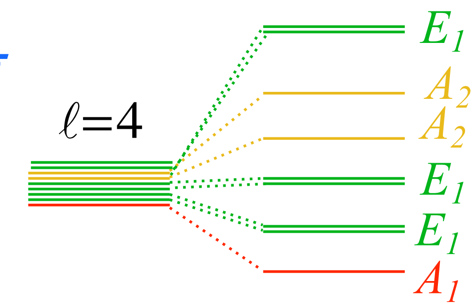
CF_4 spectral fine structure

Atomic ℓ-level or 2ℓ+1-multiplet splitting in D_3

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

Example: (ℓ=4)

$$f^{(b)} = \frac{1}{{}^{\circ}D_3} \sum_{\substack{\text{classes} \\ \kappa_k \in D_3}} {}^{\circ}\kappa_k \chi_k^{(b)*} \chi_k^{(\ell)}$$



ℓ=0, s-singlet
2ℓ+1=1
ℓ=1, p-triplet
2ℓ+1=3
ℓ=2, d-quintet
2ℓ+1=5
ℓ=3, f-septet
2ℓ+1=7
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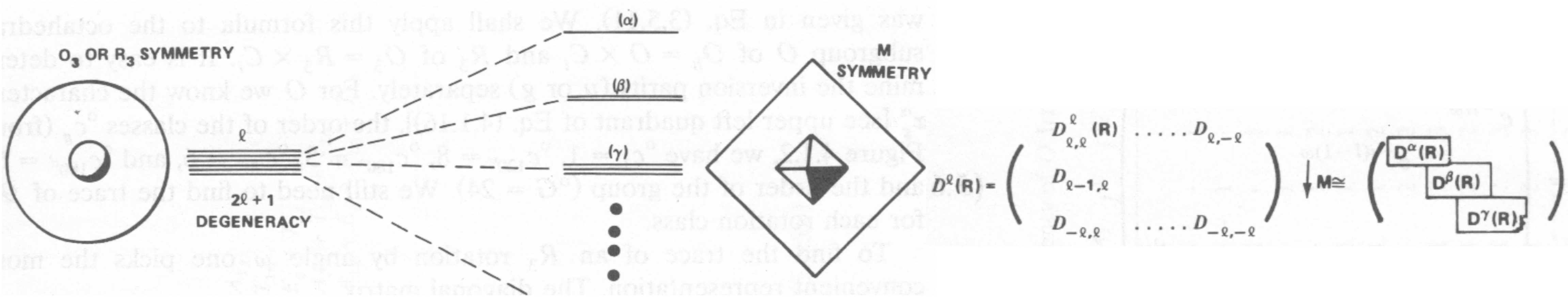
ℓ=5, h-(11)-let
2ℓ+1=11
...



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

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

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

R(3) character where: 2ℓ+1 is ℓ-orbital dimension

$\chi^{\ell}(\Theta)$	$\Theta=0$	$\frac{2\pi}{3}$	π
$\ell=0$	1	1	1
1	3	0	−1
2	5	−1	1
3	7	1	−1
4	9	0	1
5	11	−1	−1
6	13	1	1
7	15	0	−1

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

$(\mathbf{g})=$	$\{\mathbf{1}\}$	$\{\mathbf{r}^1,\mathbf{r}^2\}$	$\{\mathbf{i}_1,\mathbf{i}_2,\mathbf{i}_3\}$
$\chi^{A_1}(\mathbf{g})=$	1	1	1
$\chi^{A_2}(\mathbf{g})=$	1	1	−1
$\chi^{E_1}(\mathbf{g})=$	2	−1	0

$f^{(\alpha)}(\ell)$	f^{A_1}	f^{A_2}	f^{E_1}	
$\ell=0$	1	·	·	$1A_1$
1	·	1	1	$0A_1 \oplus A_2 \oplus E_1$
2	1	·	2	$1A_1 \quad \oplus 2E_1$

	5	−1	1
$\chi^{A_1}(\mathbf{g})=$	1	1	1
$0\chi^{A_2}(\mathbf{g})=$	0	0	0
$2\chi^{E_1}(\mathbf{g})=$	4	−2	0

trial&error??

Review :

Symmetric rigid quantum rotor analysis of R(2) Hamiltonian $\mathbf{H}=B\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$

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

Asymmetric rigid quantum rotor analysis of D_2 Hamiltonian $\mathbf{H}=A\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$

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

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

R(3)⊃D_2 character analysis of ℓ-level or 2ℓ+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 $\mathbf{H}=B\mathbf{J}\cdot\mathbf{J}+t_{044}\mathbf{T}^{[4]}$

Spherical rotor levels and RES plots of O_h tensor eigenvalues

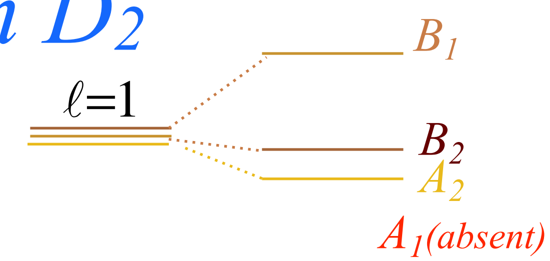
R(3)⊂O(3)⊃O_h⊃O character analysis of ℓ-level or 2ℓ+1-multiplet splitting in O

SF_6 spectral fine structure

CF_4 spectral fine structure

Atomic ℓ-level or 2ℓ+1-multiplet splitting in D_2

Here we apply that to D_2 level splitting



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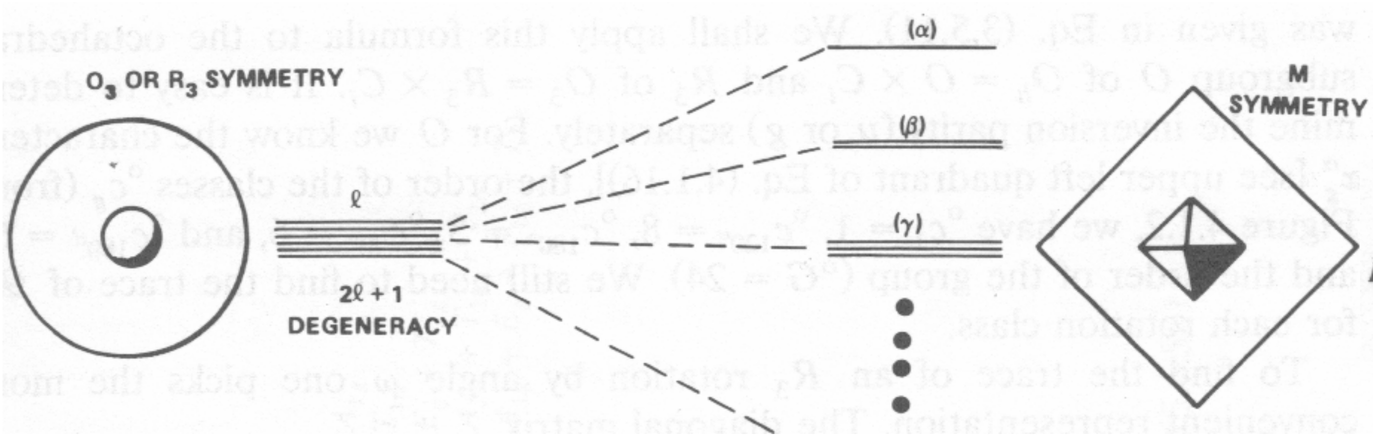
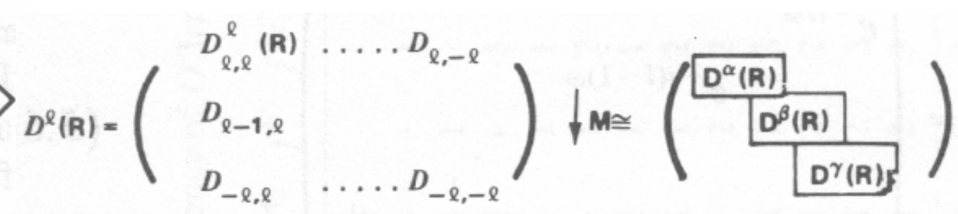
ℓ=3, f-septet
2ℓ+1=7
ℓ=4, g-nonet
2ℓ+1=9
ℓ=5, h-(11)-let
2ℓ+1=11
...

Example: (ℓ=1) $f^{(b)} = \frac{1}{{}^\circ D_2} \sum_{\substack{classes \\ \kappa_k \in D_2}} {}^\circ\kappa_k \chi_k^{(b)*} \chi_k^{(\ell)} = \frac{1}{4} \sum_{g \in D_2}^{4} \chi_k^{(b)*} \chi_k^{(\ell)}$





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

$\chi^\ell(\Theta)$	$\Theta=0$	$\mathbf{R}_x\pi$	$\mathbf{R}_y\pi$	$\mathbf{R}_z\pi$
$\ell=0$	1	1	1	1
1	3	-1	-1	-1
2	5	1	1	1
3	7	-1	-1	-1
4	9	1	1	1
5	11	-1	-1	-1
6	13	1	1	1
7	15	-1	-1	-1
8	17	1	1	1

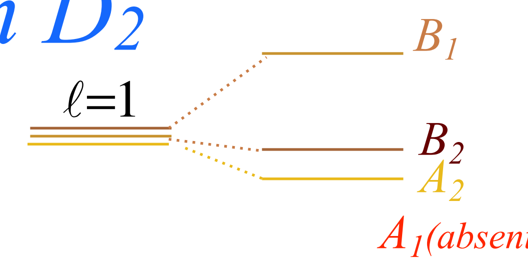
$$\chi^\ell\left(\frac{2\pi}{n}\right) = \frac{\sin\frac{(2\ell+1)\pi}{n}}{\sin\frac{\pi}{n}}$$

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

R(3) character
where: 2ℓ+1
is ℓ-orbital dimension

Atomic ℓ-level or 2ℓ+1-multiplet splitting in D_2

Here we apply that to D_2 level splitting



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2ℓ+1=7
ℓ=4, g-nonet
2ℓ+1=9
ℓ=5, h-(11)-let
2ℓ+1=11
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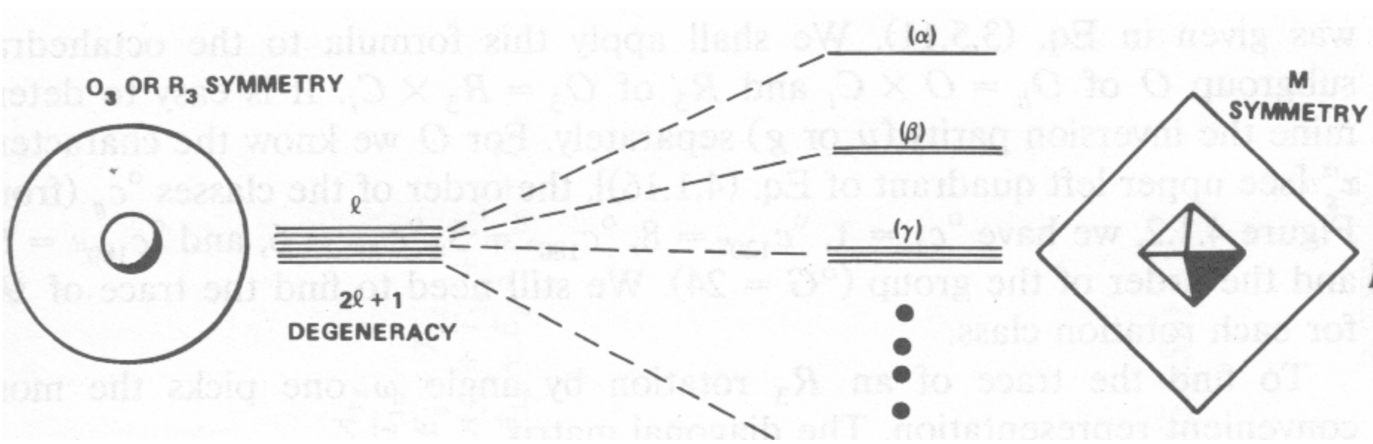
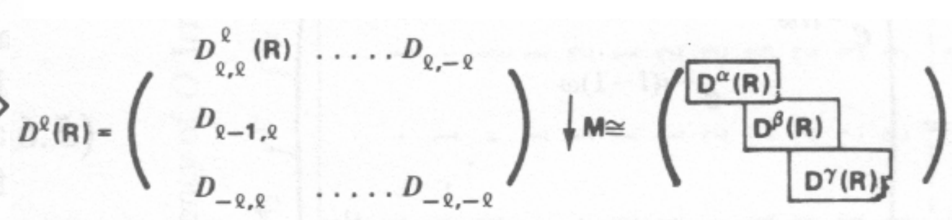
Example: (ℓ=1) $$f^{(b)} = \frac{1}{{}^{\circ}D_2} \sum_{\substack{\text{classes}\\ \kappa_k \in D_2}} {}^{\circ}\kappa_k \chi_k^{(b)*} \chi_k^{(\ell)} = \frac{1}{4} \sum_{g \in D_2}^{4} \chi_k^{(b)*} \chi_k^{(\ell)}$$





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

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

R(3) character
where: 2ℓ+1
is ℓ-orbital dimension

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

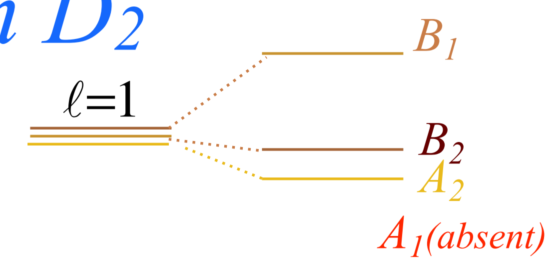
$\chi^{\ell}(\Theta)$	$\Theta=0$	$\mathbf{R}_x\pi$	$\mathbf{R}_y\pi$	$\mathbf{R}_z\pi$
$\ell=0$	1	1	1	1
1	3	-1	-1	-1
2	5	1	1	1
3	7	-1	-1	-1
4	9	1	1	1
5	11	-1	-1	-1
6	13	1	1	1
7	15	-1	-1	-1
8	17	1	1	1

...and Lect.13 p.79
D_2 characters:

D_2	**1**	$\mathbf{R}_x$	$\mathbf{R}_y$	$\mathbf{R}_z$
A_1	1	1	1	1
A_2	1	-1	1	−1
B_1	1	1	-1	−1
B_2	1	-1	-1	1

Atomic ℓ-level or 2ℓ+1-multiplet splitting in D_2

Here we apply that to D_2 level splitting



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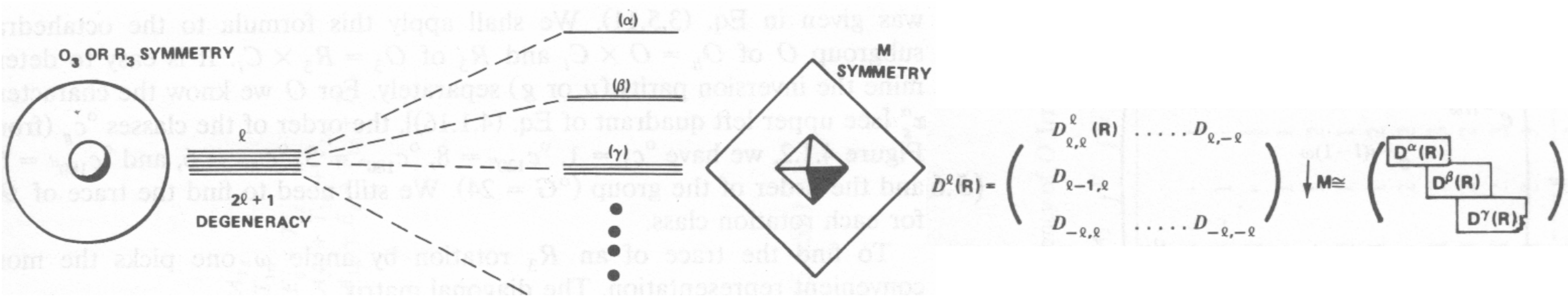
2ℓ+1=7
ℓ=4, g-nonet
2ℓ+1=9
ℓ=5, h-(11)-let
2ℓ+1=11
...

Example: (ℓ=1)
$$f^{(b)}=\frac{1}{{}^\circ D_2}\sum_{\substack{classes\\ \kappa_k\in D_2}} {}^\circ\kappa_k \chi_k^{(b)*}\chi_k^{(\ell)} = \frac{1}{4}\sum_{g\in D_2}^{4}\chi_k^{(b)*}\chi_k^{(\ell)}$$



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

$\chi^\ell(\Theta)$	$\Theta=0$	$\mathbf{R}_x\pi$	$\mathbf{R}_y\pi$	$\mathbf{R}_z\pi$
$\ell=0$	1	1	1	1
1	3	-1	-1	-1
2	5	1	1	1
3	7	-1	-1	-1
4	9	1	1	1
5	11	-1	-1	-1
6	13	1	1	1
7	15	-1	-1	-1
8	17	1	1	1

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

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

R(3) character
where: 2ℓ+1
is ℓ-orbital dimension

...and Lect.13 p.79
D_2 characters:

D_2	**1**	$\mathbf{R}_x$	$\mathbf{R}_y$	$\mathbf{R}_z$
A_1	1	1	1	1
A_2	1	-1	1	−1
B_1	1	1	-1	−1
B_2	1	-1	-1	1

$f^{(\alpha)}(\ell)$	f^{A_1}	f^{A_2}	f^{B_1}	f^{B_2}	
$\ell=0$	1	·	·		$1A_1$
1	·	1	1	1	$0A_1\oplus A_2\oplus B_1\oplus B_2$

	3	-1	-1	-1
$0\chi^{A_1}(\mathbf{g})=$	1	1	1	1
$1\chi^{A_2}(\mathbf{g})=$	1	-1	1	-1
$1\chi^{B_1}(\mathbf{g})=$	1	1	-1	-1
$1\chi^{B_2}(\mathbf{g})=$	1	-1	-1	1

trial&error??

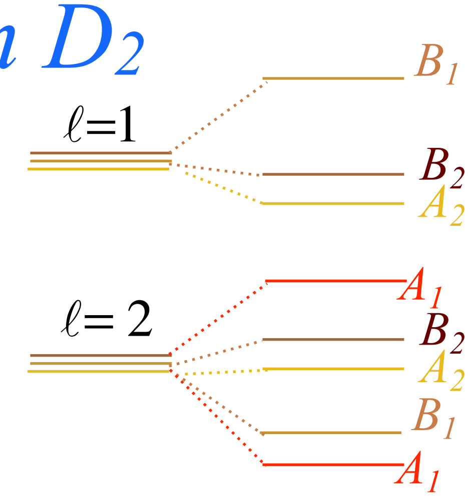
Atomic ℓ-level or 2ℓ+1-multiplet splitting in D_2

Here we apply that to D_2 level splitting

Example: (ℓ=1)

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

and: (ℓ=2)



ℓ=0, s-singlet
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ℓ=3, f-septet
2ℓ+1=7
ℓ=4, g-nonet
2ℓ+1=9
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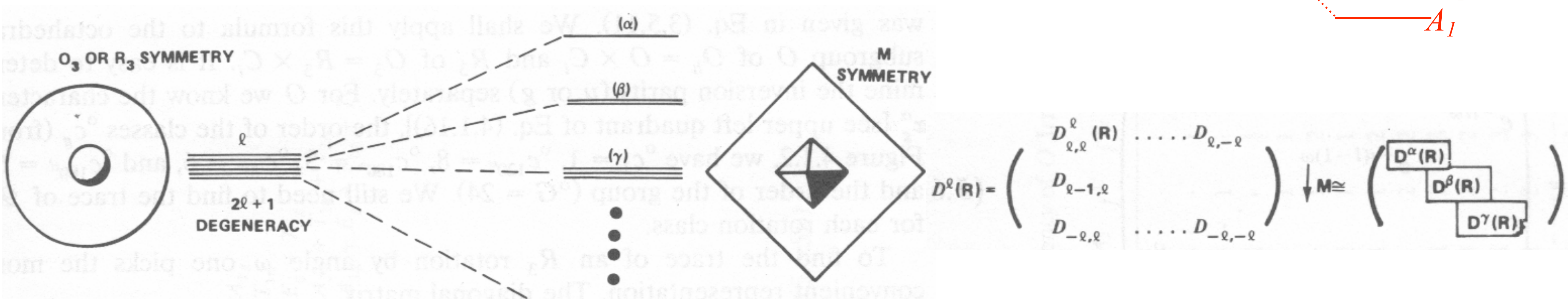


U(2) characters
from Lecture 12.6 p.134 :

$\chi^{\ell}(\Theta)$	$\Theta = 0$	$\mathbf{R}_x \pi$	$\mathbf{R}_y \pi$	$\mathbf{R}_z \pi$
$\ell = 0$	1	1	1	1
1	3	-1	-1	-1
2	5	1	1	1
3	7	-1	-1	-1
4	9	1	1	1
5	11	-1	-1	-1
6	13	1	1	1
7	15	-1	-1	-1
8	17	1	1	1

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

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

R(3) character
where: 2ℓ+1
is ℓ-orbital dimension

...and Lect.13 p.79
D_2 characters:

D_2	**1**	$\mathbf{R}_x$	$\mathbf{R}_y$	$\mathbf{R}_z$
A_1	1	1	1	1
A_2	1	-1	1	−1
B_1	1	1	-1	−1
B_2	1	-1	-1	1

$f^{(\alpha)}(\ell)$	f^{A_1}	f^{A_2}	f^{B_1}	f^{B_2}	
$\ell = 0$	1	·	·		$1A_1$
1	·	1	1	1	$0A_1 \oplus A_2 \oplus B_1 \oplus B_2$
2	2	1	1	1	$2A_1 \oplus A_2 \oplus B_1 \oplus B_2$

	5	1	1	1
$2\chi^{A_1}(\mathbf{g}) =$	2	2	2	2
$1\chi^{A_2}(\mathbf{g}) =$	1	-1	1	-1
$1\chi^{B_1}(\mathbf{g}) =$	1	1	-1	-1
$1\chi^{B_2}(\mathbf{g}) =$	1	-1	-1	1

trial&error??

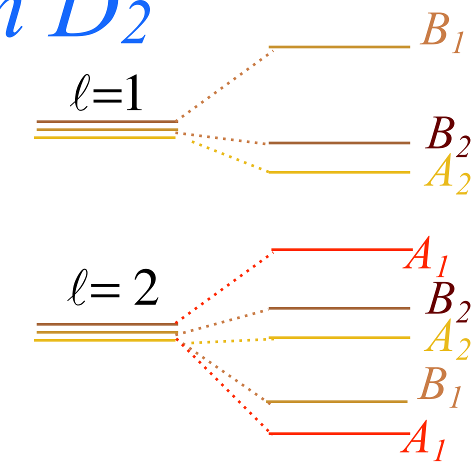
Atomic ℓ-level or $2\ell+1$-multiplet splitting in D_2

Here we apply that to D_2 level splitting

Example: $(\ell=1)$

and: $(\ell=2)$

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



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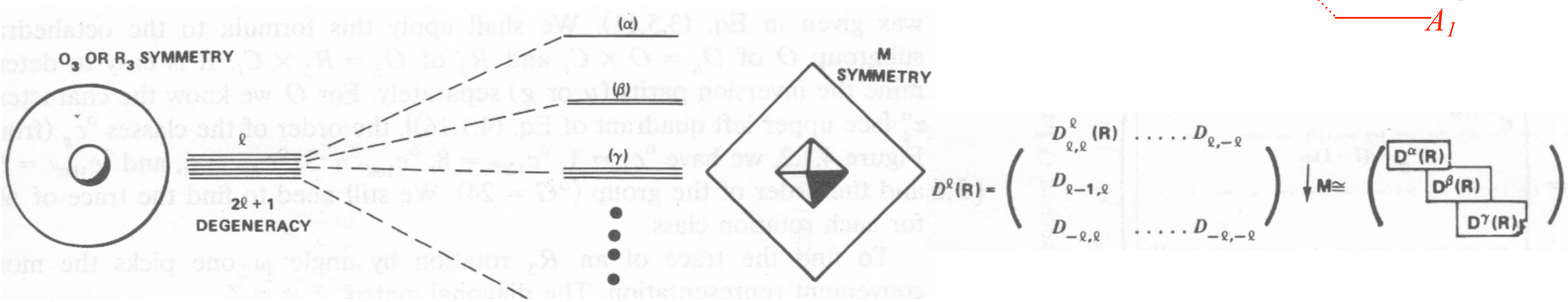

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A_2	1	-1	1	−1
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R(3) character
where: $2\ell+1$
is ℓ-orbital dimension

$f^{(\alpha)}(\ell)$	f^{A_1}	f^{A_2}	f^{B_1}	f^{B_2}	
$\ell=0$	1	·	·		$1A_1$
1	·	1	1	1	$0A_1 \oplus A_2 \oplus B_1 \oplus B_2$
2	2	1	1	1	$2A_1 \oplus A_2 \oplus B_1 \oplus B_2$

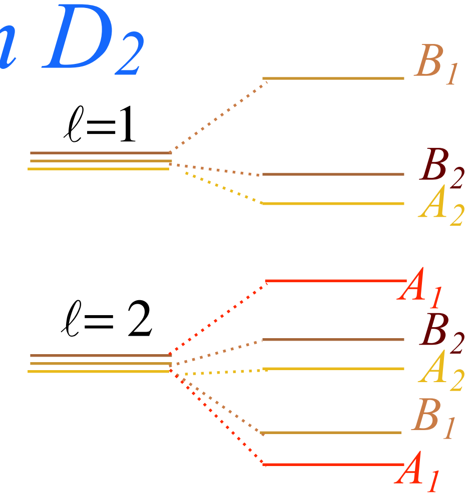
f-formula better than trial&error

$$\frac{1}{4}\begin{array}{|cc|cc|}\hline 1 & 1 & 1 & 1\\ \hline 5 & 1 & 1 & 1\\ \hline\end{array} = \frac{5+1+1+1}{4} = 2$$

$$\frac{1}{4}\begin{array}{|cc|cc|}\hline 1 & -1 & 1 & -1\\ \hline 5 & 1 & 1 & 1\\ \hline\end{array} = \frac{5-1+1-1}{4} = 1$$

Atomic ℓ-level or 2ℓ+1-multiplet splitting in D_2

Here we apply that to D_2 level splitting



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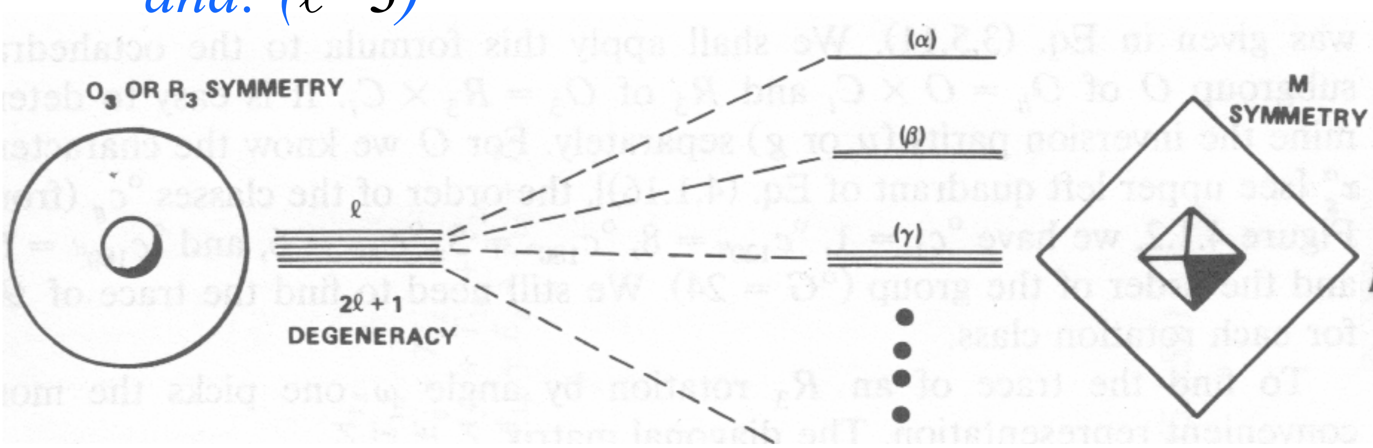
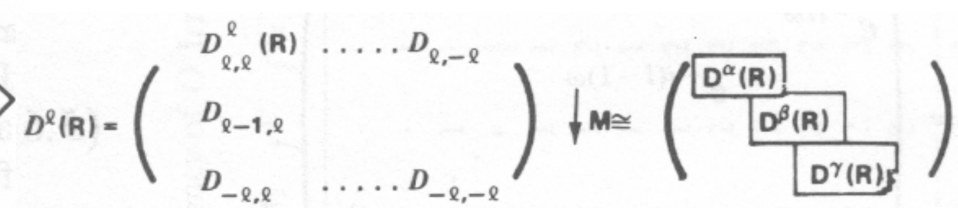
2ℓ+1=11
...

Example: (ℓ=1)
and: (ℓ=2)
and: (ℓ=3)

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





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

$\chi^\ell(\Theta)$	$\Theta = 0$	$\mathbf{R}_x\pi$	$\mathbf{R}_y\pi$	$\mathbf{R}_z\pi$
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2	5	1	1	1
3	7	-1	-1	-1
4	9	1	1	1
5	11	-1	-1	-1
6	13	1	1	1
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...and Lect.13 p.79
D_2 characters:

D_2	**1**	$\mathbf{R}_x$	$\mathbf{R}_y$	$\mathbf{R}_z$
A_1	1	1	1	1
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R(3) character
where: 2ℓ+1
is ℓ-orbital dimension

$f^{(\alpha)}(\ell)$	f^{A_1}	f^{A_2}	f^{B_1}	f^{B_2}	
$\ell = 0$	1	·	·		$1A_1$
1	·	1	1	1	$0A_1 \oplus A_2 \oplus B_1 \oplus B_2$
2	2	1	1	1	$2A_1 \oplus A_2 \oplus B_1 \oplus B_2$
3	1	2	2	2	$1A_1 \oplus 2A_2 \oplus 2B_1 \oplus 2B_2$

f-formula better than trial&error

$$\frac{1}{4}\begin{array}{|cc|cc|} 1 & 1 & 1 & 1 \\ \hline 7 & -1 & -1 & -1 \end{array} = \frac{7-1-1-1}{4} = 1$$

$$\frac{1}{4}\begin{array}{|cc|cc|} 1 & -1 & 1 & -1 \\ \hline 7 & -1 & -1 & -1 \end{array} = \frac{7+1-1+1}{4} = 2$$

Atomic ℓ-level or 2ℓ+1-multiplet splitting in D_2

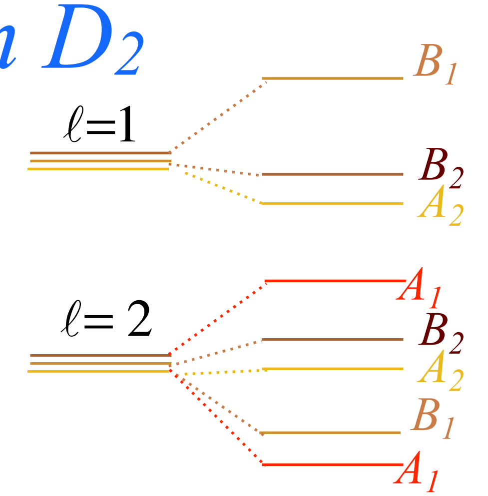
Here we apply that to D_2 level splitting

Example: $(\ell=1)$

and: $(\ell=2)$

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

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



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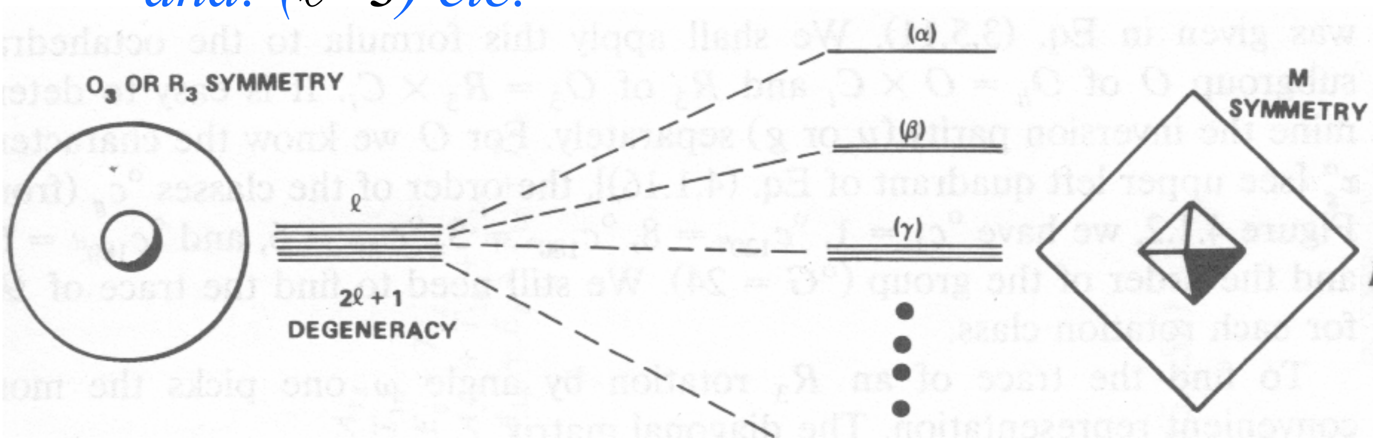
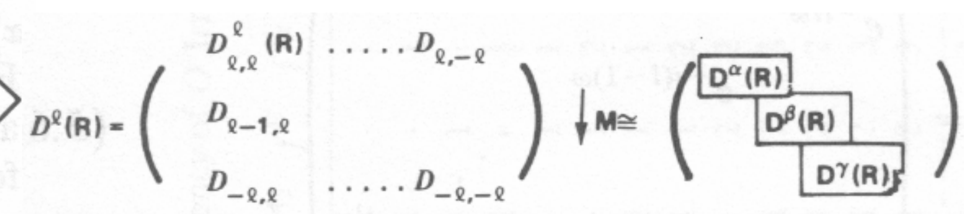
2ℓ+1=11
...





