AMOP Lecture 16
Thur. 4.10 2014

Based on QTCA Lectures 24-25
Group Theory in Quantum Mechanics

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 : *Asymmetric Top eigensolutions for J=1-2 and D_2 symmetry*

New geometric approach to rotational eigenstates and spectra
Introduction to Rotational Energy Surfaces (RES) and multipole tensor expansion
Rank-2 tensors from D^2-matrix
Building Hamiltonian $\mathbf{H} = A\mathbf{J}_x^2 + B\mathbf{J}_y^2 + C\mathbf{J}_z^2$ *out of scalar and tensor operators*
Comparing quantum and semi-classical calculations
Symmetric rotor levels and RES plots
Asymmetry rotor levels and RES plots
Spherical rotor levels and RES plots
SF_6 spectral fine structure
CF_4 spectral fine structure

As of April 3, 2014

Links to the current Harter-Soft LearnIt web apps for Physics

Bold links have default redirect pages. ***Italics*** **are not yet meant for production.Red: the final stages of testing.**

List of *production* Harter-Soft Web Apps & Textbooks (For public)

Classical Mechanics with a Bang! - URL is "http://www.uark.edu/ua/modphys/markup/CMwBangWeb.html"
Quantum Theory for the Computer Age - URL is "http://www.uark.edu/ua/modphys/markup/QTCAWeb.html"
LearnIt Web Applications - URL is "http://www.uark.edu/ua/modphys/markup/LearnItWeb.html"

Individual web-apps for current classes:

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"
JerkIt - Production; URL is "http://www.uark.edu/ua/modphys/markup/JerkItWeb.html"
MolVibes - Production; URL is "http://www.uark.edu/ua/modphys/markup/MolVibesWeb.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"

The old relativity website (2005):
Relativity - Pirelli Entrant - Production; URL is "**http://www.uark.edu/ua/pirelli**" or "http://www.uark.edu/ua/pirelli/html/default.html"

Newer relativity web-apps currently being developed (2013-)
RelativIt Production; URL is "http://www.uark.edu/ua/modphys/markup/RelativItWeb.html"
RelaWavity Production; URL is "http://www.uark.edu/ua/modphys/markup/RelaWavityWeb.html"

Additional classical wep-apps:
Trebuchet Production; URL is "http://www.uark.edu/ua/modphys/markup/TrebuchetWeb.html"
WaveIt Production; URL is "http://www.uark.edu/ua/modphys/markup/WaveItWeb.html"

Link to master list of all Harter-Soft Web Apps & Textbooks (Prod, Testing, & Developement)

http://www.uark.edu/ua/modphys/testing/markup/Harter-SoftWebApps.html

Review : *Asymmetric Top eigensolutions for J=1-2 and D_2 symmetry* *j,m,n* formulas for momentum operator matrix elements:

LAB matrix elements use the usual atomic formula:

$$\left\langle {}^{J}_{m',n'} \right| \mathbf{J}_1 \left| {}^{J}_{m,n} \right\rangle = D^J_{m',m}(\mathbf{J}_1)\delta_{n'n} = \tfrac{1}{2}\left[\delta_{m'm+1}\sqrt{(j-m)(j+m+1)} + \delta_{m'm-1}\sqrt{(j+m)(j-m+1)}\right]\delta_{n'n}$$

$$\left\langle {}^{J}_{m',n'} \right| \mathbf{J}_2 \left| {}^{J}_{m,n} \right\rangle = D^J_{m',m}(\mathbf{J}_2)\delta_{n'n} = \tfrac{-i}{2}\left[\delta_{m'm+1}\sqrt{(j-m)(j+m+1)} - \delta_{m'm-1}\sqrt{(j+m)(j-m+1)}\right]\delta_{n'n}$$

$$\left\langle {}^{J}_{m',n'} \right| \mathbf{J}_3 \left| {}^{J}_{m,n} \right\rangle = D^J_{m',m}(\mathbf{J}_3)\delta_{n'n} = \delta_{m'm}m\;\delta_{n'n}$$

BOD matrix elements are the same after switching *m's* into *n's*
and changing sign of $\mathbf{J}_2$ matrix (*-conjugation)

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

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

$$\left\langle {}^{J}_{m',n'} \right| \mathbf{J}_{\bar{3}} \left| {}^{J}_{m,n} \right\rangle = \delta_{m'm}D^{J}_{n',n}{}^{*}(\mathbf{J}_{\bar{3}}) = \delta_{m'm}n\;\delta_{n'n}$$

Hamiltonian matrices for asymmetric rotor Hamiltonian

$$\mathbf{H} = \frac{1}{2}\left(\frac{\mathbf{J}_{\bar{1}}^{\,2}}{I_{\bar{1}}} + \frac{\mathbf{J}_{\bar{2}}^{\,2}}{I_{\bar{2}}} + \frac{\mathbf{J}_{\bar{3}}^{\,2}}{I_{\bar{3}}} \right) = A\mathbf{J}_{\bar{1}}^{\,2} + B\mathbf{J}_{\bar{2}}^{\,2} + C\mathbf{J}_{\bar{3}}^{\,2}$$

First are matrix formulas for BOD J^2 components.

$$\begin{aligned}
\mathbf{J}_{\bar{1}}^2 \left|\begin{smallmatrix}J\\ m,n\end{smallmatrix}\right\rangle &= \tfrac{1}{2}\sqrt{(j-n)(j+n+1)}\,\mathbf{J}_{\bar{1}} \left|\begin{smallmatrix}J\\ m,n+1\end{smallmatrix}\right\rangle &&= \tfrac{1}{4}\sqrt{(j-n)(j+n+1)}\sqrt{(j-n-1)(j+n+2)} \left|\begin{smallmatrix}J\\ m,n+2\end{smallmatrix}\right\rangle + \tfrac{1}{4}(j-n)(j+n+1) \left|\begin{smallmatrix}J\\ m,n\end{smallmatrix}\right\rangle \\
&\quad + \tfrac{1}{2}\sqrt{(j+n)(j-n+1)}\,\mathbf{J}_{\bar{1}} \left|\begin{smallmatrix}J\\ m,n-1\end{smallmatrix}\right\rangle &&\quad + \tfrac{1}{4}\sqrt{(j+n)(j-n+1)}\sqrt{(j+n-1)(j-n+2)} \left|\begin{smallmatrix}J\\ m,n-2\end{smallmatrix}\right\rangle + \tfrac{1}{4}(j+n)(j-n+1) \left|\begin{smallmatrix}J\\ m,n\end{smallmatrix}\right\rangle
\end{aligned}$$

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

$$\begin{aligned}
\mathbf{J}_{\bar{2}}^2 \left|\begin{smallmatrix}J\\ m,n\end{smallmatrix}\right\rangle &= \tfrac{i}{2}\sqrt{(j-n)(j+n+1)}\,\mathbf{J}_{\bar{2}} \left|\begin{smallmatrix}J\\ m,n+1\end{smallmatrix}\right\rangle &&= \tfrac{-1}{4}\sqrt{(j-n)(j+n+1)}\sqrt{(j-n-1)(j+n+2)} \left|\begin{smallmatrix}J\\ m,n+2\end{smallmatrix}\right\rangle + \tfrac{1}{4}(j-n)(j+n+1) \left|\begin{smallmatrix}J\\ m,n\end{smallmatrix}\right\rangle \\
&\quad - \tfrac{i}{2}\sqrt{(j+n)(j-n+1)}\,\mathbf{J}_{\bar{2}} \left|\begin{smallmatrix}J\\ m,n-1\end{smallmatrix}\right\rangle &&\quad \tfrac{-1}{4}\sqrt{(j+n)(j-n+1)}\sqrt{(j+n-1)(j-n+2)} \left|\begin{smallmatrix}J\\ m,n-2\end{smallmatrix}\right\rangle + \tfrac{1}{4}(j+n)(j-n+1) \left|\begin{smallmatrix}J\\ m,n\end{smallmatrix}\right\rangle
\end{aligned}$$

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

$$\mathbf{J}_{\bar{3}}^2 \left|\begin{smallmatrix}J\\ m,n\end{smallmatrix}\right\rangle = n^2 \left|\begin{smallmatrix}J\\ m,n\end{smallmatrix}\right\rangle$$

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

$$(A\mathbf{J}_{\bar{1}}^2 + B\mathbf{J}_{\bar{2}}^2 + C\mathbf{J}_{\bar{3}}^2) \left|\begin{smallmatrix}J\\ m,n\end{smallmatrix}\right\rangle =$$

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

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

$$\left\langle {}^{1}_{m,n'} \middle| \mathbf{J}_{\bar{1}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} \cdot & \frac{\sqrt{2}}{2} & \cdot \\ \frac{\sqrt{2}}{2} & \cdot & \frac{\sqrt{2}}{2} \\ \cdot & \frac{\sqrt{2}}{2} & \cdot \end{pmatrix}, \quad \left\langle {}^{1}_{m,n'} \middle| \mathbf{J}_{\bar{2}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} \cdot & \frac{i\sqrt{2}}{2} & \cdot \\ \frac{-i\sqrt{2}}{2} & \cdot & \frac{i\sqrt{2}}{2} \\ \cdot & \frac{-i\sqrt{2}}{2} & \cdot \end{pmatrix}, \quad \left\langle {}^{1}_{m,n'} \middle| \mathbf{J}_{\bar{3}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} +1 & \cdot & \cdot \\ \cdot & 0 & \cdot \\ \cdot & \cdot & -1 \end{pmatrix}$$

$$\left\langle {}^{1}_{m,n'} \middle| \mathbf{J}^2_{\bar{1}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} \frac{1}{2} & \cdot & \frac{1}{2} \\ \cdot & 1 & \cdot \\ \frac{1}{2} & \cdot & \frac{1}{2} \end{pmatrix}, \quad \left\langle {}^{1}_{m,n'} \middle| \mathbf{J}^2_{\bar{2}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} \frac{1}{2} & \cdot & -\frac{1}{2} \\ \cdot & 1 & \cdot \\ -\frac{1}{2} & \cdot & \frac{1}{2} \end{pmatrix}, \quad \left\langle {}^{1}_{m,n'} \middle| \mathbf{J}^2_{\bar{3}} \middle| {}^{1}_{m,n} \right\rangle = \begin{pmatrix} +1 & \cdot & \cdot \\ \cdot & 0 & \cdot \\ \cdot & \cdot & +1 \end{pmatrix}.$$

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

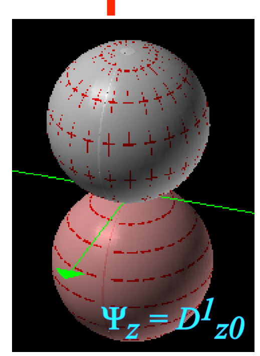
eigen-values: $\left(B+C=5,\quad A+B=3,\quad A+C=4\right)$

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

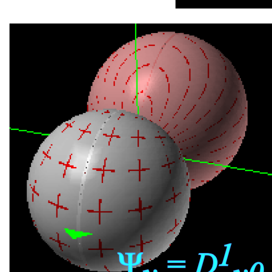
$\left|B+C\right\rangle = 1/\sqrt{2}\left|{}^{1}_{m,+1}\right\rangle \; - 1/\sqrt{2}\left|{}^{1}_{m,-1}\right\rangle$ *y-like*

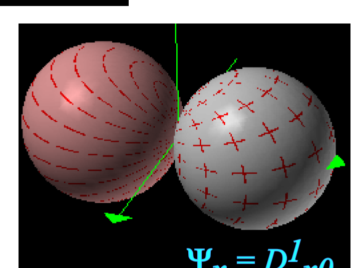
z-like $\left|A+B\right\rangle = \; +\left|{}^{1}_{m,0}\right\rangle$

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



j = 1
Standing
p-Waves

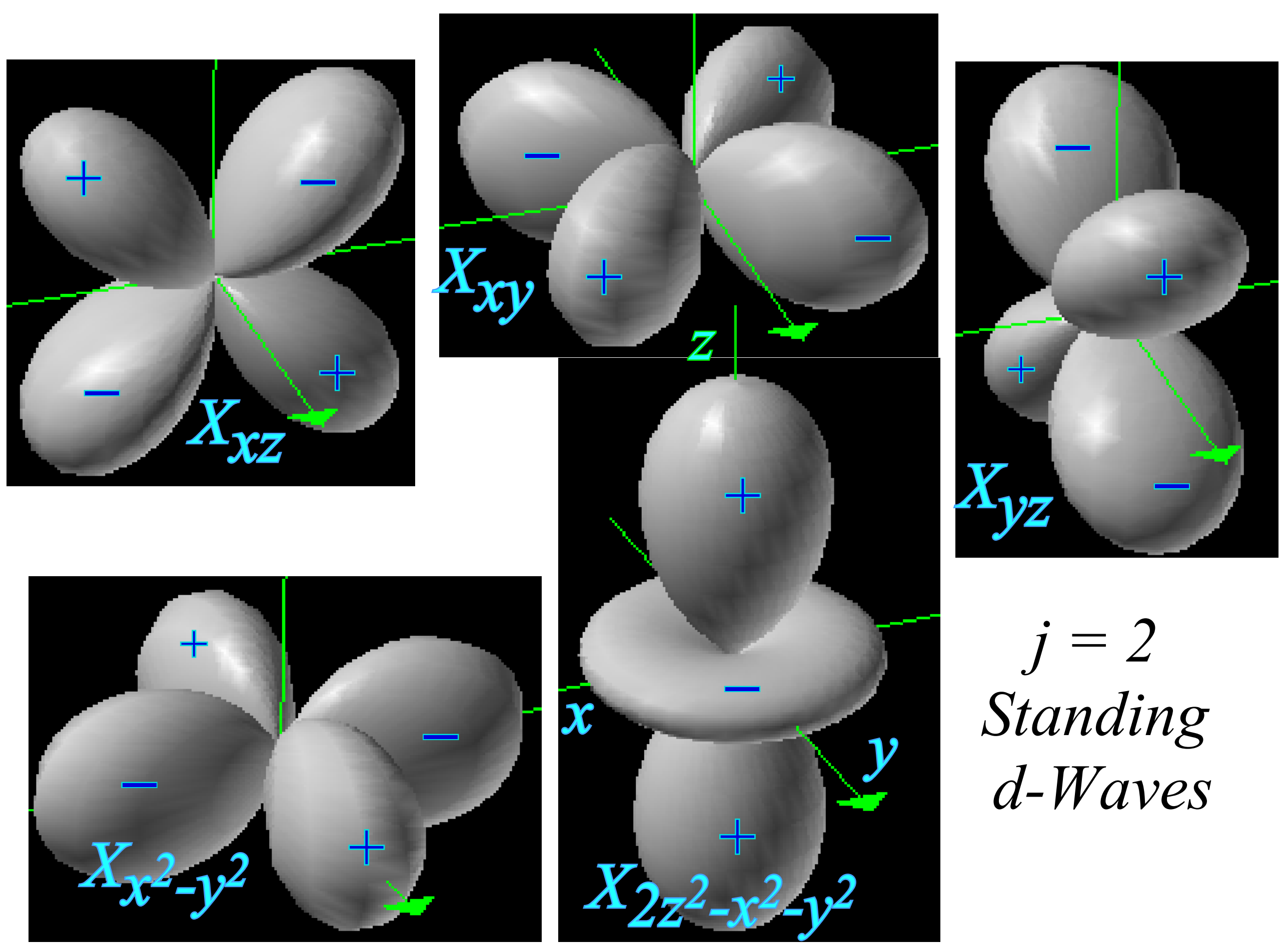




Body-based J=1
vector-like eigenfunctions

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

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



j = 2
Standing
d-Waves

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

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

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

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

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

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.

$$\left(\tfrac{1}{\sqrt{2}}\right)\begin{pmatrix} 1 & \cdot & \cdot & \cdot & 1 \\ 1 & \cdot & \cdot & \cdot & -1 \\ \cdot & 1 & \cdot & 1 & \cdot \\ \cdot & 1 & \cdot & -1 & \cdot \\ \cdot & \cdot & \sqrt{2} & \cdot & \cdot \end{pmatrix}\begin{pmatrix} 4C-\Sigma & \cdot & \frac{\sqrt{6}\Delta}{2} & \cdot & \cdot \\ \cdot & C+\frac{\Sigma}{2} & \cdot & \frac{3\Delta}{2} & \cdot \\ \frac{\sqrt{6}\Delta}{2} & \cdot & \Sigma & \cdot & \frac{\sqrt{6}\Delta}{2} \\ \cdot & \frac{3\Delta}{2} & \cdot & C+\frac{\Sigma}{2} & \cdot \\ \cdot & \cdot & \frac{\sqrt{6}\Delta}{2} & \cdot & 4C-\Sigma \end{pmatrix}\begin{pmatrix} 1 & 1 & \cdot & \cdot & \cdot \\ \cdot & \cdot & 1 & 1 & \cdot \\ \cdot & \cdot & \cdot & \cdot & \sqrt{2} \\ \cdot & \cdot & 1 & -1 & \cdot \\ 1 & -1 & \cdot & \cdot & \cdot \end{pmatrix}\left(\tfrac{1}{\sqrt{2}}\right)+2\Sigma\mathbf{1}$$

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

New D_2 basis:

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

Completing diagonalization from new D_2 basis:

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

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

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

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

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

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

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

×

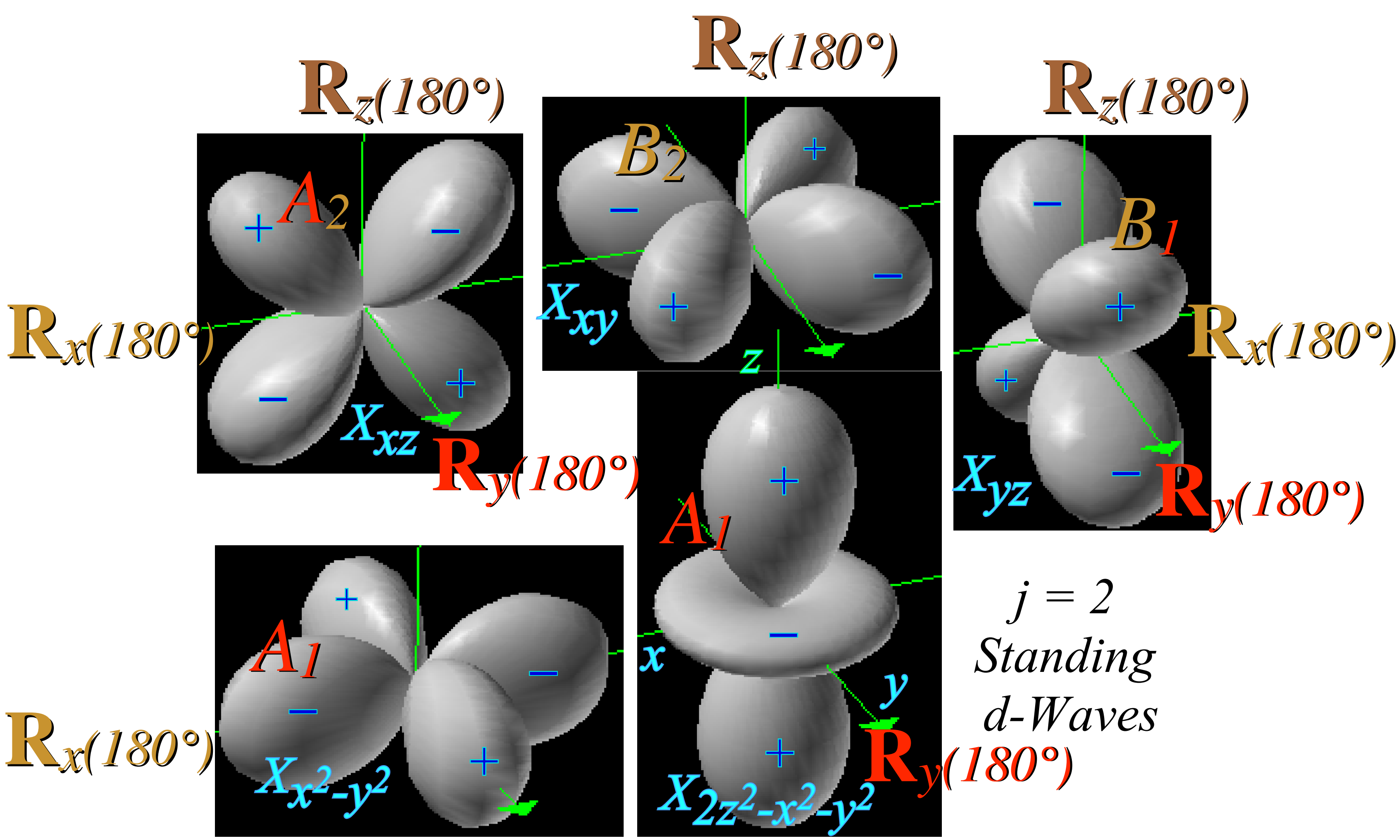
C_2^y	**1**	$\mathbf{R}_y$
+	1	1
−	1	−1

=

$C_2^x \times C_2^y$	**1·1**	$\mathbf{R}_x\cdot$**1**	**1**$\cdot\mathbf{R}_y$	$\mathbf{R}_x\cdot\mathbf{R}_y$
+·+	1·1	1·1	1·1	1·1
−·+	1·1	−1·1	1·1	−1·1
+·−	1·1	1·1	1·(−1)	1·(−1)
−·−	1·1	−1·1	1·(−1)	−1·(−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



Completing diagonalization from new D_2 basis:

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

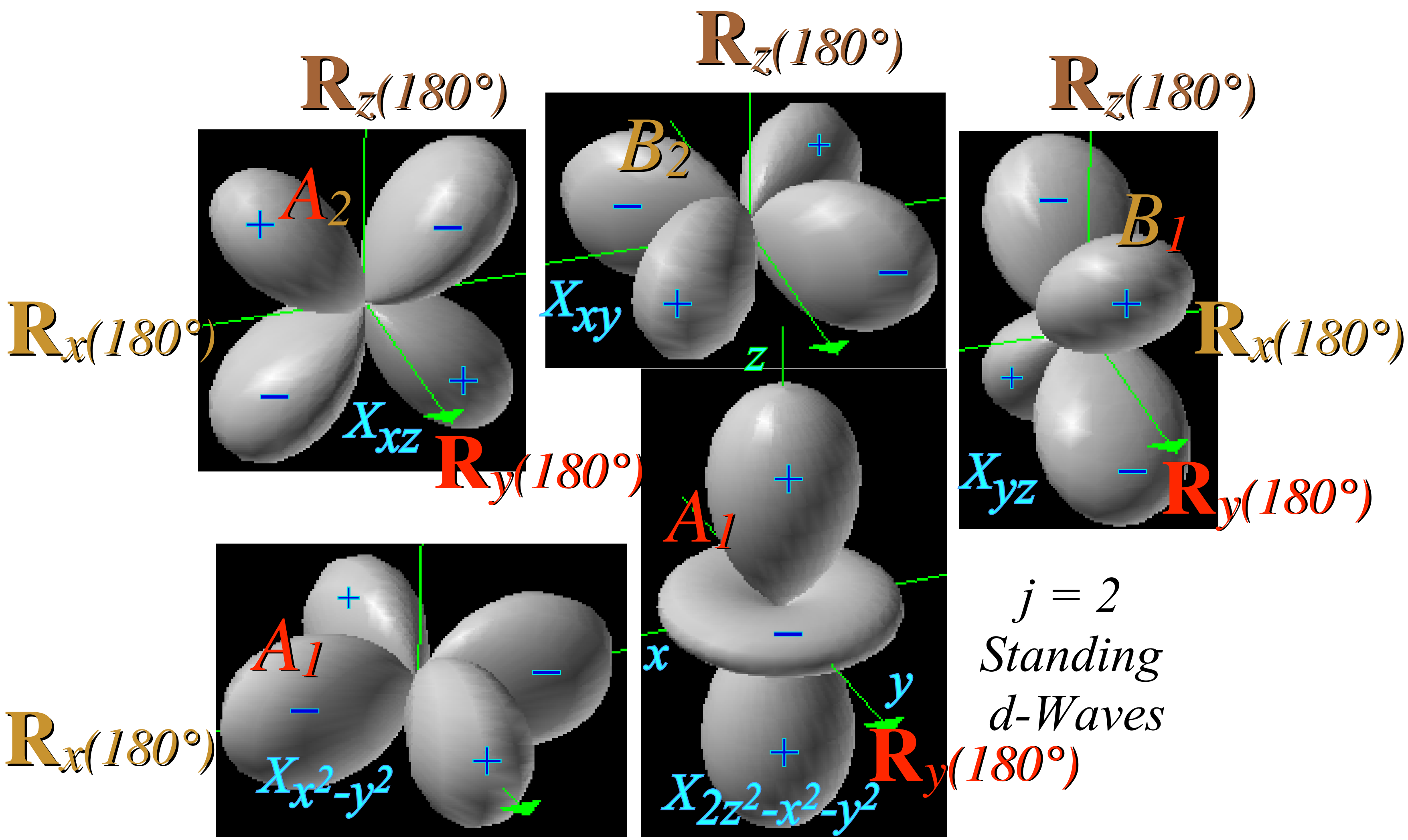
$$\left|A_1 2^+\right\rangle = \tfrac{1}{\sqrt{2}}\left|{2 \atop +2}\right\rangle + \tfrac{1}{\sqrt{2}}\left|{2 \atop -2}\right\rangle$$
$$\left|B_2 2^-\right\rangle = \tfrac{1}{\sqrt{2}}\left|{2 \atop +2}\right\rangle - \tfrac{1}{\sqrt{2}}\left|{2 \atop -2}\right\rangle$$
$$\left|B_1 1^+\right\rangle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

Need only diagonalize the two A_1's:

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

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

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:

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

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

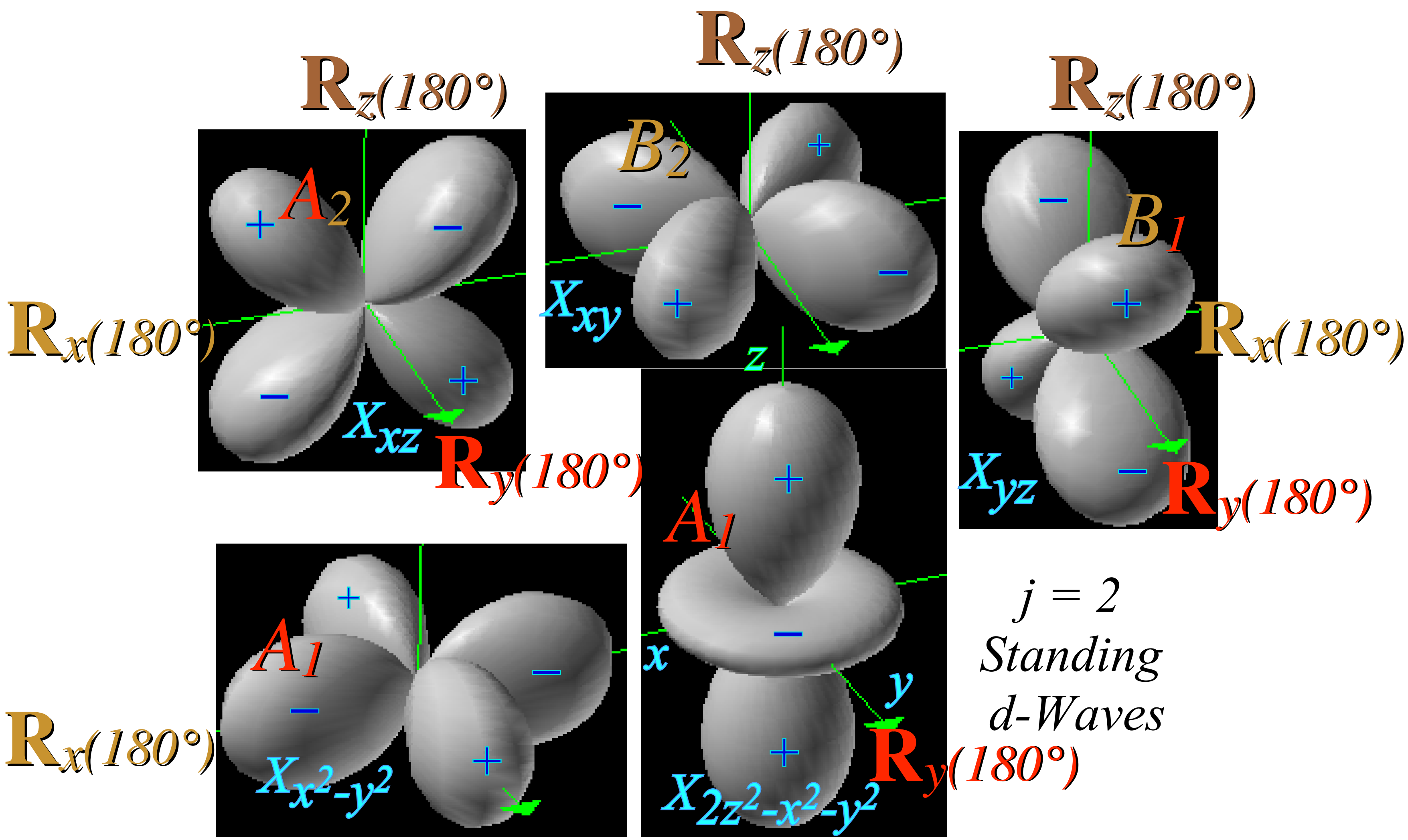
Need only diagonalize the two A_1's:

(It is n=0 versus n=2⁺)

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

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

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:

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

$$\left|A_1 2^+\right\rangle = \tfrac{1}{\sqrt{2}}\left|{2 \atop +2}\right\rangle + \tfrac{1}{\sqrt{2}}\left|{2 \atop -2}\right\rangle$$
$$\left|B_2 2^-\right\rangle = \tfrac{1}{\sqrt{2}}\left|{2 \atop +2}\right\rangle - \tfrac{1}{\sqrt{2}}\left|{2 \atop -2}\right\rangle$$
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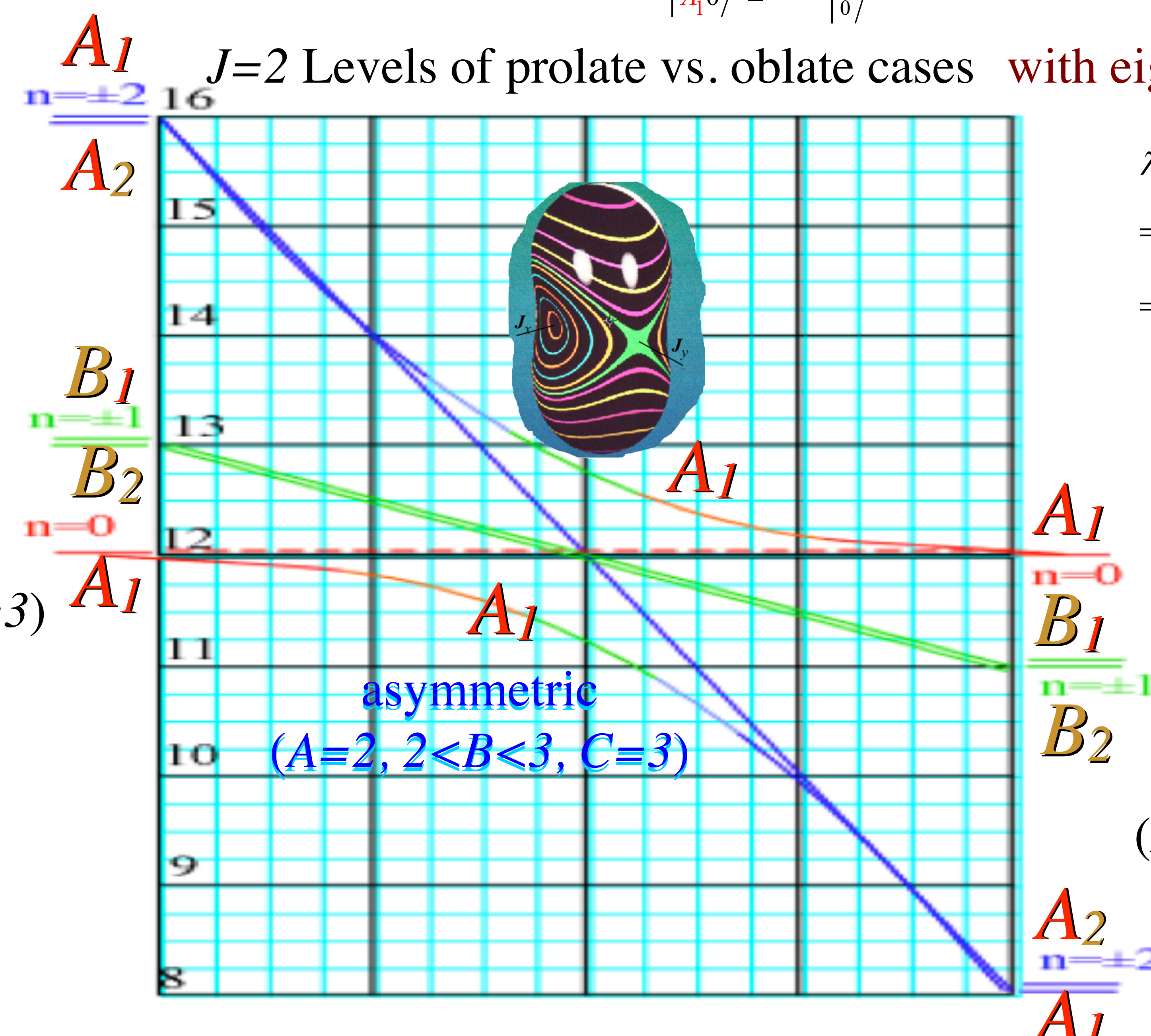
$$= (2C+2A+2B)\cdot\mathbf{1} + \begin{pmatrix} 2C-A-B & \sqrt{3}(A-B) \\ \sqrt{3}(A-B) & -(2C-A-B) \end{pmatrix}$$

with eigenvalues:

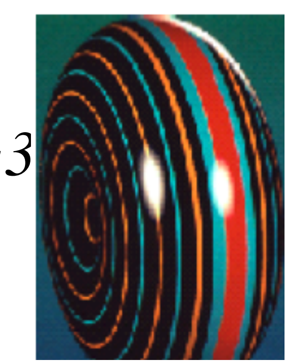
$$\lambda_\pm = 2C+2A+2B \pm \sqrt{(2C-A-B)^2 + 3(A-B)^2}$$
$$= 2(A+B+C) \pm 2\sqrt{C^2-(A+B)C+A^2-AB+B^2}$$
$$= 2C+4B \pm 2(C-B) = \begin{cases} 4C+2B \\ 6B \end{cases} \text{if: } A=B$$

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

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



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



$A=B$ 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: ($A=1$, $B=2$, $C=2$)
$B(J(J+1) + (A-B)n^2 = 2B+4A = 4+4 = 8$ ($n=\pm 2$)
$5B+A = 10+1 = 11$ ($n=\pm 1$) , $6B = 12$ ($n=0$)

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+)

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

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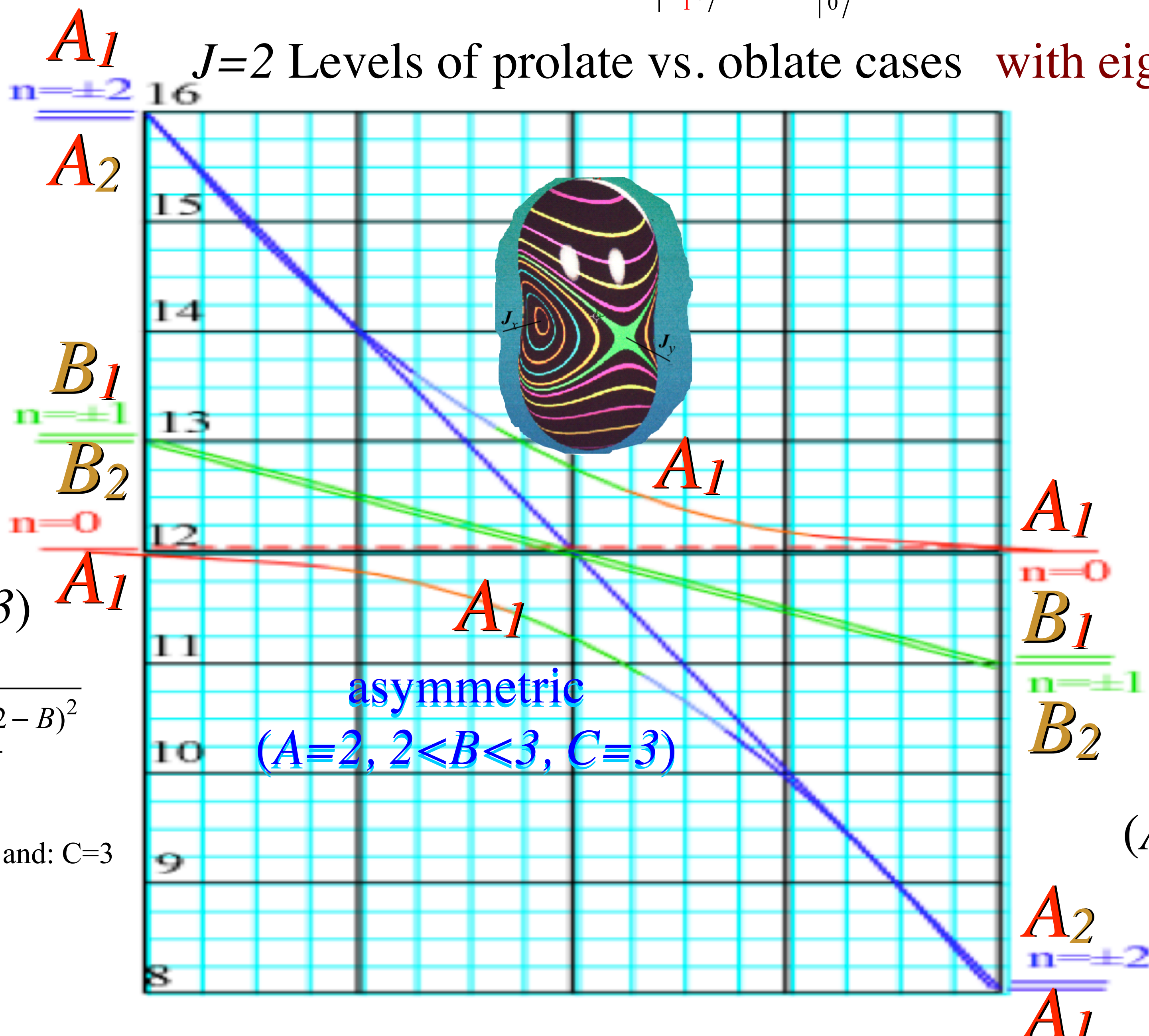
$J=2$ Levels of prolate vs. oblate cases



with eigenvalues:

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

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

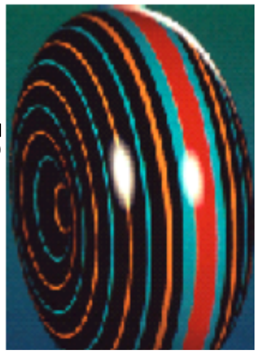
prolate

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

$$\lambda_\pm = 10+2B \pm \sqrt{(4-B)^2 + 3(2-B)^2}$$
$$= 2(5+B) \pm 2\sqrt{7-5B+B^2}$$
$$= 14 \pm 2 = \begin{cases} 16 \\ 12 \end{cases} \text{ if: } A=B=2 \text{ and: } C=3$$

oblate

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



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

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New geometric approach to rotational eigenstates and spectra

Introduction to Rotational Energy Surfaces (RES) and multipole tensor expansion

Rank-2 tensors from D^2-matrix

Building Hamiltonian $\mathbf{H} = A\mathbf{J}_x^2 + B\mathbf{J}_y^2 + C\mathbf{J}_z^2$ out of scalar and tensor operators

Comparing quantum and semi-classical calculations

Symmetric rotor levels and RES plots

Asymmetry rotor levels and RES plots

Spherical rotor levels and RES plots

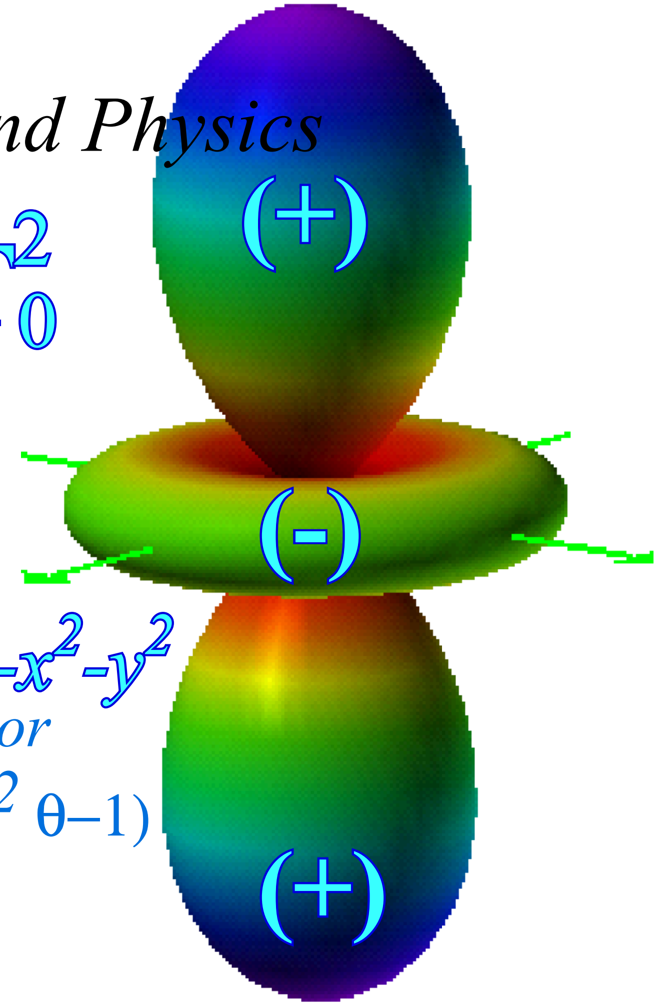
SF_6 spectral fine structure

CF_4 spectral fine structure

Review of freshman Chemistry and Physics
Electronic orbitals 101

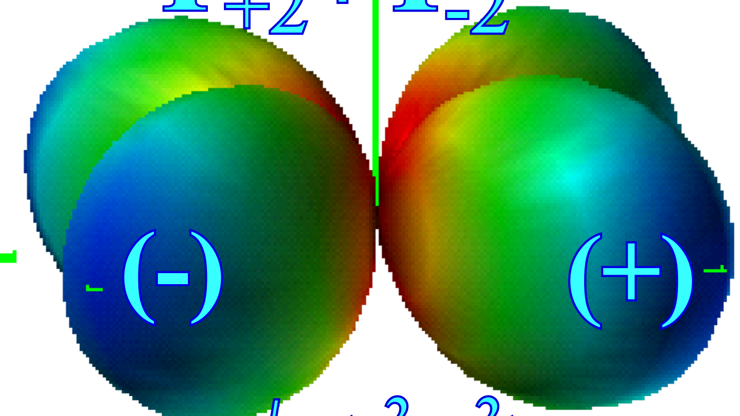
Quadrupoles
(d-orbitals)

T^2_0



$2z^2-x^2-y^2$
or
$Q(3\cos^2\theta-1)$

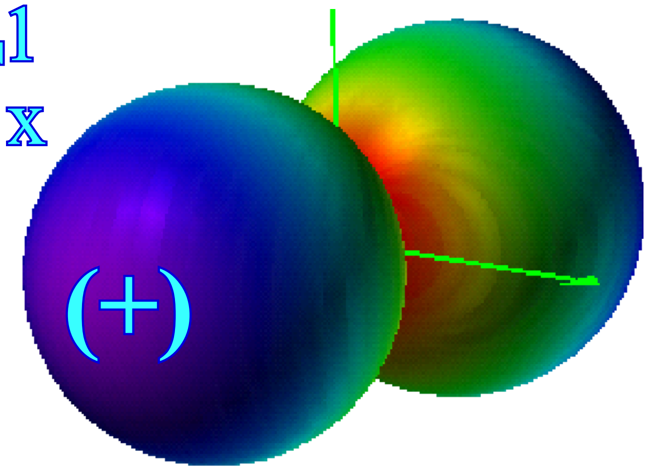
$T^2_{+2}+T^2_{-2}$



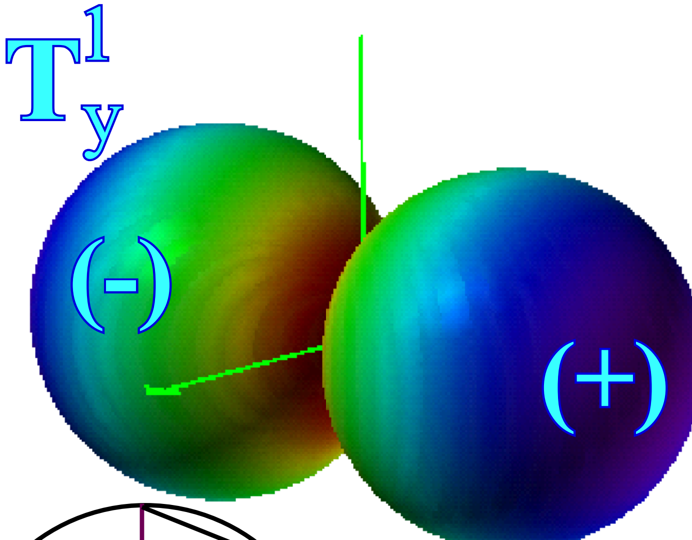
$\sqrt{3}(x^2-y^2)$

Dipoles
(p-orbitals)

T^1_x

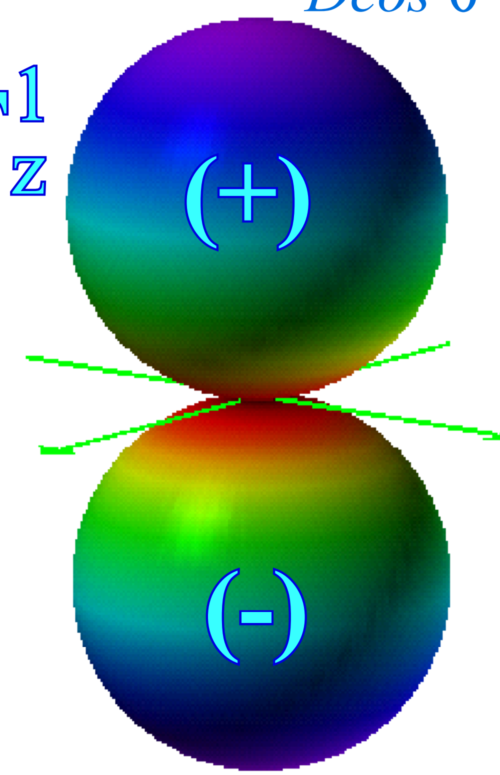


T^1_y

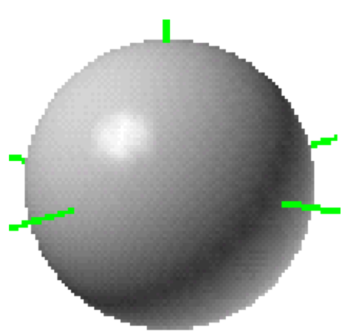


z
or
$D\cos\theta$

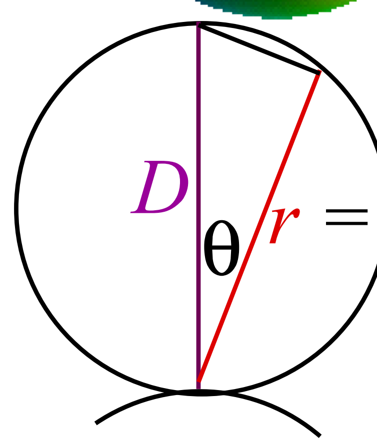
T^1_z



Monopole
(s-orbital)



T^0_0



$r = D\cos\theta$

Review of freshman Chemistry and Physics (contd)

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

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

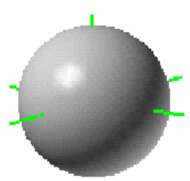
Simple Rigid Rotor Hamiltonian... (Hamiltonian H=E is <u>energy</u> in terms of <u>momentum</u>)

$BUCK$ BANG!