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

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

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

$\chi^{\ell}(\Theta)$	$\Theta=0$	$\mathbf{R}_x\pi$	$\mathbf{R}_y\pi$	$\mathbf{R}_z\pi$
$\ell=0$	1	1	1	1
1	3	-1	-1	-1
2	5	1	1	1
3	7	-1	-1	-1
4	9	1	1	1
5	11	-1	-1	-1
6	13	1	1	1
7	15	-1	-1	-1
8	17	1	1	1

...and Lect.13 p.79
D_2 characters:

D_2	**1**	$\mathbf{R}_x$	$\mathbf{R}_y$	$\mathbf{R}_z$
A_1	1	1	1	1
A_2	1	-1	1	−1
B_1	1	1	-1	−1
B_2	1	-1	-1	1

R(3) character
where: 2ℓ+1
is ℓ-orbital dimension

$f^{(\alpha)}(\ell)$	f^{A_1}	f^{A_2}	f^{B_1}	f^{B_2}	
$\ell=0$	1	·	·		$1A_1$
1	·	1	1	1	$0A_1\oplus A_2\oplus B_1\oplus B_2$
2	2	1	1	1	$2A_1\oplus A_2\oplus B_1\oplus B_2$
3	1	2	2	2	$1A_1\oplus 2A_2\oplus 2B_1\oplus 2B_2$
4	3	2	2	2	$3A_1\oplus 2A_2\oplus 2B_1\oplus 2B_2$
5	2	3	3	3	$2A_1\oplus 3A_2\oplus 3B_1\oplus 3B_2$
6	4	3	3	3	$4A_1\oplus 3A_2\oplus 3B_1\oplus 3B_2$
7	3	4	4	4	$3A_1\oplus 4A_2\oplus 4B_1\oplus 4B_2$

Review :

Symmetric rigid quantum rotor analysis of R(2) Hamiltonian $\mathbf{H}=B\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$

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

Asymmetric rigid quantum rotor analysis of D_2 Hamiltonian $\mathbf{H}=A\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$

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

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

$R(3)\supset D_2$ character analysis of ℓ-level or 2ℓ+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 $\mathbf{H}=B\mathbf{J}\cdot\mathbf{J}+t_{044}\mathbf{T}^{[4]}$

Spherical rotor levels and RES plots of O_h tensor eigenvalues

$R(3)\subset O(3)\supset O_h\supset O$ character analysis of ℓ-level or 2ℓ+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

j,m,n formulas for momentum operator matrix elements: (From Lecture 24 p. 36)

$$n_\uparrow = j+m \quad , \quad n_\downarrow = j-m$$

$$\left| \begin{smallmatrix} j \\ m \end{smallmatrix} \right\rangle = \frac{(\mathbf{a}_\uparrow^\dagger)^{j+m}(\mathbf{a}_\downarrow^\dagger)^{j-m}}{\sqrt{(j+m)!}\sqrt{(j-m)!}}\left|0,0\right\rangle = \frac{\left|n_\uparrow, n_\downarrow\right\rangle}{\sqrt{(n_\uparrow)!}\sqrt{(n_\downarrow)!}}$$

$$\mathbf{a}_\uparrow^\dagger \mathbf{a}_\downarrow \left|n_\uparrow, n_\downarrow\right\rangle = \sqrt{n_\uparrow+1}\sqrt{n_\downarrow}\left|n_\uparrow+1\ n_\downarrow-1\right\rangle \Rightarrow \mathbf{J}_+\left| \begin{smallmatrix} j \\ m \end{smallmatrix} \right\rangle = \sqrt{j+m+1}\sqrt{j-m}\left| \begin{smallmatrix} j \\ m+1 \end{smallmatrix} \right\rangle$$

$$\mathbf{a}_\downarrow^\dagger \mathbf{a}_\uparrow \left|n_\uparrow, n_\downarrow\right\rangle = \sqrt{n_\uparrow}\sqrt{n_\downarrow+1}\left|n_\uparrow-1\ n_\downarrow+1\right\rangle \Rightarrow \mathbf{J}_-\left| \begin{smallmatrix} j \\ m \end{smallmatrix} \right\rangle = \sqrt{j+m}\sqrt{j-m+1}\left| \begin{smallmatrix} j \\ m-1 \end{smallmatrix} \right\rangle$$

$$\mathbf{a}_\uparrow^\dagger \mathbf{a}_\downarrow = \mathbf{J}_+ = \mathbf{J}_X + i\mathbf{J}_Y$$

$$\mathbf{a}_\downarrow^\dagger \mathbf{a}_\uparrow = \mathbf{J}_- = \mathbf{J}_X - i\mathbf{J}_Y = \mathbf{J}_+^\dagger$$

$$\mathbf{J}_X = \tfrac{1}{2}[\mathbf{J}_+ + \mathbf{J}_-]$$

$$\mathbf{J}_Y = \tfrac{-i}{2}[\mathbf{J}_+ - \mathbf{J}_-]$$

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

j,m,n formulas for momentum operator matrix elements: (From Lecture 24 p. 36)

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$$\mathbf{a}_\downarrow^\dagger \mathbf{a}_\uparrow \left|n_\uparrow, n_\downarrow\right\rangle = \sqrt{n_\uparrow}\sqrt{n_\downarrow+1}\left|n_\uparrow-1\ n_\downarrow+1\right\rangle \Rightarrow \mathbf{J}_-\left|\begin{smallmatrix} j \\ m \end{smallmatrix}\right\rangle = \sqrt{j+m}\sqrt{j-m+1}\left|\begin{smallmatrix} j \\ m-1 \end{smallmatrix}\right\rangle$$

$$\mathbf{a}_\uparrow^\dagger \mathbf{a}_\downarrow = \mathbf{J}_+ = \mathbf{J}_X + i\mathbf{J}_Y$$

$$\mathbf{a}_\downarrow^\dagger \mathbf{a}_\uparrow = \mathbf{J}_- = \mathbf{J}_X - i\mathbf{J}_Y = \mathbf{J}_+^\dagger$$

$$\mathbf{J}_X = \tfrac{1}{2}[\mathbf{J}_+ + \mathbf{J}_-]$$

$$\mathbf{J}_Y = \tfrac{-i}{2}[\mathbf{J}_+ - \mathbf{J}_-]$$

LAB matrix elements use the usual atomic formula:

$$\left\langle\begin{smallmatrix} J \\ m',n' \end{smallmatrix}\right|\mathbf{J}_X\left|\begin{smallmatrix} J \\ m,n \end{smallmatrix}\right\rangle = D^J_{m',m}(\mathbf{J}_X)\delta_{n'n} = \tfrac{1}{2}\left[\delta_{m'm+1}\sqrt{(j-m)(j+m+1)} + \delta_{m'm-1}\sqrt{(j+m)(j-m+1)}\right]\delta_{n'n}$$

$$\left\langle\begin{smallmatrix} J \\ m',n' \end{smallmatrix}\right|\mathbf{J}_Y\left|\begin{smallmatrix} J \\ m,n \end{smallmatrix}\right\rangle = D^J_{m',m}(\mathbf{J}_Y)\delta_{n'n} = \tfrac{-i}{2}\left[\delta_{m'm+1}\sqrt{(j-m)(j+m+1)} - \delta_{m'm-1}\sqrt{(j+m)(j-m+1)}\right]\delta_{n'n}$$

$$\left\langle\begin{smallmatrix} J \\ m',n' \end{smallmatrix}\right|\mathbf{J}_Z\left|\begin{smallmatrix} J \\ m,n \end{smallmatrix}\right\rangle = D^J_{m',m}(\mathbf{J}_Z)\delta_{n'n} = \delta_{m'm}m\ \delta_{n'n}$$

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

j,m,n formulas for momentum operator matrix elements: (From Lecture 24 p. 36)

$$n_\uparrow = j+m \quad , \quad n_\downarrow = j-m$$

$$\left|\begin{matrix} j \\ m \end{matrix}\right\rangle = \frac{(\mathbf{a}_\uparrow^\dagger)^{j+m}(\mathbf{a}_\downarrow^\dagger)^{j-m}}{\sqrt{(j+m)!}\sqrt{(j-m)!}}\left|0,0\right\rangle = \frac{\left|n_\uparrow, n_\downarrow\right\rangle}{\sqrt{(n_\uparrow)!}\sqrt{(n_\downarrow)!}}$$

$$\mathbf{a}_\uparrow^\dagger \mathbf{a}_\downarrow \left|n_\uparrow, n_\downarrow\right\rangle = \sqrt{n_\uparrow+1}\sqrt{n_\downarrow}\left|n_\uparrow+1\; n_\downarrow-1\right\rangle \Rightarrow \mathbf{J}_+\left|\begin{matrix} j \\ m \end{matrix}\right\rangle = \sqrt{j+m+1}\sqrt{j-m}\left|\begin{matrix} j \\ m+1 \end{matrix}\right\rangle$$

$$\mathbf{a}_\downarrow^\dagger \mathbf{a}_\uparrow \left|n_\uparrow, n_\downarrow\right\rangle = \sqrt{n_\uparrow}\sqrt{n_\downarrow+1}\left|n_\uparrow-1\; n_\downarrow+1\right\rangle \Rightarrow \mathbf{J}_-\left|\begin{matrix} j \\ m \end{matrix}\right\rangle = \sqrt{j+m}\sqrt{j-m+1}\left|\begin{matrix} j \\ m-1 \end{matrix}\right\rangle$$

$$\mathbf{a}_\uparrow^\dagger \mathbf{a}_\downarrow = \mathbf{J}_+ = \mathbf{J}_X + i\mathbf{J}_Y$$

$$\mathbf{a}_\downarrow^\dagger \mathbf{a}_\uparrow = \mathbf{J}_- = \mathbf{J}_X - i\mathbf{J}_Y = \mathbf{J}_+^\dagger$$

$$\mathbf{J}_X = \tfrac{1}{2}[\mathbf{J}_+ + \mathbf{J}_-]$$

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LAB matrix elements use the usual atomic formula:

$$\left\langle \begin{matrix} J \\ m',n' \end{matrix}\right|\mathbf{J}_X\left|\begin{matrix} J \\ m,n \end{matrix}\right\rangle = D^J_{m',m}(\mathbf{J}_X)\delta_{n'n} = \tfrac{1}{2}\left[\delta_{m'm+1}\sqrt{(j-m)(j+m+1)} + \delta_{m'm-1}\sqrt{(j+m)(j-m+1)}\right]\delta_{n'n}$$

$$\left\langle \begin{matrix} J \\ m',n' \end{matrix}\right|\mathbf{J}_Y\left|\begin{matrix} J \\ m,n \end{matrix}\right\rangle = D^J_{m',m}(\mathbf{J}_Y)\delta_{n'n} = \tfrac{-i}{2}\left[\delta_{m'm+1}\sqrt{(j-m)(j+m+1)} - \delta_{m'm-1}\sqrt{(j+m)(j-m+1)}\right]\delta_{n'n}$$

$$\left\langle \begin{matrix} J \\ m',n' \end{matrix}\right|\mathbf{J}_Z\left|\begin{matrix} J \\ m,n \end{matrix}\right\rangle = D^J_{m',m}(\mathbf{J}_Z)\delta_{n'n} = \delta_{m'm}m\;\delta_{n'n}$$

BOD matrix elements are the same after switching *m's* into *n's*
and changing sign of $\mathbf{J}_Y$ matrix (*-conjugation)

$$\left\langle \begin{matrix} J \\ m',n' \end{matrix}\right|\mathbf{J}_{\bar{X}}\left|\begin{matrix} J \\ m,n \end{matrix}\right\rangle = \delta_{m'm}D^{J}_{n',n}{}^*(\mathbf{J}_{\bar{X}}) = \tfrac{1}{2}\;\delta_{m'm}\left[\sqrt{(j-n)(j+n+1)}\delta_{n'n+1} + \sqrt{(j+n)(j-n+1)}\delta_{n'n-1}\right]$$

$$\left\langle \begin{matrix} J \\ m',n' \end{matrix}\right|\mathbf{J}_{\bar{Y}}\left|\begin{matrix} J \\ m,n \end{matrix}\right\rangle = \delta_{m'm}D^{J}_{n',n}{}^*(\mathbf{J}_{\bar{Y}}) = \tfrac{+i}{2}\;\delta_{m'm}\left[\sqrt{(j-n)(j+n+1)}\delta_{n'n+1} - \sqrt{(j+n)(j-n+1)}\delta_{n'n-1}\right]$$

$$\left\langle \begin{matrix} J \\ m',n' \end{matrix}\right|\mathbf{J}_{\bar{Z}}\left|\begin{matrix} J \\ m,n \end{matrix}\right\rangle = \delta_{m'm}D^{J}_{n',n}{}^*(\mathbf{J}_{\bar{Z}}) = \delta_{m'm}n\;\delta_{n'n}$$

Hamiltonian matrices for asymmetric rotor Hamiltonian

$$\mathbf{H} = \tfrac{1}{2}\left(\frac{\mathbf{J}_{\bar{X}}^{\,2}}{I_{\bar{X}}} + \frac{\mathbf{J}_{\bar{Y}}^{\,2}}{I_{\bar{Y}}} + \frac{\mathbf{J}_{\bar{Z}}^{\,2}}{I_{\bar{Z}}}\right) = A\mathbf{J}_{\bar{X}}^2 + B\mathbf{J}_{\bar{Y}}^2 + C\mathbf{J}_{\bar{Z}}^2$$

First are matrix formulas for BOD J^2 components.

$$\mathbf{J}_{\bar{X}}^2\left|\begin{smallmatrix}J\\ m,n\end{smallmatrix}\right\rangle = \tfrac{1}{2}\sqrt{(j-n)(j+n+1)}\,\mathbf{J}_{\bar{X}}\left|\begin{smallmatrix}J\\ m,n+1\end{smallmatrix}\right\rangle + \tfrac{1}{2}\sqrt{(j+n)(j-n+1)}\,\mathbf{J}_{\bar{X}}\left|\begin{smallmatrix}J\\ m,n-1\end{smallmatrix}\right\rangle$$

$$= \tfrac{1}{4}\sqrt{(j-n)(j+n+1)}\sqrt{(j-n-1)(j+n+2)}\left|\begin{smallmatrix}J\\ m,n+2\end{smallmatrix}\right\rangle + \tfrac{1}{4}(j-n)(j+n+1)\left|\begin{smallmatrix}J\\ m,n\end{smallmatrix}\right\rangle$$
$$+ \tfrac{1}{4}\sqrt{(j+n)(j-n+1)}\sqrt{(j+n-1)(j-n+2)}\left|\begin{smallmatrix}J\\ m,n-2\end{smallmatrix}\right\rangle + \tfrac{1}{4}(j+n)(j-n+1)\left|\begin{smallmatrix}J\\ m,n\end{smallmatrix}\right\rangle$$

$$= \frac{\sqrt{(j-n)(j-n-1)(j+n+1)(j+n+2)}}{4}\left|\begin{smallmatrix}J\\ m,n+2\end{smallmatrix}\right\rangle + \frac{j(j+1)-n^2}{2}\left|\begin{smallmatrix}J\\ m,n\end{smallmatrix}\right\rangle + \frac{\sqrt{(j+n)(j+n-1)(j-n+1)(j-n+2)}}{4}\left|\begin{smallmatrix}J\\ m,n-2\end{smallmatrix}\right\rangle$$

$$\mathbf{J}_{\bar{Y}}^2\left|\begin{smallmatrix}J\\ m,n\end{smallmatrix}\right\rangle = \tfrac{i}{2}\sqrt{(j-n)(j+n+1)}\,\mathbf{J}_{\bar{Y}}\left|\begin{smallmatrix}J\\ m,n+1\end{smallmatrix}\right\rangle - \tfrac{i}{2}\sqrt{(j+n)(j-n+1)}\,\mathbf{J}_{\bar{Y}}\left|\begin{smallmatrix}J\\ m,n-1\end{smallmatrix}\right\rangle$$

$$= \tfrac{-1}{4}\sqrt{(j-n)(j+n+1)}\sqrt{(j-n-1)(j+n+2)}\left|\begin{smallmatrix}J\\ m,n+2\end{smallmatrix}\right\rangle + \tfrac{1}{4}(j-n)(j+n+1)\left|\begin{smallmatrix}J\\ m,n\end{smallmatrix}\right\rangle$$
$$\tfrac{-1}{4}\sqrt{(j+n)(j-n+1)}\sqrt{(j+n-1)(j-n+2)}\left|\begin{smallmatrix}J\\ m,n-2\end{smallmatrix}\right\rangle + \tfrac{1}{4}(j+n)(j-n+1)\left|\begin{smallmatrix}J\\ m,n\end{smallmatrix}\right\rangle$$

$$= -\frac{\sqrt{(j-n)(j-n-1)(j+n+1)(j+n+2)}}{4}\left|\begin{smallmatrix}J\\ m,n+2\end{smallmatrix}\right\rangle + \frac{j(j+1)-n^2}{2}\left|\begin{smallmatrix}J\\ m,n\end{smallmatrix}\right\rangle - \frac{\sqrt{(j+n)(j+n-1)(j-n+1)(j-n+2)}}{4}\left|\begin{smallmatrix}J\\ m,n-2\end{smallmatrix}\right\rangle$$

$$\mathbf{J}_{\bar{Z}}^2\left|\begin{smallmatrix}J\\ m,n\end{smallmatrix}\right\rangle = n^2\left|\begin{smallmatrix}J\\ m,n\end{smallmatrix}\right\rangle$$

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

$$(A\mathbf{J}_{\bar{X}}^2 + B\mathbf{J}_{\bar{Y}}^2 + C\mathbf{J}_{\bar{Z}}^2)\left|\begin{smallmatrix}J\\ m,n\end{smallmatrix}\right\rangle =$$

$$= (A-B)\frac{\sqrt{(j-n)(j-n-1)(j+n+1)(j+n+2)}}{4}\left|\begin{smallmatrix}J\\ m,n+2\end{smallmatrix}\right\rangle + \left[(A+B)\frac{j(j+1)-n^2}{2} + Cn^2\right]\left|\begin{smallmatrix}J\\ m,n\end{smallmatrix}\right\rangle + (A-B)\frac{\sqrt{(j+n)(j+n-1)(j-n+1)(j-n+2)}}{4}\left|\begin{smallmatrix}J\\ m,n-2\end{smallmatrix}\right\rangle$$

Review :

Symmetric rigid quantum rotor analysis of R(2) Hamiltonian $\mathbf{H}=B\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$

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

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Asymmetric rotor levels and RES plots for high-J

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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 ℓ-level or 2ℓ+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*.

$$\left\langle {}^{1}_{m,n'} \middle| \mathbf{J}_{\bar{X}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} \cdot & \frac{\sqrt{2}}{2} & \cdot \\ \frac{\sqrt{2}}{2} & \cdot & \frac{\sqrt{2}}{2} \\ \cdot & \frac{\sqrt{2}}{2} & \cdot \end{pmatrix}, \quad \left\langle {}^{1}_{m,n'} \middle| \mathbf{J}_{\bar{Y}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} \cdot & \frac{i\sqrt{2}}{2} & \cdot \\ -\frac{i\sqrt{2}}{2} & \cdot & \frac{i\sqrt{2}}{2} \\ \cdot & -\frac{i\sqrt{2}}{2} & \cdot \end{pmatrix}, \quad \left\langle {}^{1}_{m,n'} \middle| \mathbf{J}_{\bar{Z}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} +1 & \cdot & \cdot \\ \cdot & 0 & \cdot \\ \cdot & \cdot & -1 \end{pmatrix}$$

$$\left\langle {}^{1}_{m,n'} \middle| \mathbf{J}^2_{\bar{X}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} \frac{1}{2} & \cdot & \frac{1}{2} \\ \cdot & 1 & \cdot \\ \frac{1}{2} & \cdot & \frac{1}{2} \end{pmatrix}, \quad \left\langle {}^{1}_{m,n'} \middle| \mathbf{J}^2_{\bar{Y}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} \frac{1}{2} & \cdot & -\frac{1}{2} \\ \cdot & 1 & \cdot \\ -\frac{1}{2} & \cdot & \frac{1}{2} \end{pmatrix}, \quad \left\langle {}^{1}_{m,n'} \middle| \mathbf{J}^2_{\bar{Z}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} +1 & \cdot & \cdot \\ \cdot & 0 & \cdot \\ \cdot & \cdot & +1 \end{pmatrix}.$$

(*J=1*)-Matrix for *A=1*, *B=2*, *C=3*.

$$\left\langle {}^{1}_{m,n'} \middle| \mathbf{J}_{\bar{X}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} \cdot & \frac{\sqrt{2}}{2} & \cdot \\ \frac{\sqrt{2}}{2} & \cdot & \frac{\sqrt{2}}{2} \\ \cdot & \frac{\sqrt{2}}{2} & \cdot \end{pmatrix}, \quad \left\langle {}^{1}_{m,n'} \middle| \mathbf{J}_{\bar{Y}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} \cdot & \frac{i\sqrt{2}}{2} & \cdot \\ -\frac{i\sqrt{2}}{2} & \cdot & \frac{i\sqrt{2}}{2} \\ \cdot & -\frac{i\sqrt{2}}{2} & \cdot \end{pmatrix}, \quad \left\langle {}^{1}_{m,n'} \middle| \mathbf{J}_{\bar{Z}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} +1 & \cdot & \cdot \\ \cdot & 0 & \cdot \\ \cdot & \cdot & -1 \end{pmatrix}$$

$$\left\langle {}^{1}_{m,n'} \middle| \mathbf{J}^2_{\bar{X}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} \frac{1}{2} & \cdot & \frac{1}{2} \\ \cdot & 1 & \cdot \\ \frac{1}{2} & \cdot & \frac{1}{2} \end{pmatrix}, \quad \left\langle {}^{1}_{m,n'} \middle| \mathbf{J}^2_{\bar{Y}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} \frac{1}{2} & \cdot & -\frac{1}{2} \\ \cdot & 1 & \cdot \\ -\frac{1}{2} & \cdot & \frac{1}{2} \end{pmatrix}, \quad \left\langle {}^{1}_{m,n'} \middle| \mathbf{J}^2_{\bar{Z}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} +1 & \cdot & \cdot \\ \cdot & 0 & \cdot \\ \cdot & \cdot & +1 \end{pmatrix}.$$

$$\left\langle A\mathbf{J}^2_{\bar{X}} + B\mathbf{J}^2_{\bar{Y}} + C\mathbf{J}^2_{\bar{Z}} \right\rangle^{J=1} = \begin{pmatrix} \frac{A}{2}+\frac{B}{2}+C & \cdot & \frac{A}{2}-\frac{B}{2} \\ \cdot & A+B & \cdot \\ \frac{A}{2}-\frac{B}{2} & \cdot & \frac{A}{2}+\frac{B}{2}+C \end{pmatrix} = \begin{pmatrix} \frac{1}{2}+\frac{2}{2}+3 & \cdot & \frac{1}{2}-\frac{2}{2} \\ \cdot & 1+2 & \cdot \\ \frac{1}{2}-\frac{2}{2} & \cdot & \frac{1}{2}+\frac{2}{2}+3 \end{pmatrix} = \begin{pmatrix} \frac{9}{2} & \cdot & -\frac{1}{2} \\ \cdot & 3 & \cdot \\ -\frac{1}{2} & \cdot & \frac{9}{2} \end{pmatrix}$$

$f^{(\alpha)}(\ell)$	f^{A_1}	f^{A_2}	f^{B_1}	f^{B_2}	
$\ell=0$	1	·	·		$1A_1$
1	·	1	1	1	$0A_1 \oplus A_2 \oplus B_1 \oplus B_2$

($J=1$)-Matrix for $A=1$, $B=2$, $C=3$.

$$\left\langle {}^{1}_{m,n'} \middle| \mathbf{J}_{\bar{X}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} \cdot & \frac{\sqrt{2}}{2} & \cdot \\ \frac{\sqrt{2}}{2} & \cdot & \frac{\sqrt{2}}{2} \\ \cdot & \frac{\sqrt{2}}{2} & \cdot \end{pmatrix}, \quad \left\langle {}^{1}_{m,n'} \middle| \mathbf{J}_{\bar{Y}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} \cdot & \frac{i\sqrt{2}}{2} & \cdot \\ \frac{-i\sqrt{2}}{2} & \cdot & \frac{i\sqrt{2}}{2} \\ \cdot & \frac{-i\sqrt{2}}{2} & \cdot \end{pmatrix}, \quad \left\langle {}^{1}_{m,n'} \middle| \mathbf{J}_{\bar{Z}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} +1 & \cdot & \cdot \\ \cdot & 0 & \cdot \\ \cdot & \cdot & -1 \end{pmatrix}$$

$$\left\langle {}^{1}_{m,n'} \middle| \mathbf{J}^2_{\bar{X}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} \frac{1}{2} & \cdot & \frac{1}{2} \\ \cdot & 1 & \cdot \\ \frac{1}{2} & \cdot & \frac{1}{2} \end{pmatrix}, \quad \left\langle {}^{1}_{m,n'} \middle| \mathbf{J}^2_{\bar{Y}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} \frac{1}{2} & \cdot & -\frac{1}{2} \\ \cdot & 1 & \cdot \\ -\frac{1}{2} & \cdot & \frac{1}{2} \end{pmatrix}, \quad \left\langle {}^{1}_{m,n'} \middle| \mathbf{J}^2_{\bar{Z}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} +1 & \cdot & \cdot \\ \cdot & 0 & \cdot \\ \cdot & \cdot & +1 \end{pmatrix}.$$

$$\left\langle A\mathbf{J}^2_{\bar{X}} + B\mathbf{J}^2_{\bar{Y}} + C\mathbf{J}^2_{\bar{Z}} \right\rangle^{J=1} = \begin{pmatrix} \frac{A}{2}+\frac{B}{2}+C & \cdot & \frac{A}{2}-\frac{B}{2} \\ \cdot & A+B & \cdot \\ \frac{A}{2}-\frac{B}{2} & \cdot & \frac{A}{2}+\frac{B}{2}+C \end{pmatrix} = \begin{pmatrix} \frac{1}{2}+\frac{2}{2}+3 & \cdot & \frac{1}{2}-\frac{2}{2} \\ \cdot & 1+2 & \cdot \\ \frac{1}{2}-\frac{2}{2} & \cdot & \frac{1}{2}+\frac{2}{2}+3 \end{pmatrix} = \begin{pmatrix} \frac{9}{2} & \cdot & -\frac{1}{2} \\ \cdot & 3 & \cdot \\ -\frac{1}{2} & \cdot & \frac{9}{2} \end{pmatrix}$$

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

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

$f^{(\alpha)}(\ell)$	f^{A_1}	f^{A_2}	f^{B_1}	f^{B_2}	
$\ell=0$	1	·	·		$1A_1$
1	·	1	1	1	$0A_1 \oplus A_2 \oplus B_1 \oplus B_2$

$(J=1)$-Matrix for $A=1$, $B=2$, $C=3$.

$$\left\langle {}^{1}_{m,n'}\middle|\mathbf{J}_{\bar{X}}\middle|{}^{1}_{m,n}\right\rangle=\begin{pmatrix} \cdot & \frac{\sqrt{2}}{2} & \cdot \\ \frac{\sqrt{2}}{2} & \cdot & \frac{\sqrt{2}}{2} \\ \cdot & \frac{\sqrt{2}}{2} & \cdot \end{pmatrix},\quad \left\langle {}^{1}_{m,n'}\middle|\mathbf{J}_{\bar{Y}}\middle|{}^{1}_{m,n}\right\rangle=\begin{pmatrix} \cdot & \frac{i\sqrt{2}}{2} & \cdot \\ \frac{-i\sqrt{2}}{2} & \cdot & \frac{i\sqrt{2}}{2} \\ \cdot & \frac{-i\sqrt{2}}{2} & \cdot \end{pmatrix},\quad \left\langle {}^{1}_{m,n'}\middle|\mathbf{J}_{\bar{Z}}\middle|{}^{1}_{m,n}\right\rangle=\begin{pmatrix} +1 & \cdot & \cdot \\ \cdot & 0 & \cdot \\ \cdot & \cdot & -1 \end{pmatrix}$$

$$\left\langle {}^{1}_{m,n'}\middle|\mathbf{J}^2_{\bar{X}}\middle|{}^{1}_{m,n}\right\rangle=\begin{pmatrix} \frac{1}{2} & \cdot & \frac{1}{2} \\ \cdot & 1 & \cdot \\ \frac{1}{2} & \cdot & \frac{1}{2} \end{pmatrix},\quad \left\langle {}^{1}_{m,n'}\middle|\mathbf{J}^2_{\bar{Y}}\middle|{}^{1}_{m,n}\right\rangle=\begin{pmatrix} \frac{1}{2} & \cdot & -\frac{1}{2} \\ \cdot & 1 & \cdot \\ -\frac{1}{2} & \cdot & \frac{1}{2} \end{pmatrix},\quad \left\langle {}^{1}_{m,n'}\middle|\mathbf{J}^2_{\bar{Z}}\middle|{}^{1}_{m,n}\right\rangle=\begin{pmatrix} +1 & \cdot & \cdot \\ \cdot & 0 & \cdot \\ \cdot & \cdot & +1 \end{pmatrix}.$$

$$\left\langle A\mathbf{J}^2_{\bar{X}}+B\mathbf{J}^2_{\bar{Y}}+C\mathbf{J}^2_{\bar{Z}}\right\rangle^{J=1}=\begin{pmatrix} \frac{A}{2}+\frac{B}{2}+C & \cdot & \frac{A}{2}-\frac{B}{2} \\ \cdot & A+B & \cdot \\ \frac{A}{2}-\frac{B}{2} & \cdot & \frac{A}{2}+\frac{B}{2}+C \end{pmatrix}=\begin{pmatrix} \frac{1}{2}+\frac{2}{2}+3 & \cdot & \frac{1}{2}-\frac{2}{2} \\ \cdot & 1+2 & \cdot \\ \frac{1}{2}-\frac{2}{2} & \cdot & \frac{1}{2}+\frac{2}{2}+3 \end{pmatrix}=\begin{pmatrix} \frac{9}{2} & \cdot & -\frac{1}{2} \\ \cdot & 3 & \cdot \\ -\frac{1}{2} & \cdot & \frac{9}{2} \end{pmatrix}$$

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

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

$f^{(\alpha)}(\ell)$	f^{A_1}	f^{A_2}	f^{B_1}	f^{B_2}	
$\ell=0$	1	·	·		$1A_1$
1	·	1	1	1	$0A_1\oplus A_2\oplus B_1\oplus B_2$

D_2	**1**	$\mathbf{R}_x$	$\mathbf{R}_y$	$\mathbf{R}_z$
A_1	1	1	1	1
A_2	1	-1	1	–1
B_1	1	1	-1	–1
B_2	1	-1	-1	1

$(J{=}1)$-Matrix for $A{=}1,\ B{=}2,\ C{=}3$.

$$\left\langle {}^{1}_{m,n'} \middle| \mathbf{J}_{\bar{X}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} \cdot & \frac{\sqrt{2}}{2} & \cdot \\ \frac{\sqrt{2}}{2} & \cdot & \frac{\sqrt{2}}{2} \\ \cdot & \frac{\sqrt{2}}{2} & \cdot \end{pmatrix}, \quad \left\langle {}^{1}_{m,n'} \middle| \mathbf{J}_{\bar{Y}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} \cdot & \frac{i\sqrt{2}}{2} & \cdot \\ -\frac{i\sqrt{2}}{2} & \cdot & \frac{i\sqrt{2}}{2} \\ \cdot & -\frac{i\sqrt{2}}{2} & \cdot \end{pmatrix}, \quad \left\langle {}^{1}_{m,n'} \middle| \mathbf{J}_{\bar{Z}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} +1 & \cdot & \cdot \\ \cdot & 0 & \cdot \\ \cdot & \cdot & -1 \end{pmatrix}$$

$$\left\langle {}^{1}_{m,n'} \middle| \mathbf{J}^2_{\bar{X}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} \frac{1}{2} & \cdot & \frac{1}{2} \\ \cdot & 1 & \cdot \\ \frac{1}{2} & \cdot & \frac{1}{2} \end{pmatrix}, \quad \left\langle {}^{1}_{m,n'} \middle| \mathbf{J}^2_{\bar{Y}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} \frac{1}{2} & \cdot & -\frac{1}{2} \\ \cdot & 1 & \cdot \\ -\frac{1}{2} & \cdot & \frac{1}{2} \end{pmatrix}, \quad \left\langle {}^{1}_{m,n'} \middle| \mathbf{J}^2_{\bar{Z}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} +1 & \cdot & \cdot \\ \cdot & 0 & \cdot \\ \cdot & \cdot & +1 \end{pmatrix}.$$

$$\left\langle A\mathbf{J}^2_{\bar{X}} + B\mathbf{J}^2_{\bar{Y}} + C\mathbf{J}^2_{\bar{Z}} \right\rangle^{J=1} = \begin{pmatrix} \frac{A}{2}+\frac{B}{2}+C & \cdot & \frac{A}{2}-\frac{B}{2} \\ \cdot & A+B & \cdot \\ \frac{A}{2}-\frac{B}{2} & \cdot & \frac{A}{2}+\frac{B}{2}+C \end{pmatrix} = \begin{pmatrix} \frac{1}{2}+\frac{2}{2}+3 & \cdot & \frac{1}{2}-\frac{2}{2} \\ \cdot & 1+2 & \cdot \\ \frac{1}{2}-\frac{2}{2} & \cdot & \frac{1}{2}+\frac{2}{2}+3 \end{pmatrix} = \begin{pmatrix} \frac{9}{2} & \cdot & -\frac{1}{2} \\ \cdot & 3 & \cdot \\ -\frac{1}{2} & \cdot & \frac{9}{2} \end{pmatrix}$$

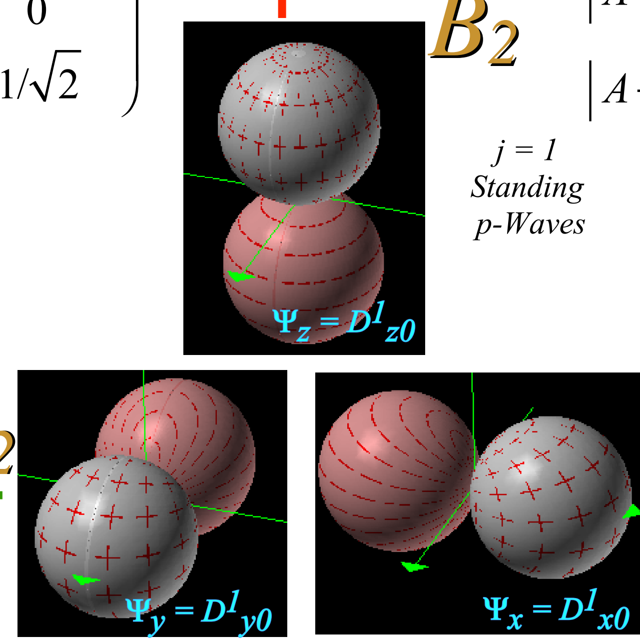
eigen-values: $(B+C=5,\quad A+B=3,\quad A+C=4)$

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

$$\left|B+C\right\rangle = 1/\sqrt{2}\left|{}^{1}_{m,+1}\right\rangle \qquad -1/\sqrt{2}\left|{}^{1}_{m,-1}\right\rangle$$

$$\left|A+B\right\rangle = \qquad +\left|{}^{1}_{m,0}\right\rangle$$

$$\left|A+C\right\rangle = 1/\sqrt{2}\left|{}^{1}_{m,+1}\right\rangle \qquad +1/\sqrt{2}\left|{}^{1}_{m,-1}\right\rangle$$



j = 1 Standing p-Waves

Body-based J=1 vector-like eigenfunctions

D_2	**1**	$\mathbf{R}_x$	$\mathbf{R}_y$	$\mathbf{R}_z$
A_1	1	1	1	1
A_2	1	-1	1	−1
B_1	1	1	-1	−1
B_2	1	-1	-1	1

Review :

Symmetric rigid quantum rotor analysis of R(2) Hamiltonian $\mathbf{H}=B\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$

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

Asymmetric rigid quantum rotor analysis of D_2 Hamiltonian $\mathbf{H}=A\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$

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

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

R(3)⊃D_2 character analysis of ℓ-level or 2ℓ+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 $\mathbf{H}=B\mathbf{J}\cdot\mathbf{J}+t_{044}\mathbf{T}^{[4]}$

Spherical rotor levels and RES plots of O_h tensor eigenvalues

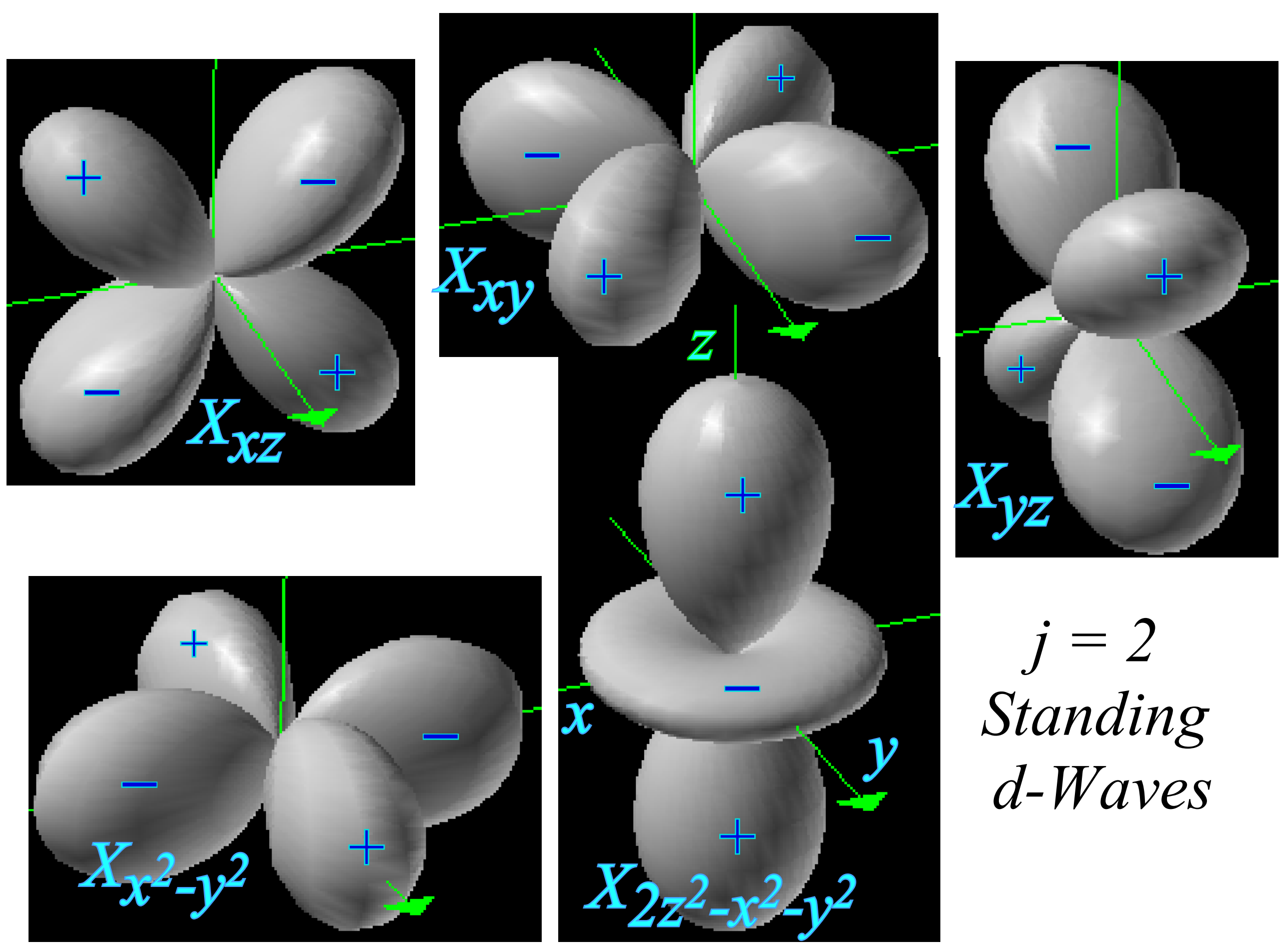
R(3)⊂O(3)⊃O_h⊃O character analysis of ℓ-level or 2ℓ+1-multiplet splitting in O

SF_6 spectral fine structure

CF_4 spectral fine structure

($J=2$)-Matrix for $A=1$, $B=2$, $C=3$.

$$\left\langle A\mathbf{J}_{\bar{1}}^{2}+B\mathbf{J}_{\bar{2}}^{2}+C\mathbf{J}_{\bar{3}}^{2}\right\rangle^{J=2}=\begin{pmatrix} (A+B)+4C & \cdot & \frac{\sqrt{6}}{2}(A-B) & \cdot & \cdot \\ \cdot & \frac{5}{2}(A+B)+C & \cdot & \frac{3}{2}(A-B) & \cdot \\ \frac{\sqrt{6}}{2}(A-B) & \cdot & 3(A+B) & \cdot & \frac{\sqrt{6}}{2}(A-B) \\ \cdot & \frac{3}{2}(A-B) & \cdot & \frac{5}{2}(A+B)+C & \cdot \\ \cdot & \cdot & \frac{\sqrt{6}}{2}(A-B) & \cdot & (A+B)+4C \end{pmatrix}=\begin{pmatrix} 15 & & -\frac{\sqrt{6}}{2} & & \\ & \frac{15}{2} & & \frac{-3}{2} & \\ -\frac{\sqrt{6}}{2} & & 6 & & -\frac{\sqrt{6}}{2} \\ & \frac{-3}{2} & & \frac{15}{2} & \\ & & -\frac{\sqrt{6}}{2} & & 15 \end{pmatrix}$$



$j=2$
Standing d-Waves

$f^{(\alpha)}(\ell)$	f^{A_1}	f^{A_2}	f^{B_1}	f^{B_2}
$\ell=0$	1	·	·	
1	·	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

$(J=2)$-Matrix for $A=1$, $B=2$, $C=3$.

$$\left\langle A\mathbf{J}_{\bar{1}}^2 + B\mathbf{J}_{\bar{2}}^2 + C\mathbf{J}_{\bar{3}}^2 \right\rangle^{J=2} = \begin{pmatrix} (A+B)+4C & \cdot & \frac{\sqrt{6}}{2}(A-B) & \cdot & \cdot \\ \cdot & \frac{5}{2}(A+B)+C & \cdot & \frac{3}{2}(A-B) & \cdot \\ \frac{\sqrt{6}}{2}(A-B) & \cdot & 3(A+B) & \cdot & \frac{\sqrt{6}}{2}(A-B) \\ \cdot & \frac{3}{2}(A-B) & \cdot & \frac{5}{2}(A+B)+C & \cdot \\ \cdot & \cdot & \frac{\sqrt{6}}{2}(A-B) & \cdot & (A+B)+4C \end{pmatrix} = \begin{pmatrix} 15 & & \frac{-\sqrt{6}}{2} & & \\ & \frac{15}{2} & & \frac{-3}{2} & \\ \frac{-\sqrt{6}}{2} & & 6 & & \frac{-\sqrt{6}}{2} \\ & \frac{-3}{2} & & \frac{15}{2} & \\ & & \frac{-\sqrt{6}}{2} & & 15 \end{pmatrix}$$

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

$$\left|A_1 2^+\right\rangle = \tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\+2\end{smallmatrix}\right\rangle + \tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\-2\end{smallmatrix}\right\rangle, \quad \left|B_1 1^+\right\rangle = \tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\+1\end{smallmatrix}\right\rangle + \tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\-1\end{smallmatrix}\right\rangle, \quad \left|A_1 0\right\rangle = \left|\begin{smallmatrix}2\\0\end{smallmatrix}\right\rangle$$

$$\left|B_2 2^-\right\rangle = \tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\+2\end{smallmatrix}\right\rangle - \tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\-2\end{smallmatrix}\right\rangle, \quad \left|A_2 1^-\right\rangle = \tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\+1\end{smallmatrix}\right\rangle - \tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\-1\end{smallmatrix}\right\rangle$$