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

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

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



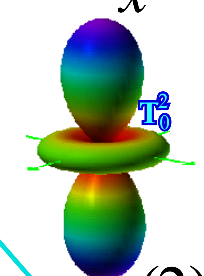
$\mathbf{T}_0^0$

Spherical Top

(A=B=C)

$\mathbf{H} = B\,\mathbf{J}^2$

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



$\mathbf{T}_0^2$

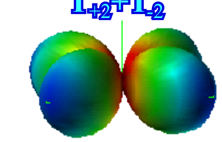
Symmetric Top

(A=B≠C)

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

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

$\mathbf{T}_{+2}^2 + \mathbf{T}_{-2}^2$



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

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 follows…)

New geometric approach to rotational eigenstates and spectra

Introduction to Rotational Energy Surfaces (RES) and multipole tensor expansion

➡ *Rank-2 tensors from D^2-matrix*

Building Hamiltonian $\mathbf{H} = A\mathbf{J}_x^{\ 2} + B\mathbf{J}_y^{\ 2} + C\mathbf{J}_z^{\ 2}$ *out of scalar and tensor operators*

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SF_6 spectral fine structure

CF_4 spectral fine structure

Spherical 2^k-*multipole functions* $X^k_{\ q}$ or *X-functions* are D^*-functions times the k^{th} power of radius (r^k).

$$\sqrt{4\pi/5}\,Y^{\ell=2}_{m=2}(\phi\theta) = D^{2*}_{2,0}(\phi\theta 0) = \sqrt{\frac{3}{8}}e^{i2\phi}\sin^2\theta = \sqrt{\frac{3}{8}}\frac{(x+iy)^2}{r^2}$$

$$\sqrt{4\pi/5}\,Y^{\ell=2}_{m=1}(\phi\theta) = D^{2*}_{1,0}(\phi\theta 0) = -\sqrt{\frac{3}{2}}e^{i\phi}\sin\theta\cos\theta = -\sqrt{\frac{3}{2}}\frac{(x+iy)z}{r^2}$$

$$\sqrt{4\pi/5}\,Y^{\ell=2}_{m=0}(\phi\theta) = D^{2*}_{0,0}(\phi\theta 0) = \frac{3\cos^2\theta-1}{2} = \frac{3z^2-r^2}{2r^2}$$

$$\sqrt{4\pi/5}\,Y^{\ell=2}_{m=-1}(\phi\theta) = D^{2*}_{-1,0}(\phi\theta 0) = \sqrt{\frac{3}{2}}e^{-i\phi}\sin\theta\cos\theta = \sqrt{\frac{3}{2}}\frac{(x-iy)z}{r^2}$$

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$$X^k_q = r^k D^{k*}_{q,0} = \sqrt{\frac{4\pi}{2k+1}}\,r^k Y^k_q$$

Spherical 2^k*-multipole functions* $X^k{}_q$ or *X-functions* are D^*-functions times the k^{th} power of radius (r^k).

$$X_q^k = r^k D_{q,0}^{k*} = \sqrt{\frac{4\pi}{2k+1}} r^k Y_q^k$$

$$\sqrt{4\pi/5}\, Y_{m=2}^{\ell=2}(\phi\theta) = D_{2,0}^{2*}(\phi\theta 0) = \sqrt{\frac{3}{8}} e^{i2\phi} \sin^2\theta = \sqrt{\frac{3}{8}} \frac{(x+iy)^2}{r^2}$$

$$\sqrt{4\pi/5}\, Y_{m=1}^{\ell=2}(\phi\theta) = D_{1,0}^{2*}(\phi\theta 0) = -\sqrt{\frac{3}{2}} e^{i\phi} \sin\theta\cos\theta = -\sqrt{\frac{3}{2}} \frac{(x+iy)z}{r^2}$$

$$\sqrt{4\pi/5}\, Y_{m=0}^{\ell=2}(\phi\theta) = D_{0,0}^{2*}(\phi\theta 0) = \frac{3\cos^2\theta - 1}{2} = \frac{3z^2 - r^2}{2r^2}$$

$$\longrightarrow \quad \sqrt{4\pi/5}\, Y_{m=0}^{\ell=2}(\phi\theta) = X_0^2(\phi\theta 0) = r^2 \frac{3\cos^2\theta - 1}{2} = \frac{3z^2 - r^2}{2} = \frac{2z^2 - x^2 - y^2}{2}$$

$$\sqrt{4\pi/5}\, Y_{m=-1}^{\ell=2}(\phi\theta) = D_{-1,0}^{2*}(\phi\theta 0) = \sqrt{\frac{3}{2}} e^{-i\phi} \sin\theta\cos\theta = \sqrt{\frac{3}{2}} \frac{(x-iy)z}{r^2}$$

$$\sqrt{4\pi/5}\, Y_{m=-2}^{\ell=2}(\phi\theta) = D_{-2,0}^{2*}(\phi\theta 0) = \sqrt{\frac{3}{8}} e^{-i2\phi} \sin^2\theta = \sqrt{\frac{3}{8}} \frac{(x-iy)^2}{r^2}$$

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$$\sqrt{4\pi/5}\, Y_{m=2}^{\ell=2}(\phi\theta) = D_{2,0}^{2*}(\phi\theta 0) = \sqrt{\frac{3}{8}} e^{i2\phi}\sin^2\theta = \sqrt{\frac{3}{8}}\frac{(x+iy)^2}{r^2}$$

$$\sqrt{4\pi/5}\, Y_{m=1}^{\ell=2}(\phi\theta) = D_{1,0}^{2*}(\phi\theta 0) = -\sqrt{\frac{3}{2}} e^{i\phi}\sin\theta\cos\theta = -\sqrt{\frac{3}{2}}\frac{(x+iy)z}{r^2}$$

$$\sqrt{4\pi/5}\, Y_{m=0}^{\ell=2}(\phi\theta) = D_{0,0}^{2*}(\phi\theta 0) = \frac{3\cos^2\theta - 1}{2} = \frac{3z^2 - r^2}{2r^2}$$

$$\sqrt{4\pi/5}\, Y_{m=-1}^{\ell=2}(\phi\theta) = D_{-1,0}^{2*}(\phi\theta 0) = \sqrt{\frac{3}{2}} e^{-i\phi}\sin\theta\cos\theta = \sqrt{\frac{3}{2}}\frac{(x-iy)z}{r^2}$$

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$$\longrightarrow \sqrt{4\pi/5}\, Y_{m=0}^{\ell=2}(\phi\theta) = X_0^2(\phi\theta 0) = r^2\frac{3\cos^2\theta - 1}{2} = \frac{3z^2 - r^2}{2} = \frac{2z^2 - x^2 - y^2}{2}$$

The (x,y,z) polynomials become $(\mathbf{J}_x, \mathbf{J}_y, \mathbf{J}_z)$ rotor tensor operators

$$\mathbf{T}_0^2 = \frac{2\mathbf{J}_z{}^2 - \mathbf{J}_x{}^2 - \mathbf{J}_y{}^2}{2} = \mathbf{J}^2\frac{3\cos^2\theta - 1}{2} = \mathbf{J}^2 P_2(\cos\theta)$$

Spherical 2^k-*multipole functions* $X^k{}_q$ or *X-functions* are D^*-functions times the k^{th} power of radius (r^k).

$$X^k_q = r^k D^{k*}_{q,0} = \sqrt{\frac{4\pi}{2k+1}} r^k Y^k_q$$

$$\sqrt{4\pi/5}\, Y^{\ell=2}_{m=2}(\phi\theta) = D^{2*}_{2,0}(\phi\theta 0) = \sqrt{\frac{3}{8}} e^{i2\phi}\sin^2\theta = \sqrt{\frac{3}{8}}\frac{(x+iy)^2}{r^2}$$

$$\sqrt{4\pi/5}\, Y^{\ell=2}_{m=1}(\phi\theta) = D^{2*}_{1,0}(\phi\theta 0) = -\sqrt{\frac{3}{2}} e^{i\phi}\sin\theta\cos\theta = -\sqrt{\frac{3}{2}}\frac{(x+iy)z}{r^2}$$

$$\sqrt{4\pi/5}\, Y^{\ell=2}_{m=0}(\phi\theta) = D^{2*}_{0,0}(\phi\theta 0) = \frac{3\cos^2\theta - 1}{2} = \frac{3z^2 - r^2}{2r^2}$$

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-

$$= \quad X^2_2(\phi\theta 0) - X^2_{-2}(\phi\theta 0) = \sqrt{\frac{3}{2}} r^2 \frac{e^{i2\phi} - e^{-i2\phi}}{2}\sin^2\theta = \sqrt{\frac{3}{8}}(i4xy) = i\sqrt{6}xy = i\sqrt{\frac{3}{2}} r^2 \sin 2\phi \sin^2\theta \longrightarrow \mathbf{T}^2_2 - \mathbf{T}^2_{-2} = i\sqrt{6}\,\mathbf{J}_x\mathbf{J}_y$$

etc.

And, don't forget scalar: $\mathbf{T}^0_0 = \mathbf{J}_x{}^2 + \mathbf{J}_y{}^2 + \mathbf{J}_z{}^2 = \mathbf{J}^2$

New geometric approach to rotational eigenstates and spectra

Introduction to Rotational Energy Surfaces (RES) and multipole tensor expansion

Rank-2 tensors from D^2-matrix

➡ *Building Hamiltonian* $\mathbf{H} = A\mathbf{J}_x^{\,2} + B\mathbf{J}_y^{\,2} + C\mathbf{J}_z^{\,2}$ *out of scalar and tensor operators*

Comparing quantum and semi-classical calculations

Symmetric rotor levels and RES plots

Asymmetry rotor levels and RES plots

Spherical rotor levels and RES plots

SF_6 spectral fine structure

CF_4 spectral fine structure

Building Hamiltonian $\mathbf{H} = A\mathbf{J}_x{}^2 + B\mathbf{J}_y{}^2 + C\mathbf{J}_z{}^2$ *out of scalar and tensor operators*

$\mathbf{T}_0^0 = \mathbf{J}_x{}^2 + \mathbf{J}_y{}^2 + \mathbf{J}_z{}^2 = \mathbf{J}^2$	$\mathbf{T}_0^2 = \dfrac{2\mathbf{J}_z{}^2 - \mathbf{J}_x{}^2 - \mathbf{J}_y{}^2}{2} = \mathbf{J}^2 \dfrac{3\cos^2\theta - 1}{2} = \mathbf{J}^2 P_2(\cos\theta)$	$\mathbf{T}_2^2 + \mathbf{T}_{-2}^2 = \sqrt{6}\dfrac{\mathbf{J}_x{}^2 - \mathbf{J}_y{}^2}{2} = \sqrt{\dfrac{3}{2}}\mathbf{J}^2 \sin^2\theta \cos 2\phi$

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$\mathbf{T}_0^0 = \mathbf{J}_x{}^2 + \mathbf{J}_y{}^2 + \mathbf{J}_z{}^2 = \mathbf{J}^2$	$\mathbf{T}_0^2 = \frac{2\mathbf{J}_z{}^2 - \mathbf{J}_x{}^2 - \mathbf{J}_y{}^2}{2} = \mathbf{J}^2 \frac{3\cos^2\theta - 1}{2} = \mathbf{J}^2 P_2(\cos\theta)$	$\mathbf{T}_2^2 + \mathbf{T}_{-2}^2 = \sqrt{6}\frac{\mathbf{J}_x{}^2 - \mathbf{J}_y{}^2}{2} = \sqrt{\frac{3}{2}}\mathbf{J}^2 \sin^2\theta\cos 2\phi$

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$$= \left(\frac{1}{3}A + \frac{1}{3}B + \frac{1}{3}C\right)\left(\mathbf{J}_x{}^2 + \mathbf{J}_y{}^2 + \mathbf{J}_z{}^2\right)$$

$$+\left(\frac{-1}{6}A + \frac{-1}{6}B + \frac{2}{6}C\right)\left(-\mathbf{J}_x{}^2 - \mathbf{J}_y{}^2 + 2\mathbf{J}_z{}^2\right)$$

$$+\left(\frac{1}{2}A + \frac{-1}{2}B + 0\cdot C\right)\left(\mathbf{J}_x{}^2 - \mathbf{J}_y{}^2 + 0\right)$$

Building Hamiltonian $\mathbf{H} = A\mathbf{J}_x{}^2 + B\mathbf{J}_y{}^2 + C\mathbf{J}_z{}^2$ *out of scalar and tensor operators*

$$\mathbf{T}_0^0 = \mathbf{J}_x{}^2 + \mathbf{J}_y{}^2 + \mathbf{J}_z{}^2 = \mathbf{J}^2$$

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$\mathbf{T}^0_0 = \mathbf{J}_x{}^2 + \mathbf{J}_y{}^2 + \mathbf{J}_z{}^2 = \mathbf{J}^2$	$\mathbf{T}^2_0 = \dfrac{2\mathbf{J}_z{}^2 - \mathbf{J}_x{}^2 - \mathbf{J}_y{}^2}{2} = \mathbf{J}^2 \dfrac{3\cos^2\theta - 1}{2} = \mathbf{J}^2 P_2(\cos\theta)$	$\mathbf{T}^2_2 + \mathbf{T}^2_{-2} = \sqrt{6}\dfrac{\mathbf{J}_x{}^2 - \mathbf{J}_y{}^2}{2} = \sqrt{\dfrac{3}{2}}\mathbf{J}^2 \sin^2\theta \cos 2\phi$

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$$+\left(\frac{1}{\sqrt{6}}A + \frac{-1}{\sqrt{6}}B + 0\cdot C\right)\left(\sqrt{6}\frac{\mathbf{J}_x{}^2 - \mathbf{J}_y{}^2}{2}\right)$$

$$= \frac{1}{3}(A + B + C)(\mathbf{T}^0_0)$$
$$+\frac{1}{3}(-A - B + 2C)(\mathbf{T}^2_0)$$
$$+\frac{1}{\sqrt{6}}(A - B)(\mathbf{T}^2_2 + \mathbf{T}^2_{-2})$$

Building Hamiltonian $\mathbf{H} = A\mathbf{J}_x^2 + B\mathbf{J}_y^2 + C\mathbf{J}_z^2$ *out of scalar and tensor operators*

$\mathbf{T}_0^0 = \mathbf{J}_x^2 + \mathbf{J}_y^2 + \mathbf{J}_z^2 = \mathbf{J}^2$	$\mathbf{T}_0^2 = \frac{2\mathbf{J}_z^2 - \mathbf{J}_x^2 - \mathbf{J}_y^2}{2} = \mathbf{J}^2 \frac{3\cos^2\theta - 1}{2} = \mathbf{J}^2 P_2(\cos\theta)$	$\mathbf{T}_2^2 + \mathbf{T}_{-2}^2 = \sqrt{6}\frac{\mathbf{J}_x^2 - \mathbf{J}_y^2}{2} = \sqrt{\frac{3}{2}}\mathbf{J}^2 \sin^2\theta \cos 2\phi$

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

$$= (\tfrac{1}{3}A + \tfrac{1}{3}B + \tfrac{1}{3}C)(\mathbf{J}_x^2 + \mathbf{J}_y^2 + \mathbf{J}_z^2) \qquad = (\tfrac{1}{3}A + \tfrac{1}{3}B + \tfrac{1}{3}C)(\mathbf{J}_x^2 + \mathbf{J}_y^2 + \mathbf{J}_z^2) \qquad = \tfrac{1}{3}(A + B + C)(\mathbf{T}_0^0)$$

$$+(\tfrac{-1}{6}A + \tfrac{-1}{6}B + \tfrac{2}{6}C)(-\mathbf{J}_x^2 - \mathbf{J}_y^2 + 2\mathbf{J}_z^2) \qquad +(\tfrac{-1}{3}A + \tfrac{-1}{3}B + \tfrac{2}{3}C)(\frac{2\mathbf{J}_z^2 - \mathbf{J}_x^2 - \mathbf{J}_y^2}{2}) \qquad +\tfrac{1}{3}(-A - B + 2C)(\mathbf{T}_0^2)$$

$$+(\tfrac{1}{2}A + \tfrac{-1}{2}B + 0\cdot C)(\mathbf{J}_x^2 - \mathbf{J}_y^2 + 0) \qquad +(\tfrac{1}{\sqrt{6}}A + \tfrac{-1}{\sqrt{6}}B + 0\cdot C)(\sqrt{6}\frac{\mathbf{J}_x^2 - \mathbf{J}_y^2}{2}) \qquad +\tfrac{1}{\sqrt{6}}(A - B)(\mathbf{T}_2^2 + \mathbf{T}_{-2}^2)$$

Resulting ***asymmetric*** *top Hamiltonian expansion:*

asymmetry term

$$\mathbf{H} = A\mathbf{J}_x^2 + B\mathbf{J}_y^2 + C\mathbf{J}_z^2 = \frac{1}{3}(A + B + C)(\mathbf{T}_0^0) + \frac{1}{3}(2C - A - B)(\mathbf{T}_0^2) + \frac{A - B}{\sqrt{6}}(\mathbf{T}_2^2 + \mathbf{T}_{-2}^2)$$

Building Hamiltonian $\mathbf{H} = A\mathbf{J}_x^{\,2} + B\mathbf{J}_y^{\,2} + C\mathbf{J}_z^{\,2}$ *out of scalar and tensor operators*

$\mathbf{T}_0^0 = \mathbf{J}_x^{\,2} + \mathbf{J}_y^{\,2} + \mathbf{J}_z^{\,2} = \mathbf{J}^2$	$\mathbf{T}_0^2 = \frac{2\mathbf{J}_z^{\,2} - \mathbf{J}_x^{\,2} - \mathbf{J}_y^{\,2}}{2} = \mathbf{J}^2 \frac{3\cos^2\theta - 1}{2} = \mathbf{J}^2 P_2(\cos\theta)$	$\mathbf{T}_2^2 + \mathbf{T}_{-2}^2 = \sqrt{6}\frac{\mathbf{J}_x^{\,2} - \mathbf{J}_y^{\,2}}{2} = \sqrt{\frac{3}{2}}\mathbf{J}^2 \sin^2\theta \cos 2\phi$

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

$$= (\tfrac{1}{3}A + \tfrac{1}{3}B + \tfrac{1}{3}C)(\mathbf{J}_x^{\,2} + \mathbf{J}_y^{\,2} + \mathbf{J}_z^{\,2}) \quad = (\tfrac{1}{3}A + \tfrac{1}{3}B + \tfrac{1}{3}C)(\mathbf{J}_x^{\,2} + \mathbf{J}_y^{\,2} + \mathbf{J}_z^{\,2}) \quad = \tfrac{1}{3}(A + B + C)(\mathbf{T}_0^0)$$

$$+(\tfrac{-1}{6}A + \tfrac{-1}{6}B + \tfrac{2}{6}C)(-\mathbf{J}_x^{\,2} - \mathbf{J}_y^{\,2} + 2\mathbf{J}_z^{\,2}) \quad +(\tfrac{-1}{3}A + \tfrac{-1}{3}B + \tfrac{2}{3}C)(\frac{2\mathbf{J}_z^{\,2} - \mathbf{J}_x^{\,2} - \mathbf{J}_y^{\,2}}{2}) \quad + \tfrac{1}{3}(-A - B + 2C)(\mathbf{T}_0^2)$$

$$+(\tfrac{1}{2}A + \tfrac{-1}{2}B + 0\cdot C)(\mathbf{J}_x^{\,2} - \mathbf{J}_y^{\,2} + 0) \quad +(\tfrac{1}{\sqrt{6}}A + \tfrac{-1}{\sqrt{6}}B + 0\cdot C)(\sqrt{6}\frac{\mathbf{J}_x^{\,2} - \mathbf{J}_y^{\,2}}{2}) \quad + \tfrac{1}{\sqrt{6}}(A - B)(\mathbf{T}_2^2 + \mathbf{T}_{-2}^2)$$

Resulting asymmetric top Hamiltonian expansion:

$$\mathbf{H} = A\mathbf{J}_x^{\,2} + B\mathbf{J}_y^{\,2} + C\mathbf{J}_z^{\,2} = \frac{1}{3}(A + B + C)(\mathbf{T}_0^0) + \frac{1}{3}(2C - A - B)(\mathbf{T}_0^2) + \overbrace{\frac{A - B}{\sqrt{6}}}^{\textit{asymmetry term}}(\mathbf{T}_2^2 + \mathbf{T}_{-2}^2)$$

Resulting semi-classical asymmetric top Hamiltonian expansion:

$$\mathbf{H} = A\mathbf{J}_x^{\,2} + B\mathbf{J}_y^{\,2} + C\mathbf{J}_z^{\,2} = \frac{1}{3}(A + B + C)(\mathbf{J}^2) + \frac{1}{3}(2C - A - B)(\mathbf{J}^2\frac{3\cos^2\theta - 1}{2}) + \overbrace{\frac{A - B}{\sqrt{6}}}^{\textit{asymmetry term}}(\sqrt{\frac{3}{2}}\mathbf{J}^2 \sin^2\theta \cos 2\phi)$$

Building Hamiltonian $\mathbf{H} = A\mathbf{J}_x^2 + B\mathbf{J}_y^2 + C\mathbf{J}_z^2$ *out of scalar and tensor operators*

$\mathbf{T}_0^0 = \mathbf{J}_x^2 + \mathbf{J}_y^2 + \mathbf{J}_z^2 = \mathbf{J}^2$	$\mathbf{T}_0^2 = \frac{2\mathbf{J}_z^2 - \mathbf{J}_x^2 - \mathbf{J}_y^2}{2} = \mathbf{J}^2 \frac{3\cos^2\theta - 1}{2} = \mathbf{J}^2 P_2(\cos\theta)$	$\mathbf{T}_2^2 + \mathbf{T}_{-2}^2 = \sqrt{6}\frac{\mathbf{J}_x^2 - \mathbf{J}_y^2}{2} = \sqrt{\frac{3}{2}}\mathbf{J}^2 \sin^2\theta \cos 2\phi$

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

$$= (\tfrac{1}{3}A + \tfrac{1}{3}B + \tfrac{1}{3}C)(\mathbf{J}_x^2 + \mathbf{J}_y^2 + \mathbf{J}_z^2) \quad = (\tfrac{1}{3}A + \tfrac{1}{3}B + \tfrac{1}{3}C)(\mathbf{J}_x^2 + \mathbf{J}_y^2 + \mathbf{J}_z^2) \quad = \tfrac{1}{3}(A + B + C)(\mathbf{T}_0^0)$$

$$+(\tfrac{-1}{6}A + \tfrac{-1}{6}B + \tfrac{2}{6}C)(-\mathbf{J}_x^2 - \mathbf{J}_y^2 + 2\mathbf{J}_z^2) \quad +(\tfrac{-1}{3}A + \tfrac{-1}{3}B + \tfrac{2}{3}C)(\frac{2\mathbf{J}_z^2 - \mathbf{J}_x^2 - \mathbf{J}_y^2}{2}) \quad +\tfrac{1}{3}(-A - B + 2C)(\mathbf{T}_0^2)$$

$$+(\tfrac{1}{2}A + \tfrac{-1}{2}B + 0\cdot C)(\mathbf{J}_x^2 - \mathbf{J}_y^2 + 0) \quad +(\tfrac{1}{\sqrt{6}}A + \tfrac{-1}{\sqrt{6}}B + 0\cdot C)(\sqrt{6}\frac{\mathbf{J}_x^2 - \mathbf{J}_y^2}{2}) \quad +\tfrac{1}{\sqrt{6}}(A - B)(\mathbf{T}_2^2 + \mathbf{T}_{-2}^2)$$

Resulting asymmetric top Hamiltonian expansion:

asymmetry term

$$\mathbf{H} = A\mathbf{J}_x^2 + B\mathbf{J}_y^2 + C\mathbf{J}_z^2 = \frac{1}{3}(A + B + C)(\mathbf{T}_0^0) + \frac{1}{3}(2C - A - B)(\mathbf{T}_0^2) + \frac{A - B}{\sqrt{6}}(\mathbf{T}_2^2 + \mathbf{T}_{-2}^2)$$

Resulting semi-classical asymmetric top Hamiltonian expansion:

asymmetry term

$$\mathbf{H} = A\mathbf{J}_x^2 + B\mathbf{J}_y^2 + C\mathbf{J}_z^2 = \frac{1}{3}(A + B + C)(\mathbf{J}^2) + \frac{1}{3}(2C - A - B)(\mathbf{J}^2\frac{3\cos^2\theta - 1}{2}) + \frac{A - B}{\sqrt{6}}(\sqrt{\frac{3}{2}}\mathbf{J}^2 \sin^2\theta\cos 2\phi)$$

$$\mathbf{H} = A\mathbf{J}_x^2 + B\mathbf{J}_y^2 + C\mathbf{J}_z^2 = \mathbf{J}^2\left[\frac{A + B + C}{3} + \frac{2C - A - B}{6}(3\cos^2\theta - 1) + \frac{A - B}{2}\sin^2\theta\cos 2\phi\right]$$

Building Hamiltonian $\mathbf{H} = A\mathbf{J}_x^{\,2} + B\mathbf{J}_y^{\,2} + C\mathbf{J}_z^{\,2}$ *out of scalar and tensor operators*

$$\mathbf{T}_0^0 = \mathbf{J}_x^{\,2} + \mathbf{J}_y^{\,2} + \mathbf{J}_z^{\,2} = \mathbf{J}^2$$

$$\mathbf{T}_0^2 = \frac{2\mathbf{J}_z^{\,2} - \mathbf{J}_x^{\,2} - \mathbf{J}_y^{\,2}}{2} = \mathbf{J}^2 \frac{3\cos^2\theta - 1}{2} = \mathbf{J}^2 P_2(\cos\theta)$$

$$\mathbf{T}_2^2 + \mathbf{T}_{-2}^2 = \sqrt{6}\frac{\mathbf{J}_x^{\,2} - \mathbf{J}_y^{\,2}}{2} = \sqrt{\frac{3}{2}}\mathbf{J}^2 \sin^2\theta\cos 2\phi$$

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

$$= (\tfrac{1}{3}A + \tfrac{1}{3}B + \tfrac{1}{3}C)(\mathbf{J}_x^{\,2} + \mathbf{J}_y^{\,2} + \mathbf{J}_z^{\,2}) + (\tfrac{-1}{6}A + \tfrac{-1}{6}B + \tfrac{2}{6}C)(-\mathbf{J}_x^{\,2} - \mathbf{J}_y^{\,2} + 2\mathbf{J}_z^{\,2}) + (\tfrac{1}{2}A + \tfrac{-1}{2}B + 0\cdot C)(\mathbf{J}_x^{\,2} - \mathbf{J}_y^{\,2} + 0)$$

$$= (\tfrac{1}{3}A + \tfrac{1}{3}B + \tfrac{1}{3}C)(\mathbf{J}_x^{\,2} + \mathbf{J}_y^{\,2} + \mathbf{J}_z^{\,2}) + (\tfrac{-1}{3}A + \tfrac{-1}{3}B + \tfrac{2}{3}C)\left(\frac{2\mathbf{J}_z^{\,2} - \mathbf{J}_x^{\,2} - \mathbf{J}_y^{\,2}}{2}\right) + (\tfrac{1}{\sqrt{6}}A + \tfrac{-1}{\sqrt{6}}B + 0\cdot C)\left(\sqrt{6}\frac{\mathbf{J}_x^{\,2} - \mathbf{J}_y^{\,2}}{2}\right)$$

$$= \tfrac{1}{3}(A + B + C)(\mathbf{T}_0^0) + \tfrac{1}{3}(-A - B + 2C)(\mathbf{T}_0^2) + \tfrac{1}{\sqrt{6}}(A - B)(\mathbf{T}_2^2 + \mathbf{T}_{-2}^2)$$

Resulting asymmetric top Hamiltonian expansion:

asymmetry term

$$\mathbf{H} = A\mathbf{J}_x^{\,2} + B\mathbf{J}_y^{\,2} + C\mathbf{J}_z^{\,2} = \frac{1}{3}(A + B + C)(\mathbf{T}_0^0) + \frac{1}{3}(2C - A - B)(\mathbf{T}_0^2) + \frac{A - B}{\sqrt{6}}(\mathbf{T}_2^2 + \mathbf{T}_{-2}^2)$$

Resulting semi-classical asymmetric top Hamiltonian expansion:

asymmetry term

$$\mathbf{H} = A\mathbf{J}_x^{\,2} + B\mathbf{J}_y^{\,2} + C\mathbf{J}_z^{\,2} = \frac{1}{3}(A + B + C)(\mathbf{J}^2) + \frac{1}{3}(2C - A - B)\left(\mathbf{J}^2\frac{3\cos^2\theta - 1}{2}\right) + \frac{A - B}{\sqrt{6}}\left(\sqrt{\frac{3}{2}}\mathbf{J}^2 \sin^2\theta\cos 2\phi\right)$$

$$\mathbf{H} = A\mathbf{J}_x^{\,2} + B\mathbf{J}_y^{\,2} + C\mathbf{J}_z^{\,2} = \mathbf{J}^2\left[\frac{A + B + C}{3} + \frac{2C - A - B}{6}(3\cos^2\theta - 1) + \frac{A - B}{2}\sin^2\theta\cos 2\phi\right]$$

Resulting semi-classical symmetric top Hamiltonian expansion:

$$\mathbf{H} = B\mathbf{J}_x^{\,2} + B\mathbf{J}_y^{\,2} + C\mathbf{J}_z^{\,2} = \mathbf{J}^2\left[\frac{B + B + C}{3} + \frac{2C - B - B}{6}(3\cos^2\theta - 1) + \frac{B - B}{2}\sin^2\theta\cos 2\phi\right] = \mathbf{J}^2\left[B + \frac{C - B}{3}3\cos^2\theta\right]$$

Building Hamiltonian $\mathbf{H} = A\mathbf{J}_x{}^2 + B\mathbf{J}_y{}^2 + C\mathbf{J}_z{}^2$ *out of scalar and tensor operators*

$\mathbf{T}_0^0 = \mathbf{J}_x{}^2 + \mathbf{J}_y{}^2 + \mathbf{J}_z{}^2 = \mathbf{J}^2$	$\mathbf{T}_0^2 = \frac{2\mathbf{J}_z{}^2 - \mathbf{J}_x{}^2 - \mathbf{J}_y{}^2}{2} = \mathbf{J}^2 \frac{3\cos^2\theta - 1}{2} = \mathbf{J}^2 P_2(\cos\theta)$	$\mathbf{T}_2^2 + \mathbf{T}_{-2}^2 = \sqrt{6}\frac{\mathbf{J}_x{}^2 - \mathbf{J}_y{}^2}{2} = \sqrt{\frac{3}{2}}\mathbf{J}^2 \sin^2\theta\cos 2\phi$

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

$$= \left(\frac{1}{3}A + \frac{1}{3}B + \frac{1}{3}C\right)\left(\mathbf{J}_x{}^2 + \mathbf{J}_y{}^2 + \mathbf{J}_z{}^2\right) = \left(\frac{1}{3}A + \frac{1}{3}B + \frac{1}{3}C\right)\left(\mathbf{J}_x{}^2 + \mathbf{J}_y{}^2 + \mathbf{J}_z{}^2\right) = \frac{1}{3}(A + B + C)(\mathbf{T}_0^0)$$

$$+\left(\frac{-1}{6}A + \frac{-1}{6}B + \frac{2}{6}C\right)\left(-\mathbf{J}_x{}^2 - \mathbf{J}_y{}^2 + 2\mathbf{J}_z{}^2\right) \quad +\left(\frac{-1}{3}A + \frac{-1}{3}B + \frac{2}{3}C\right)\left(\frac{2\mathbf{J}_z{}^2 - \mathbf{J}_x{}^2 - \mathbf{J}_y{}^2}{2}\right) \quad +\frac{1}{3}(-A - B + 2C)(\mathbf{T}_0^2)$$

$$+\left(\frac{1}{2}A + \frac{-1}{2}B + 0\cdot C\right)\left(\mathbf{J}_x{}^2 - \mathbf{J}_y{}^2 + 0\right) \quad +\left(\frac{1}{\sqrt{6}}A + \frac{-1}{\sqrt{6}}B + 0\cdot C\right)\left(\sqrt{6}\frac{\mathbf{J}_x{}^2 - \mathbf{J}_y{}^2}{2}\right) \quad +\frac{1}{\sqrt{6}}(A - B)(\mathbf{T}_2^2 + \mathbf{T}_{-2}^2)$$

Resulting asymmetric top Hamiltonian expansion:

asymmetry term

$$\mathbf{H} = A\mathbf{J}_x{}^2 + B\mathbf{J}_y{}^2 + C\mathbf{J}_z{}^2 = \frac{1}{3}(A + B + C)(\mathbf{T}_0^0) + \frac{1}{3}(2C - A - B)(\mathbf{T}_0^2) + \frac{A - B}{\sqrt{6}}(\mathbf{T}_2^2 + \mathbf{T}_{-2}^2)$$

Resulting semi-classical asymmetric top Hamiltonian expansion:

asymmetry term

$$\mathbf{H} = A\mathbf{J}_x{}^2 + B\mathbf{J}_y{}^2 + C\mathbf{J}_z{}^2 = \frac{1}{3}(A + B + C)(\mathbf{J}^2) + \frac{1}{3}(2C - A - B)\left(\mathbf{J}^2\frac{3\cos^2\theta - 1}{2}\right) + \frac{A - B}{\sqrt{6}}\left(\sqrt{\frac{3}{2}}\mathbf{J}^2\sin^2\theta\cos 2\phi\right)$$

$$\mathbf{H} = A\mathbf{J}_x{}^2 + B\mathbf{J}_y{}^2 + C\mathbf{J}_z{}^2 = \mathbf{J}^2\left[\frac{A + B + C}{3} + \frac{2C - A - B}{6}(3\cos^2\theta - 1) + \frac{A - B}{2}\sin^2\theta\cos 2\phi\right]$$

Resulting semi-classical symmetric top Hamiltonian expansion:

$$\mathbf{H} = B\mathbf{J}_x{}^2 + B\mathbf{J}_y{}^2 + C\mathbf{J}_z{}^2 = \mathbf{J}^2\left[\frac{B + B + C}{3} + \frac{2C - B - B}{6}(3\cos^2\theta - 1) + \frac{B - B}{2}\sin^2\theta\cos 2\phi\right] = \mathbf{J}^2\left[B + (C - B)\cos^2\theta\right]$$

$$= B\mathbf{J}^2 + (C - B)\mathbf{J}_z{}^2 = B\mathbf{J}^2 + (C - B)\mathbf{J}^2\cos^2\theta$$