$f^{(\alpha)}(\ell)$	f^{A_1}	f^{A_2}	f^{B_1}	f^{B_2}
$\ell=0$	1	·	·	
1	·	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

$(J=2)$-Matrix for $A=1$, $B=2$, $C=3$.

$$\left\langle A\mathbf{J}_{\bar 1}^2 + B\mathbf{J}_{\bar 2}^2 + C\mathbf{J}_{\bar 3}^2 \right\rangle^{J=2} = \begin{pmatrix} (A+B)+4C & \cdot & \frac{\sqrt6}{2}(A-B) & \cdot & \cdot \\ \cdot & \frac52(A+B)+C & \cdot & \frac32(A-B) & \cdot \\ \frac{\sqrt6}{2}(A-B) & \cdot & 3(A+B) & \cdot & \frac{\sqrt6}{2}(A-B) \\ \cdot & \frac32(A-B) & \cdot & \frac52(A+B)+C & \cdot \\ \cdot & \cdot & \frac{\sqrt6}{2}(A-B) & \cdot & (A+B)+4C \end{pmatrix} = \begin{pmatrix} 15 & & \frac{-\sqrt6}{2} & & \\ & \frac{15}{2} & & \frac{-3}{2} & \\ \frac{-\sqrt6}{2} & & 6 & & \frac{-\sqrt6}{2} \\ & \frac{-3}{2} & & \frac{15}{2} & \\ & & \frac{-\sqrt6}{2} & & 15 \end{pmatrix}$$

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

$$\left|A_1 2^+\right\rangle = \tfrac{1}{\sqrt2}\left|\begin{smallmatrix}2\\+2\end{smallmatrix}\right\rangle + \tfrac{1}{\sqrt2}\left|\begin{smallmatrix}2\\-2\end{smallmatrix}\right\rangle, \quad \left|B_1 1^+\right\rangle = \tfrac{1}{\sqrt2}\left|\begin{smallmatrix}2\\+1\end{smallmatrix}\right\rangle + \tfrac{1}{\sqrt2}\left|\begin{smallmatrix}2\\-1\end{smallmatrix}\right\rangle, \quad \left|A_1 0\right\rangle = \left|\begin{smallmatrix}2\\0\end{smallmatrix}\right\rangle$$

$$\left|B_2 2^-\right\rangle = \tfrac{1}{\sqrt2}\left|\begin{smallmatrix}2\\+2\end{smallmatrix}\right\rangle - \tfrac{1}{\sqrt2}\left|\begin{smallmatrix}2\\-2\end{smallmatrix}\right\rangle, \quad \left|A_2 1^-\right\rangle = \tfrac{1}{\sqrt2}\left|\begin{smallmatrix}2\\+1\end{smallmatrix}\right\rangle - \tfrac{1}{\sqrt2}\left|\begin{smallmatrix}2\\-1\end{smallmatrix}\right\rangle$$

The following basis transformation "almost diagonalizes" $\langle \mathbf{H}\rangle^{J=2}$ by reducing it to block form.
Let: $\Sigma = A+B$ and $\Delta = A-B$ to shorten expressions.

$$\left(\tfrac{1}{\sqrt2}\right)\begin{pmatrix} 1 & \cdot & \cdot & \cdot & 1 \\ 1 & \cdot & \cdot & \cdot & -1 \\ \cdot & 1 & \cdot & 1 & \cdot \\ \cdot & 1 & \cdot & -1 & \cdot \\ \cdot & \cdot & \sqrt2 & \cdot & \cdot \end{pmatrix}\begin{pmatrix} 4C-\Sigma & \cdot & \frac{\sqrt6\Delta}{2} & \cdot & \cdot \\ \cdot & C+\frac{\Sigma}{2} & \cdot & \frac{3\Delta}{2} & \cdot \\ \frac{\sqrt6\Delta}{2} & \cdot & \Sigma & \cdot & \frac{\sqrt6\Delta}{2} \\ \cdot & \frac{3\Delta}{2} & \cdot & C+\frac{\Sigma}{2} & \cdot \\ \cdot & \cdot & \frac{\sqrt6\Delta}{2} & \cdot & 4C-\Sigma \end{pmatrix}\begin{pmatrix} 1 & 1 & \cdot & \cdot & \cdot \\ \cdot & \cdot & 1 & 1 & \cdot \\ \cdot & \cdot & \cdot & \cdot & \sqrt2 \\ \cdot & \cdot & 1 & -1 & \cdot \\ 1 & -1 & \cdot & \cdot & \cdot \end{pmatrix}\left(\tfrac{1}{\sqrt2}\right) + 2\Sigma\mathbf{1}$$

$$= \begin{pmatrix} 4C+\Sigma & \cdot & \cdot & \cdot & \sqrt3\Delta \\ \cdot & 4C+\Sigma & \cdot & \cdot & \cdot \\ \cdot & \cdot & C+\frac{5\Sigma}{2}+\frac{3\Delta}{2} & \cdot & \cdot \\ \cdot & \cdot & \cdot & C+\frac{5\Sigma}{2}-\frac{3\Delta}{2} & \cdot \\ \sqrt3\Delta & \cdot & \cdot & \cdot & 3\Sigma \end{pmatrix} = \begin{pmatrix} 4C+A+B & \cdot & \cdot & \cdot & \sqrt3(A-B) \\ \cdot & 4C+A+B & \cdot & \cdot & \cdot \\ \cdot & \cdot & C+4A+B & \cdot & \cdot \\ \cdot & \cdot & \cdot & C+A+4B & \cdot \\ \sqrt3(A-B) & \cdot & \cdot & \cdot & 3A+3B \end{pmatrix}$$

New D_2 basis:

$$\left|A_1 2^+\right\rangle = \tfrac{1}{\sqrt2}\left|\begin{smallmatrix}2\\+2\end{smallmatrix}\right\rangle + \tfrac{1}{\sqrt2}\left|\begin{smallmatrix}2\\-2\end{smallmatrix}\right\rangle$$

$$\left|B_2 2^-\right\rangle = \tfrac{1}{\sqrt2}\left|\begin{smallmatrix}2\\+2\end{smallmatrix}\right\rangle - \tfrac{1}{\sqrt2}\left|\begin{smallmatrix}2\\-2\end{smallmatrix}\right\rangle$$

$$\left|B_1 1^+\right\rangle = \tfrac{1}{\sqrt2}\left|\begin{smallmatrix}2\\+1\end{smallmatrix}\right\rangle + \tfrac{1}{\sqrt2}\left|\begin{smallmatrix}2\\-1\end{smallmatrix}\right\rangle$$

$$\left|A_2 1^-\right\rangle = \tfrac{1}{\sqrt2}\left|\begin{smallmatrix}2\\+1\end{smallmatrix}\right\rangle - \tfrac{1}{\sqrt2}\left|\begin{smallmatrix}2\\-1\end{smallmatrix}\right\rangle$$

$$\left|A_1 0\right\rangle = \left|\begin{smallmatrix}2\\0\end{smallmatrix}\right\rangle$$

Completing diagonalization from new D_2 basis:

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

$$\left|A_1 2^+\right\rangle = \frac{1}{\sqrt{2}}\left|\begin{matrix}2\\+2\end{matrix}\right\rangle + \frac{1}{\sqrt{2}}\left|\begin{matrix}2\\-2\end{matrix}\right\rangle$$

$$\left|B_2 2^-\right\rangle = \frac{1}{\sqrt{2}}\left|\begin{matrix}2\\+2\end{matrix}\right\rangle - \frac{1}{\sqrt{2}}\left|\begin{matrix}2\\-2\end{matrix}\right\rangle$$

$$\left|B_1 1^+\right\rangle = \frac{1}{\sqrt{2}}\left|\begin{matrix}2\\+1\end{matrix}\right\rangle + \frac{1}{\sqrt{2}}\left|\begin{matrix}2\\-1\end{matrix}\right\rangle$$

$$\left|A_2 1^-\right\rangle = \frac{1}{\sqrt{2}}\left|\begin{matrix}2\\+1\end{matrix}\right\rangle - \frac{1}{\sqrt{2}}\left|\begin{matrix}2\\-1\end{matrix}\right\rangle$$

$$\left|A_1 0\right\rangle = \left|\begin{matrix}2\\0\end{matrix}\right\rangle$$

D_2	**1**	$\mathbf{R}_x$	$\mathbf{R}_y$	$\mathbf{R}_z$
A_1	1	1	1	1
A_2	1	-1	1	−1
B_1	1	1	-1	−1
B_2	1	-1	-1	1

C_2^x	**1**	$\mathbf{R}_x$
+	1	1
−	1	−1

×

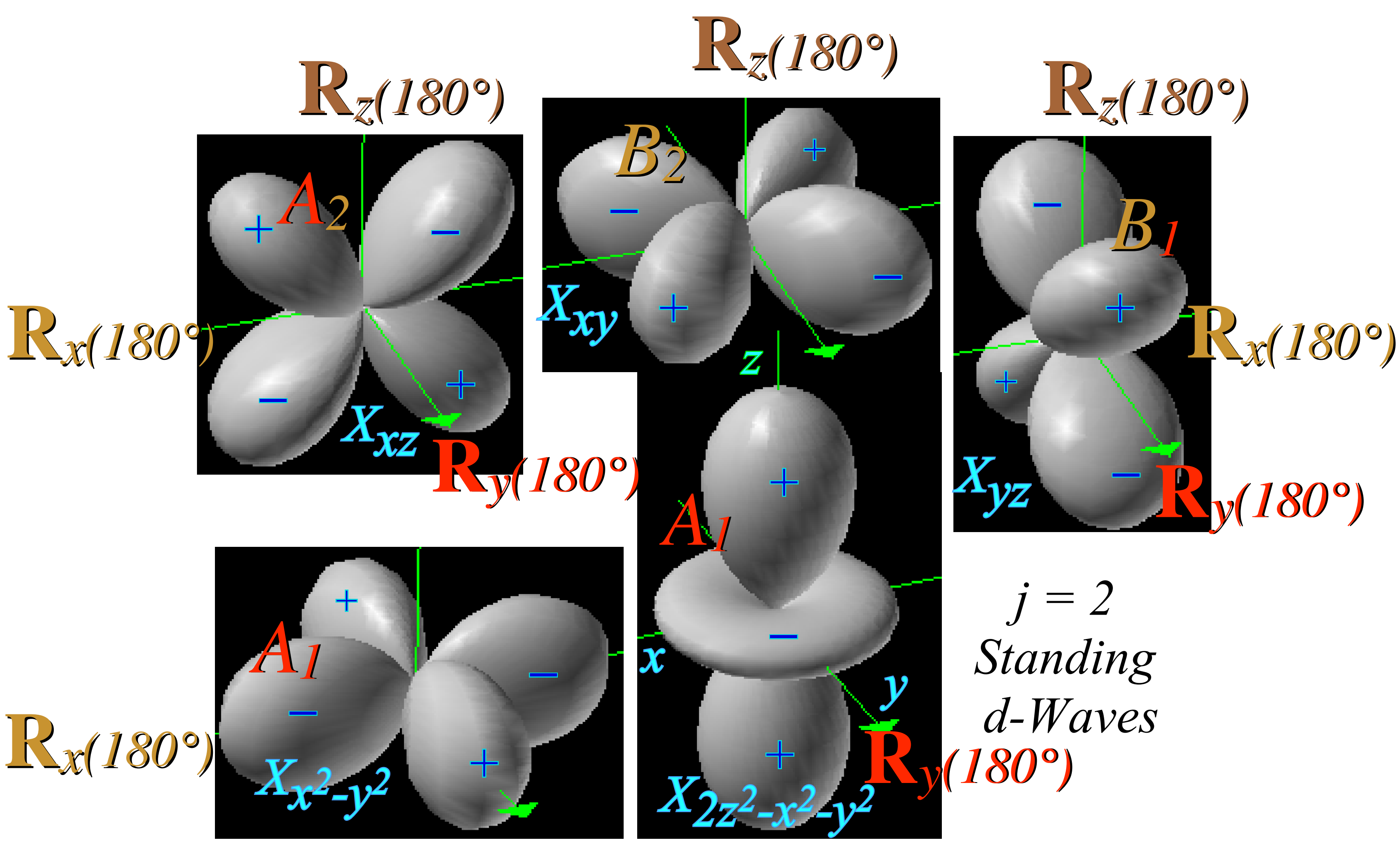
C_2^y	**1**	$\mathbf{R}_y$
+	1	1
−	1	−1

=

$C_2^x \times C_2^y$	$\mathbf{1}\cdot\mathbf{1}$	$\mathbf{R}_x\cdot\mathbf{1}$	$\mathbf{1}\cdot\mathbf{R}_y$	$\mathbf{R}_x\cdot\mathbf{R}_y$
$+\cdot+$	$1\cdot1$	$1\cdot1$	$1\cdot1$	$1\cdot1$
$-\cdot+$	$1\cdot1$	$-1\cdot1$	$1\cdot1$	$-1\cdot1$
$+\cdot-$	$1\cdot1$	$1\cdot1$	$1\cdot(-1)$	$1\cdot(-1)$
$-\cdot-$	$1\cdot1$	$-1\cdot1$	$1\cdot(-1)$	$-1\cdot(-1)$

=

D_2	**1**	$\mathbf{R}_x$	$\mathbf{R}_y$	$\mathbf{R}_z$
$+\cdot+=A_1$	1	1	1	1
$-\cdot+=A_2$	1	-1	1	−1
$+\cdot-=B_1$	1	1	-1	−1
$-\cdot-=B_2$	1	-1	-1	1



Completing diagonalization from new D_2 basis:

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

$$\left|A_1 2^+\right\rangle = \tfrac{1}{\sqrt{2}}\left|{2 \atop +2}\right\rangle + \tfrac{1}{\sqrt{2}}\left|{2 \atop -2}\right\rangle$$

$$\left|B_2 2^-\right\rangle = \tfrac{1}{\sqrt{2}}\left|{2 \atop +2}\right\rangle - \tfrac{1}{\sqrt{2}}\left|{2 \atop -2}\right\rangle$$

$$\left|B_1 1^+\right\rangle = \tfrac{1}{\sqrt{2}}\left|{2 \atop +1}\right\rangle + \tfrac{1}{\sqrt{2}}\left|{2 \atop -1}\right\rangle$$

$$\left|A_2 1^-\right\rangle = \tfrac{1}{\sqrt{2}}\left|{2 \atop +1}\right\rangle - \tfrac{1}{\sqrt{2}}\left|{2 \atop -1}\right\rangle$$

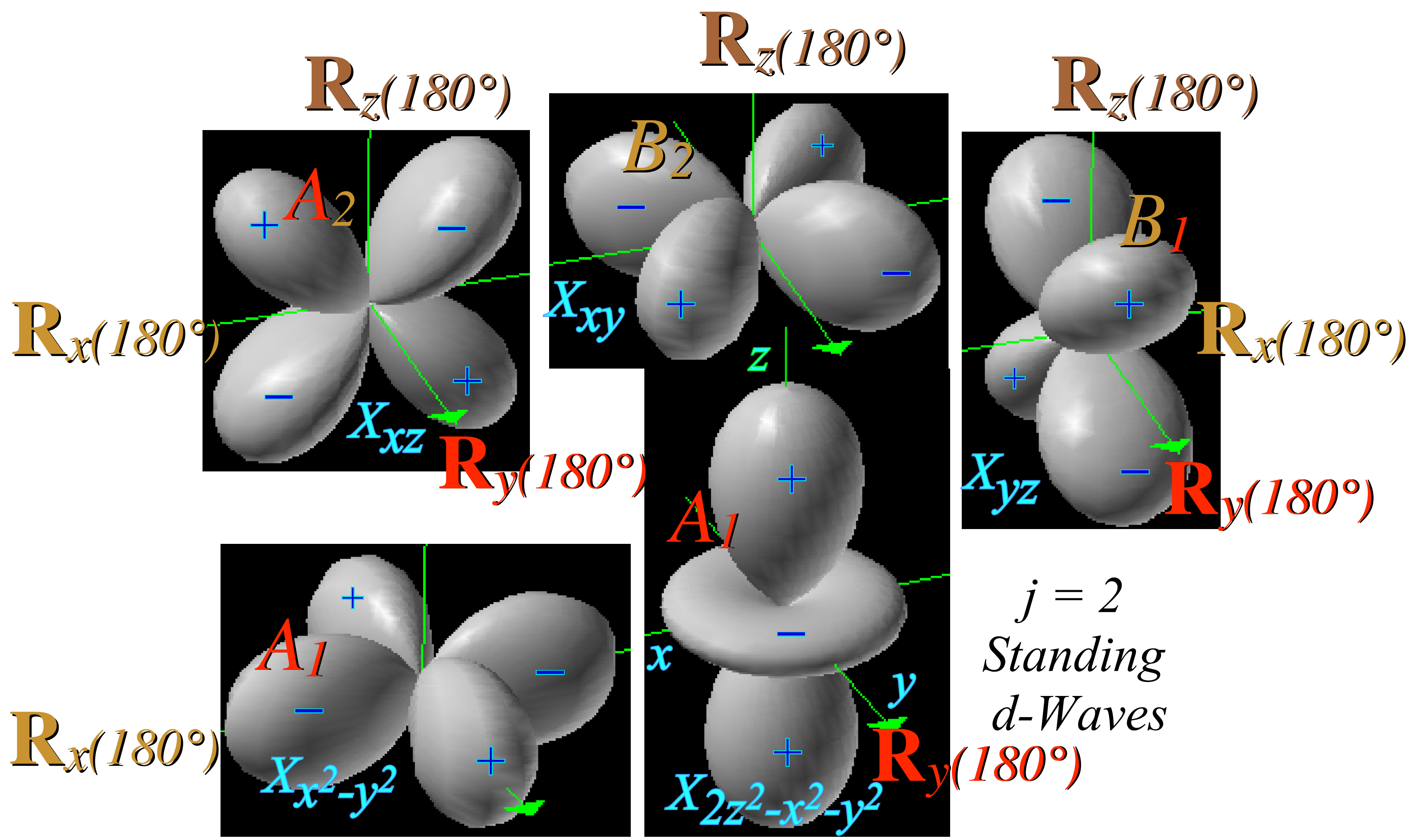
$$\left|A_1 0\right\rangle = \left|{2 \atop 0}\right\rangle$$

Need only diagonalize the two A_1's:

(It is n=0 versus n=2⁺)

$$\begin{pmatrix} 4C+A+B & \sqrt{3}(A-B) \\ \sqrt{3}(A-B) & 3A+3B \end{pmatrix} \begin{matrix} \left|A_1 2^+\right\rangle = \tfrac{1}{\sqrt{2}}\left|{2 \atop +2}\right\rangle + \tfrac{1}{\sqrt{2}}\left|{2 \atop -2}\right\rangle \\ \left|A_1 0\right\rangle = \left|{2 \atop 0}\right\rangle \end{matrix}$$

D_2	**1**	$\mathbf{R}_x$	$\mathbf{R}_y$	$\mathbf{R}_z$
A_1	1	1	1	1
A_2	1	-1	1	−1
B_1	1	1	-1	−1
B_2	1	-1	-1	1



Completing diagonalization from new D_2 basis:

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

$$\left|A_1 2^+\right\rangle = \tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\+2\end{smallmatrix}\right\rangle + \tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\-2\end{smallmatrix}\right\rangle$$
$$\left|B_2 2^-\right\rangle = \tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\+2\end{smallmatrix}\right\rangle - \tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\-2\end{smallmatrix}\right\rangle$$
$$\left|B_1 1^+\right\rangle = \tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\+1\end{smallmatrix}\right\rangle + \tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\-1\end{smallmatrix}\right\rangle$$
$$\left|A_2 1^-\right\rangle = \tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\+1\end{smallmatrix}\right\rangle - \tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\-1\end{smallmatrix}\right\rangle$$
$$\left|A_1 0\right\rangle = \left|\begin{smallmatrix}2\\0\end{smallmatrix}\right\rangle$$

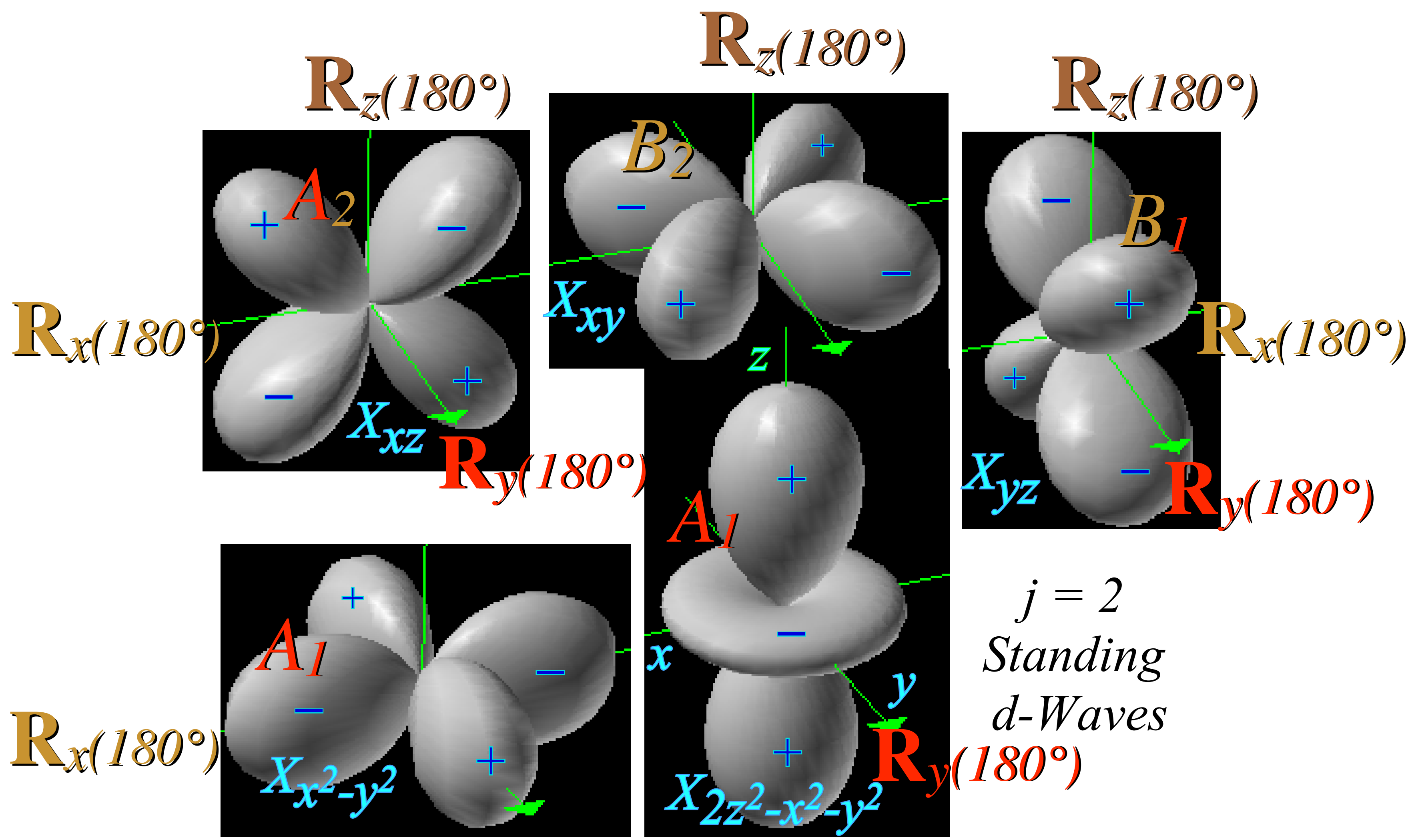
D_2	**1**	$\mathbf{R}_x$	$\mathbf{R}_y$	$\mathbf{R}_z$
A_1	1	1	1	1
A_2	1	-1	1	−1
B_1	1	1	-1	−1
B_2	1	-1	-1	1

Need only diagonalize the two A_1's:

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

$$\begin{pmatrix} 4C+A+B & \sqrt{3}(A-B) \\ \sqrt{3}(A-B) & 3A+3B \end{pmatrix} \begin{matrix} \left|A_1 2^+\right\rangle = \tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\+2\end{smallmatrix}\right\rangle + \tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\-2\end{smallmatrix}\right\rangle \\ \left|A_1 0\right\rangle = \left|\begin{smallmatrix}2\\0\end{smallmatrix}\right\rangle \end{matrix}$$

$$= (2C+2A+2B)\cdot\mathbf{1} + \begin{pmatrix} 2C-A-B & \sqrt{3}(A-B) \\ \sqrt{3}(A-B) & -(2C-A-B) \end{pmatrix}$$



Completing diagonalization from new D_2 basis:

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

$$\left|A_1 2^+\right\rangle = \tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\+2\end{smallmatrix}\right\rangle + \tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\-2\end{smallmatrix}\right\rangle$$

$$\left|B_2 2^-\right\rangle = \tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\+2\end{smallmatrix}\right\rangle - \tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\-2\end{smallmatrix}\right\rangle$$

$$\left|B_1 1^+\right\rangle = \tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\+1\end{smallmatrix}\right\rangle + \tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\-1\end{smallmatrix}\right\rangle$$

$$\left|A_2 1^-\right\rangle = \tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\+1\end{smallmatrix}\right\rangle - \tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\-1\end{smallmatrix}\right\rangle$$

$$\left|A_1 0\right\rangle = \left|\begin{smallmatrix}2\\0\end{smallmatrix}\right\rangle$$

Need only diagonalize the two A_1's:

(It is n=0 versus n=2⁺)

$$\begin{pmatrix} 4C+A+B & \sqrt{3}(A-B) \\ \sqrt{3}(A-B) & 3A+3B \end{pmatrix} \begin{matrix} \left|A_1 2^+\right\rangle = \tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\+2\end{smallmatrix}\right\rangle + \tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\-2\end{smallmatrix}\right\rangle \\ \left|A_1 0\right\rangle = \left|\begin{smallmatrix}2\\0\end{smallmatrix}\right\rangle \end{matrix}$$

$$= (2C+2A+2B)\cdot\mathbf{1} + \begin{pmatrix} 2C-A-B & \sqrt{3}(A-B) \\ \sqrt{3}(A-B) & -(2C-A-B) \end{pmatrix}$$

with eigenvalues:

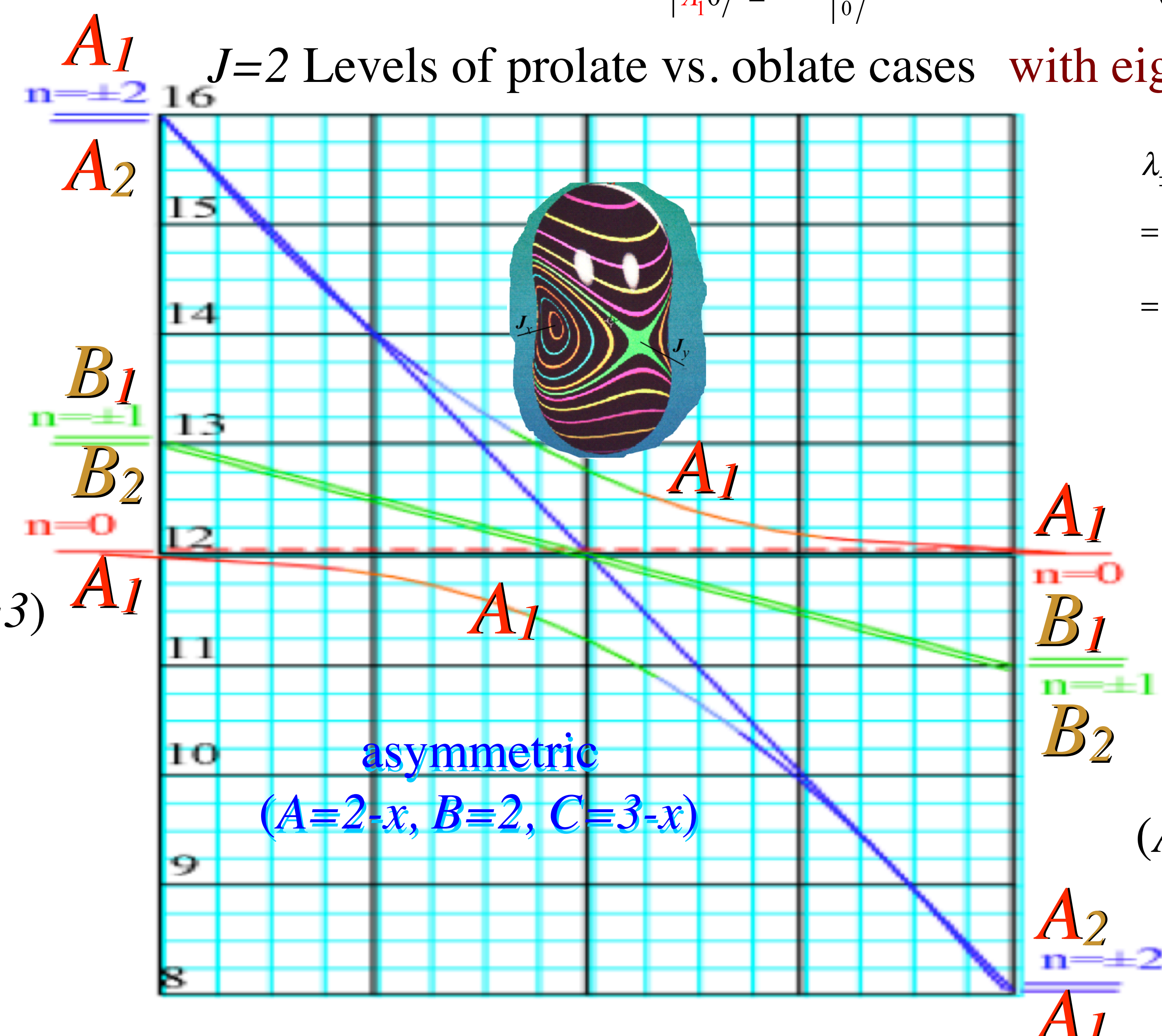
$$\lambda_{\pm} = 2C+2A+2B \pm \sqrt{(2C-A-B)^2 + 3(A-B)^2}$$

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

$$= 2C+4B \pm 2(C-B) = \begin{cases} 4C+2B \\ 6B \end{cases} \quad \text{if: } A=B$$

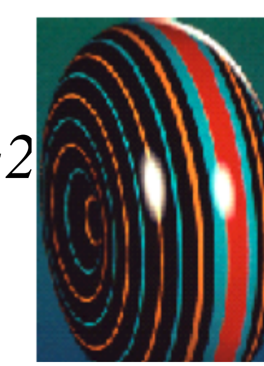
J=2 Levels of prolate vs. oblate cases

prolate
(A=2, B=2, C=3)



J=2

oblate
(A=1, B=2, C=2)



$A=B$ 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)

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

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

Completing diagonalization from new D_2 basis:

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

$$\left|A_1 2^+\right\rangle = \tfrac{1}{\sqrt{2}}\left|{2 \atop +2}\right\rangle + \tfrac{1}{\sqrt{2}}\left|{2 \atop -2}\right\rangle$$

$$\left|B_2 2^-\right\rangle = \tfrac{1}{\sqrt{2}}\left|{2 \atop +2}\right\rangle - \tfrac{1}{\sqrt{2}}\left|{2 \atop -2}\right\rangle$$

$$\left|B_1 1^+\right\rangle = \tfrac{1}{\sqrt{2}}\left|{2 \atop +1}\right\rangle + \tfrac{1}{\sqrt{2}}\left|{2 \atop -1}\right\rangle$$

$$\left|A_2 1^-\right\rangle = \tfrac{1}{\sqrt{2}}\left|{2 \atop +1}\right\rangle - \tfrac{1}{\sqrt{2}}\left|{2 \atop -1}\right\rangle$$

$$\left|A_1 0\right\rangle = \left|{2 \atop 0}\right\rangle$$

Need only diagonalize the two A_1's:

(It is n=0 versus n=2⁺)

$$\begin{pmatrix} 4C+A+B & \sqrt{3}(A-B) \\ \sqrt{3}(A-B) & 3A+3B \end{pmatrix} \quad \left|A_1 2^+\right\rangle = \tfrac{1}{\sqrt{2}}\left|{2 \atop +2}\right\rangle + \tfrac{1}{\sqrt{2}}\left|{2 \atop -2}\right\rangle, \quad \left|A_1 0\right\rangle = \left|{2 \atop 0}\right\rangle$$

$$= (2C+2A+2B)\cdot\mathbf{1} + \begin{pmatrix} 2C-A-B & \sqrt{3}(A-B) \\ \sqrt{3}(A-B) & -(2C-A-B) \end{pmatrix}$$

$J=2$ Levels of prolate vs. oblate cases

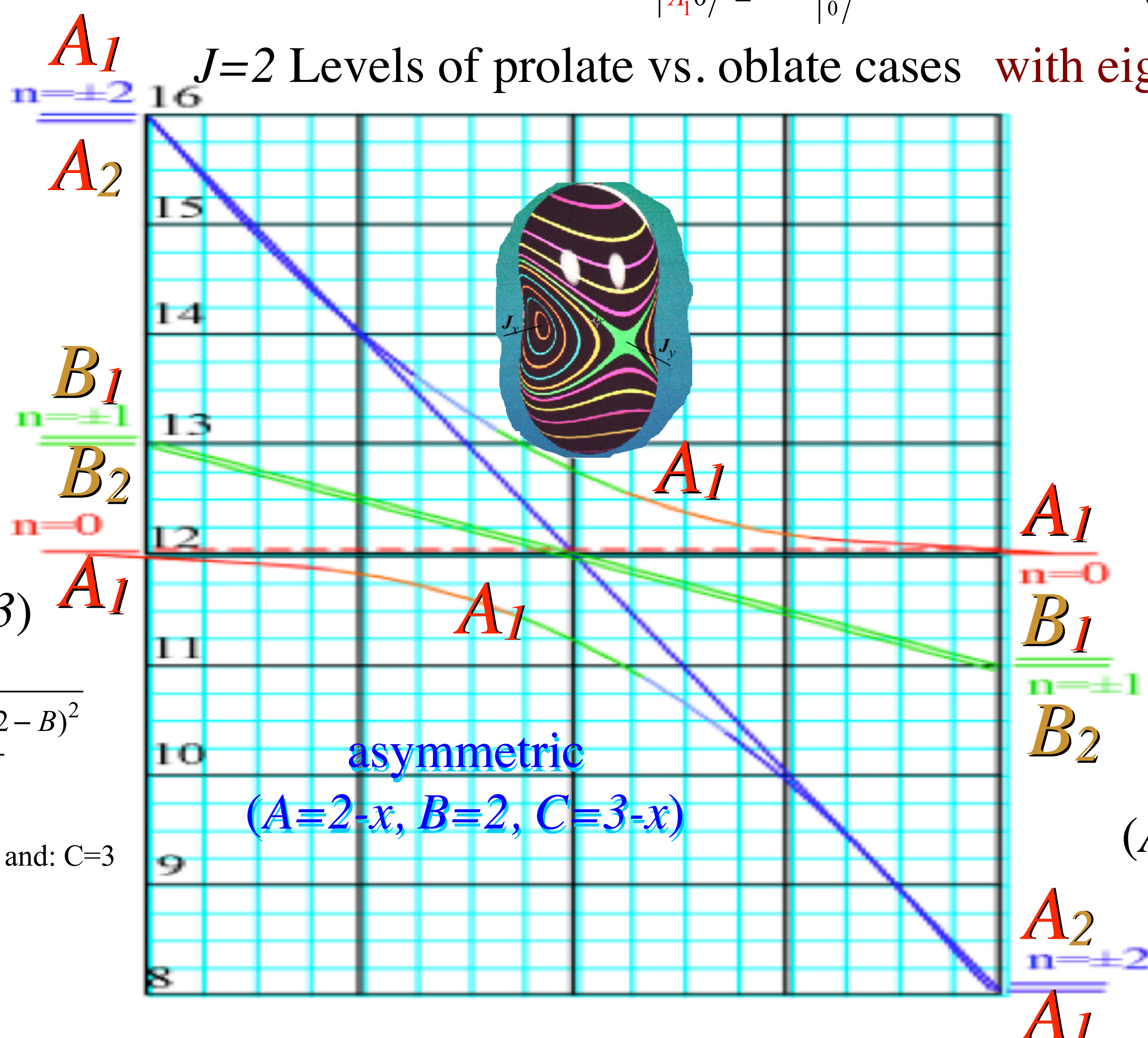
with eigenvalues:

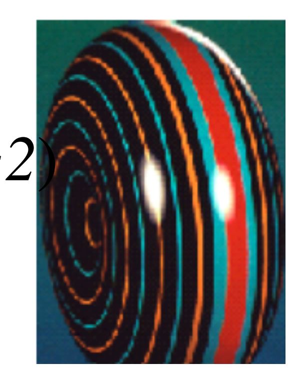
$$\begin{pmatrix} 14+B & \sqrt{3}(2-B) \\ \sqrt{3}(2-B) & 6+3B \end{pmatrix} =$$

$$(10+2B)\cdot\mathbf{1} + \begin{pmatrix} 4-B & \sqrt{3}(2-B) \\ \sqrt{3}(2-B) & -(4-B) \end{pmatrix}$$

prolate

$(A=2, B=2, C=3)$





oblate

$(A=1, B=2, C=2)$

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

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

$$= 14 \pm 2 = \begin{cases} 16 \\ 12 \end{cases} \text{ if: } A=B=2 \text{ and: } C=3$$

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

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

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

Review :

Symmetric rigid quantum rotor analysis of R(2) Hamiltonian $\mathbf{H}=B\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$

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

Asymmetric rigid quantum rotor analysis of D_2 Hamiltonian $\mathbf{H}=A\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$

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

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

$R(3)\supset D_2$ character analysis of ℓ-level or 2ℓ+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 $\mathbf{H}=B\mathbf{J}\cdot\mathbf{J}+t_{044}\mathbf{T}^{[4]}$