New geometric approach to rotational eigenstates and spectra

Introduction to Rotational Energy Surfaces (RES) and multipole tensor expansion

Rank-2 tensors from D^2-matrix

Building Hamiltonian $\mathbf{H} = A\mathbf{J}_x^2 + B\mathbf{J}_y^2 + C\mathbf{J}_z^2$ *out of scalar and tensor operators*

➡ *Comparing quantum and semi-classical calculations*

Symmetric rotor levels and RES plots

Asymmetry rotor levels and RES plots

Spherical rotor levels and RES plots

SF_6 spectral fine structure

CF_4 spectral fine structure

Some New Approaches for Treating Rotor Hamiltonians

(Q) Quantum: *Find H-matrix rep and diagonalize by computer*

$$\left\langle \begin{matrix} J' \\ K' \end{matrix} \middle| \mathbf{T}_0^{(0)} \middle| \begin{matrix} J \\ K \end{matrix} \right\rangle = \delta_{K'K}^{J'J} J(J+1)$$

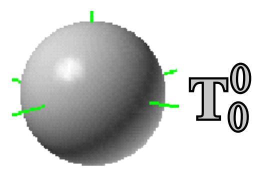
(But, is there life after diagonalization?!?)

$$\left\langle \begin{matrix} J' \\ K' \end{matrix} \middle| \mathbf{T}_0^{(2)} \middle| \begin{matrix} J \\ K \end{matrix} \right\rangle = C_{0\,K\,K'}^{2\,J\,J'} \left\langle J' \| 2 \| J \right\rangle$$

$$\left\langle \begin{matrix} J' \\ K' \end{matrix} \middle| \mathbf{T}_q^{(2)} \middle| \begin{matrix} J \\ K \end{matrix} \right\rangle = C_{q\,K\,K'}^{2\,J\,J'} \left\langle J' \| 2 \| J \right\rangle$$

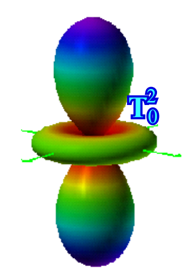
(P) Classical RES Plot: *Rotational Energy (RE) surfaces and/or H-phase paths*

$$\left\langle \mathbf{T}_0^{(0)} \right\rangle = cY_0^0 = J(J+1)$$

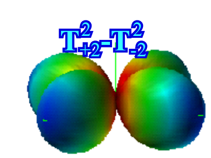


(tensor operator $\mathbf{T}_q^k$ *is replaced by spherical harmonic* $Y_q^k[\beta,\gamma]$*)*

$$\left\langle 2\mathbf{T}_0^{(2)} \right\rangle = cY_0^2 = J(J+1)\left(3\cos^2\beta - 1\right)$$



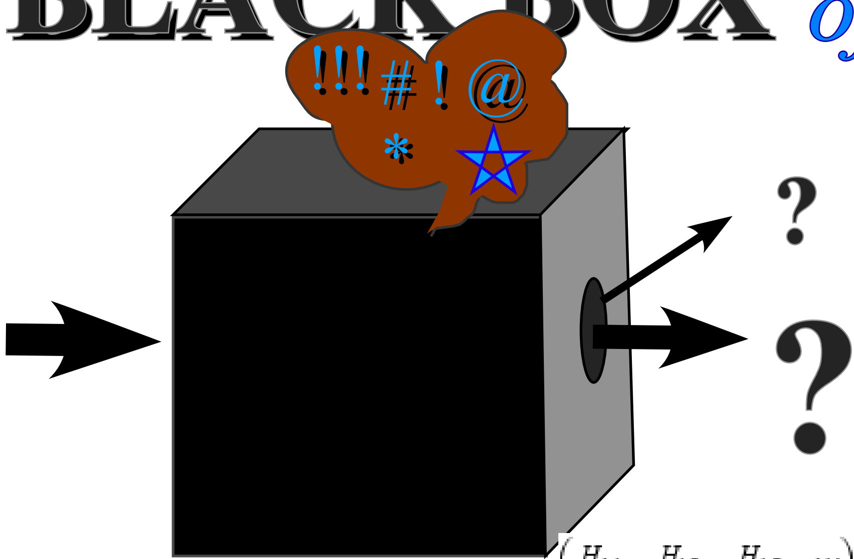
$$\sqrt{\frac{2}{3}}\left\langle \left(\mathbf{T}_2^{(2)} - \mathbf{T}_{-2}^{(2)}\right) \right\rangle = c\left(Y_2^2 - Y_2^2\right) = J(J+1)\left(\sin^2\beta\cos 2\gamma\right)$$



(S) Semiclassical: *Some of both*

Peeking into **BLACK BOX** *of matrix diagonalization:*

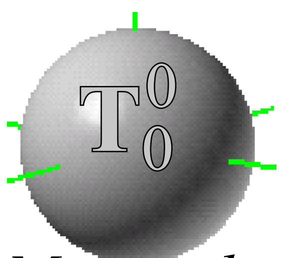
$$\mathbf{H}=\begin{pmatrix} H_{11} & H_{12} & H_{13} & \cdots \\ H_{21} & H_{22} & H_{23} & \cdots \\ H_{31} & H_{32} & H_{33} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$



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 +..*

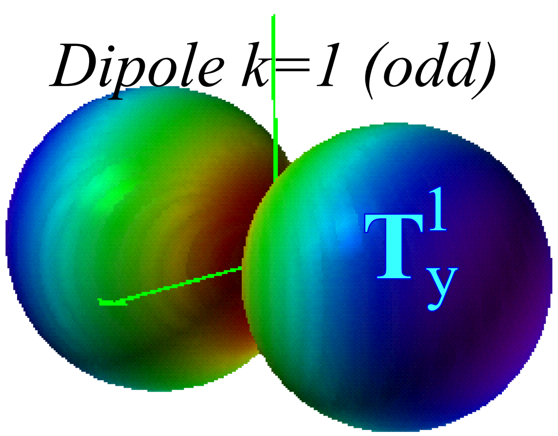
$$\mathbf{H}= a\mathbf{T}^0_0+b\mathbf{T}^1_0+c\mathbf{T}^1_1+\ldots+d\mathbf{T}^2_0+e\mathbf{T}^2_1+\ldots=\Sigma c^k_q\,\mathbf{T}^k_q$$



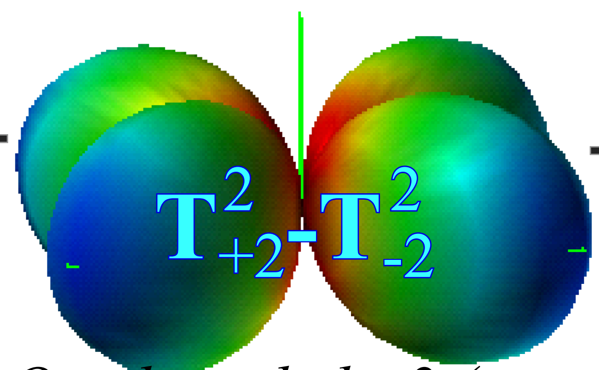
Monopole
k=0 (even)

+

Dipole k=1 (odd)



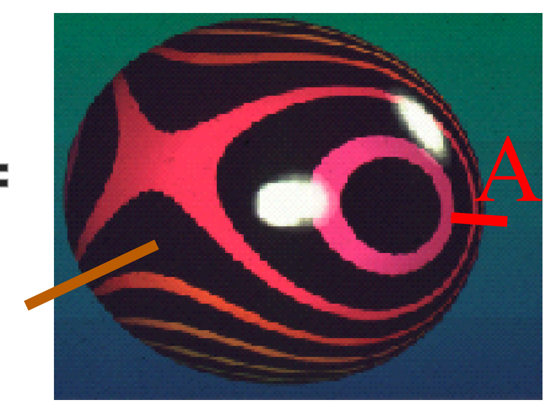
+



Quadrupole k=2 (even)

+... =

mixed-k



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

2-by-2 case:

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

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

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

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)

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)*

$$\mathbf{u}^2_{+2}=\begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 0 & 0 & 0\end{pmatrix} \quad \mathbf{u}^2_{+1}=\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0\end{pmatrix}\frac{1}{\sqrt{2}} \quad \mathbf{u}^2_{0}=\begin{pmatrix} 1 & 0 & 0 \\ 0 & -2 & 0 \\ 0 & 0 & 1\end{pmatrix}\frac{1}{\sqrt{6}} \quad \mathbf{u}^2_{-1}=\begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & 0\end{pmatrix}\frac{1}{\sqrt{2}} \quad \mathbf{u}^2_{-2}=\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 1 & 0 & 0\end{pmatrix}$$

rank-2 (tensor)

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

rank-1 (vector)

$$\mathbf{u}^0_{0}=\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1\end{pmatrix}\frac{1}{\sqrt{3}}$$

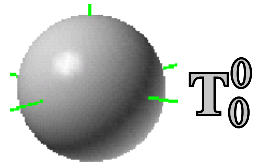
rank-0 (scalar)

Mutually commuting diagonal operators

Some New Approaches for Treating Rotor Hamiltonians (contd)

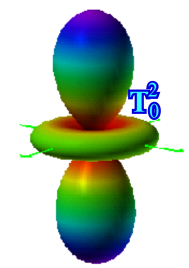
(P) Classical RE Plot: *Rotational Energy (RE) surfaces and/or H-phase paths*

$$\left\langle \mathbf{T}_0^{(0)} \right\rangle = cY_0^0 = J(J+1)$$

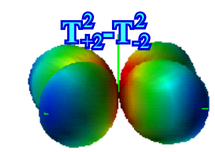


(But, there IS life before AND after diagonalization!)

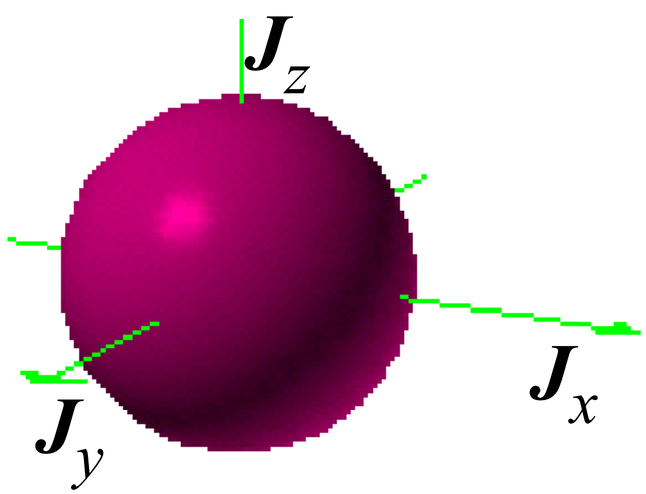
$$\left\langle 2\mathbf{T}_0^{(2)} \right\rangle = cY_0^2 = J(J+1)\left(3\cos^2\beta - 1\right)$$



$$\sqrt{\frac{2}{3}}\left\langle \left(\mathbf{T}_2^{(2)} - \mathbf{T}_{-2}^{(2)}\right) \right\rangle = c\left(Y_2^2 - Y_{-2}^2\right) = J(J+1)\left(\sin^2\beta\cos 2\gamma\right)$$

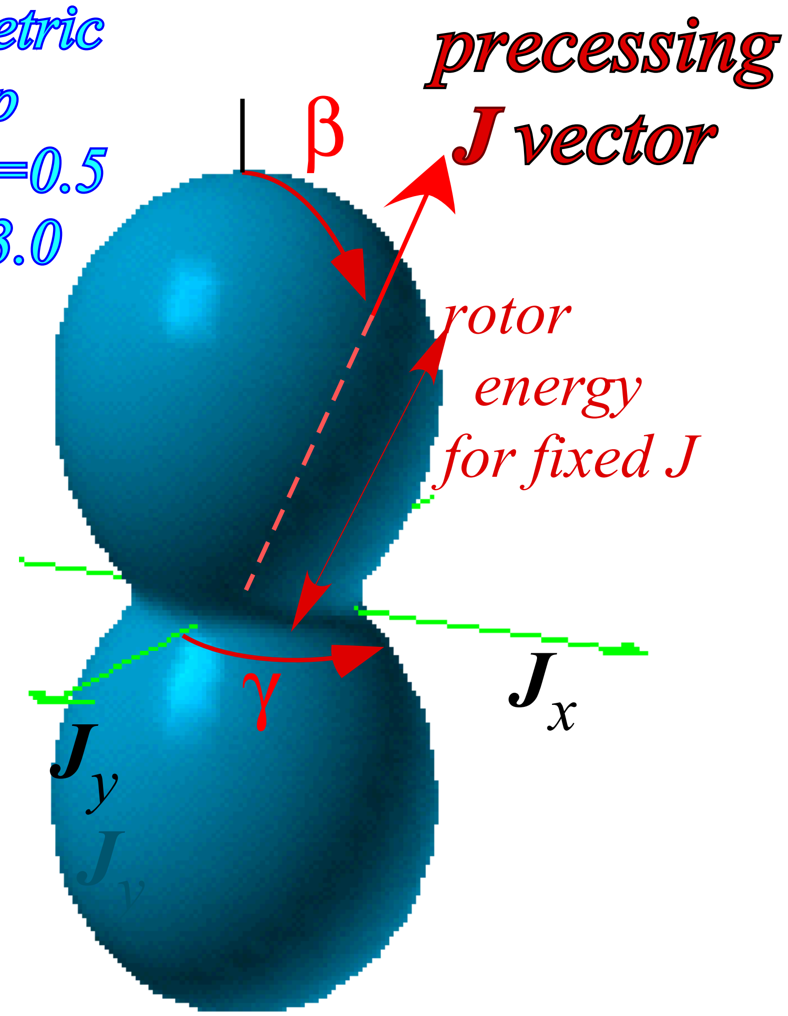


Spherical Top
$A = B = C = 1.0$

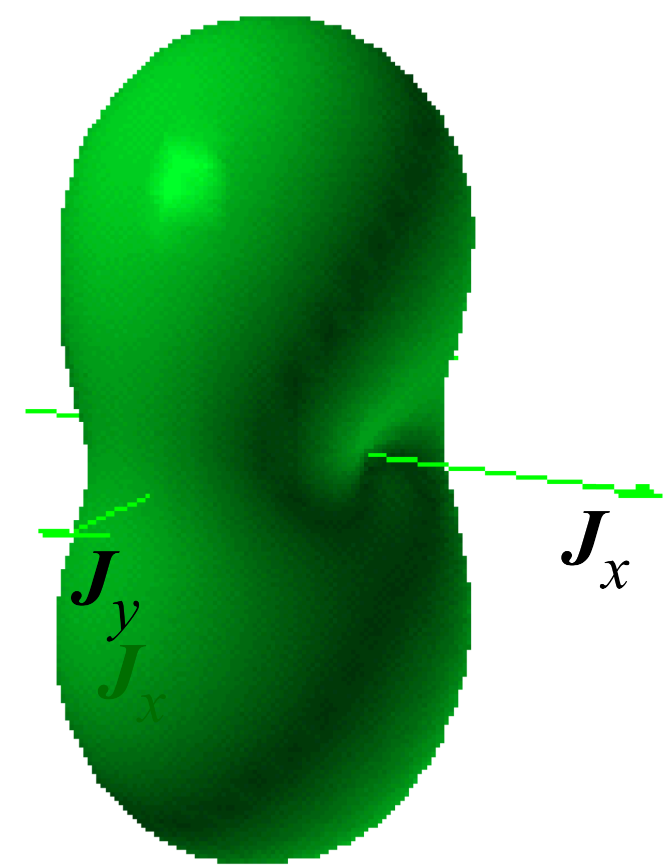


RE surface
Energy plotted radially
vs.
direction of J-vector
|for fixed magnitude |J

Symmetric Top
$A = B = 0.5$
$C = 3.0$



Asymmetric Top
$A = 0.5$
$B = 1.5$
$C = 3.0$



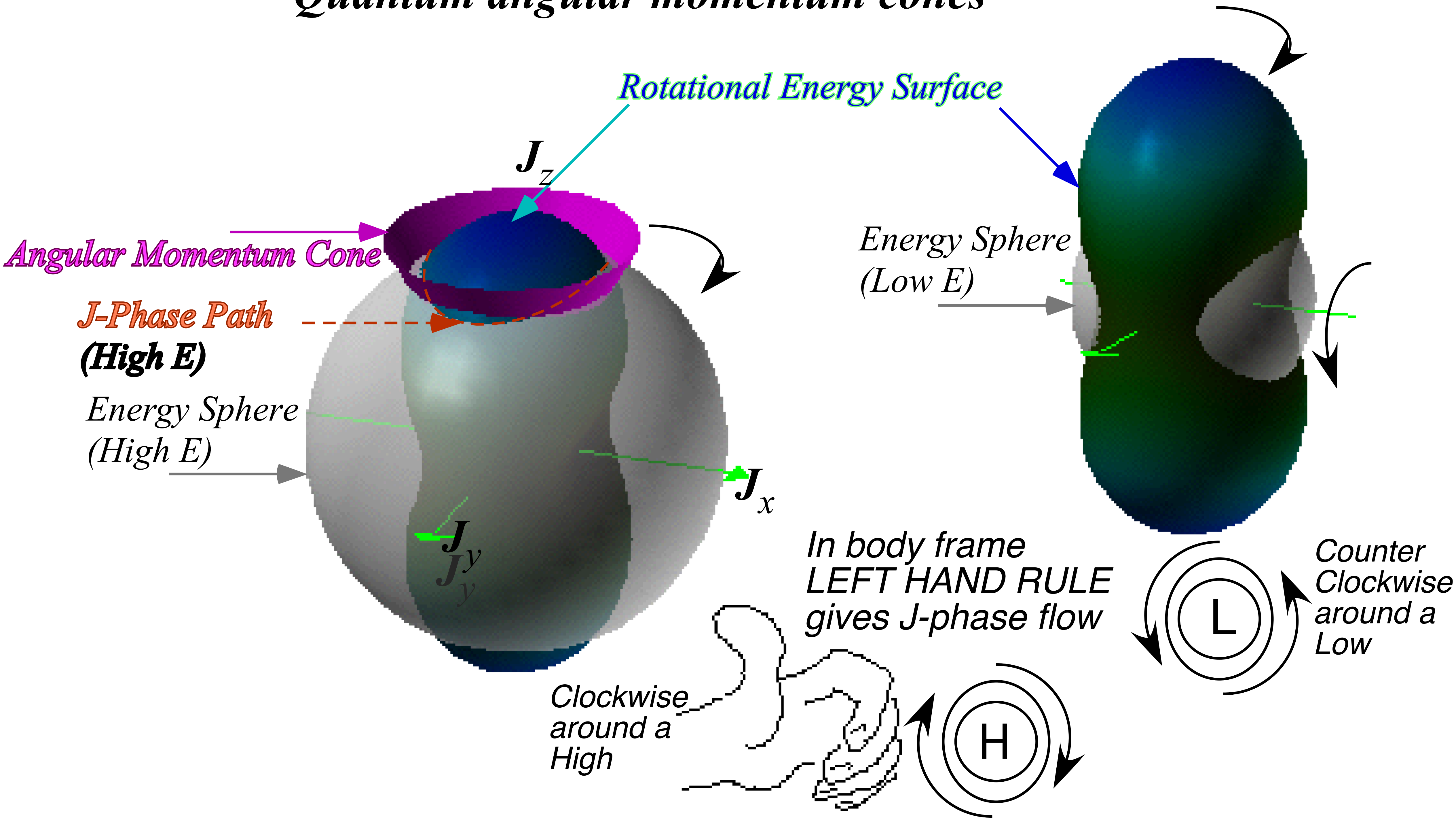
(S) Semiclassical Analysis

Uses

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

and

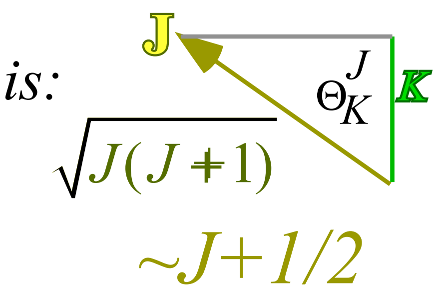
Quantum angular momentum cones



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

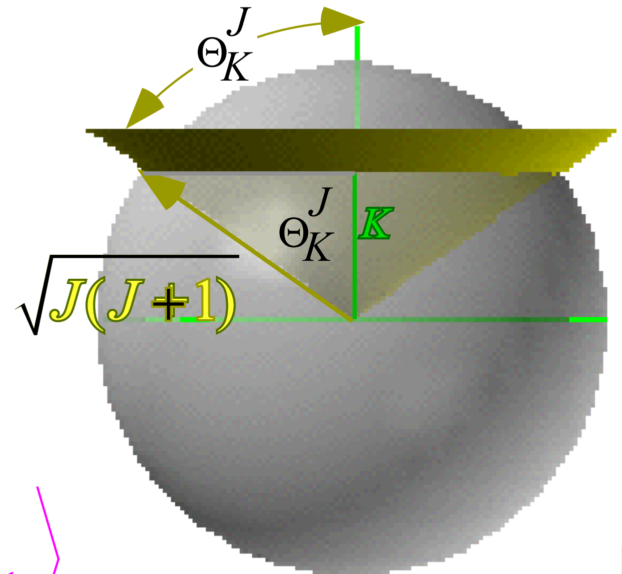
$$\mathbf{J}_z \left| \begin{matrix} J \\ K \end{matrix} \right\rangle = K \left| \begin{matrix} J \\ K \end{matrix} \right\rangle$$

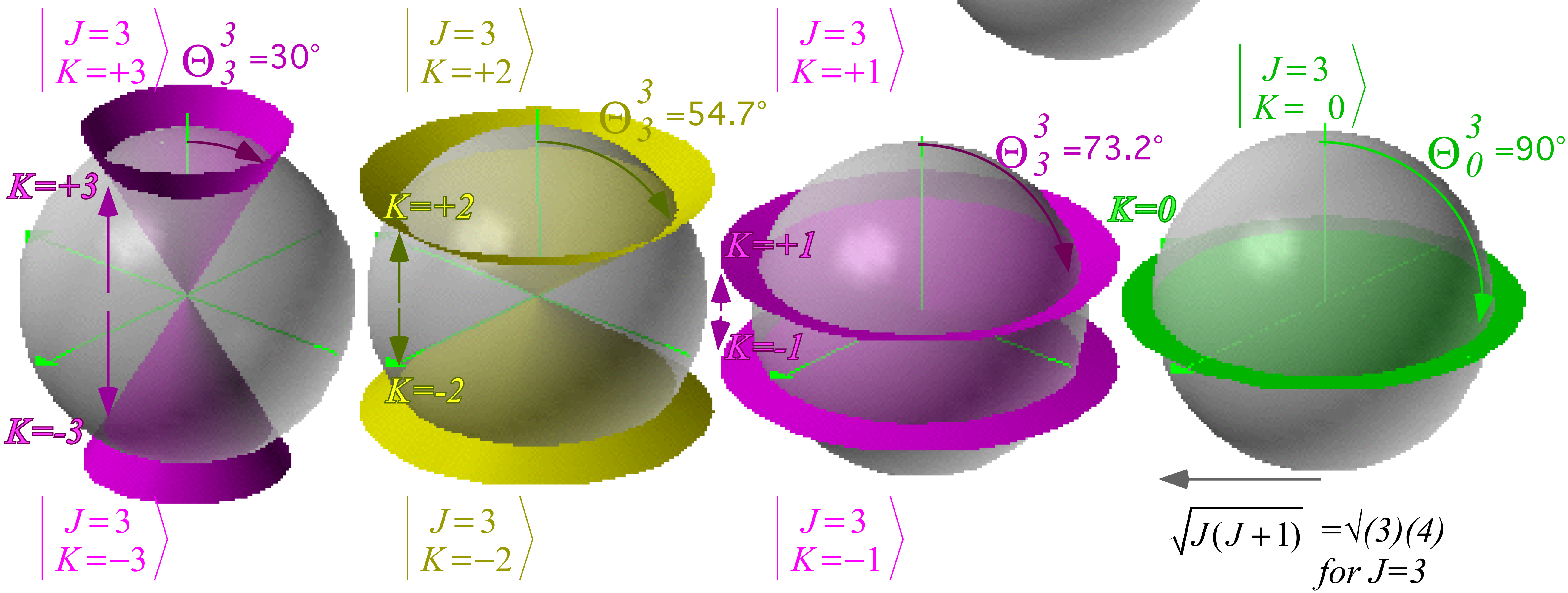
Interpreted "Literally" is:



Quantum Angular Cone Uncertainty Angles

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





New geometric approach to rotational eigenstates and spectra

Introduction to Rotational Energy Surfaces (RES) and multipole tensor expansion

Rank-2 tensors from D^2-matrix

Building Hamiltonian $\mathbf{H} = A\mathbf{J}_x^2 + B\mathbf{J}_y^2 + C\mathbf{J}_z^2$ *out of scalar and tensor operators*

Comparing quantum and semi-classical calculations

➡ *Symmetric rotor levels and RES plots*

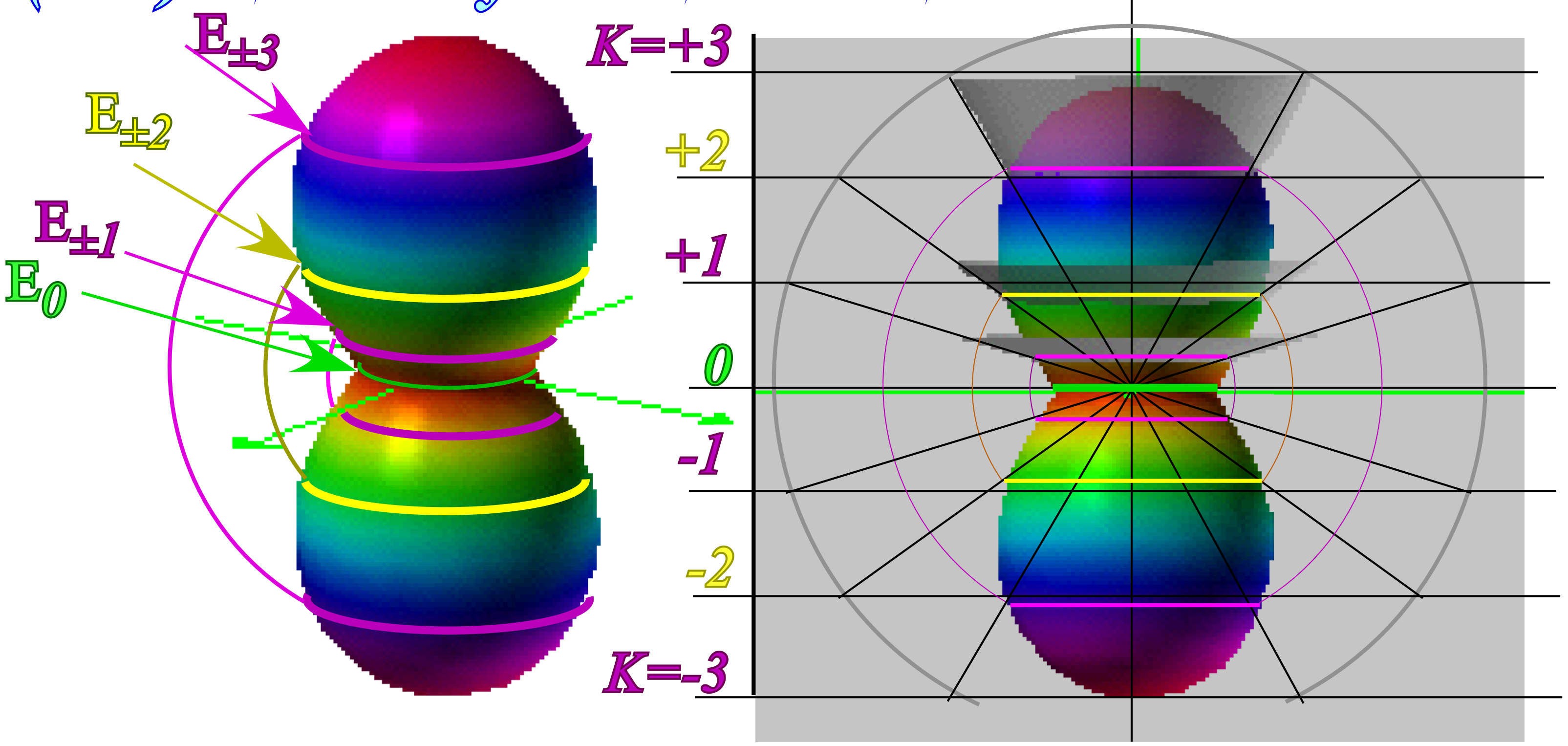
Asymmetry rotor levels and RES plots

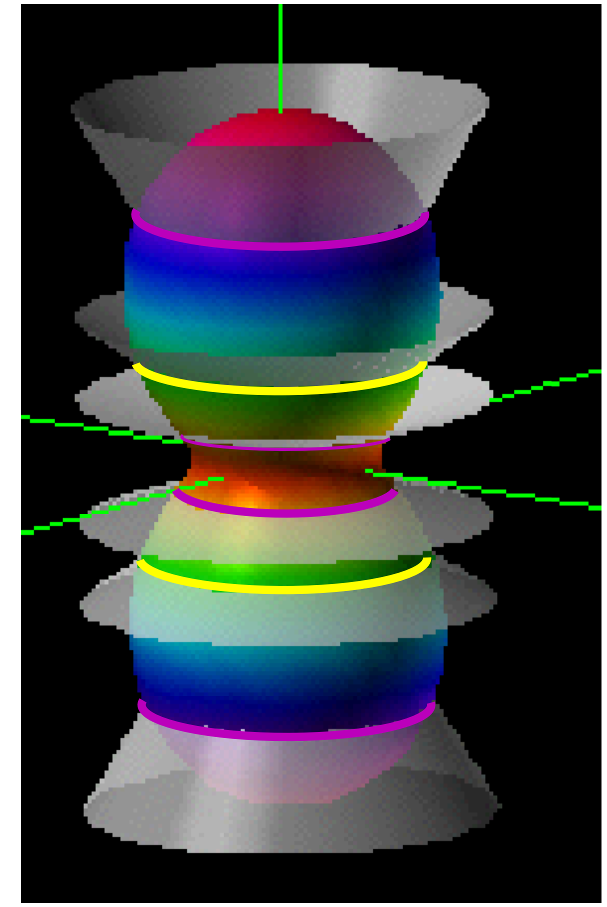
Spherical rotor levels and RES plots

SF_6 spectral fine structure

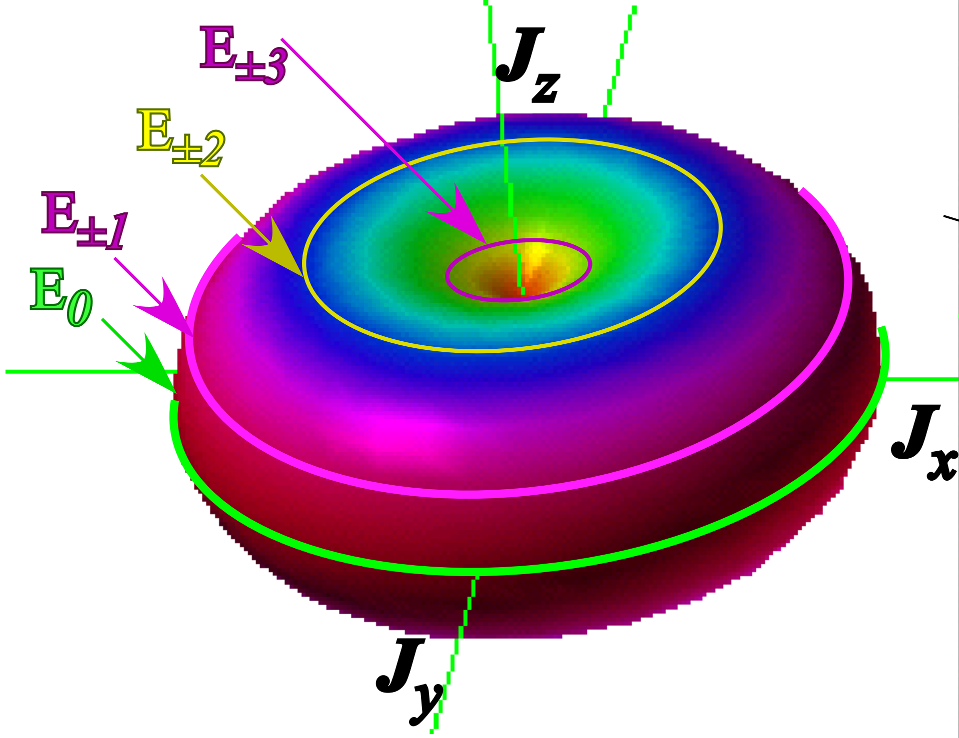
CF_4 spectral fine structure

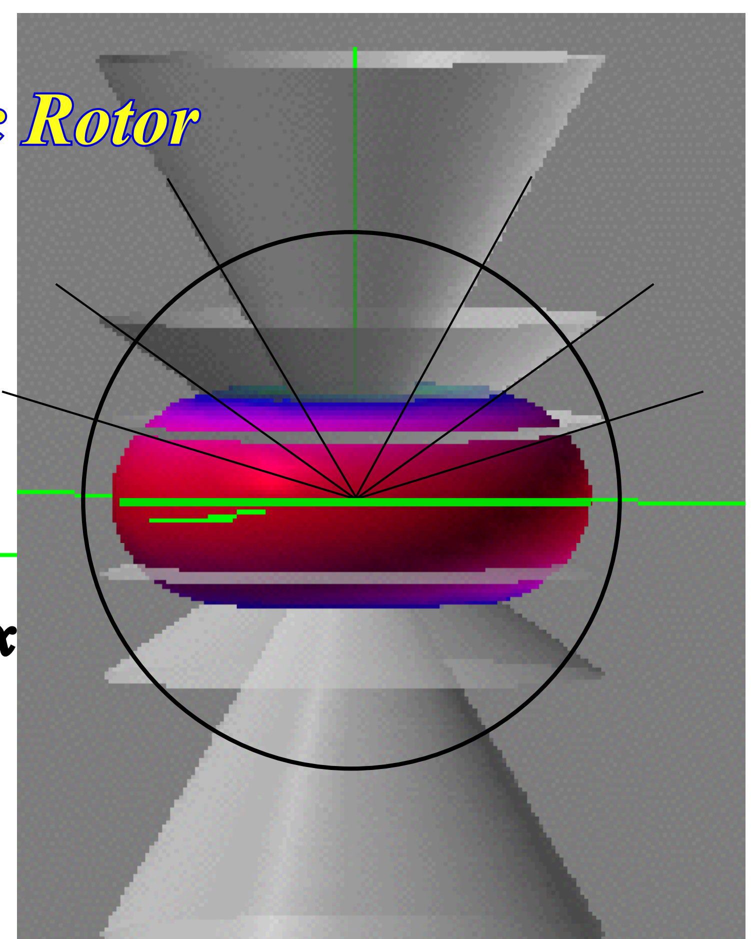
(S) Semiclassical J-Phase Paths for
(J=3) Prolate Symmetric Rotor