Spherical rotor levels and RES plots of O_h tensor eigenvalues

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

SF_6 spectral fine structure

CF_4 spectral fine structure

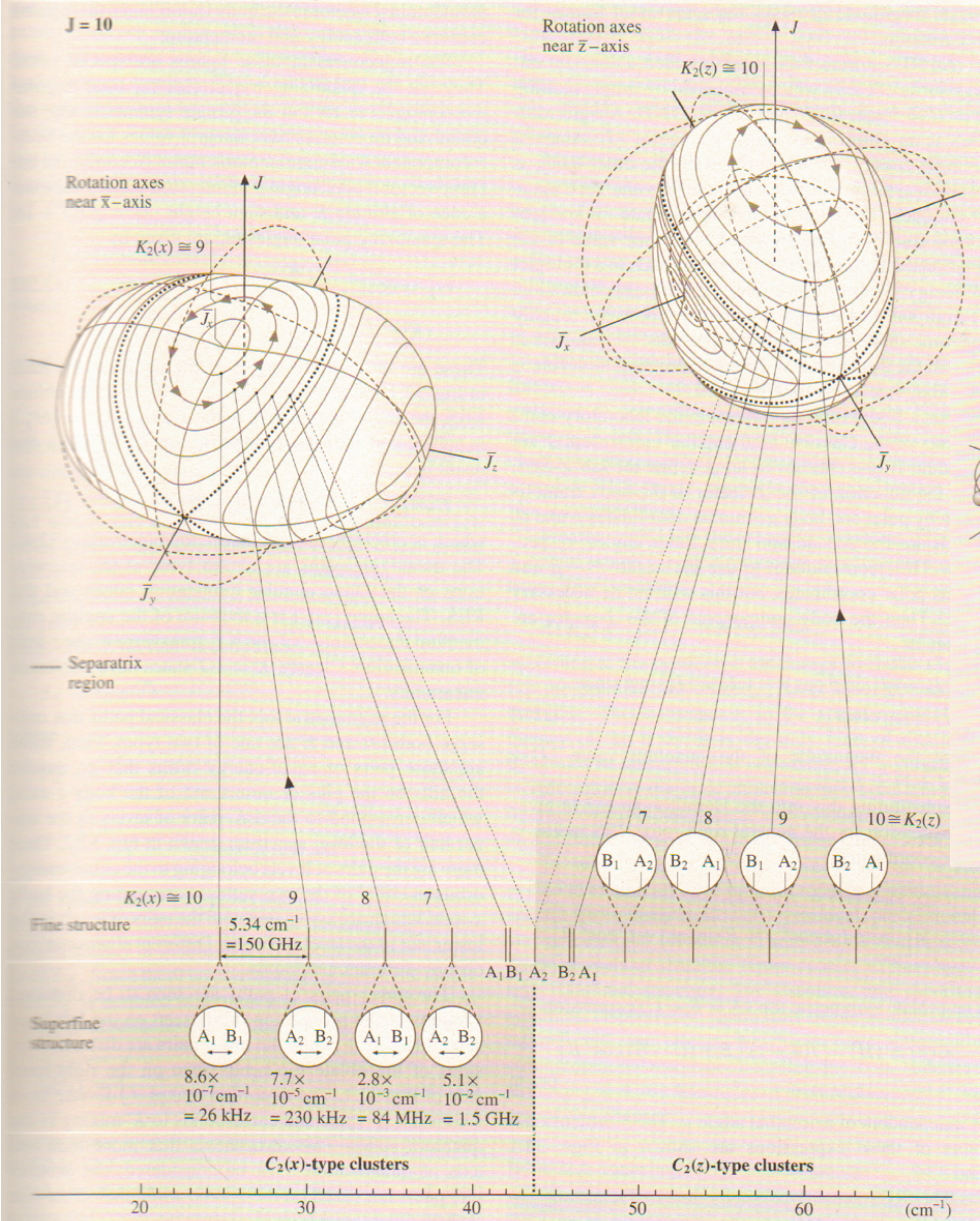
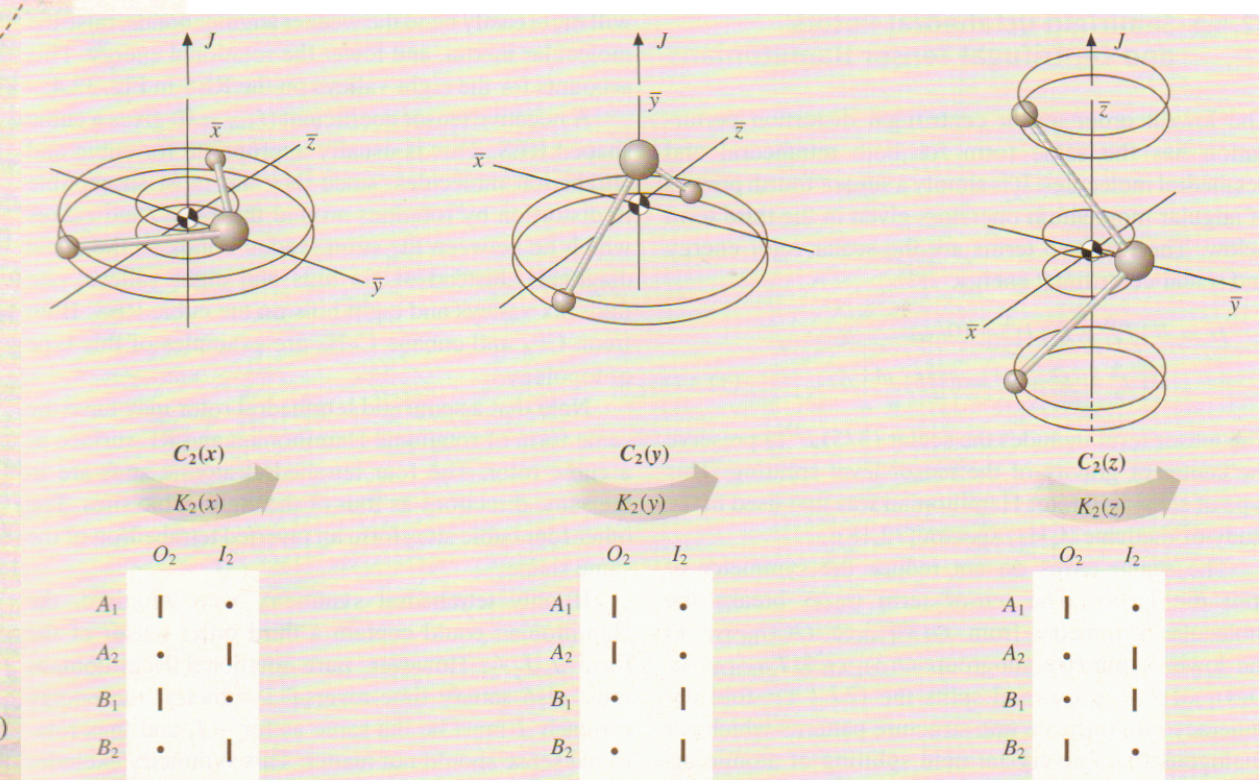


Fig. 32.2 $J = 10$ rotational energy surface and related level spectrum for an asymmetric rigid rotator ($A = 0.2$, $B = 0.4$, $C = 0.6\,\text{cm}^{-1}$)

Examples of Group⊃Sub-group correlation

$D_2 \supset C_2(x)$ $D_2 \supset C_2(y)$ $D_2 \supset C_2(z)$



Springer 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

$D_2 \supset C_2(x)$ $D_2 \supset C_2(y)$ $D_2 \supset C_2(z)$

D_2	$\mathbf{1}$	$\mathbf{R}_x$	$\mathbf{R}_y$	$\mathbf{R}_z$
A_1	1	1	1	1
A_2	1	-1	1	−1
B_1	1	1	-1	−1
B_2	1	-1	-1	1

Original color mixing scheme gives

yellow $1_2=(A_2B_1)$

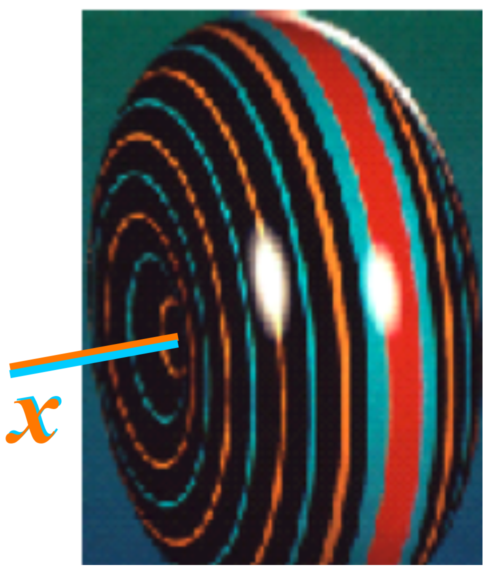
purple $0_2=(A_1B_2)$

for z-prolate axis

orange $0_2=(A_1B_1)$

cyan $1_2=(A_2B_2)$

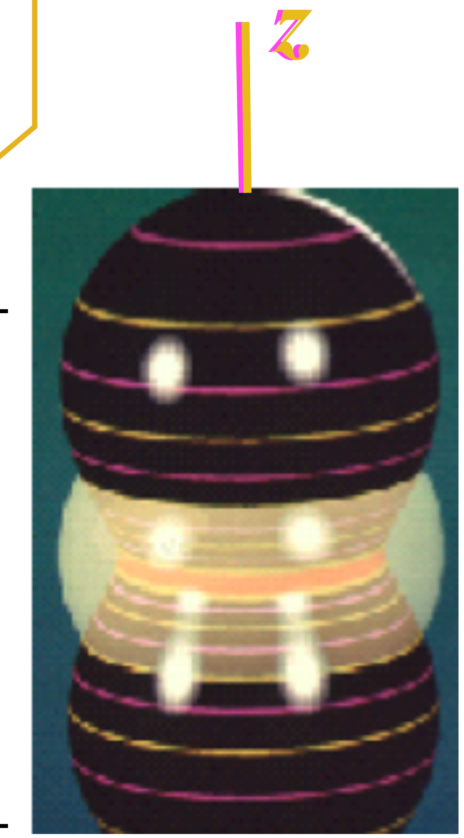
for x-oblate axis



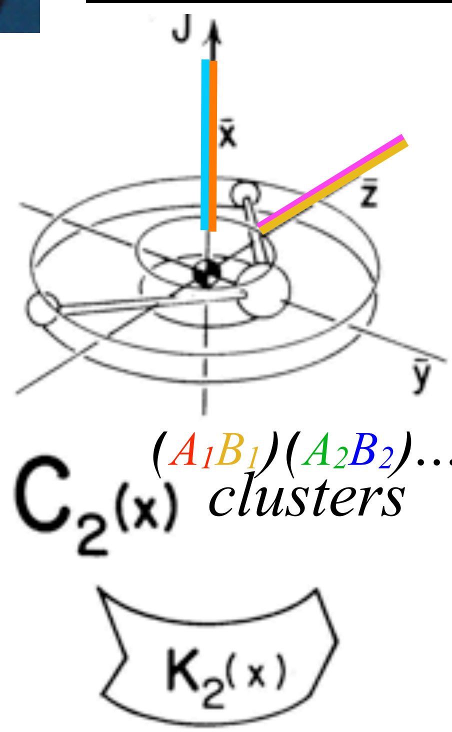
C_{2x}	0_2	1_2
A_1	1	·
A_2	·	1
B_1	1	·
B_2	·	1

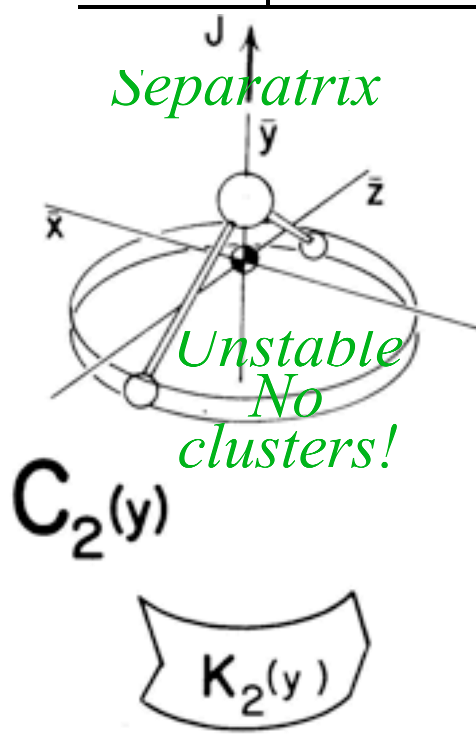
C_{2y}	0_2	1_2
A_1	1	·
A_2	1	·
B_1	·	1
B_2	·	1

C_{2z}	0_2	1_2
A_1	1	·
A_2	·	1
B_1	·	1
B_2	1	·



Review:
Asymmetric
vs
Symmetric
rotor levels





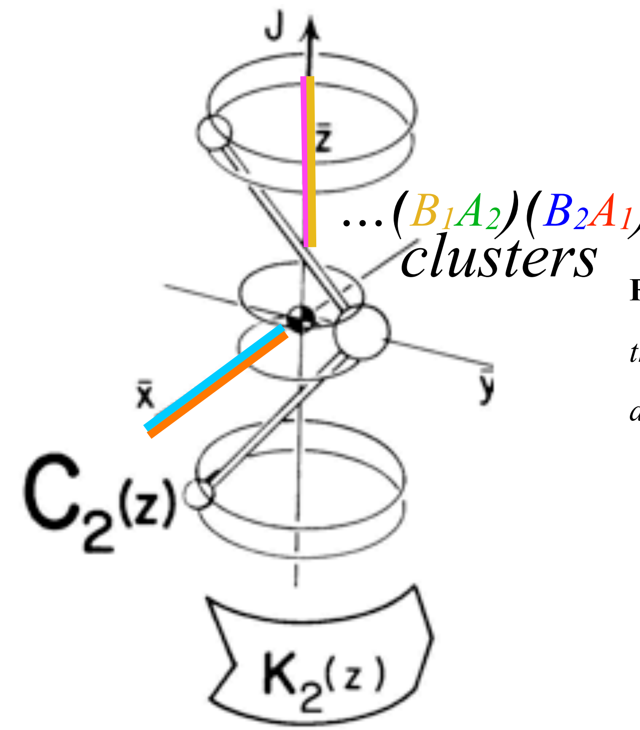
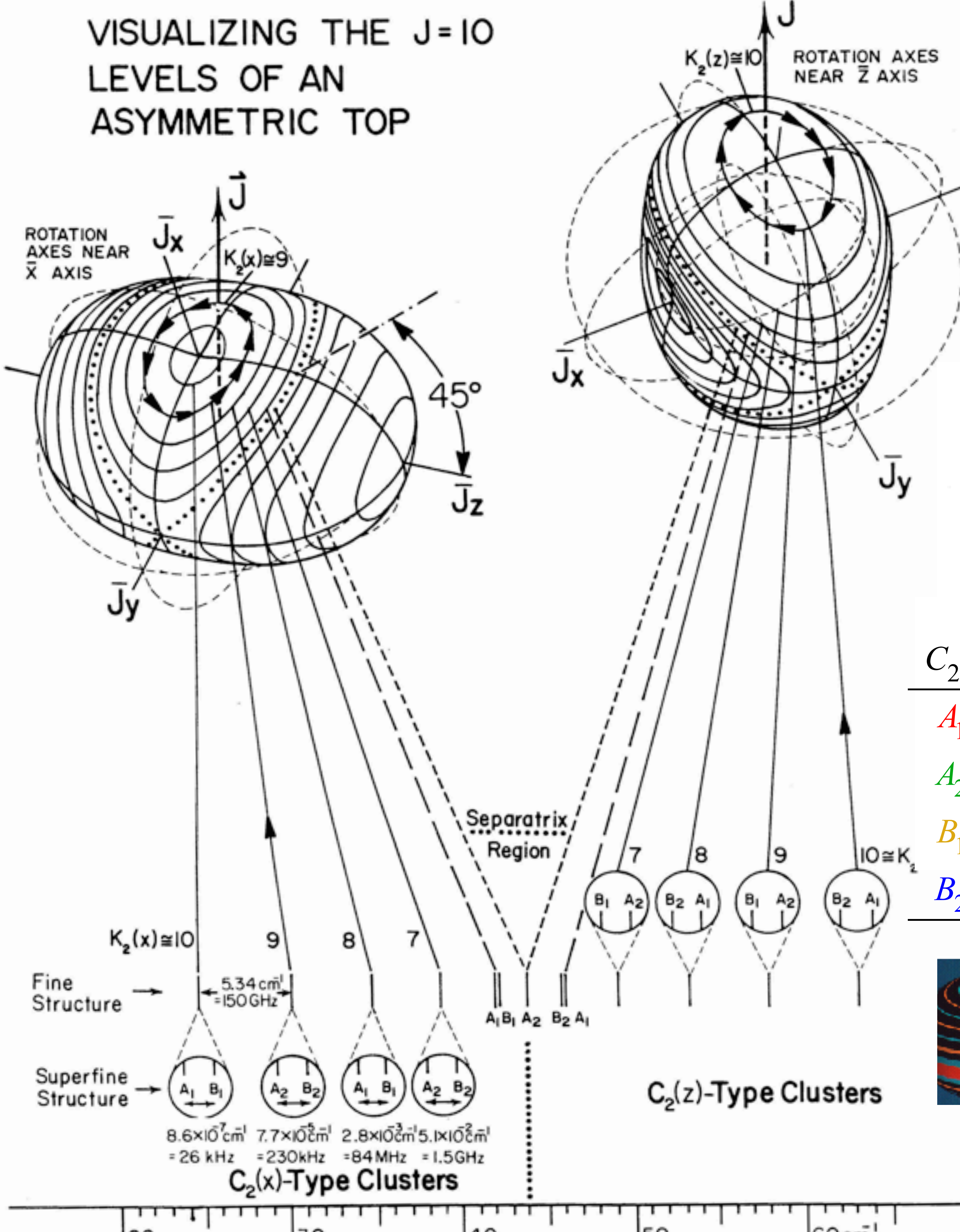


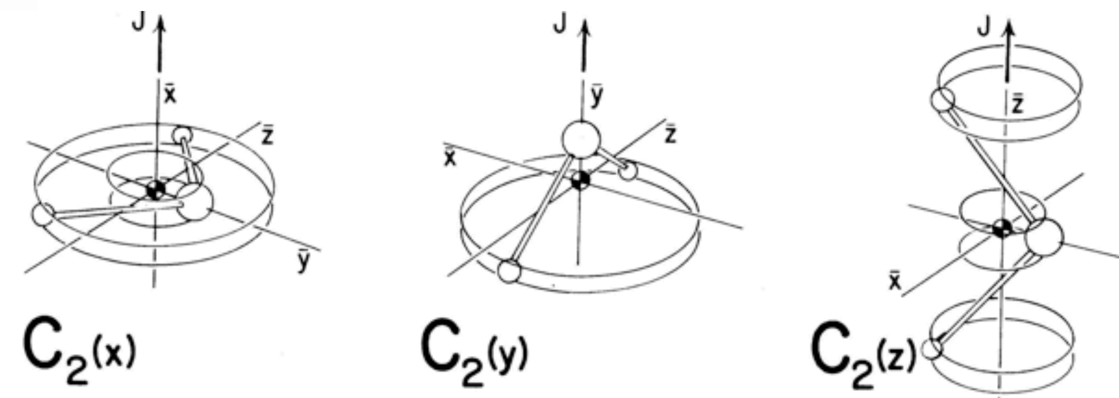
Fig. 25.4.3 *Correlations between the asymmetric top symmetry D_2 and subgroups $C_2(x)$, $C_2(y)$, and $C_2(z)$.*



D_2	**1**	$\mathbf{R}_x$	$\mathbf{R}_y$	$\mathbf{R}_z$
A_1	1	1	1	1
A_2	1	-1	1	−1
B_1	1	1	-1	−1
B_2	1	-1	-1	1

Examples of Group⊃Sub-group correlation

$D_2\supset C_2(x)$ *$D_2\supset C_2(y)$* *$D_2\supset C_2(z)$*



C_{2x}	0_2	1_2
A_1	1	·
A_2	·	1
B_1	1	·
B_2	·	1

C_{2y}	0_2	1_2
A_1	1	·
A_2	1	·
B_1	·	1
B_2	·	1

C_{2z}	0_2	1_2
A_1	1	·
A_2	·	1
B_1	·	1
B_2	1	·

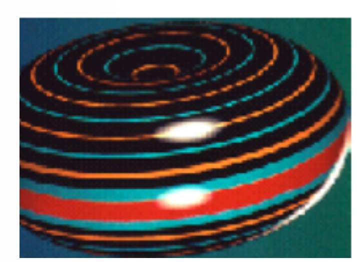
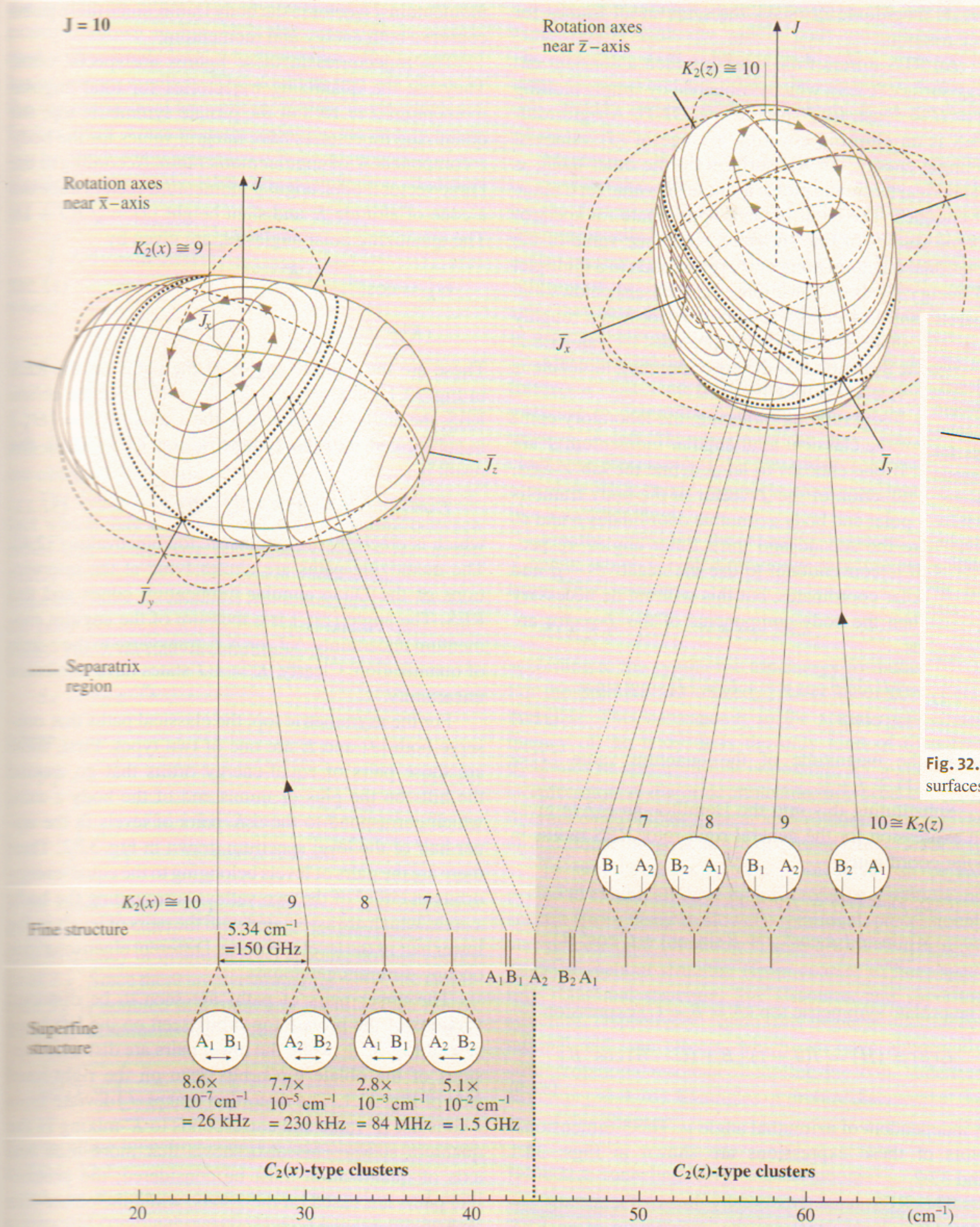


Fig. 25.4.2 *$J = 10$ asymmetric top energy levels and related RE surface paths ($A = 0.2$, $B = 0.4$, $C = 0.6$). Clustered pairs of levels are indicated in magnifying circles that show superfine splittings.*



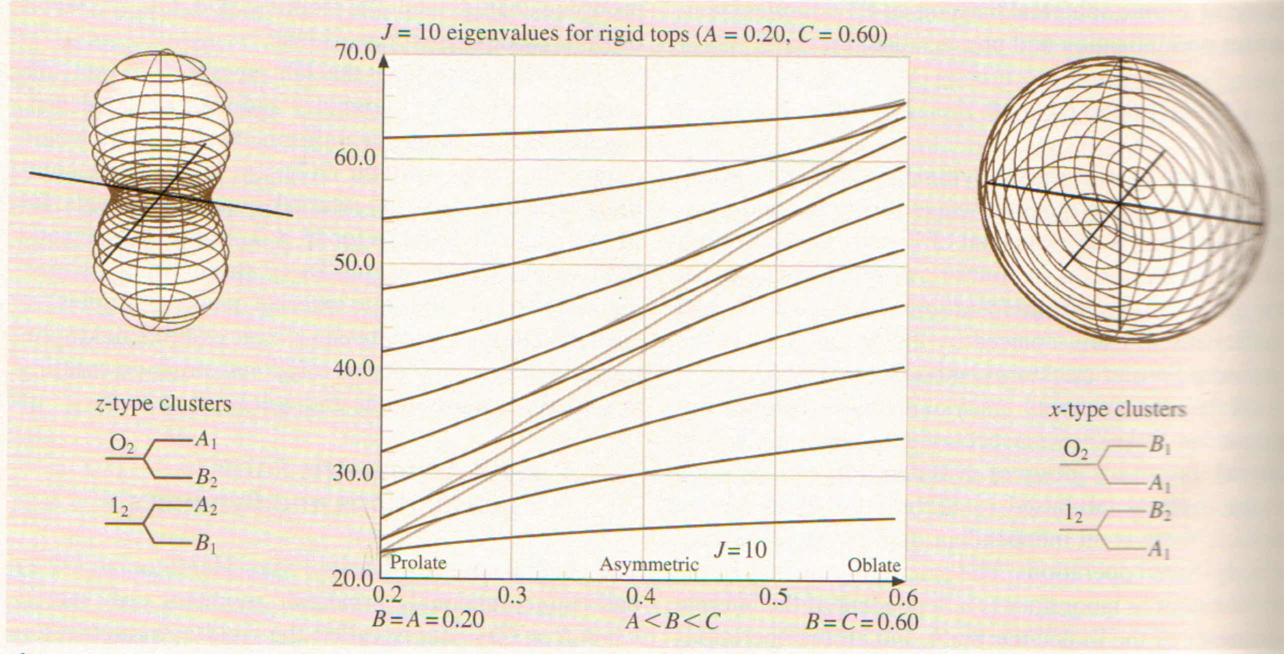
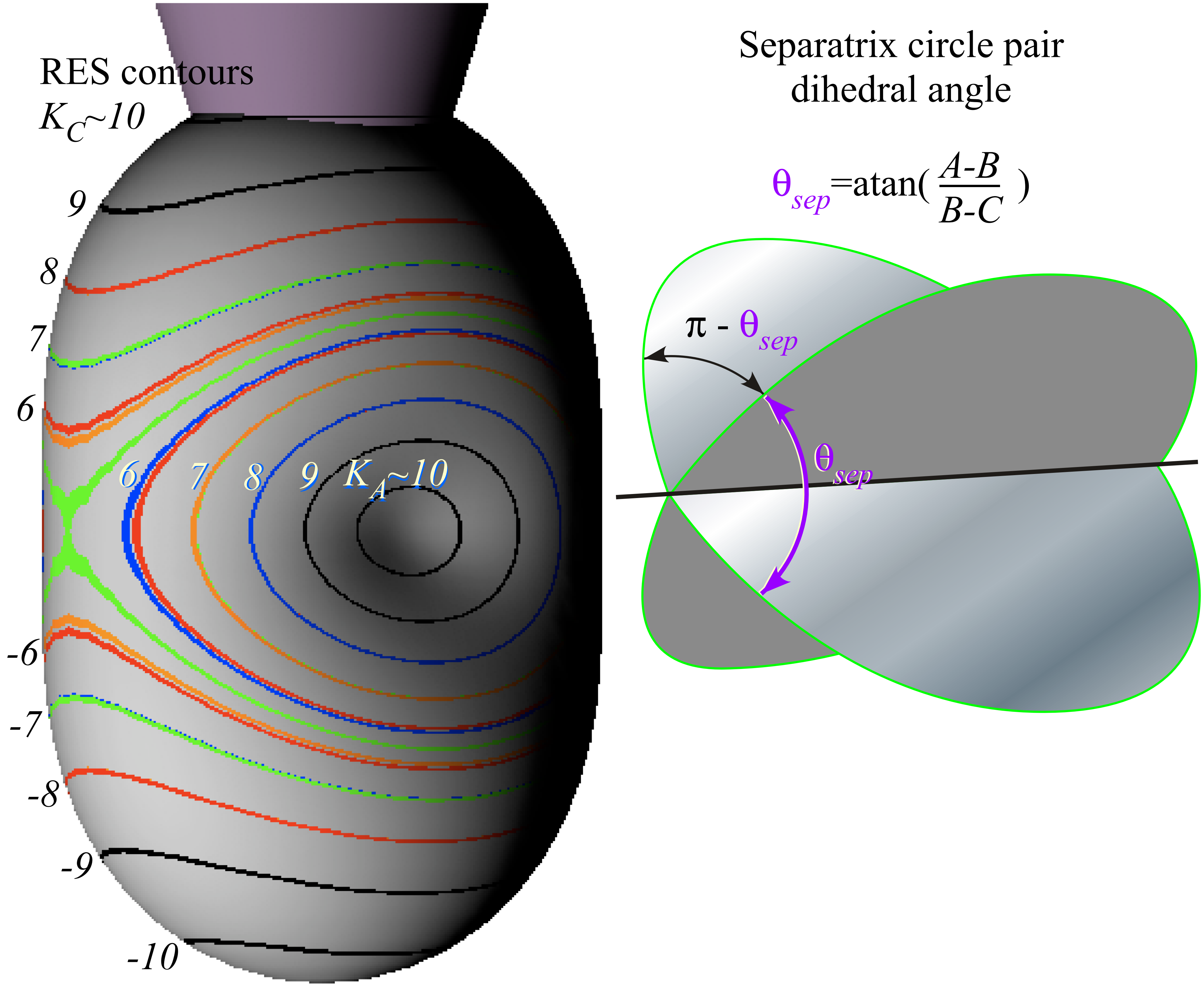


Fig. 32.1 $J = 10$ eigenvalue plot for symmetric rigid rotors. ($A = 0.2$, $C = 0.6\,\text{cm}^{-1}$ $A < B < C$). Prolate and oblate RE surfaces are shown

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

Springer Handbook
of
Atomic, Molecular, and Optical Physics (2005)
Fig.32.1 and 32.2 p. 494-495



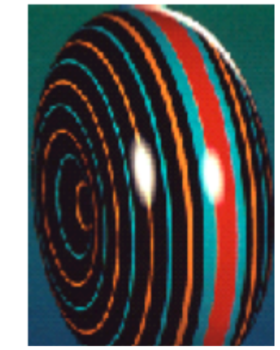
Int.J.Molecular Science 14.(2013) Fig.3 p. 733

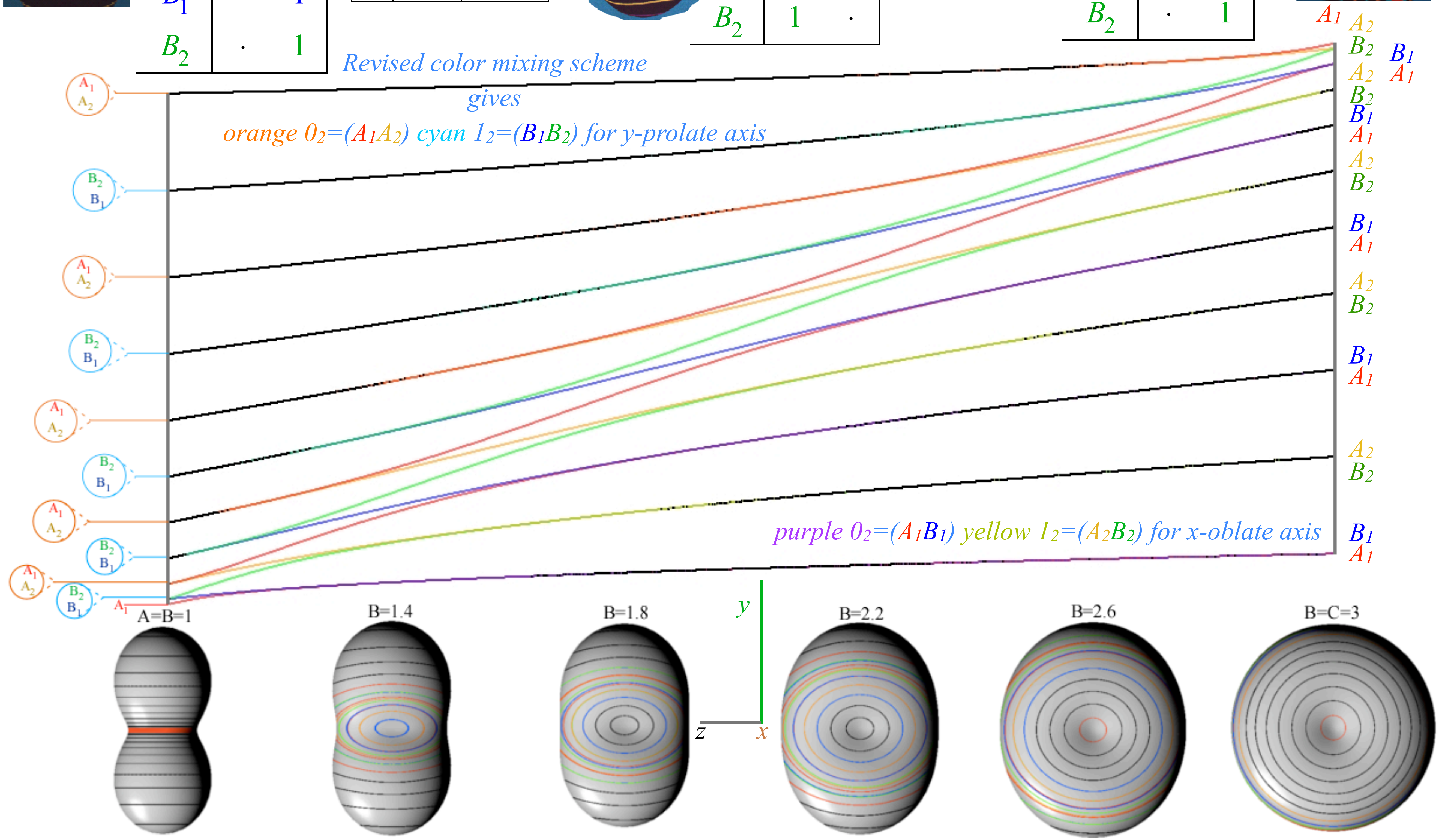
C_{2y}	0_2	1_2
A_1	1	·
A_2	1	·
B_1	·	1
B_2	·	1

D_2	**1**	$\mathbf{R}_x$	$\mathbf{R}_y$	$\mathbf{R}_z$
A_1	1	1	1	1
A_2	1	-1	1	−1
B_1	1	1	-1	−1
B_2	1	-1	-1	1

C_{2z}	0_2	1_2
A_1	1	·
A_2	·	1
B_1	·	1
B_2	1	·

C_{2x}	0_2	1_2
A_1	1	·
A_2	·	1
B_1	1	·
B_2	·	1





(Revised color mixing scheme used here) *Int.J.Molecular Science 14.(2013)* Fig.4 p. 734

Review :

Symmetric rigid quantum rotor analysis of R(2) Hamiltonian $\mathbf{H}=B\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$

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

Asymmetric rigid quantum rotor analysis of D_2 Hamiltonian $\mathbf{H}=A\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$

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

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

$R(3)\supset D_2$ character analysis of ℓ-level or 2ℓ+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 $\mathbf{H}=B\mathbf{J}\cdot\mathbf{J}+t_{044}\mathbf{T}^{[4]}$

Spherical rotor levels and RES plots of O_h tensor eigenvalues

$R(3)\subset O(3)\supset O_h\supset O$ character analysis of ℓ-level or 2ℓ+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 ℓ-level starts on p. 10 of Lecture 27

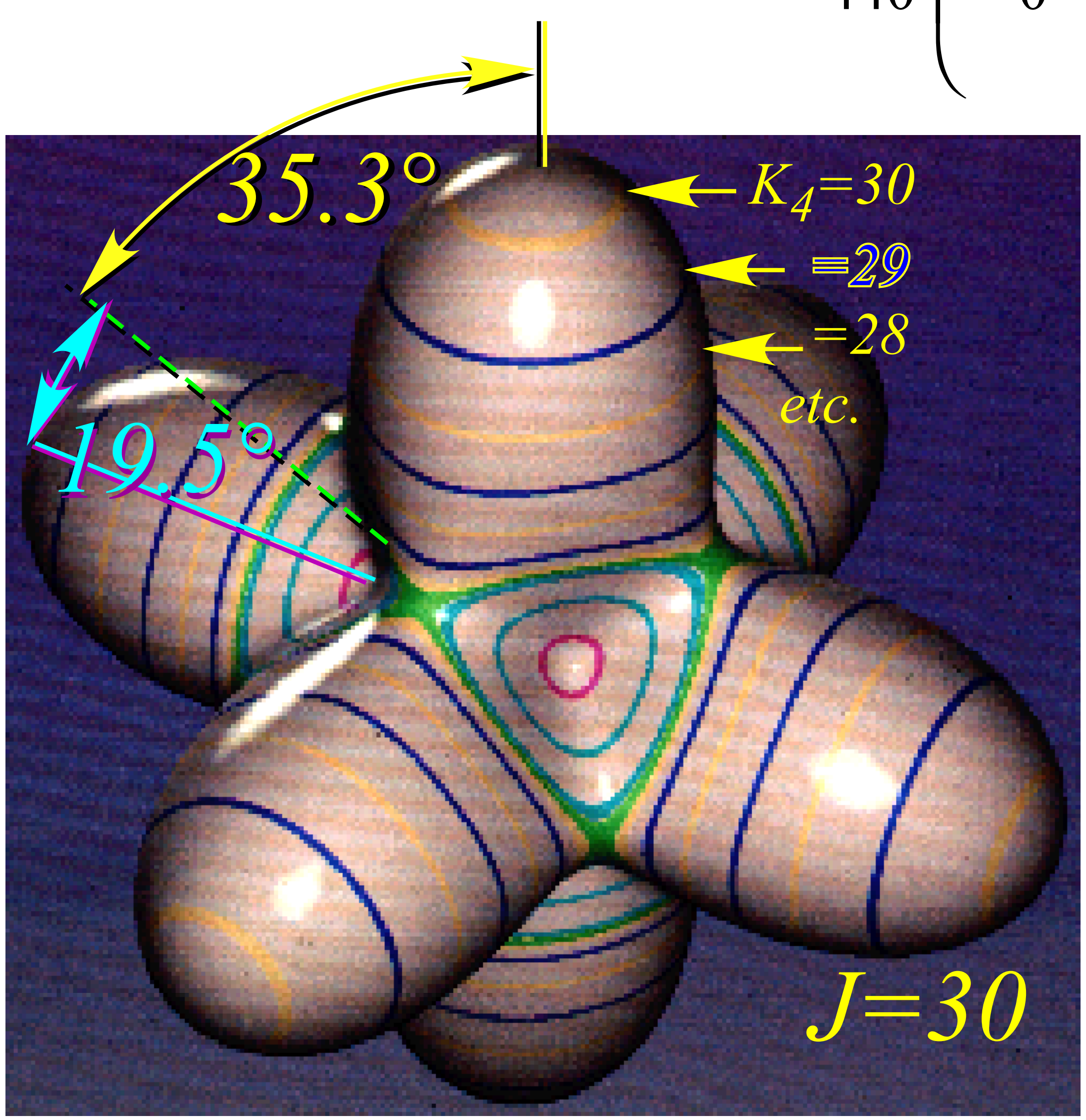
Semi Rigid Rotor Hamiltonian: *Centrifugal and Coriolis terms...*

$$\mathbf{H} = A\mathbf{J}_x^2 + B\mathbf{J}_y^2 + C\mathbf{J}_z^2 + t_{xxxx}\mathbf{J}_x^4 + t_{xxyy}\mathbf{J}_x^2\mathbf{J}_y^2 + \cdots$$

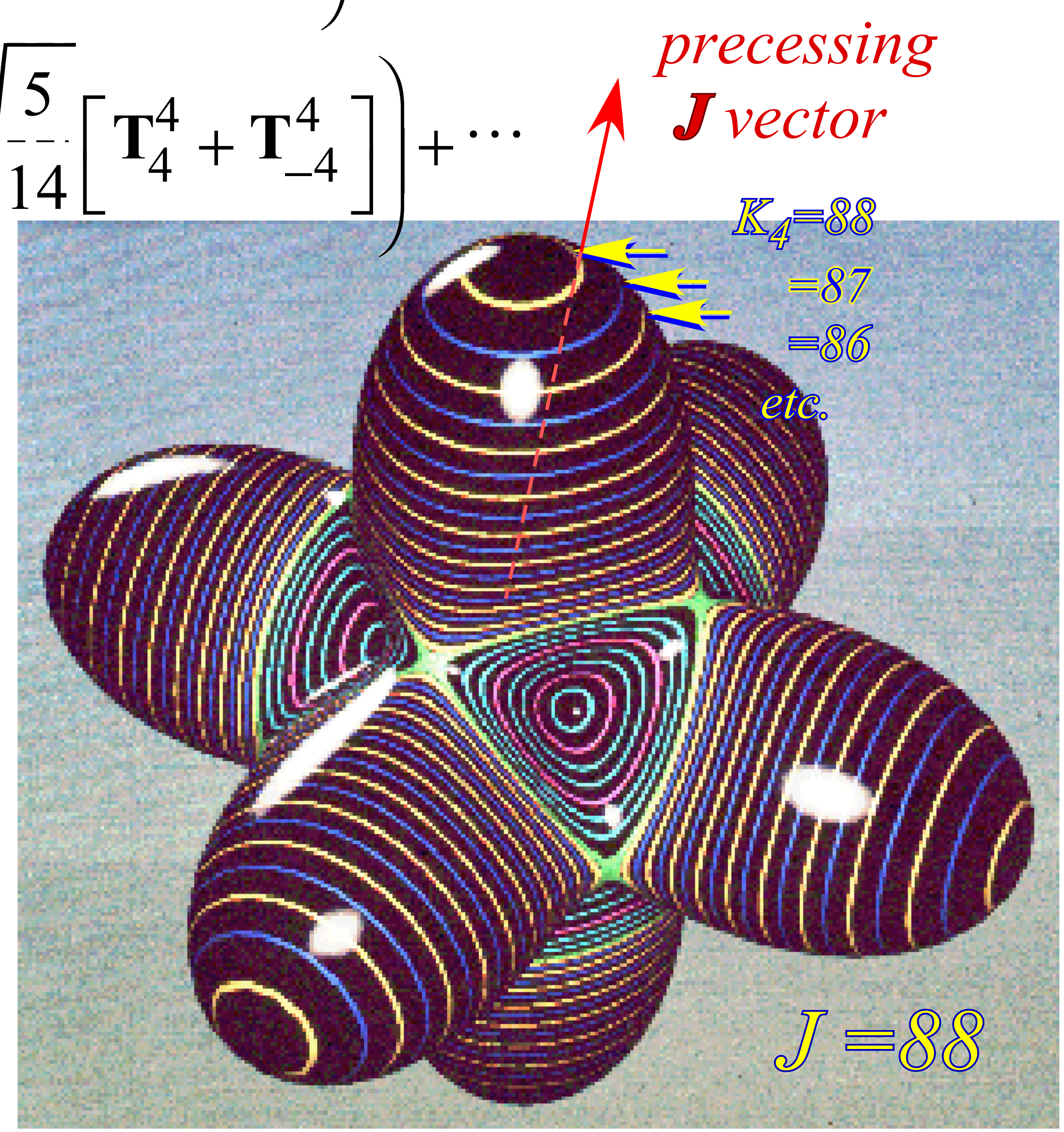
Semi Rigid O_h or T_d Spherical Top: *(Hecht Hamiltonian 1960)*

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

$$= \quad B\mathbf{J}^2 \quad + t_{440}\left(\mathbf{T}_0^4 + \sqrt{\frac{5}{14}}\left[\mathbf{T}_4^4 + \mathbf{T}_{-4}^4\right]\right) + \cdots$$



after QTforCA Unit 8. Ch. 25 Fig. 25.4.5



Review :

Symmetric rigid quantum rotor analysis of R(2) Hamiltonian $\mathbf{H}=B\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$

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

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

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

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

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Asymmetric rotor levels and RES plots for high-J

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

Spherical rotor levels and RES plots of O_h tensor eigenvalues

$R(3)\subset O(3)\supset O_h\supset O$ character analysis of ℓ-level or 2ℓ+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)

$R(3) \subset O(3) \supset O_h \supset O$ character analysis (From Principles of Symmetry Dynamics & Spectroscopy Ch.5 p.384)

	Trace $\mathscr{D}^l(\omega 00)$					Single Electron Orbital Spectroscopic Labeling
	$\omega = 0°$	$\omega = 120°$	$\omega = 180°$	$\omega = 90°$	$\omega = 180°$	
$l = 0$	1	1	1	1	1	s_g
1	3	0	−1	1	−1	P_u
2	5	−1	1	−1	1	d_g
3	7	1	−1	−1	−1	f_u
4	9	0	1	1	1	g_g
5	11	−1	−1	1	−1	h_u
6	13	1	1	−1	1	i_g
7	15	0	−1	−1	−1	k_u
8	17	−1	1	1	1	l_g
9	19	1	−1	1	−1	m_u
10	21	0	1	−1	1	n_g
11	23	−1	−1	−1	−1	o_u
12	25	1	1	1	1	q_g
13	27	0	−1	1	−1	r_u
14	29	−1	1	−1	1	t_g
15	31	1	−1	−1	−1	u_u
16	33	0	1	1	1	
17	35	−1	−1	1	−1	
18	37	1	1	−1	1	
19	39	0	−1	−1	−1	
20	41	−1	1	1	1	

(5.6.5a)

	Frequency of O Irreps					
	f^{A_1}	f^{A_2}	f^E	f^{T_1}	f^{T_2}	
$l = 0$	1	·	·	·	·	A_{1g}
1	·	·	·	1	·	T_{1u}
2	·	·	1	·	1	$E_g + T_{2g}$
3	·	1	·	1	1	$A_{2u} + T_{1u} + T_{2u}$
4	1	·	1	1	1	$A_{1g} + E_g + T_{1g} + T_{2g}$
5	·	·	1	2	1	
6	1	1	1	1	2	
7	·	1	1	2	2	
8	1	·	2	2	2	
9	1	1	1	3	2	
10	1	1	2	2	3	
11	·	1	2	3	3	
12	2	1	2	3	3	
13	1	1	2	4	3	
14	1	1	3	3	4	
15	1	2	2	4	4	
16	2	1	3	4	4	
17	1	1	3	5	4	
18	2	2	3	4	5	
19	1	2	3	5	5	
20	2	1	4	5	5	

(5.6.5b)

R(3) characters

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

O characters

O	**1**	**r**	$\mathbf{R}^2$	$\mathbf{R}^3$	$\mathbf{i}_k$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
T_1	3	0	-1	1	-1
T_2	3	0	-1	-1	1

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

Frequency of O Irreps

	f^{A_1}	f^{A_2}	f^{E}	f^{T_1}	f^{T_2}	
$l=0$	1	·	·	·	·	A_{1g}
1	·	·	·	1	·	T_{1u}
2	·	·	1	·	1	$E_g + T_{2g}$
3	·	1	·	1	1	$A_{2u} + T_{1u} + T_{2u}$
4	1	·	1	1	1	$A_{1g} + E_g + T_{1g} + T_{2g}$

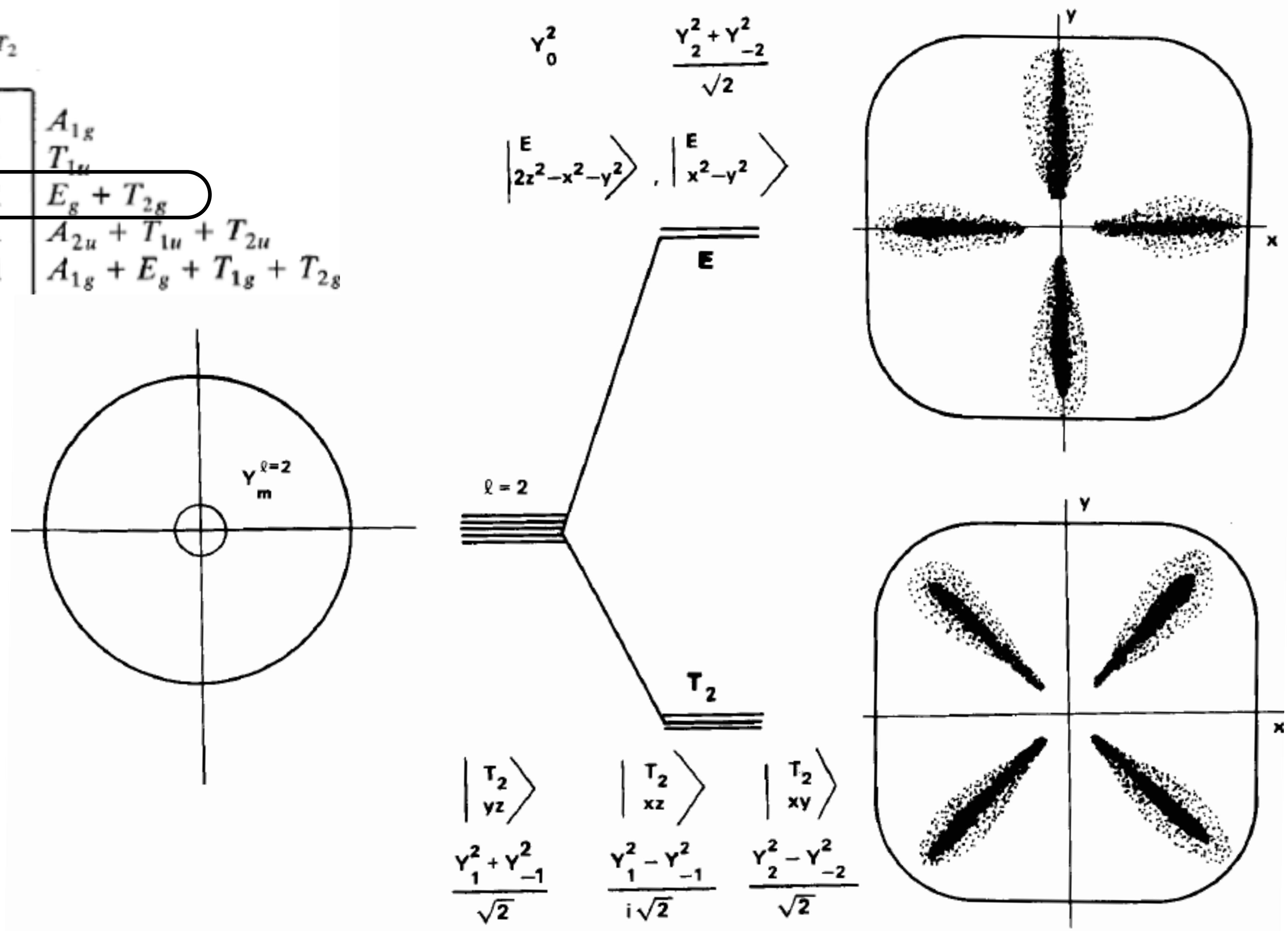


Figure 5.6.3 Detailed sketch of octahedral splitting of a d orbital. The wave functions $\left\langle\begin{matrix}E\\2\end{matrix}\right\rangle$ and $\left\langle\begin{matrix}T_2\\3\end{matrix}\right\rangle$ are sketched inside the equipotential contour $x^4 + y^4 = \text{constant}$ ($z = 0$).

$R(3)\subset O(3)\supset O_h\supset O$ character analysis (From Principles of Symmetry Dynamics & Spectroscopy Ch.5 p.403)

$(A_1\ T_1\ E)_{0_4}\ (T_2\ T_1)_{3_4}\ (E\ T_2\ A_2)_{2_4}\ (T_2\ T_1)_{1_4}\ldots(A_2\ T_2\ T_1\ A_1)_{0_3}\ (T_1\ E\ T_2)_{1_3}\ (T_1\ E\ T_2)_{2_3}\ \ldots$

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)*

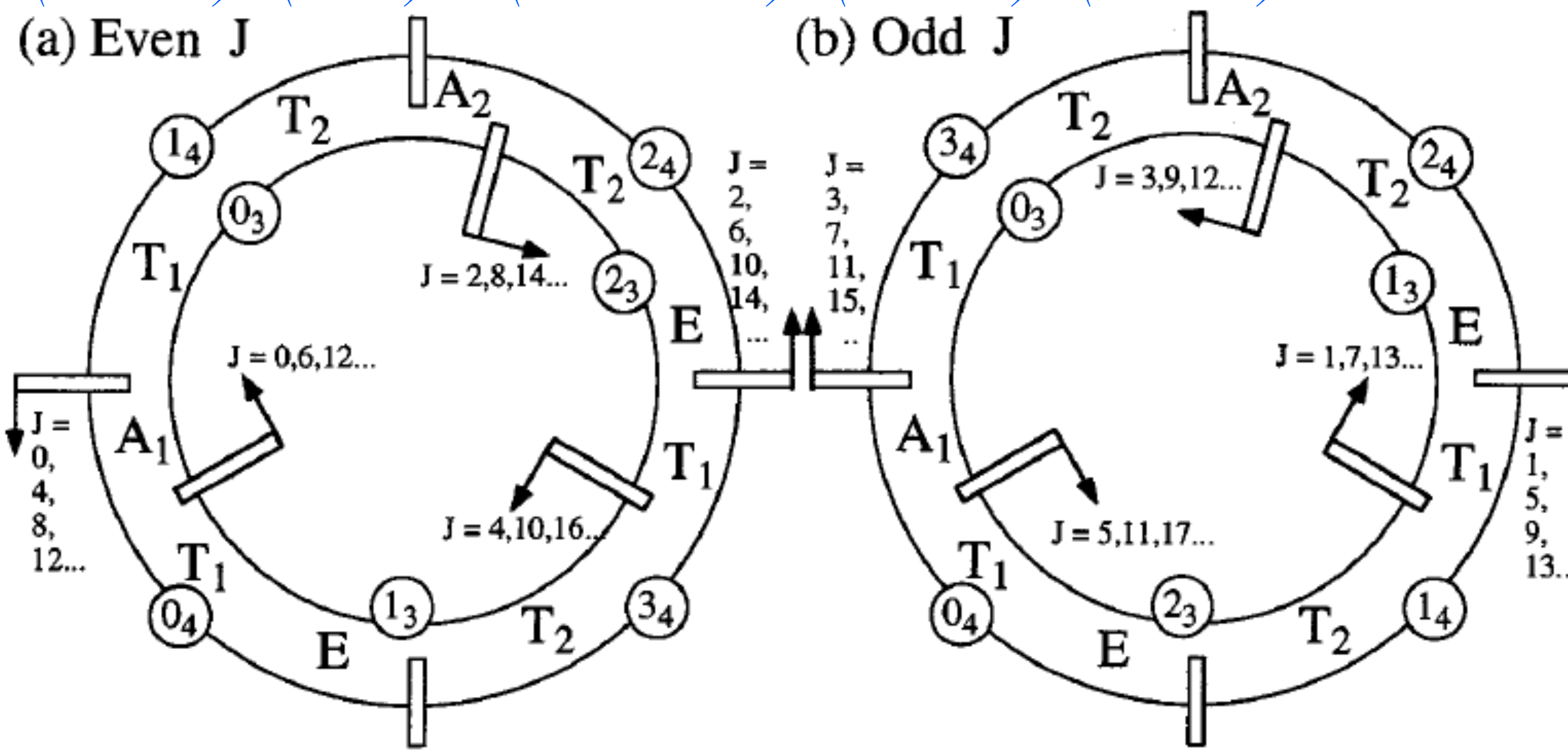


Figure 5.6.9 Mnemonic wheels for octahedral-O orbital. Splitting of J levels for (a) even J and (b) odd J.

$R(3) \subset O(3) \supset O_h \supset O$ character analysis (From Principles of Symmetry Dynamics & Spectroscopy Ch.5 p.403)

$(A_1\ T_1\ E)_{0_4}\ (T_2\ T_1)_{3_4}\ (E\ T_2\ A_2)_{2_4}\ (T_2\ T_1)_{1_4} \ldots (A_2\ T_2\ T_1\ A_1)_{0_3}\ (T_1\ E\ T_2)_{1_3}\ (T_1\ E\ T_2)_{2_3}\ \ldots$

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)*

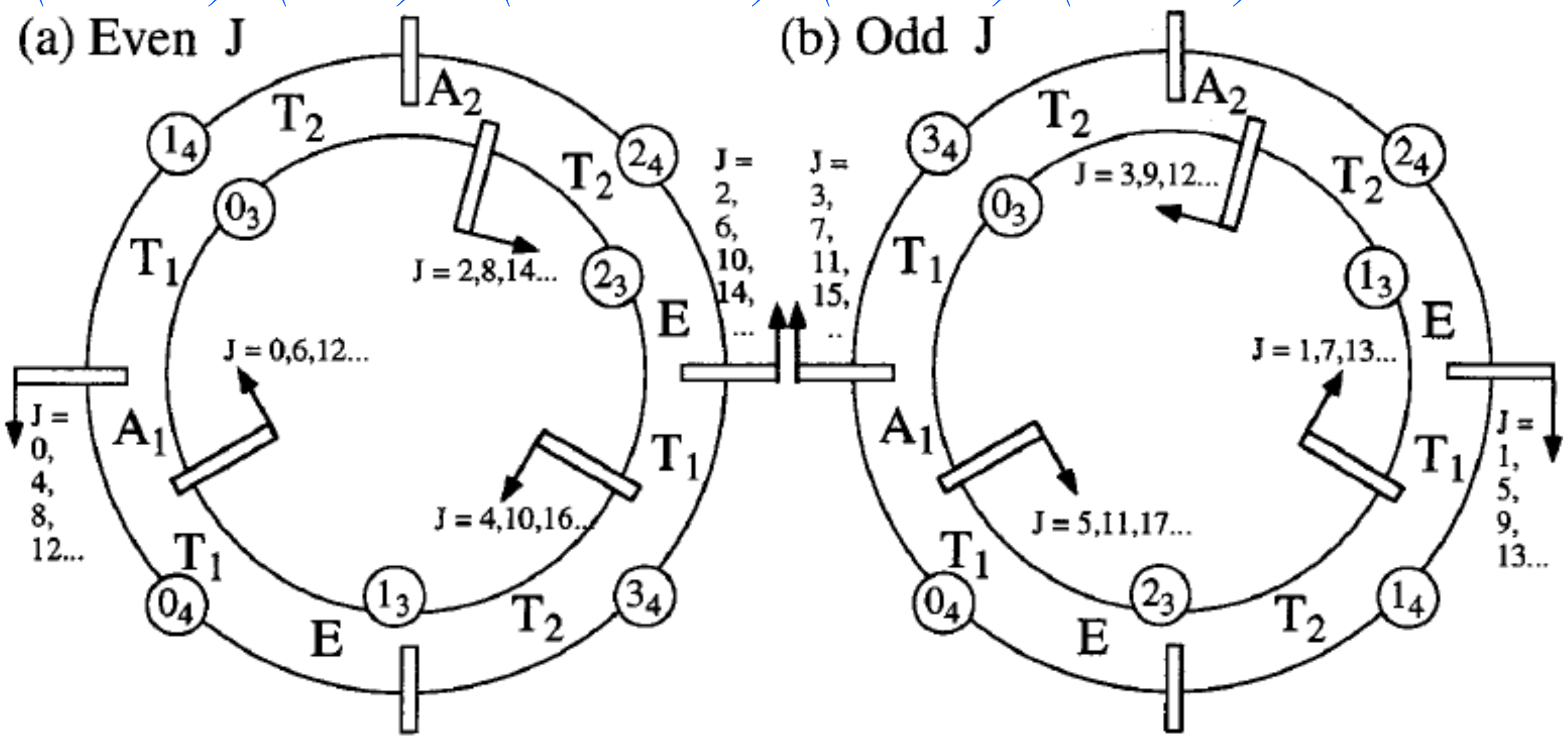
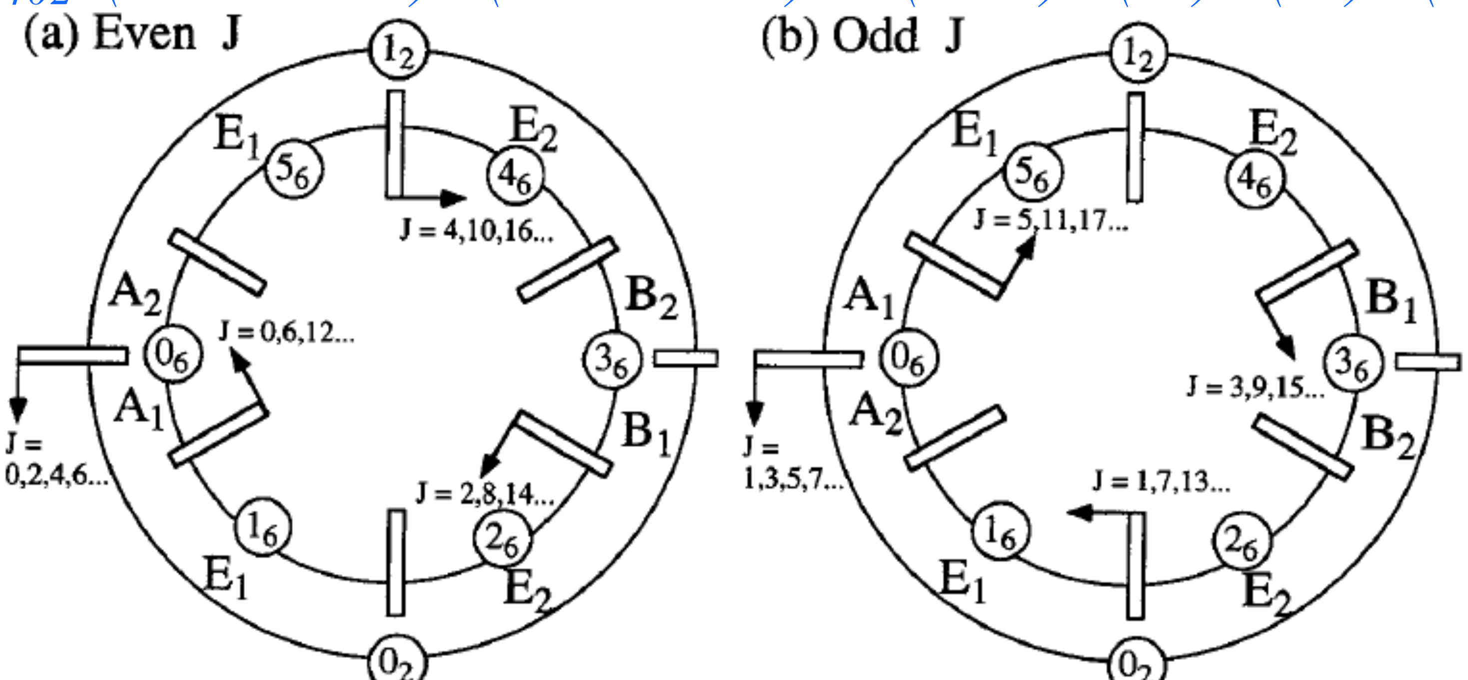


Figure 5.6.9 Mnemonic wheels for octahedral-*O* orbital. Splitting of *J* levels for (a) even *J* and (b) odd *J*.

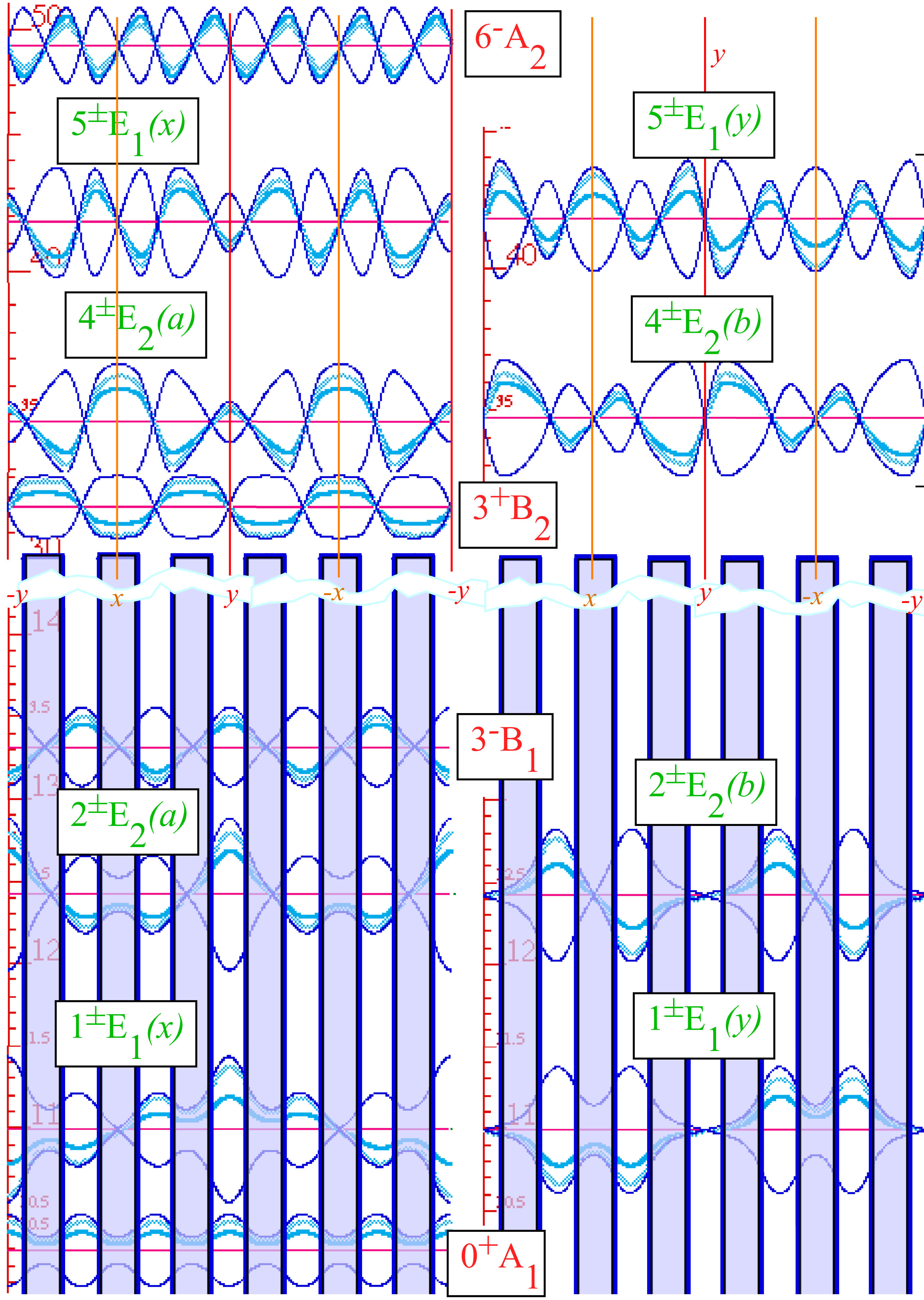
D_6 wheel

Ch.5 p.402 $(A_1\ E_1\ E_2\ B_1)_{0_2}\ (B_2\ E_2\ E_1\ A_2)_{1_2} \ldots (A_2 A_1)_{0_6}\ (E_1)_{1_6}\ (E_2)_{2_6}\ (B_1\ B_2)_{3_6} (E_2)_{4_6}\ (E_1)_{5_6} \ldots$



(see p. 68-72 of Lect. 18 where "band" and "gap" spacing varies with energy)

D_6 Band structure and related induced representations (Mac OS-9)



$D_6 \supset C_3(h)$	0_6	1_6	2_6	3_6	4_6	5_6
A_1	1	·	·	·	·	·
A_2	1	·	·	·	·	·
E_2	·	·	1	·	1	·
B_2	·	·	·	1	·	·
B_1	·	·	·	1	·	·
E_1	·	1	·	·	·	1

$1_2 \uparrow D_3 \sim A_2 \oplus E_2 \oplus E_1 \oplus B_2$

Odd Band or Cluster

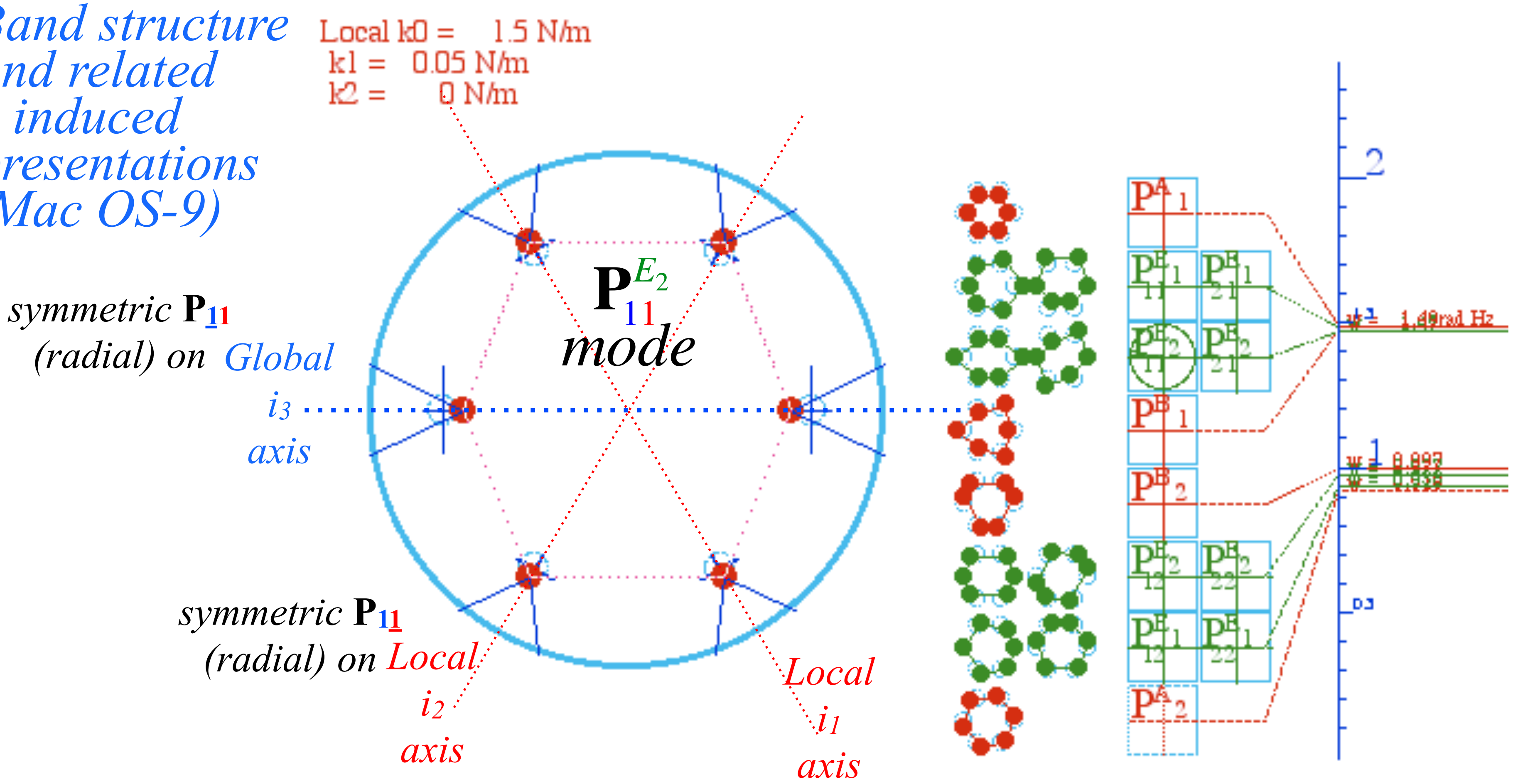
$0_2 \uparrow D_3 \sim A_1 \oplus E_1 \oplus E_2 \oplus B_1$

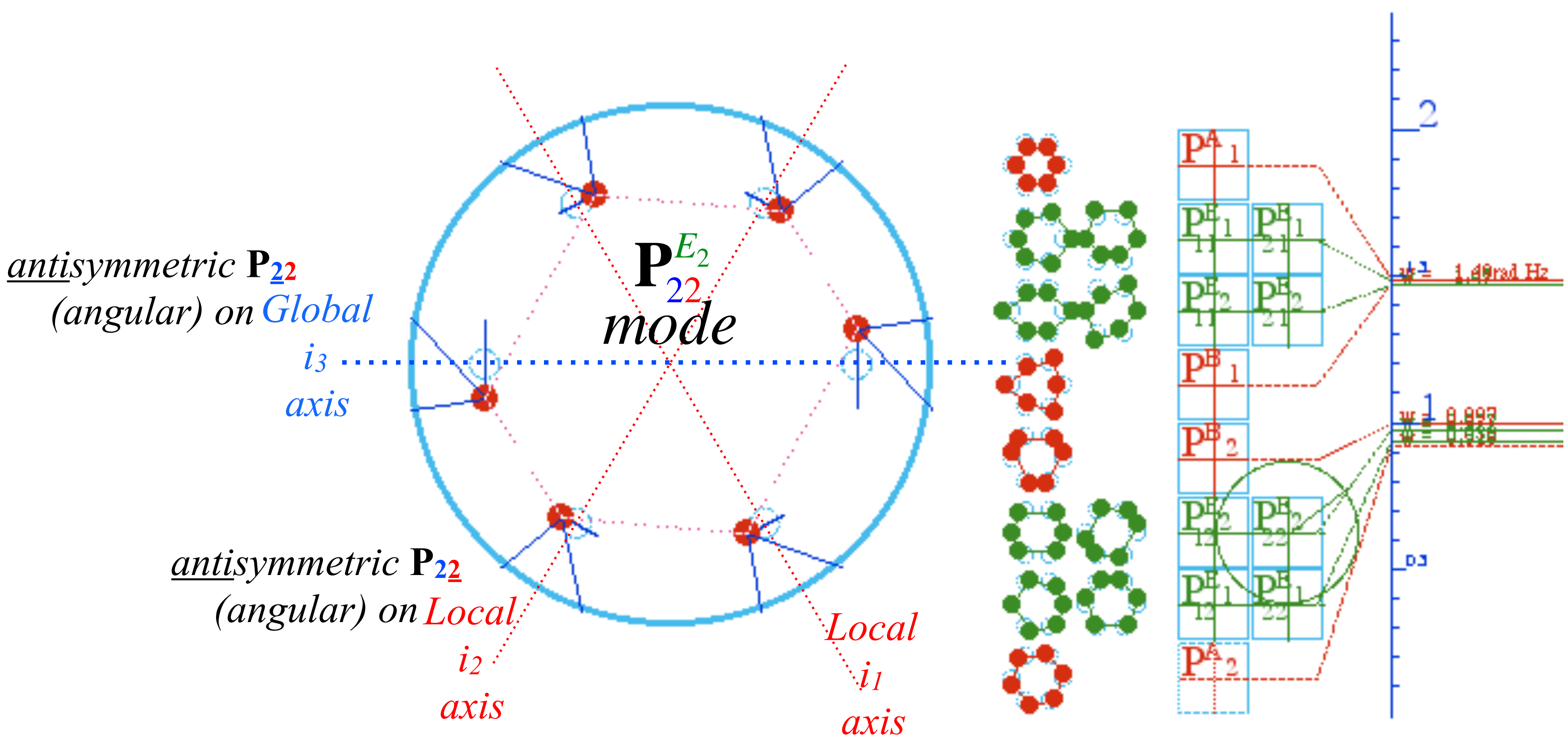
Even Band or Cluster

$D_3 \supset C_2(j_3)$	0_2	1_2
A_1	1	·
A_2	·	1
E_2	1	1
B_2	·	1
B_1	1	·
E_1	1	1

(p. 68 of Lect. 18)

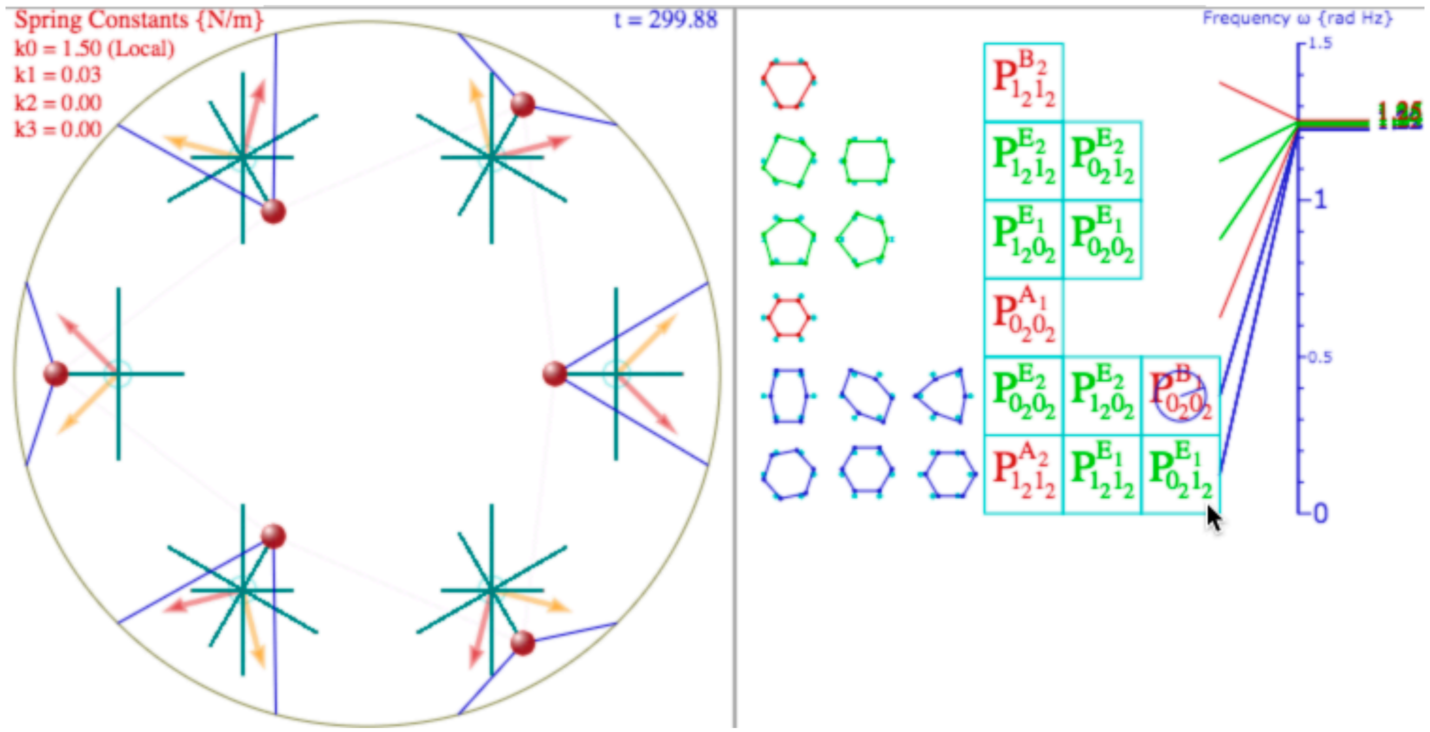
D_6 Band structure and related induced representations (Mac OS-9)



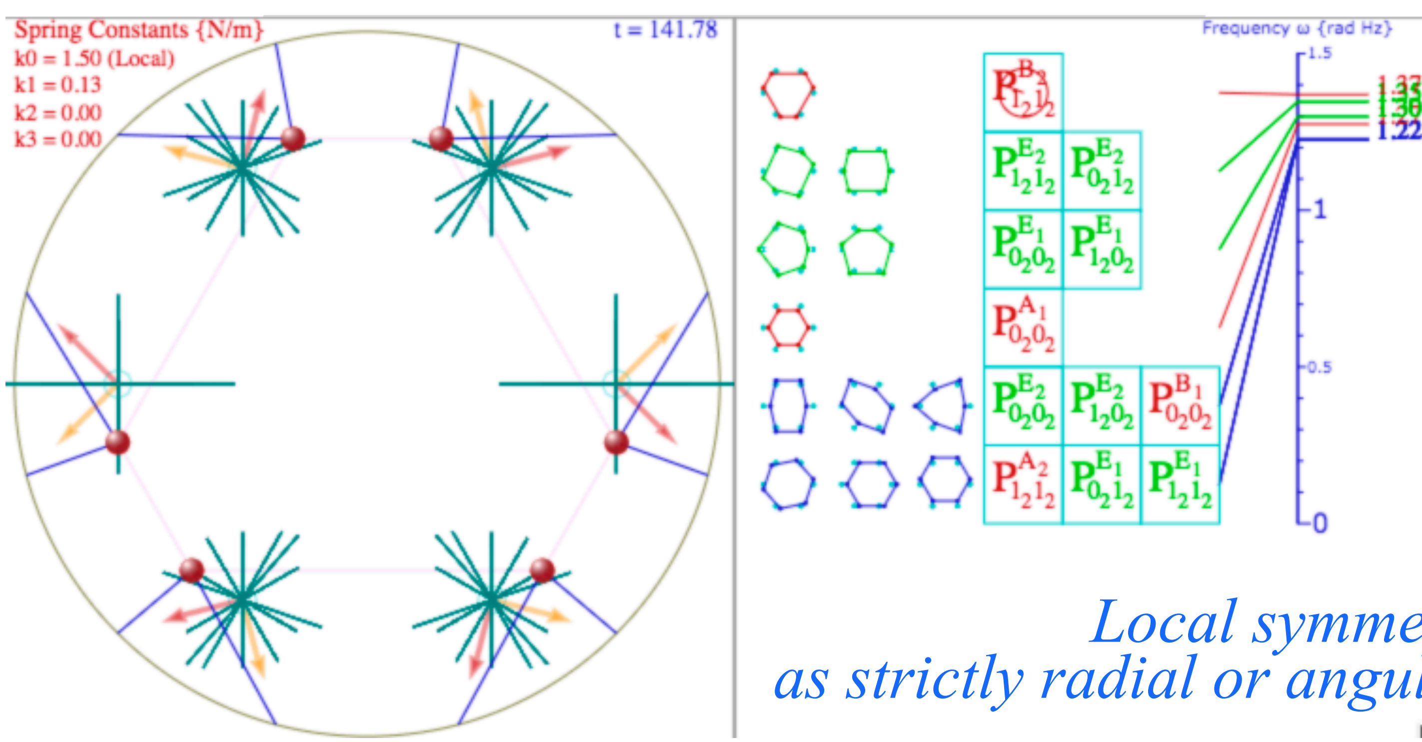


(p. 69 of Lect. 18)

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

Review :

Symmetric rigid quantum rotor analysis of R(2) Hamiltonian $\mathbf{H}=B\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$

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R(3)⊂O(3)⊃O_h⊃O character analysis of ℓ-level or 2ℓ+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)

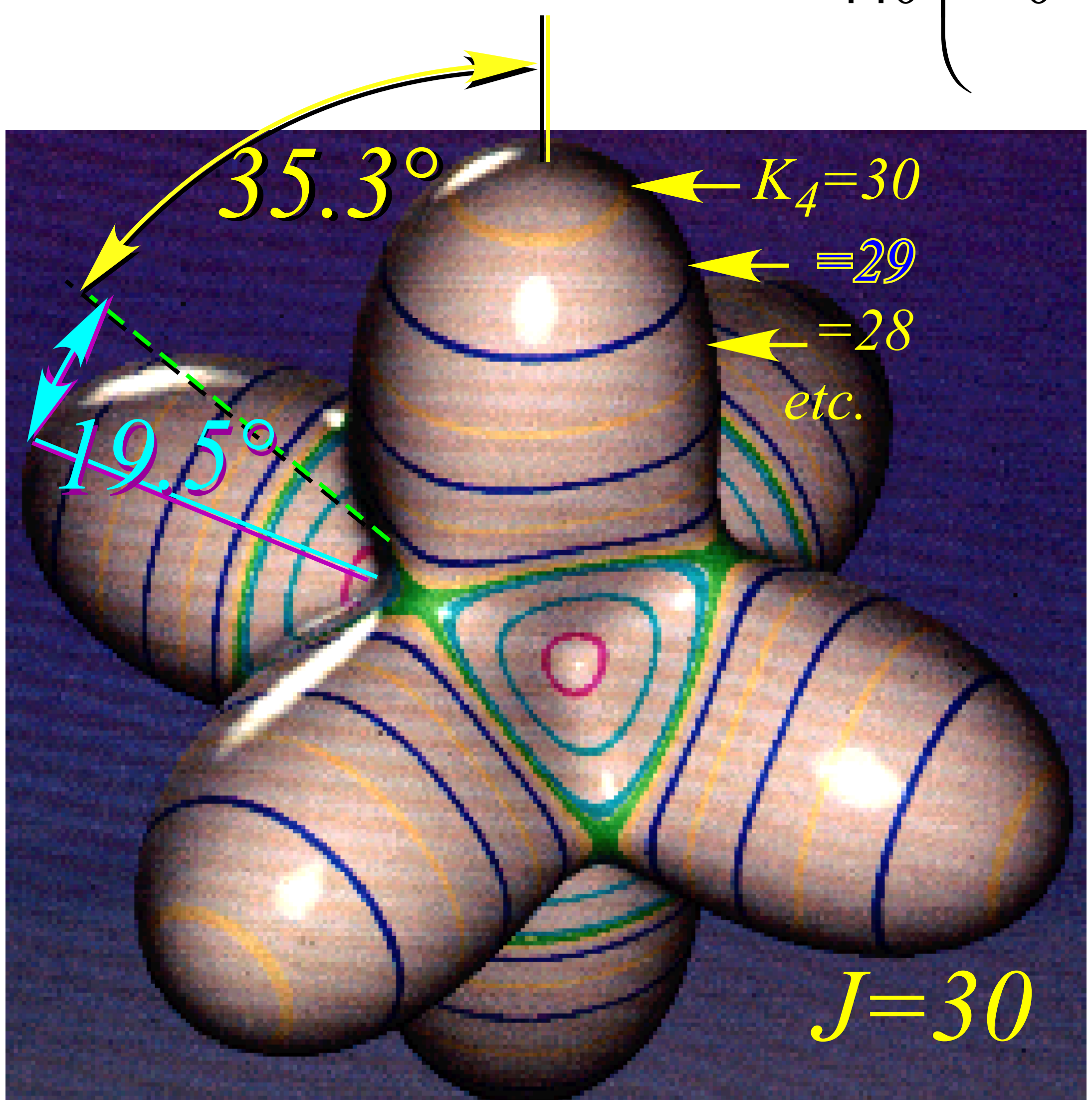
Semi Rigid Rotor Hamiltonian: *Centrifugal and Coriolis terms...*

$$\mathbf{H} = A\mathbf{J}_x^2 + B\mathbf{J}_y^2 + C\mathbf{J}_z^2 + t_{xxxx}\mathbf{J}_x^4 + t_{xxyy}\mathbf{J}_x^2\mathbf{J}_y^2 + \cdots$$

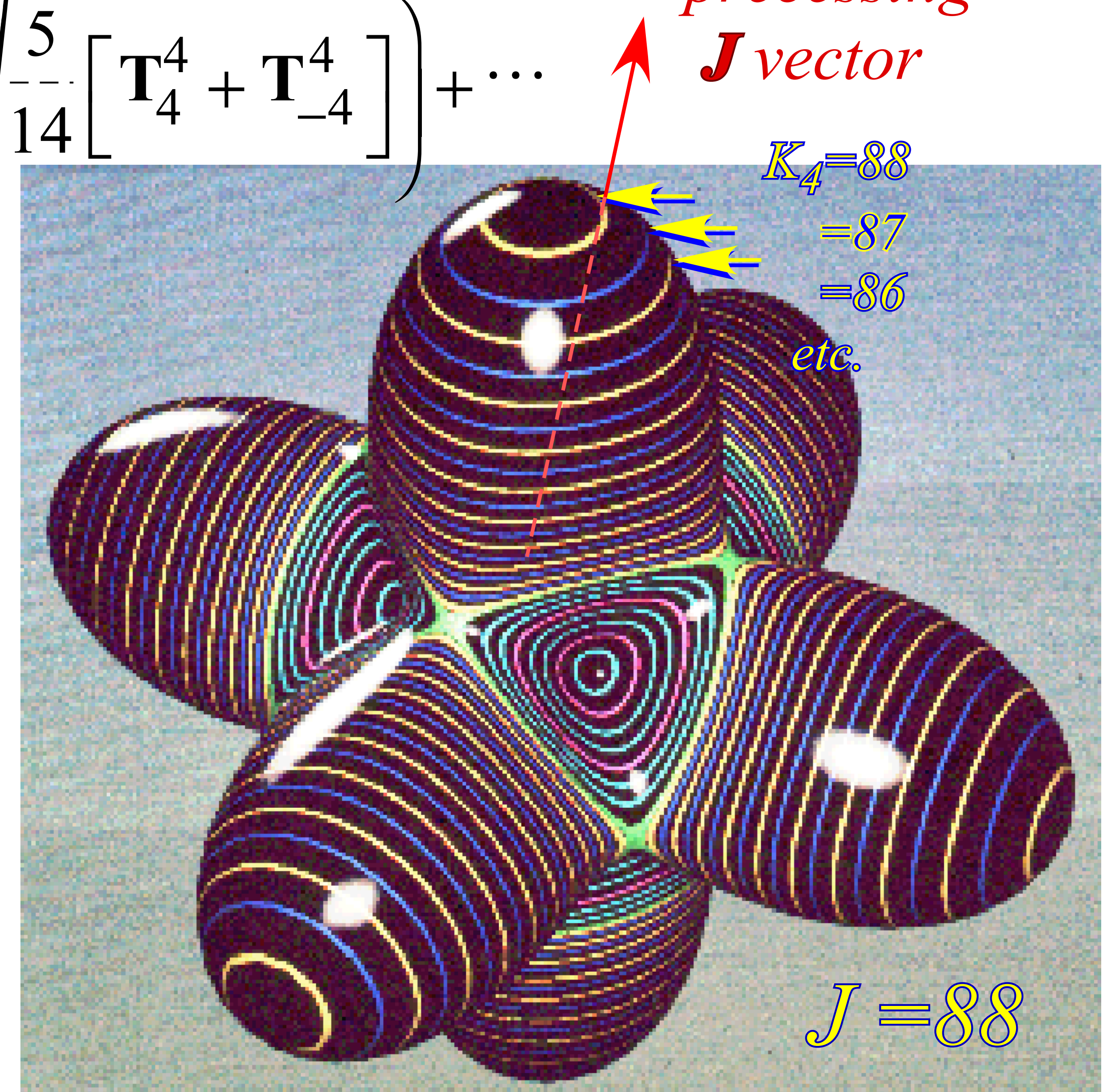
Semi Rigid O_h or T_d Spherical Top: *(Hecht Hamiltonian 1960)*

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

$$= BJ^2 + t_{440}\left(\mathbf{T}_0^4 + \sqrt{\frac{5}{14}}\left[\mathbf{T}_4^4 + \mathbf{T}_{-4}^4\right]\right) + \cdots$$

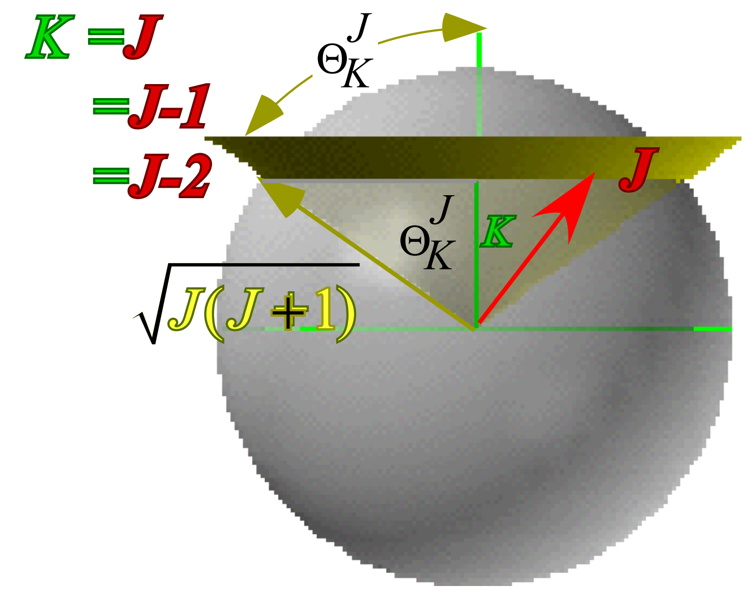


after QTforCA Unit 8. Ch. 25 Fig. 25.4.5



Finding Hamiltonian Eigensolutions by Geometry using Uncertainty Cone Angles

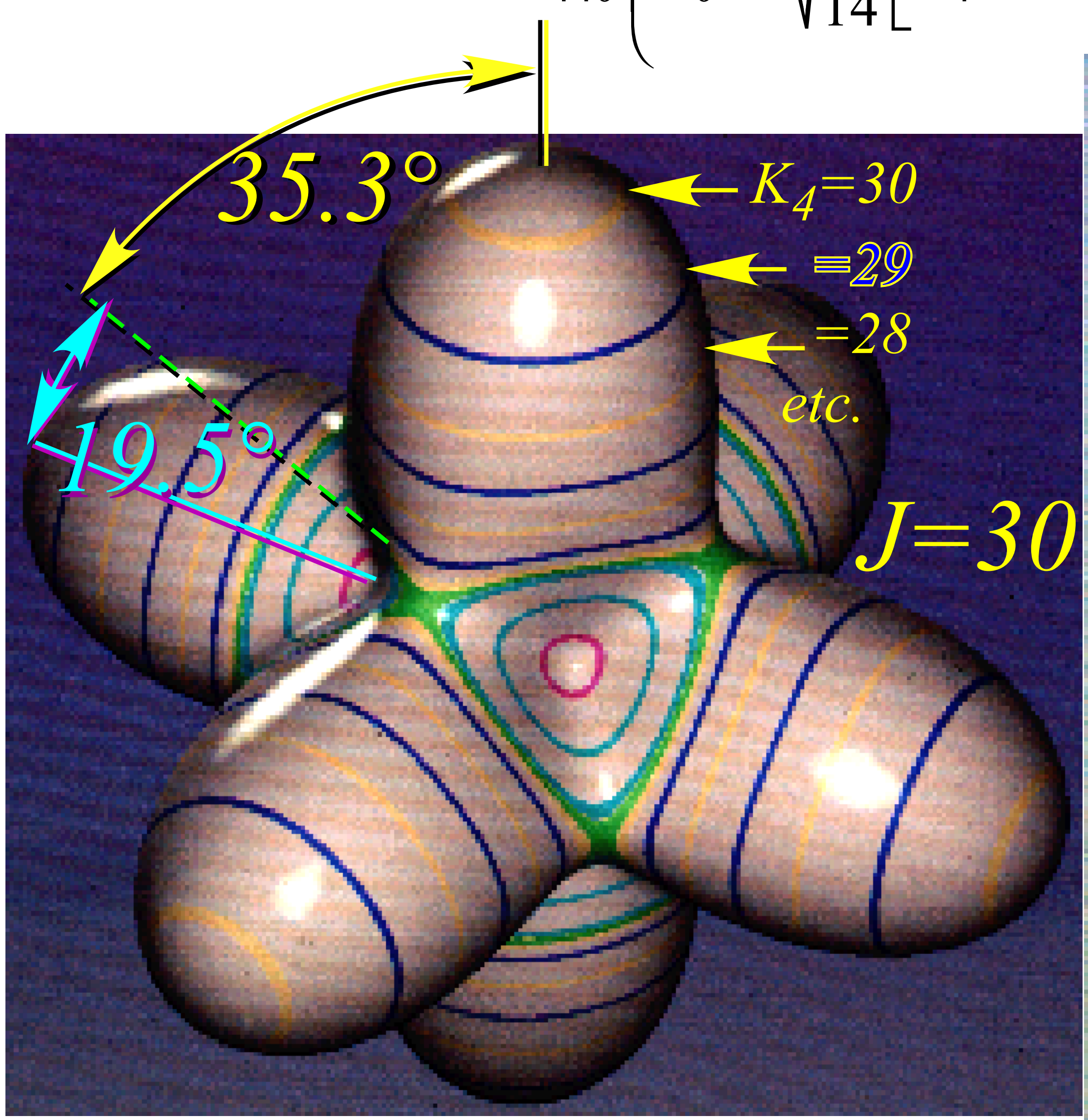
$$\cos\Theta_K^J = \frac{K}{\sqrt{J(J+1)}}$$

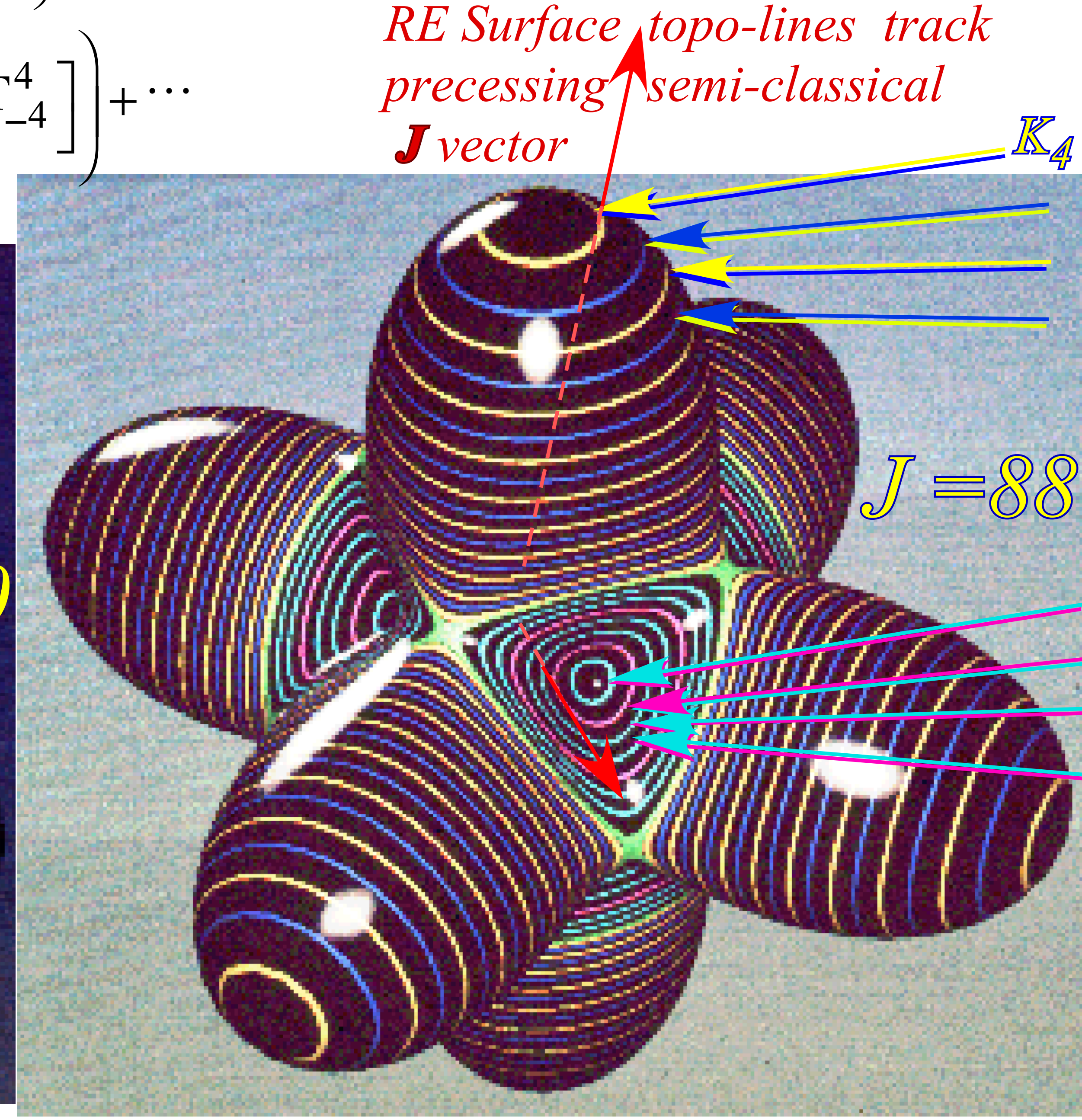


O_h or T_d Spherical Top: *(Hecht Ro-vib Hamiltonian 1960)*

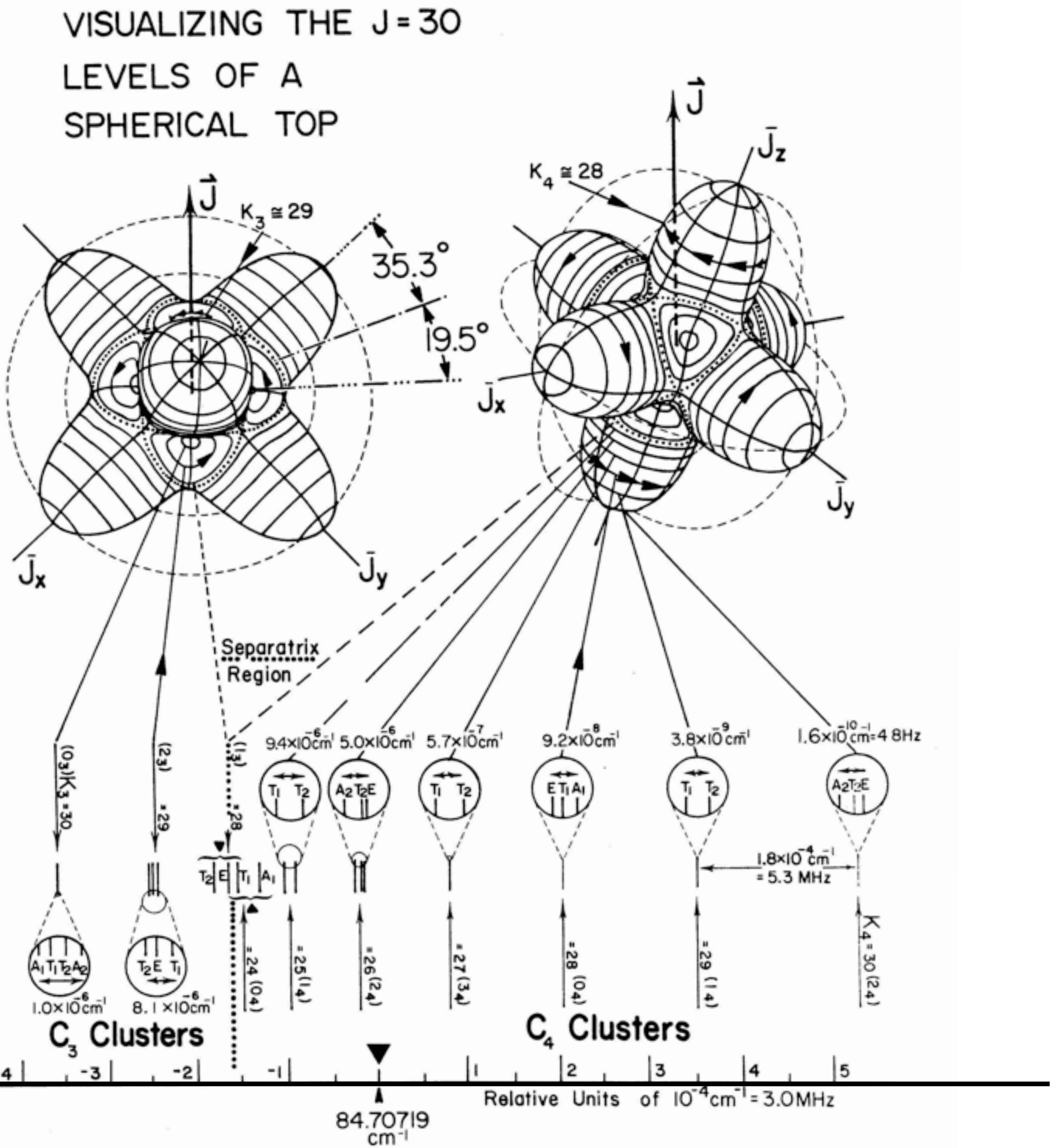
$$\mathbf{H} = B\left(\mathbf{J}_x^2 + \mathbf{J}_y^2 + \mathbf{J}_z^2\right) + t_{440}\left(\mathbf{J}_x^4 + \mathbf{J}_y^4 + \mathbf{J}_z^4 - \frac{3}{5}J^4\right) + \cdots$$

$$= B\mathbf{J}^2 + t_{440}\left(\mathbf{T}_0^4 + \sqrt{\frac{5}{14}}\left[\mathbf{T}_4^4 + \mathbf{T}_{-4}^4\right]\right) + \cdots$$

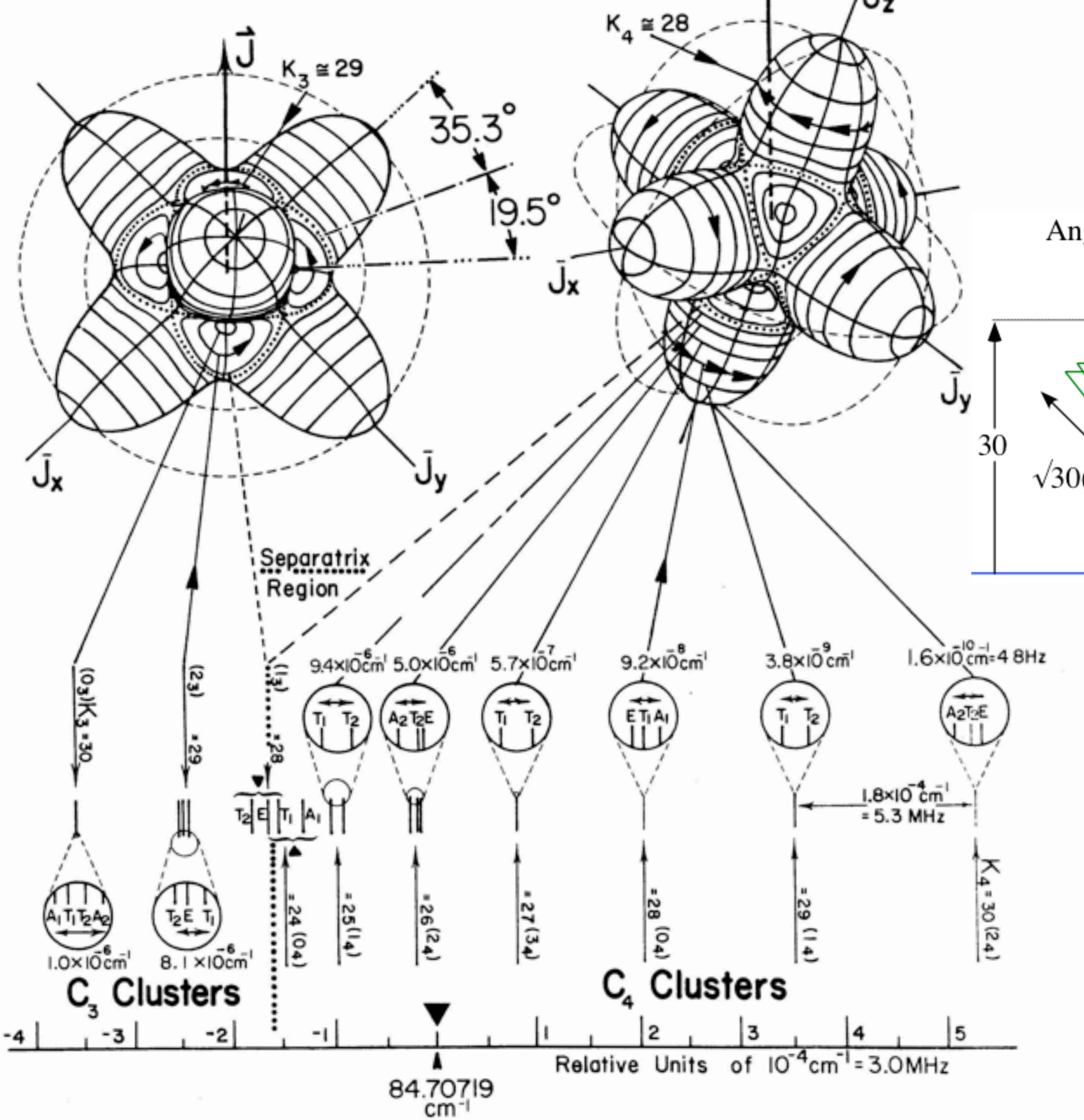


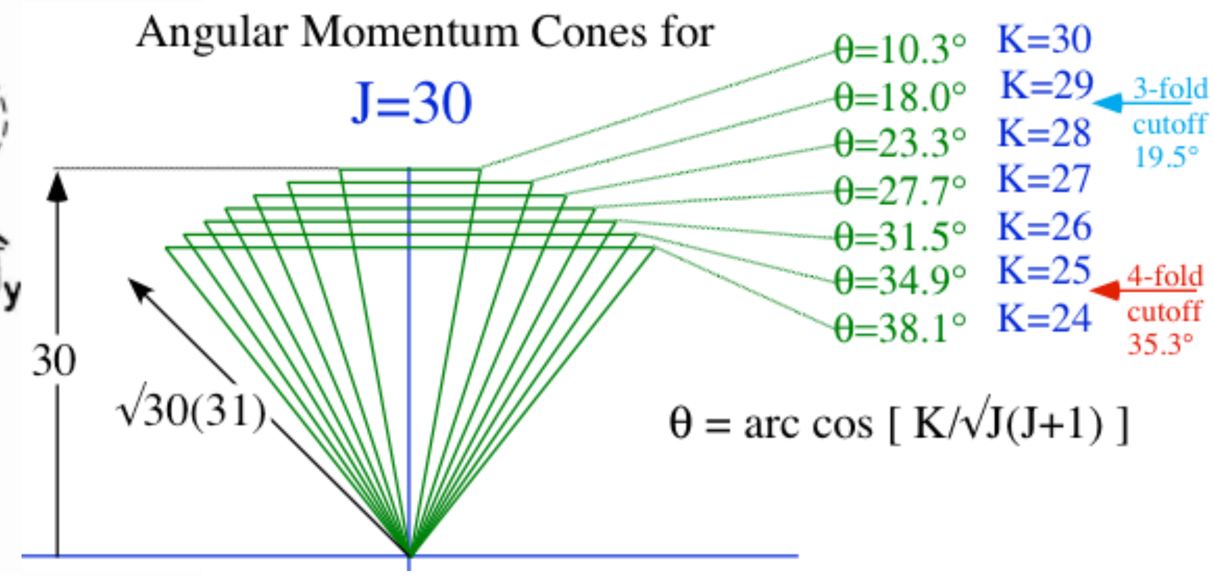


page 75 shows slice

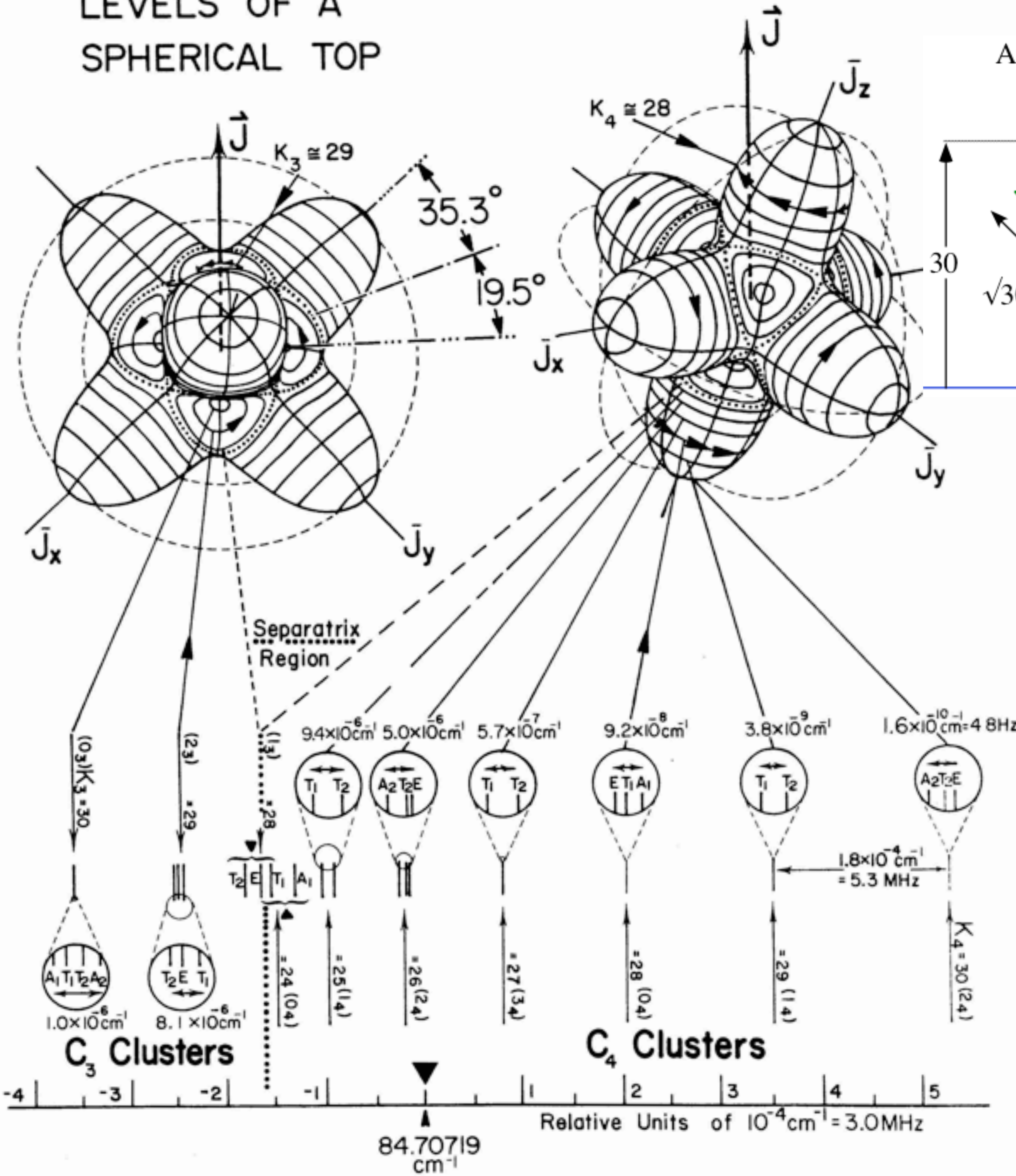

VISUALIZING THE J = 30
LEVELS OF A
SPHERICAL TOP
J
K3 ≅ 29
35.3°
19.5°
Jx
Jy
K4 ≅ 28
J
Jz
Jx
Jy
Separatrix
Region
(03)K3 = 30
(23) = 29
(13) = 28
9.4×10⁻⁶cm⁻¹
5.0×10⁻⁶cm⁻¹
5.7×10⁻⁷cm⁻¹
9.2×10⁻⁸cm⁻¹
3.8×10⁻⁹cm⁻¹
1.6×10⁻¹⁰cm⁻¹ = 4.8Hz
T1 T2
A2 T2 E
T1 T2
E T1 A1
T1 T2
A2 T2 E
T2 E T1 A1
1.8×10⁻⁴cm⁻¹
= 5.3 MHz
A1 T1 T2 A2
T2 E T1
1.0×10⁻⁶cm⁻¹
8.1×10⁻⁶cm⁻¹
= 24 (04)
= 25 (14)
= 26 (24)
= 27 (34)
= 28 (04)
= 29 (14)
K4 = 30 (24)
C3 Clusters
C4 Clusters
-4
-3
-2
-1
1
2
3
4
5
Relative Units of 10⁻⁴cm⁻¹ = 3.0MHz
84.70719
cm⁻¹

VISUALIZING THE J = 30 LEVELS OF A SPHERICAL TOP



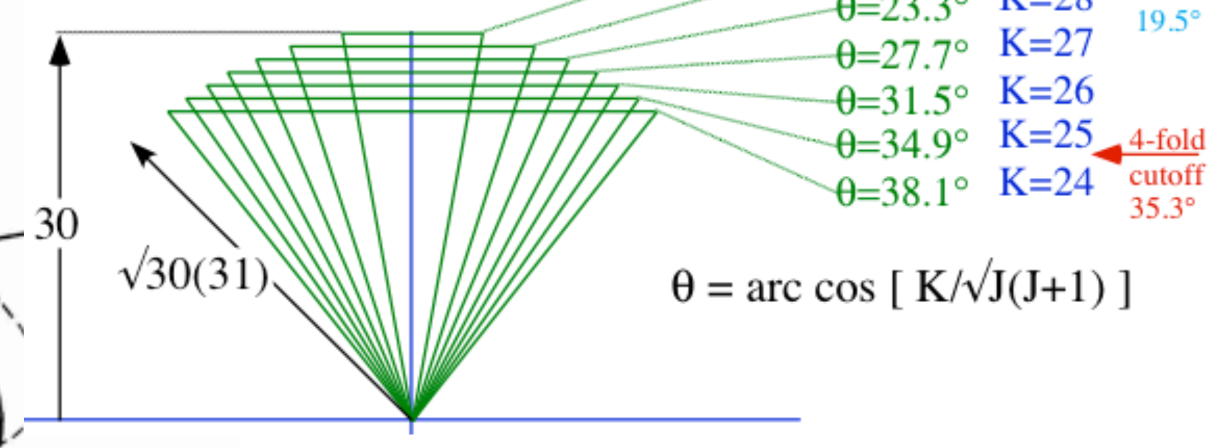


VISUALIZING THE J = 30 LEVELS OF A SPHERICAL TOP

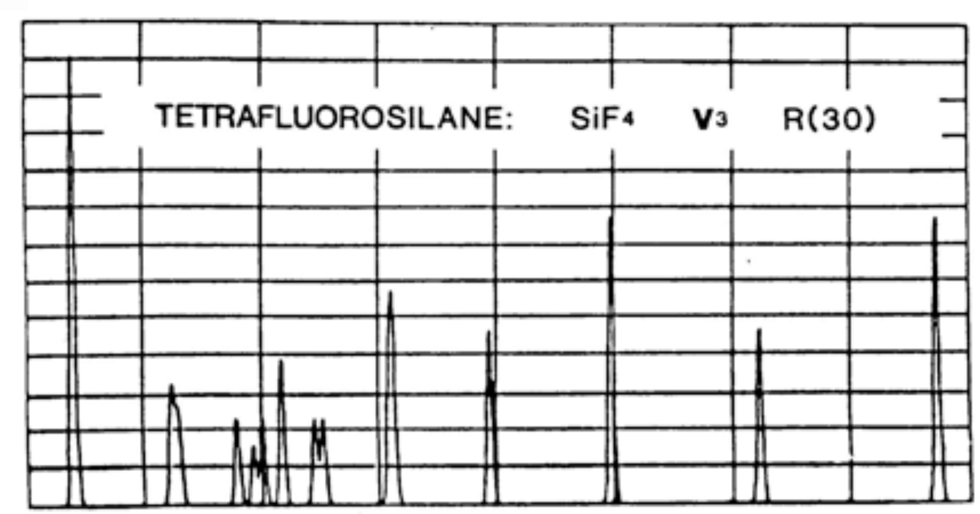


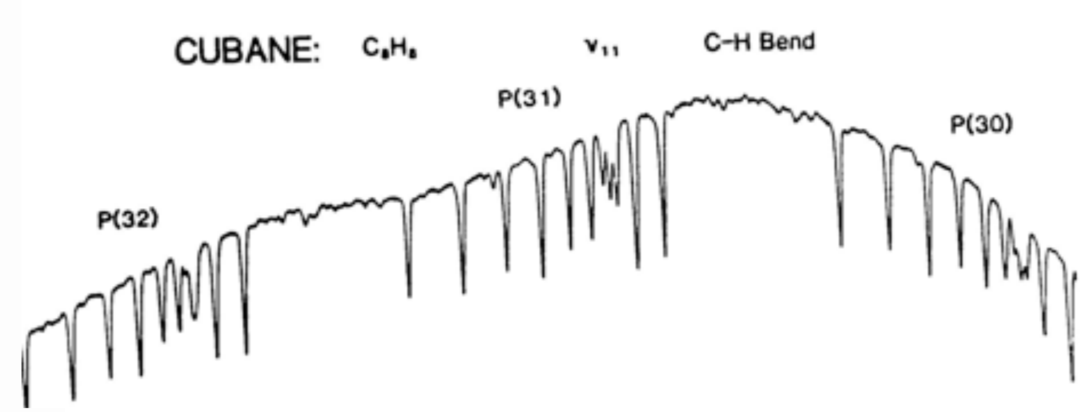
Angular Momentum Cones for

J=30

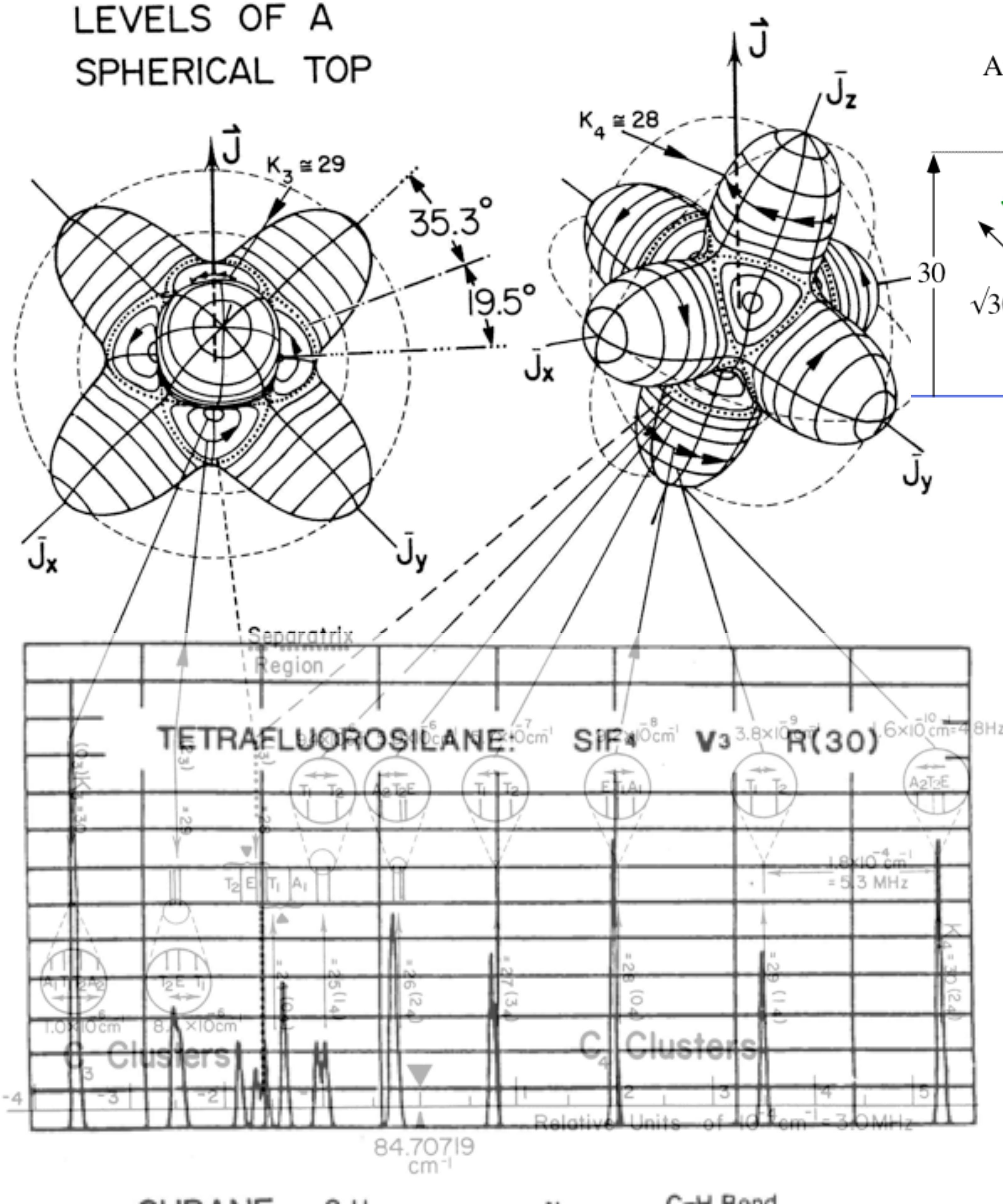


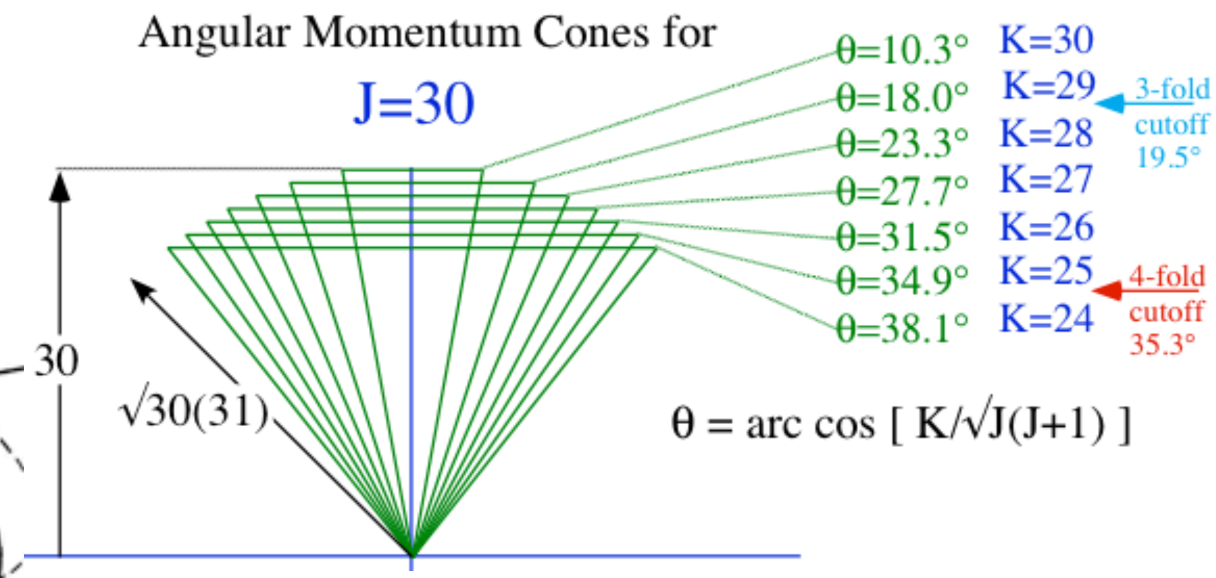
Two molecular examples: SiF_4 and C_8H_8





VISUALIZING THE J = 30 LEVELS OF A SPHERICAL TOP





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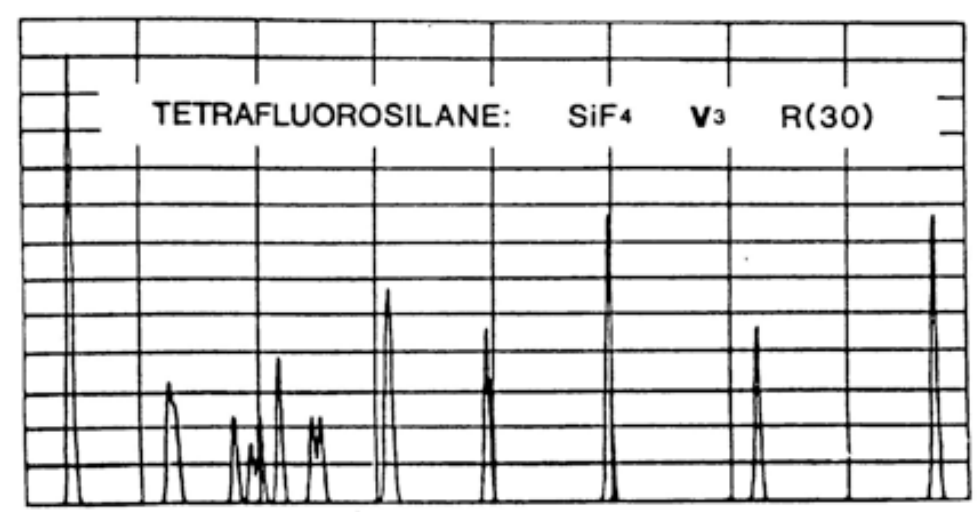
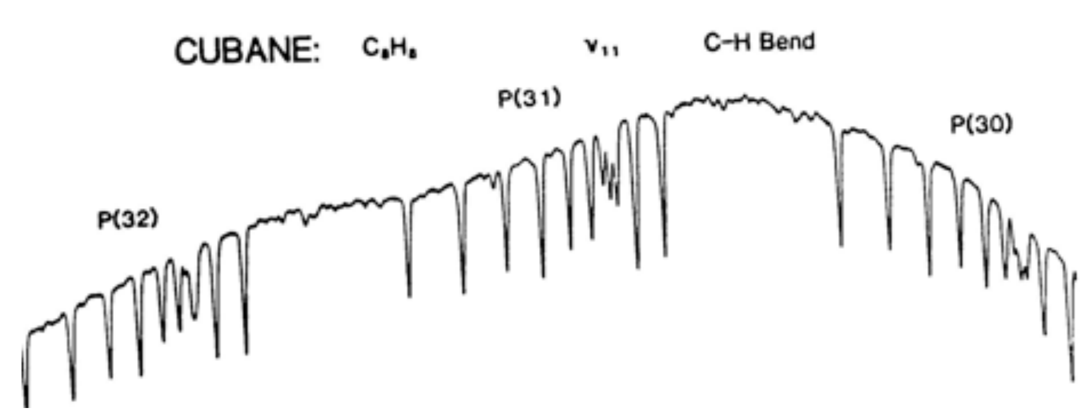
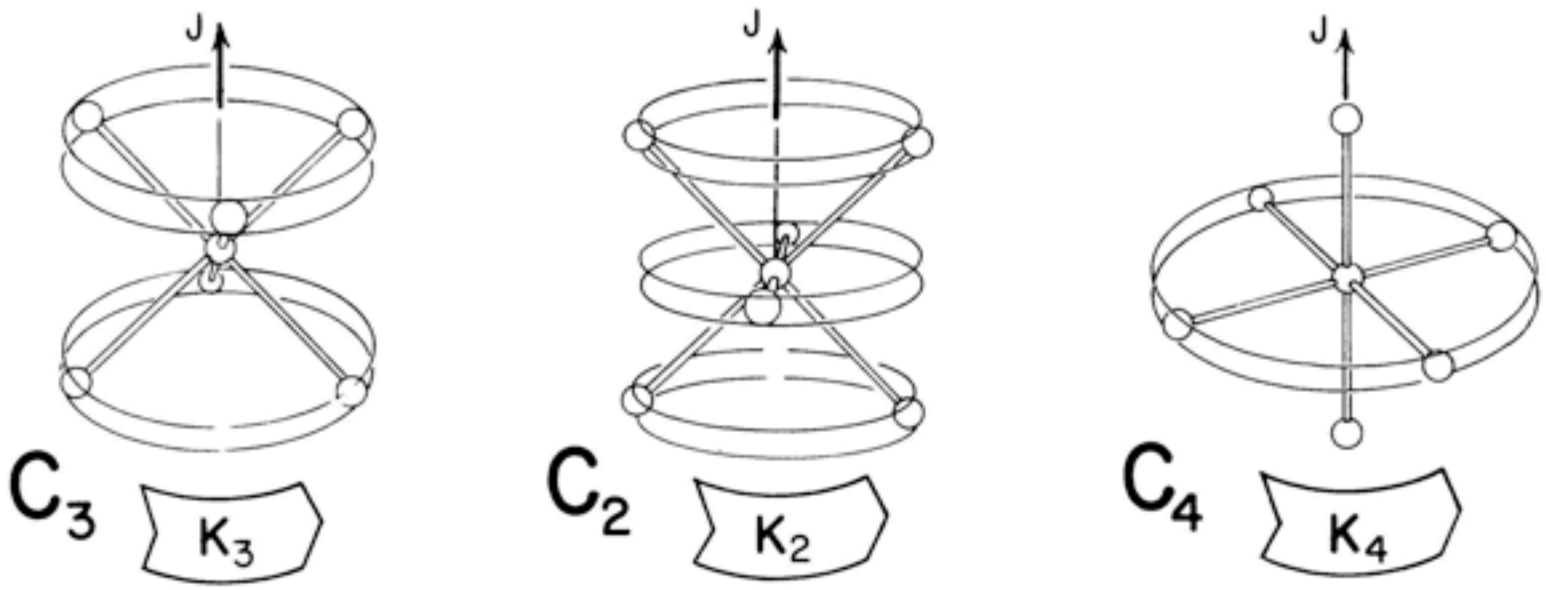




Previous page: QTforCA Unit 8. Ch. 25 Fig. 25.4.9

Fig. 25.4.9 *Infrared spectra showing fine structure clusters. Tetrafluorosilane (SiF_4) spectrum from a ν_3 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).*
[Cubane (C_8H_8) spectrum from ν_{11} P(30), P(31), and P(32), transitions; cubane (C_8H_8) spectrum from ν_{12} R(36), transition.
[After A. S. Pine, A. G. Maki, A. G. Robiette, B. J. Krohn, J. K. G. Watson, and Th Urbanek, J. Am. Chem. Soc., ***106****, 891 (1984).]*



	0_3	1_3	2_3
A_1	1	·	·
A_2	1	·	·
E	·	1	1
T_1	1	1	1
T_2	1	1	1

	0_2	1_2
A_1	1	·
A_2	·	1
E	1	1
T_1	1	2
T_2	2	1

	0_4	1_4	2_4	3_4
A_1	1	·	·	·
A_2	·	·	1	·
E	1	·	1	·
T_1	1	1	·	1
T_2	·	1	1	1

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.*

QTforCA Unit 8. Ch. 25 Fig. 25.4.7

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Symmetric rigid quantum rotor analysis of R(2) Hamiltonian $\mathbf{H}=B\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$

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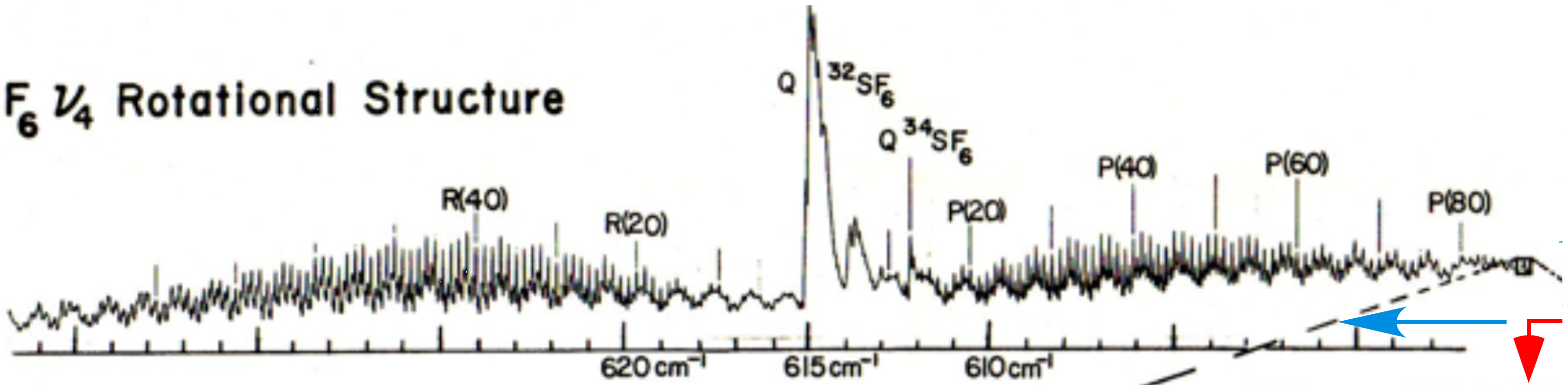
R(3)⊂O(3)⊃O_h⊃O character analysis of ℓ-level or 2ℓ+1-multiplet splitting in O

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

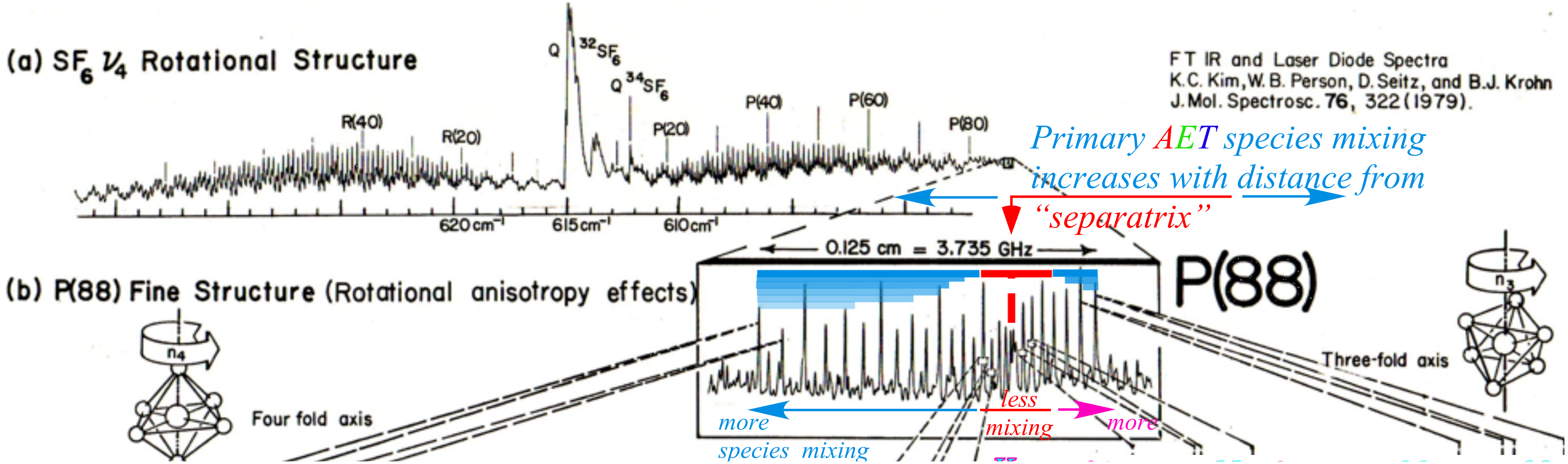
SF_6 spectral fine structure P(88)

CF_4 spectral fine structure P(54)

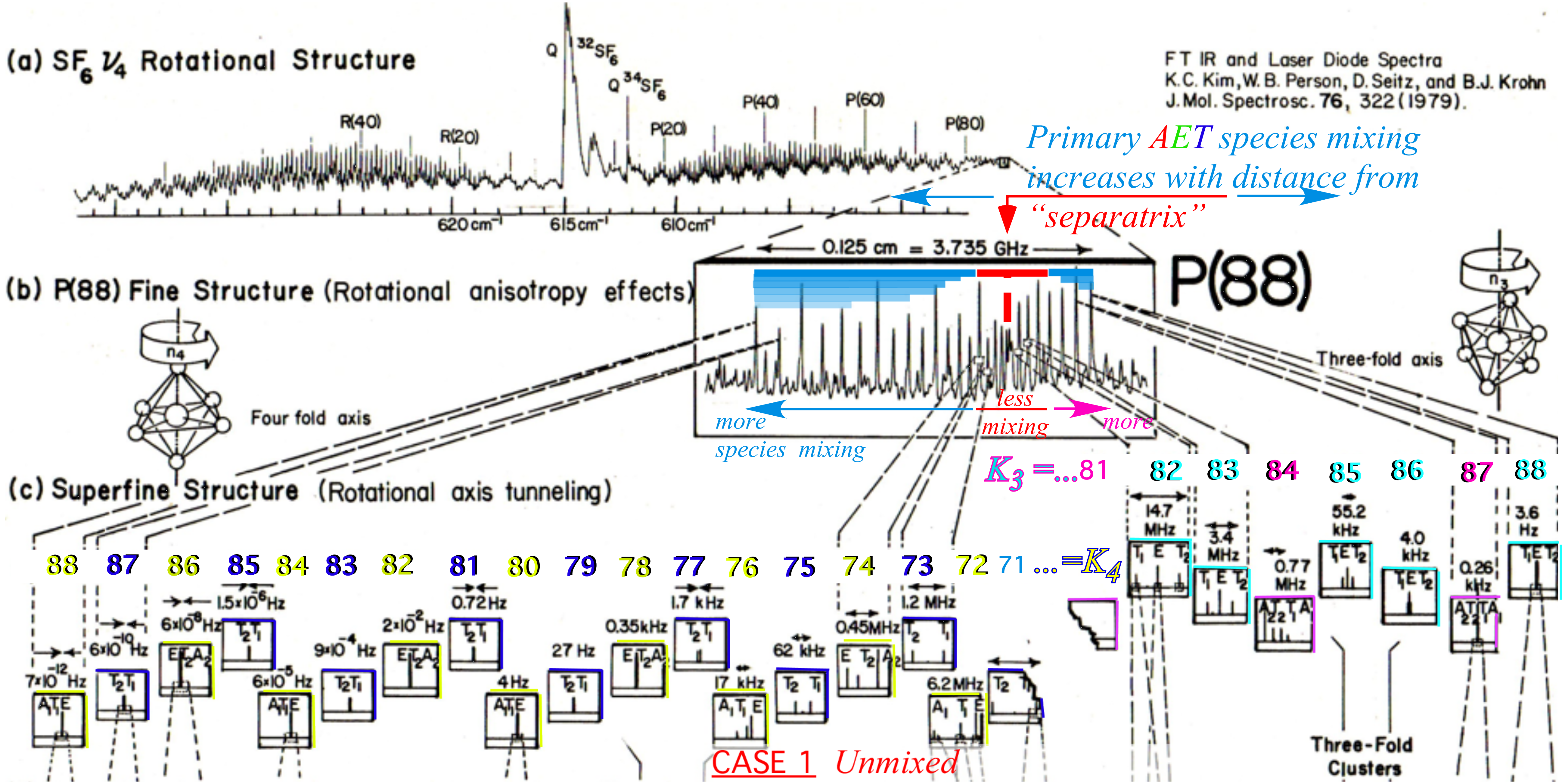
(a) SF_6 ν_4 Rotational Structure



FT IR and Laser Diode Spectra
K.C. Kim, W. B. Person, D. Seitz, and B.J. Krohn
J. Mol. Spectrosc. **76**, 322 (1979).



(a) SF6 ν4 Rotational Structure
Q
32SF6
Q 34SF6
R(40)
R(20)
P(20)
P(40)
P(60)
P(80)
620 cm-1
615 cm-1
610 cm-1
FT IR and Laser Diode Spectra
K.C. Kim, W. B. Person, D. Seitz, and B.J. Krohn
J. Mol. Spectrosc. 76, 322 (1979).
Primary AET species mixing
increases with distance from
"separatrix"
(b) P(88) Fine Structure (Rotational anisotropy effects)
0.125 cm = 3.735 GHz
P(88)
n4
Four fold axis
n3
Three-fold axis
more
species mixing
less
mixing
more



(a) SF6 ν4 Rotational Structure
FT IR and Laser Diode Spectra
K.C. Kim, W.B. Person, D. Seitz, and B.J. Krohn
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R(40)
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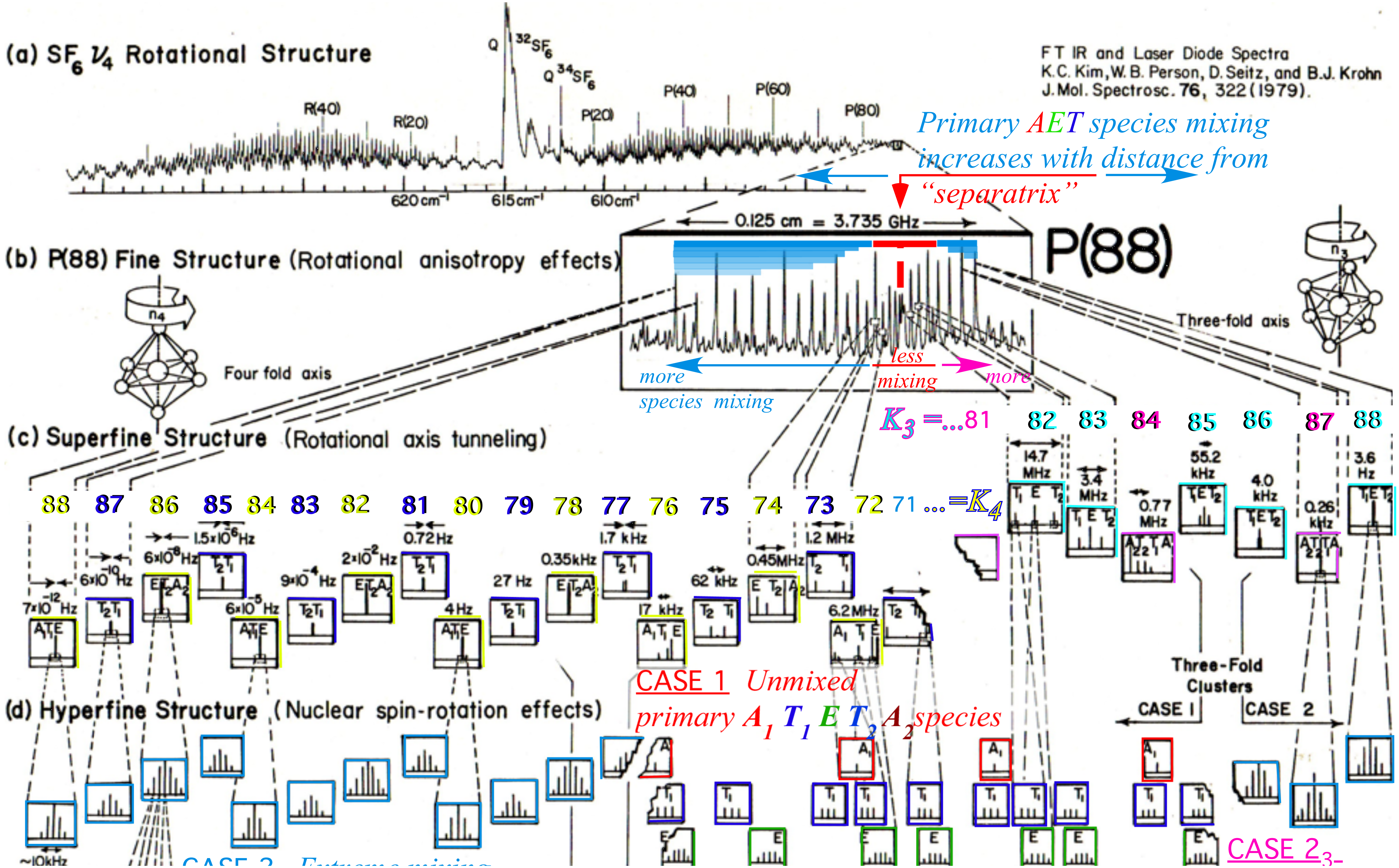
P(20)
P(40)
P(60)
P(80)
620 cm-1
615 cm-1
610 cm-1
Primary AET species mixing increases with distance from "separatrix"
(b) P(88) Fine Structure (Rotational anisotropy effects)
0.125 cm = 3.735 GHz
P(88)
Four fold axis
Three-fold axis
more species mixing
less mixing
more
(c) Superfine Structure (Rotational axis tunneling)
K3 = ...81 82 83 84 85 86 87 88
88 87 86 85 84 83 82 81 80 79 78 77 76 75 74 73 72 71 ... = K4
CASE 1 Unmixed
Three-Fold Clusters



(a) SF6 ν4 Rotational Structure
FT IR and Laser Diode Spectra
K.C. Kim, W.B. Person, D. Seitz, and B.J. Krohn
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Q 32SF6
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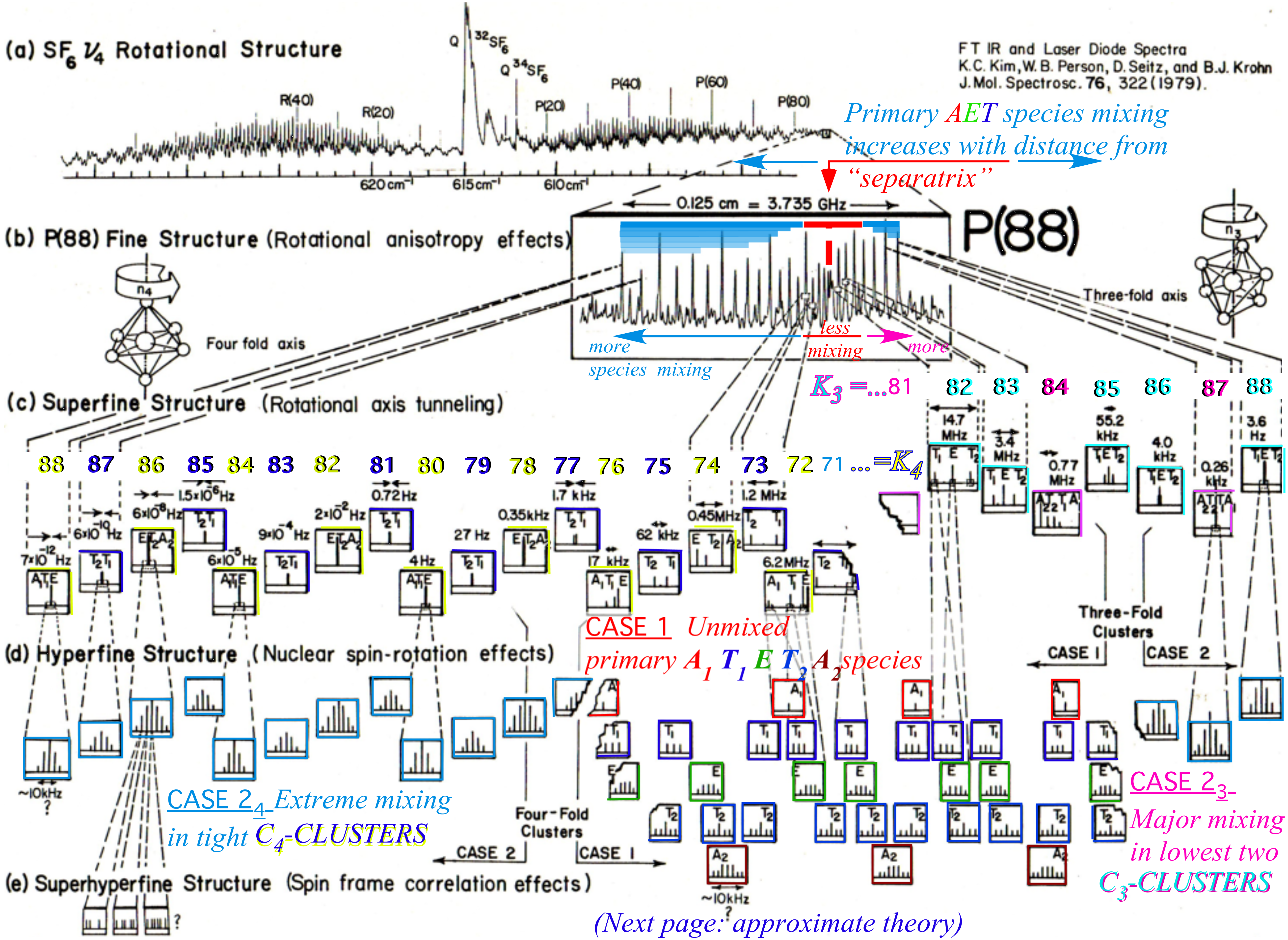
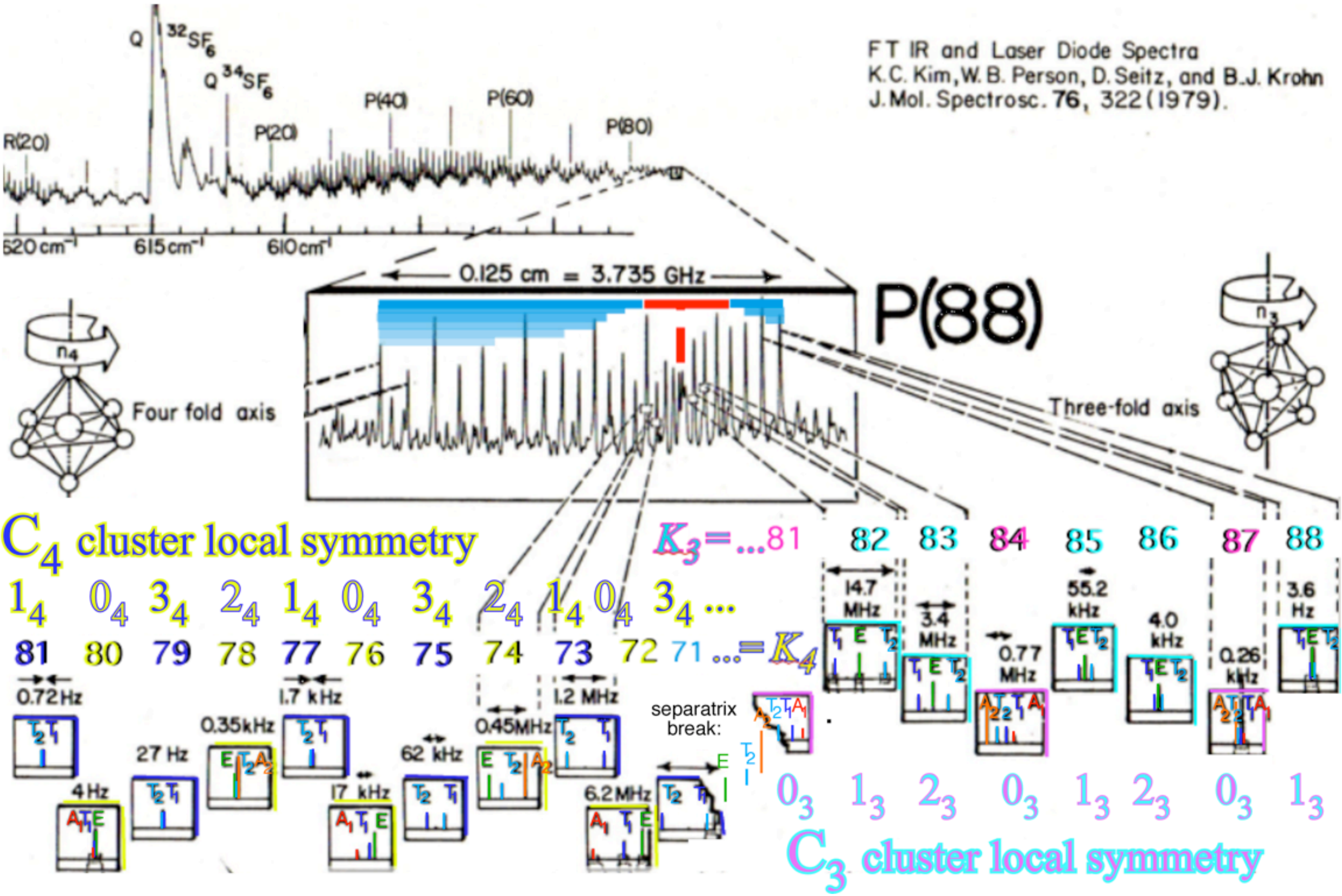
620 cm-1
615 cm-1
610 cm-1
Primary AET species mixing
increases with distance from
"separatrix"
0.125 cm = 3.735 GHz
P(88)
(b) P(88) Fine Structure (Rotational anisotropy effects)
Four fold axis
Three-fold axis
more species mixing
less mixing
more
(c) Superfine Structure (Rotational axis tunneling)
K3 =...81 82 83 84 85 86 87 88
88 87 86 85 84 83 82 81 80 79 78 77 76 75 74 73 72 71 ...=K4
CASE 1 Unmixed
primary A1 T1 E T2 A2 species
Three-Fold Clusters
CASE 1
CASE 2
(d) Hyperfine Structure (Nuclear spin-rotation effects)
~10kHz
CASE 23



(a) SF6 ν4 Rotational Structure
FT IR and Laser Diode Spectra
K.C. Kim, W.B. Person, D. Seitz, and B.J. Krohn
J. Mol. Spectrosc. 76, 322 (1979).
Primary AET species mixing increases with distance from "separatrix"
(b) P(88) Fine Structure (Rotational anisotropy effects)
0.125 cm = 3.735 GHz
P(88)
Four fold axis
Three-fold axis
more species mixing
less mixing
more
(c) Superfine Structure (Rotational axis tunneling)
K3 =...81 82 83 84 85 86 87 88
88 87 86 85 84 83 82 81 80 79 78 77 76 75 74 73 72 71 ...=K4
CASE 1 Unmixed primary A1 T1 E T2 A2 species
(d) Hyperfine Structure (Nuclear spin-rotation effects)
Three-Fold Clusters
CASE 1
CASE 2
CASE 2_4 Extreme mixing in tight C4-CLUSTERS
Four-Fold Clusters
CASE 2
CASE 1
CASE 2_3 Major mixing in lowest two C3-CLUSTERS
(e) Superhyperfine Structure (Spin frame correlation effects)
(Next page: approximate theory)

IR Spectra of SF6 ν₄ P(88)



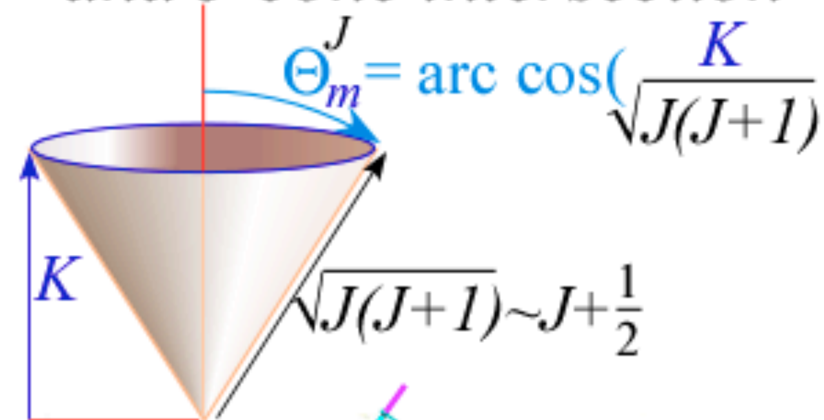
Int.J.Molecular Science 14.(2013) Fig.26 p. 783

SF_6 Spectra of O_h Ro-vibronic Hamiltonian described by RE Tensor Topography

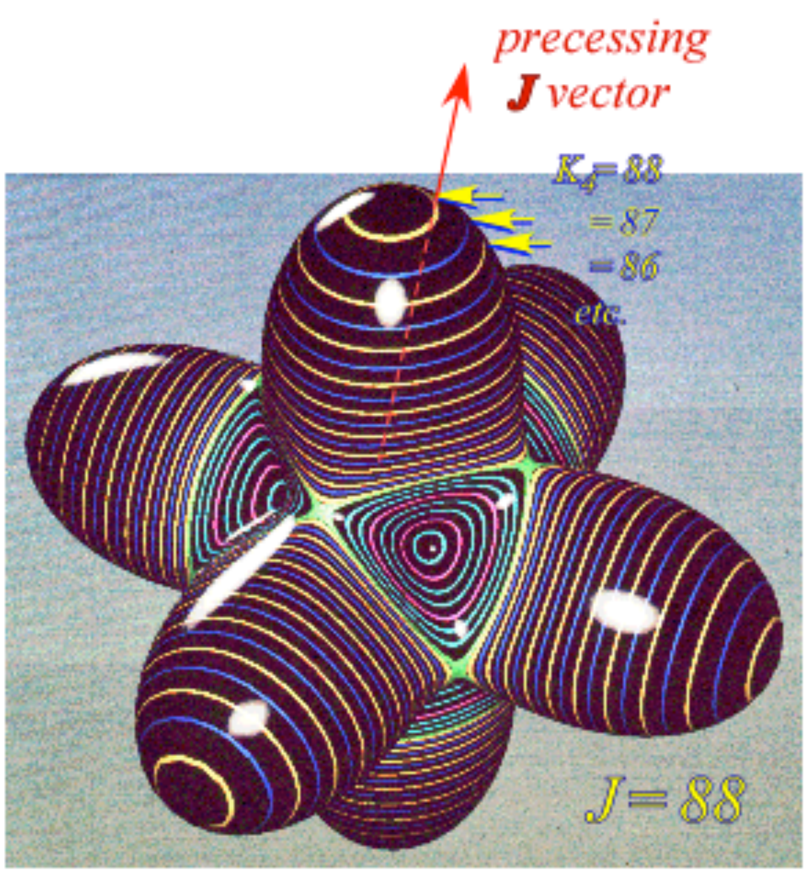
and J-cone intersection

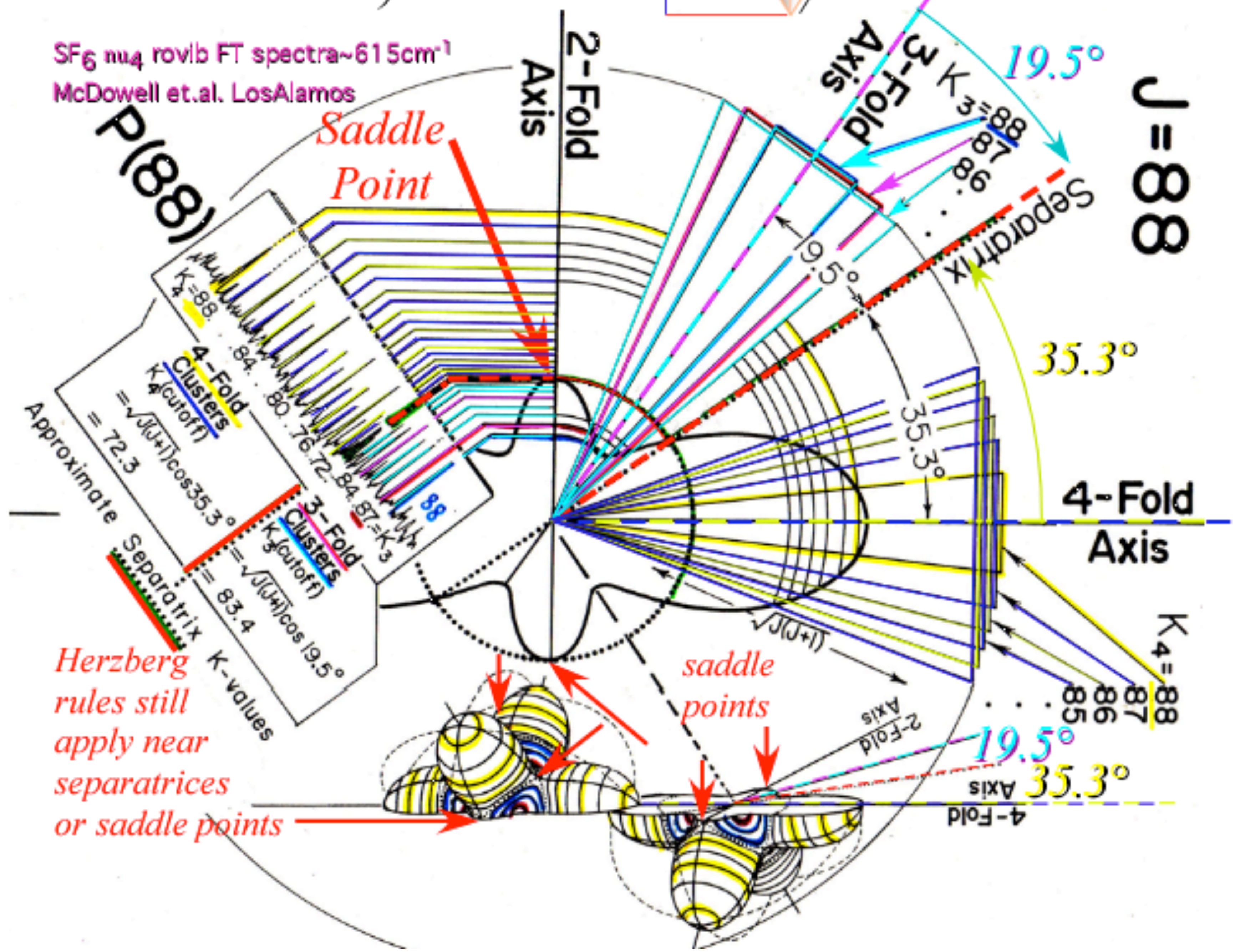
$$\mathbf{H} = B\left(\mathbf{J}_x^2 + \mathbf{J}_y^2 + \mathbf{J}_z^2\right) + t_{440}\left(\mathbf{J}_x^4 + \mathbf{J}_y^4 + \mathbf{J}_z^4 - \frac{3}{5}J^4\right) + \cdots$$

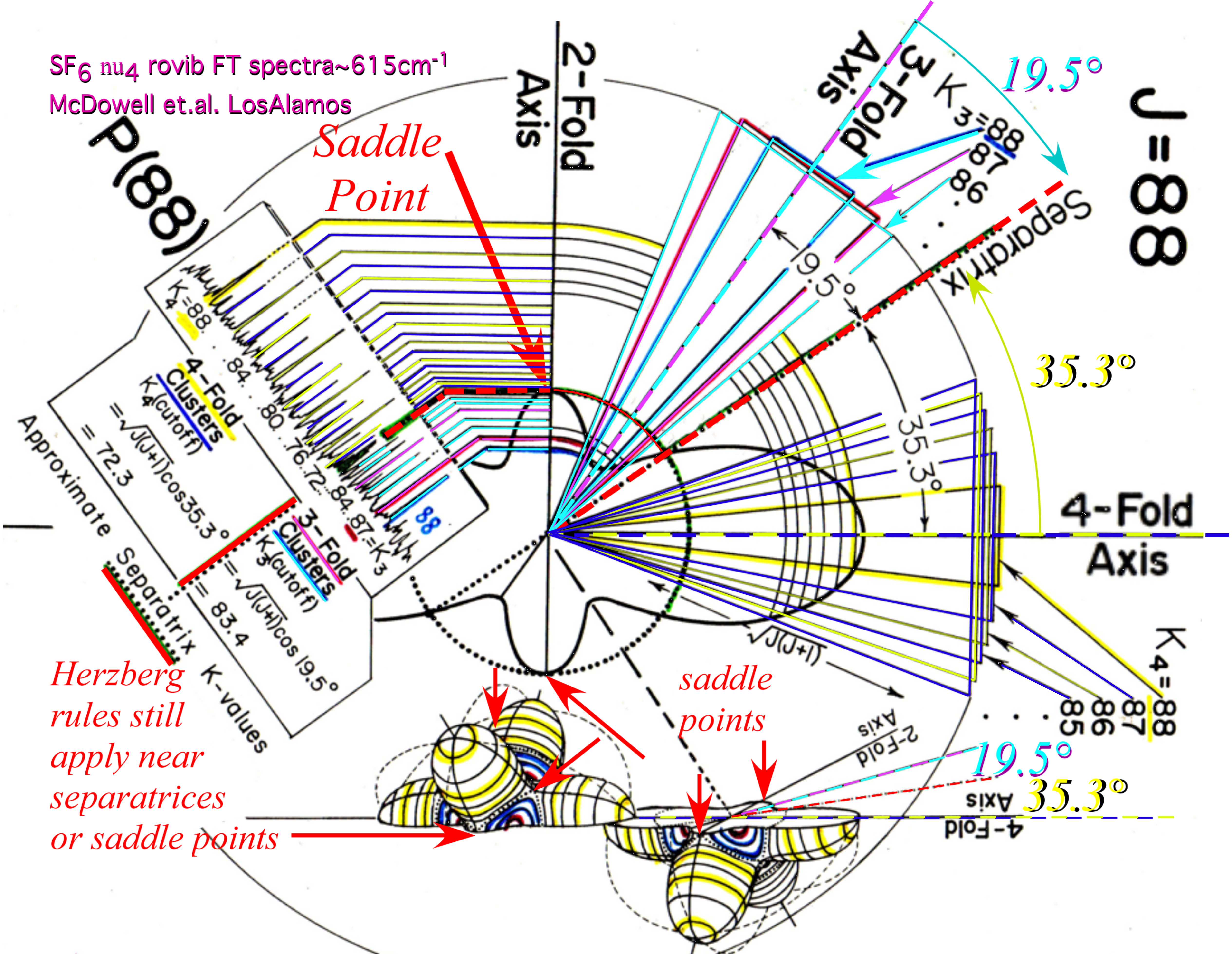
$$= \quad B\mathbf{J}^2 \quad + t_{440}\left(\mathbf{T}_0^4 + \sqrt{\frac{5}{14}}\left[\mathbf{T}_4^4 + \mathbf{T}_{-4}^4\right]\right) + \cdots$$



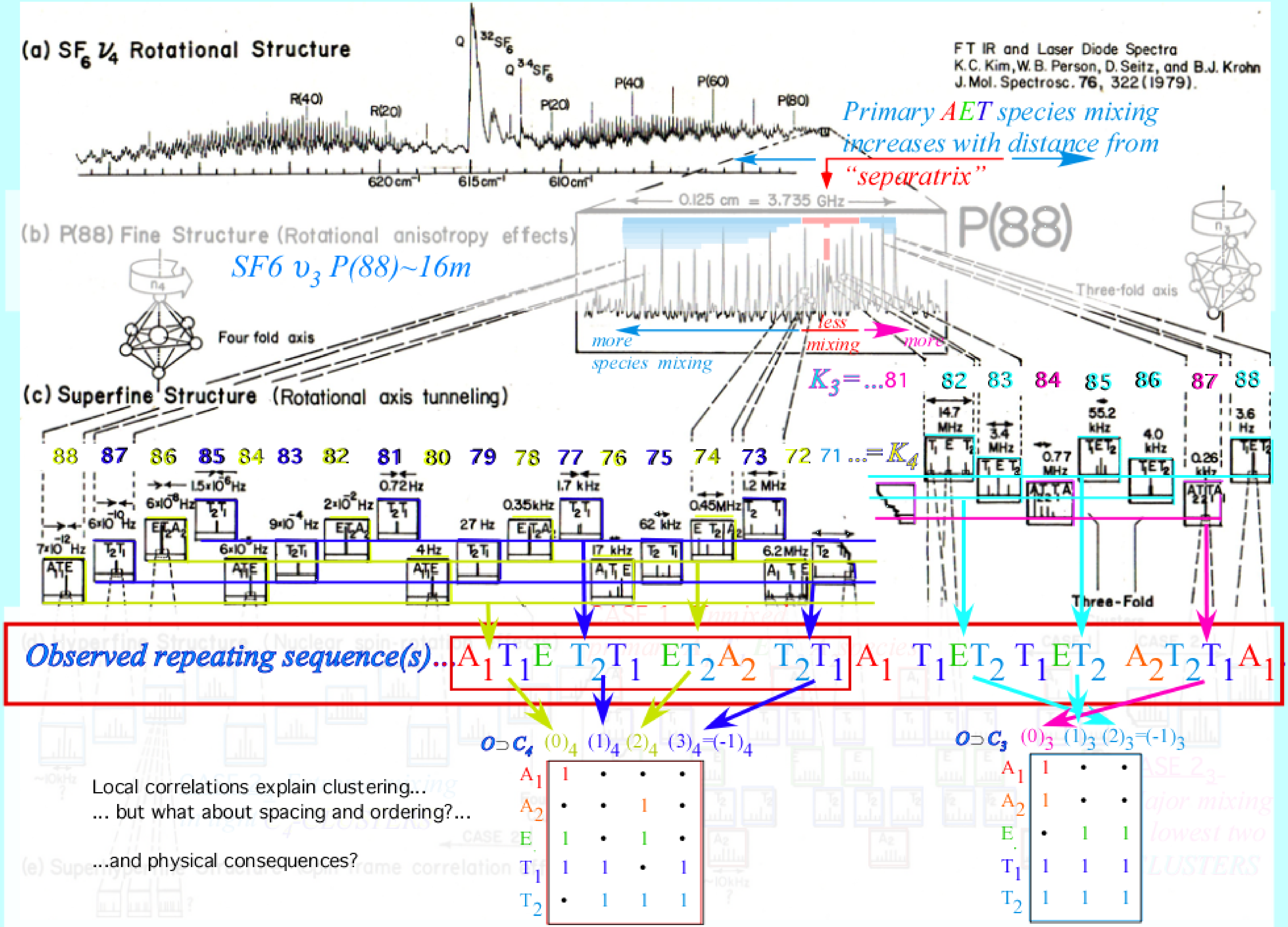
Rovibronic Energy (RE)
Tensor Surface





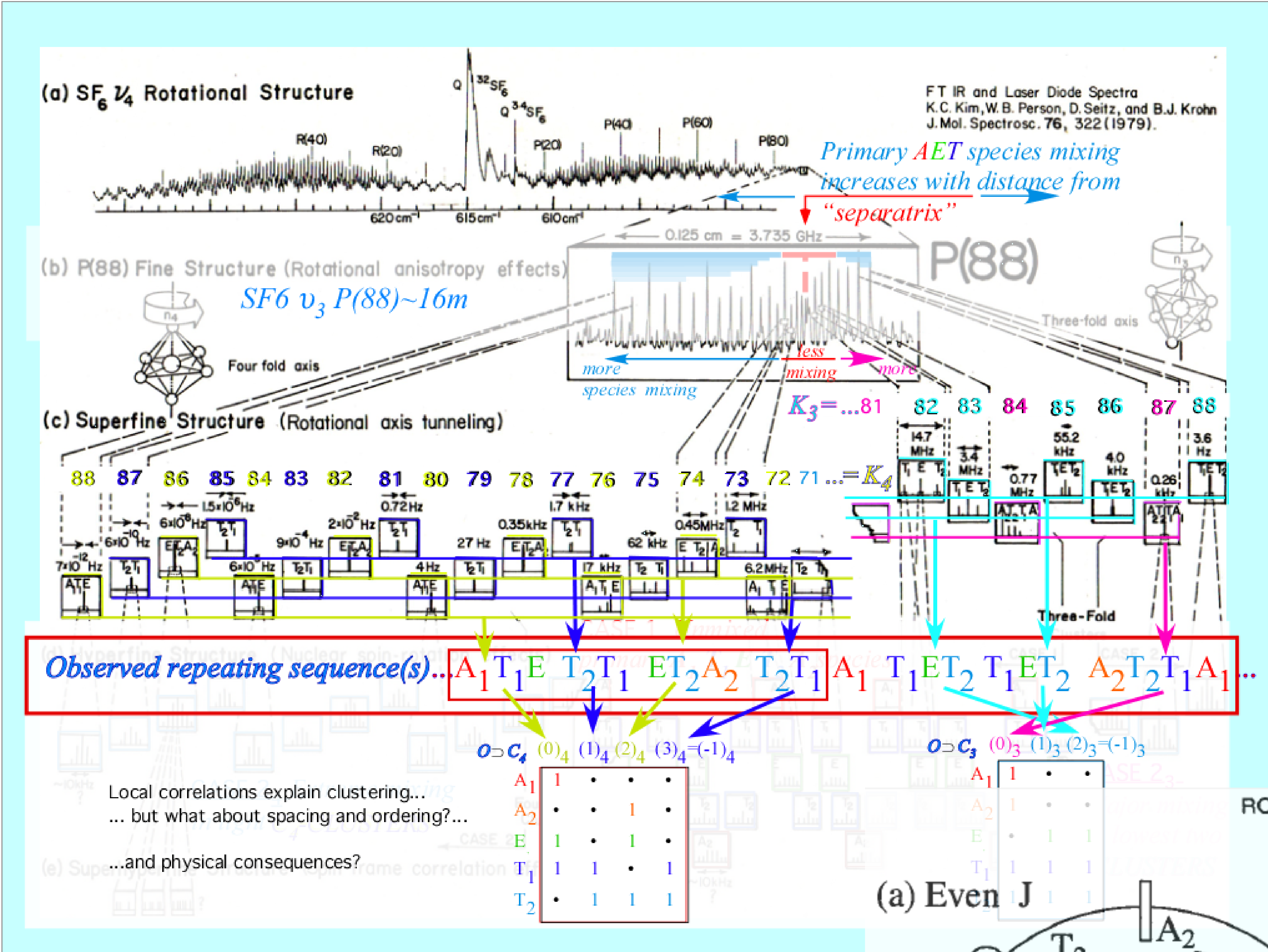


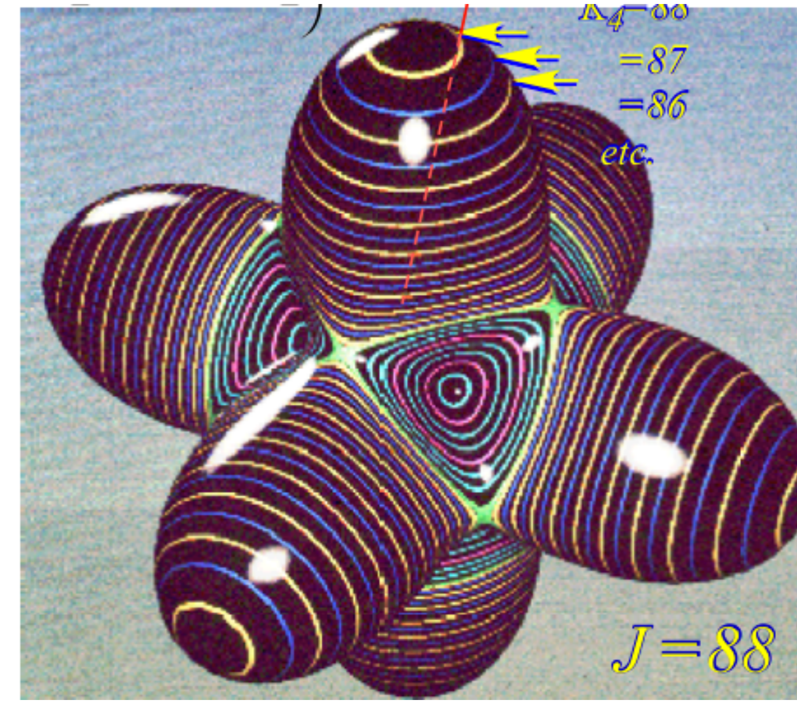
SF6 nu4 rovib FT spectra~615cm-1
McDowell et.al. LosAlamos
P(88)
2-Fold Axis
3-Fold Axis
J=88
Saddle Point
19.5°
35.3°
Separatrix
4-Fold Axis
4-Fold Clusters
K4(cutoff) = √J(J+1) cos35.3° = 72.3
3-Fold Clusters
K3(cutoff) = √J(J+1) cos 19.5° = 83.4
Approximate Separatrix K-values
√J(J+1)
saddle points
Herzberg rules still apply near separatrices or saddle points



	$(0)_4$	$(1)_4$	$(2)_4$	$(3)_4$
A_1	1	•	•	•
A_2	•	•	1	•
E	1	•	1	•
T_1	1	1	•	1
T_2	•	1	1	1

	$(0)_3$	$(1)_3$	$(2)_3$
A_1	1	•	•
A_2	1	•	•
E	•	1	1
T_1	1	1	1
T_2	1	1	1





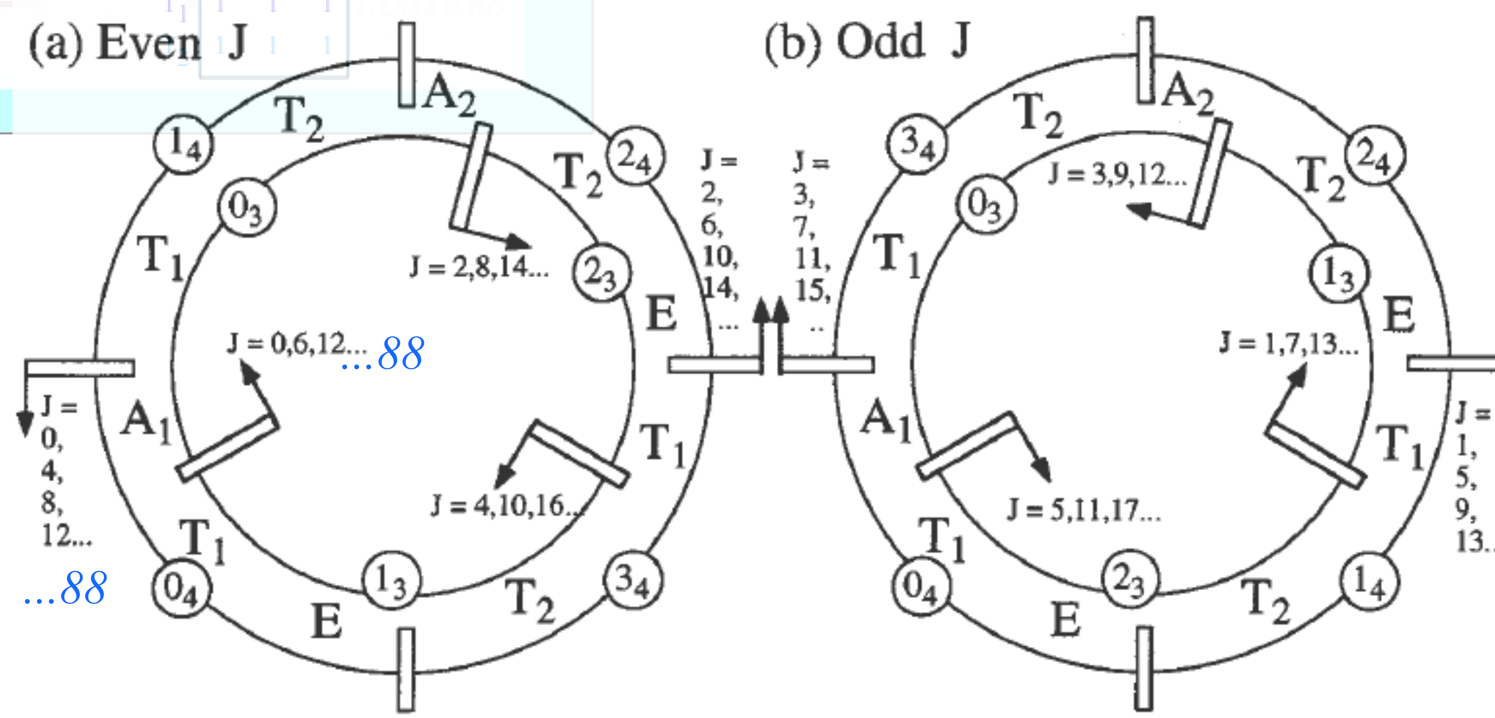


Figure 5.6.9 Mnemonic wheels for octahedral-O orbital. Splitting of J levels for (a) even J and (b) odd J.

SF₆ 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.

Review :

Symmetric rigid quantum rotor analysis of R(2) Hamiltonian $\mathbf{H}=B\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$

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

Asymmetric rigid quantum rotor analysis of D_2 Hamiltonian $\mathbf{H}=A\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$

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

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

$R(3)\supset D_2$ character analysis of ℓ-level or 2ℓ+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 $\mathbf{H}=B\mathbf{J}\cdot\mathbf{J}+t_{044}\mathbf{T}^{[4]}$

Spherical rotor levels and RES plots of O_h tensor eigenvalues

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

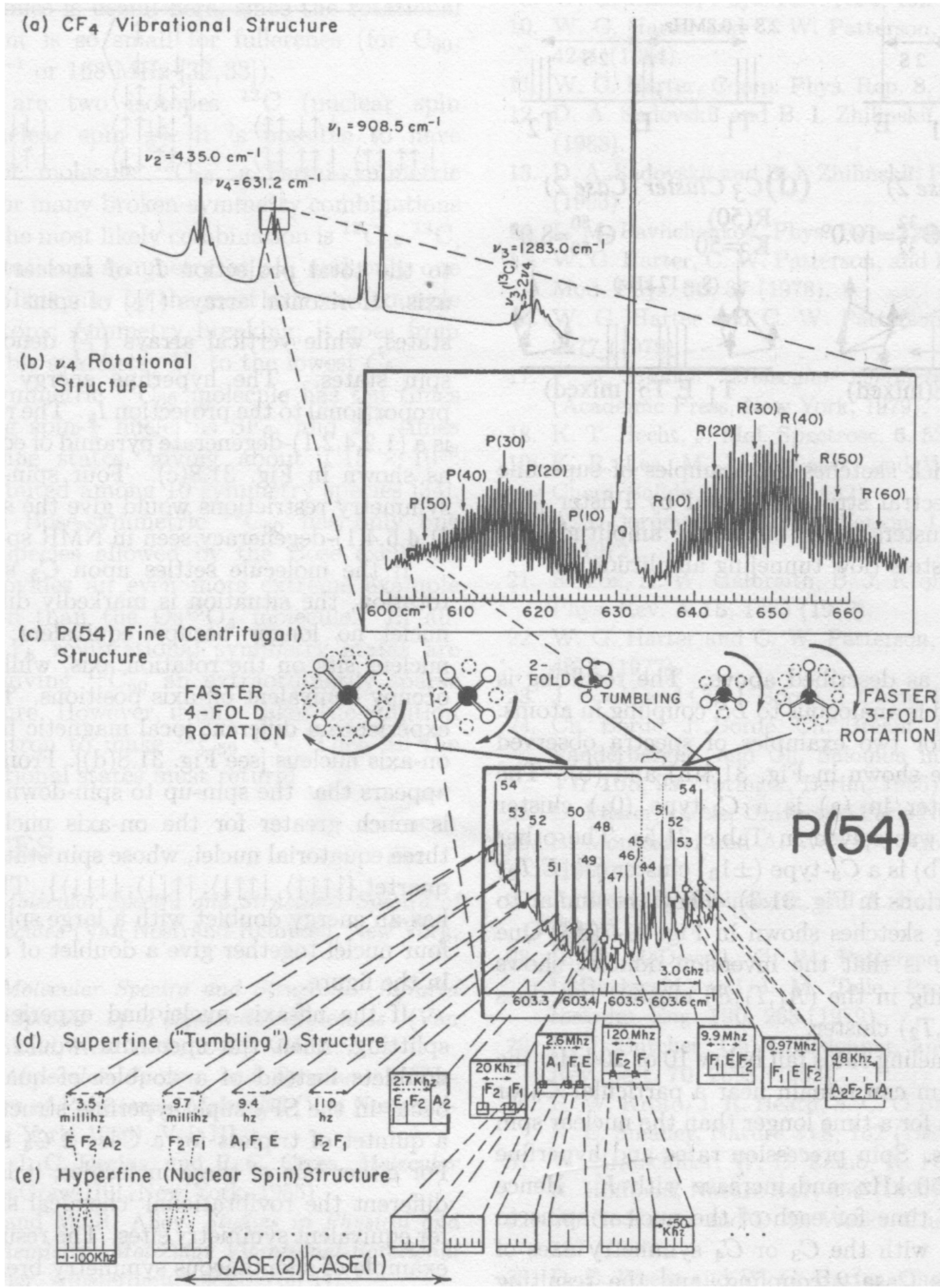
Visualizing J=30 quantum levels of cubic, octahedral, and tetrahedral molecules

SF_6 spectral fine structure P(88)

➡ *CF_4 spectral fine structure P(54)* ⬅

Example of frequency hierarchy for 16μm spectra of CF_4 (Freon-14)

W.G.Harter
Ch. 31
Atomic, Molecular, & Optical Physics Handbook
Am. Int. of Physics
Gordon Drake Editor
(1996)



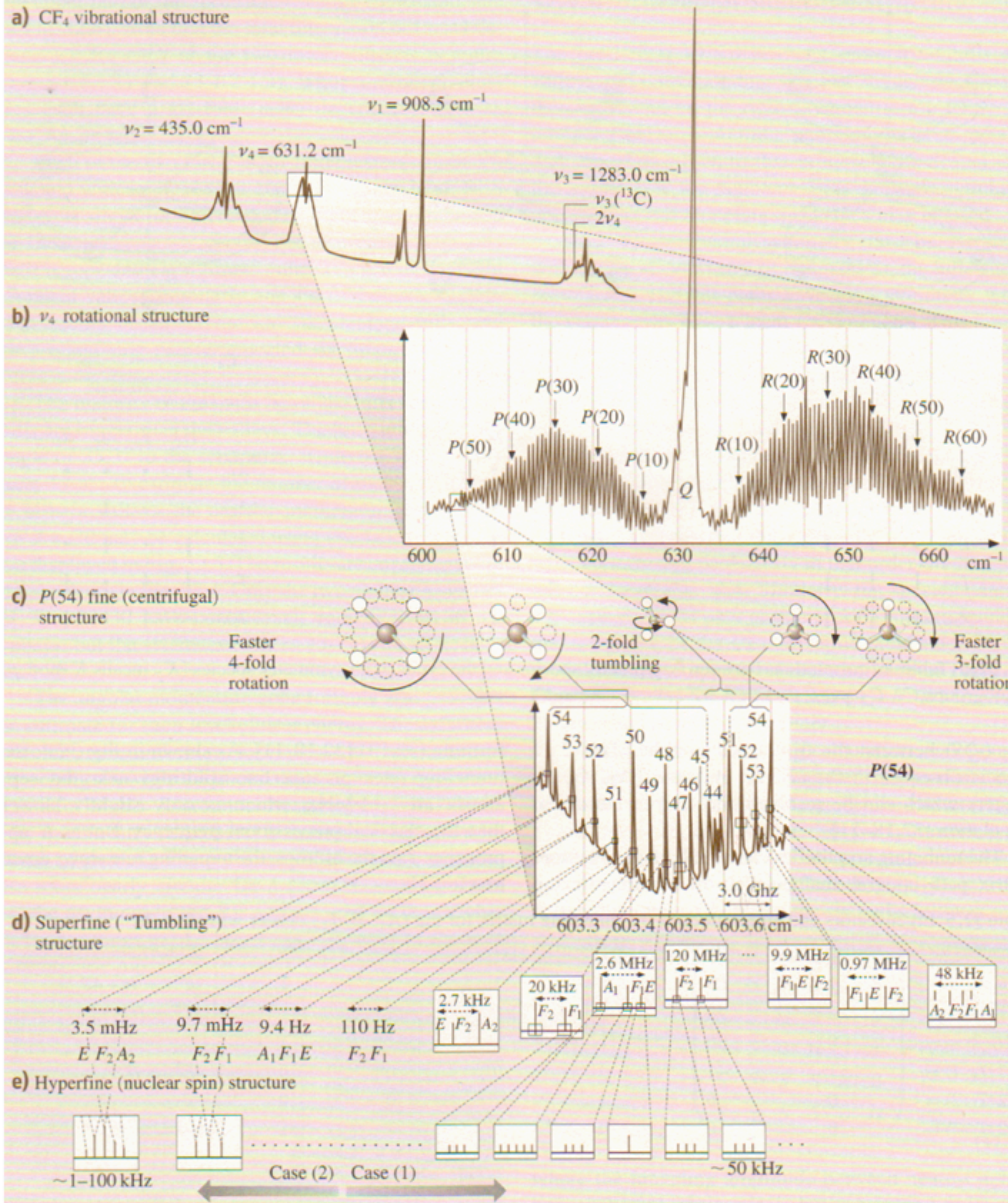
Example of frequency hierarchy for 16μm spectra of CF_4 (Freon-14)

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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BohrIt - Production; URL is "http://www.uark.edu/ua/modphys/markup/BohrItWeb.html"
BounceIt - Production; URL is "http://www.uark.edu/ua/modphys/markup/BounceItWeb.html"
BoxIt - Production; URL is "http://www.uark.edu/ua/modphys/markup/BoxItWeb.html"
CoulIt - Production; URL is "http://www.uark.edu/ua/modphys/markup/CoulItWeb.html"
Cycloidulum - Production; URL is "http://www.uark.edu/ua/modphys/markup/CycloidulumWeb.html"
LearnIt - Production; URL is "**http://www.uark.edu/ua/modphys**" or "http://www.uark.edu/ua/modphys/markup/LearnItWeb.html"
JerkIt - Production; URL is "http://www.uark.edu/ua/modphys/markup/JerkItWeb.html"
Pendulum - Production; URL is "http://www.uark.edu/ua/modphys/markup/PendulumWeb.html"
QuantIt - Production; URL is "http://www.uark.edu/ua/modphys/markup/QuantItWeb.html"
Relativity - Pirelli Entrant: URL is "http://www.uark.edu/ua/pirelli" or "http://www.uark.edu/ua/pirelli/html/default.html"
Trebuchet Production; URL is "http://www.uark.edu/ua/modphys/markup/TrebuchetWeb.html"

Testing Links - ***For internal use and testing by Harter & Heyoka***

BohrIt - Testing; URL is "http://www.uark.edu/ua/modphys/testing/markup/BohrItWeb.html"
BounceIt - Testing; URL is "http://www.uark.edu/ua/modphys/testing/markup/BounceItWeb.html"
BounceIt Title Page - Testing; URL is "http://www.uark.edu/ua/modphys/testing/markup/BounceItTitlePage.html"
BoxIt - Testing; URL is "http://www.uark.edu/ua/modphys/testing/markup/BoxItWeb.html"
CoulIt - Testing; URL is "http://www.uark.edu/ua/modphys/testing/markup/CoulItWeb.html"
Cycloidulum - Testing; URL is "http://www.uark.edu/ua/modphys/testing/markup/CycloidulumWeb.html"
Harter-Soft Web Apps - Quick Reference - Testing; URL is "http://www.uark.edu/ua/modphys/testing/markup/JerkItWeb.html"
JerkIt - Testing; URL is "http://www.uark.edu/ua/modphys/testing/markup/JerkItWeb.html"
ModernPhysics - Testing; URL is "http://www.uark.edu/ua/modphys/testing/markup/IntroCover.html"
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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