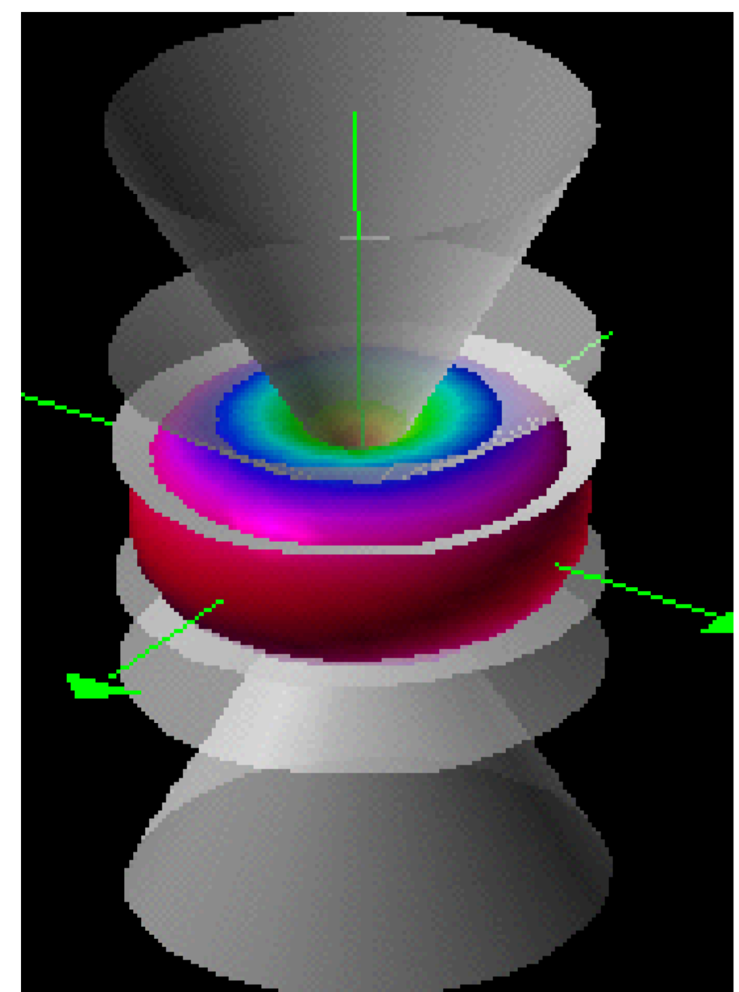




(J=3) Oblate Symmetric Rotor







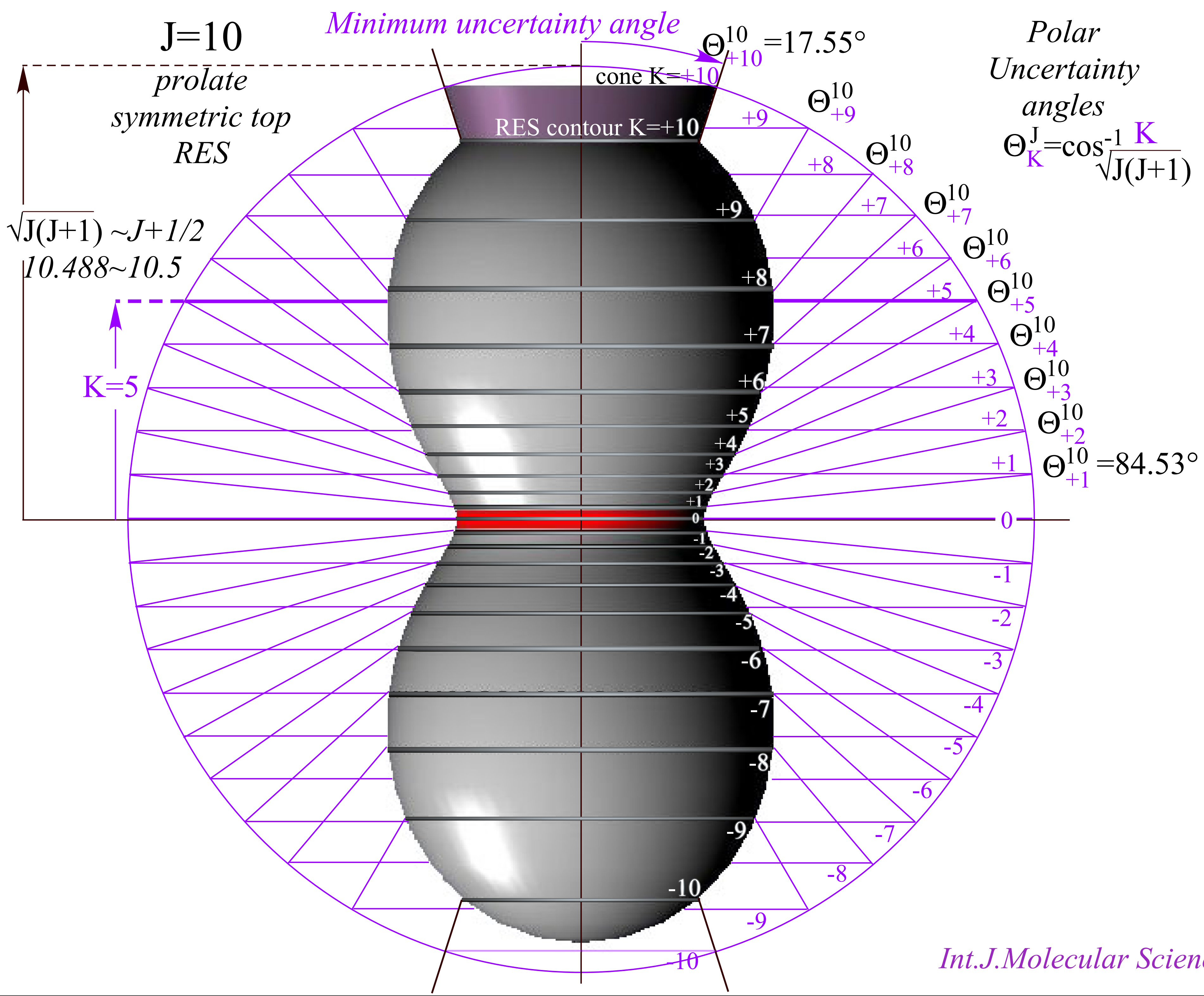
Rotational Energy Surface (RES):

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

$\left|\begin{matrix} j \\ m,n \end{matrix}\right\rangle$

Conventional notation: $n=K$

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



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

Rotational Energy Surface (RES):

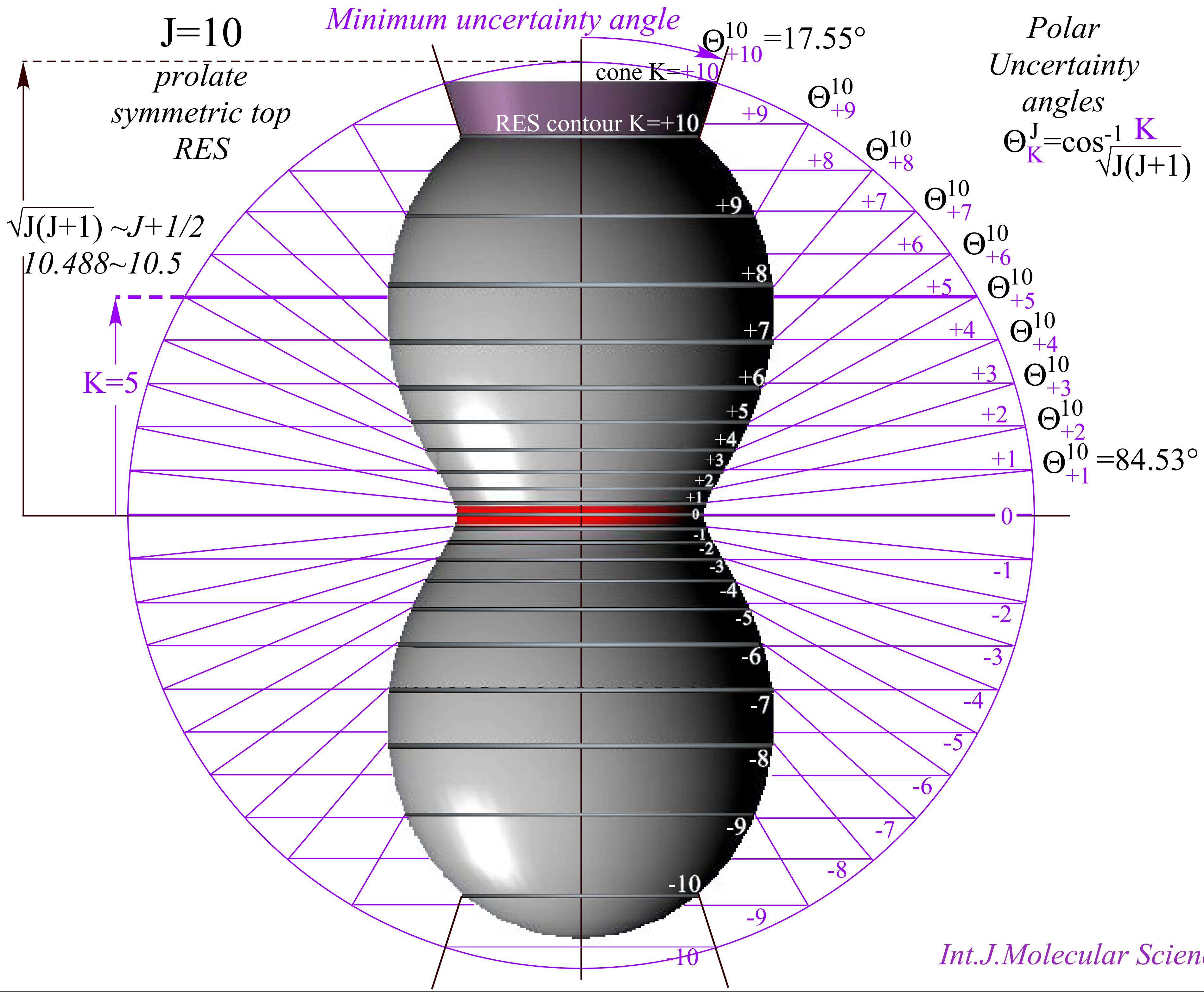
Plot Hamiltonian $\mathbf{H}=B\mathbf{J}^2+(C-B)\mathbf{J}_z^{\,2}$ radially as $H(\Theta)=BJ(J+1)+(C-B)J(J+1)\cos^2\Theta$

$\left|\begin{matrix} j \\ m,n \end{matrix}\right\rangle$

Conventional notation: $n=K$

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

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



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

Rotational Energy Surface (RES):

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

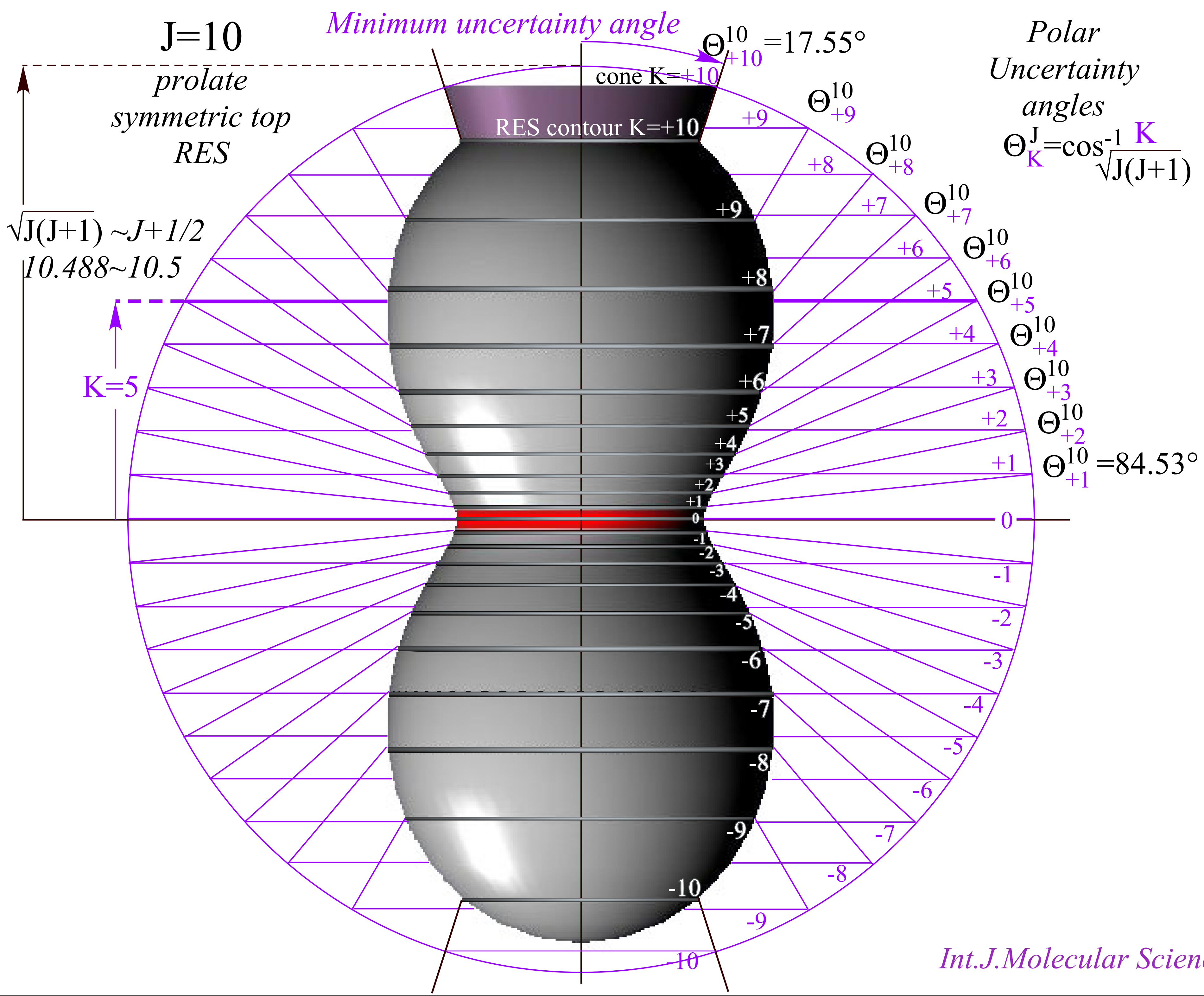
$\left|\begin{matrix} j \\ m,n \end{matrix}\right\rangle$

Conventional notation: $n=K$

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

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

(Here this gives exact quantum eigenvalues!)



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

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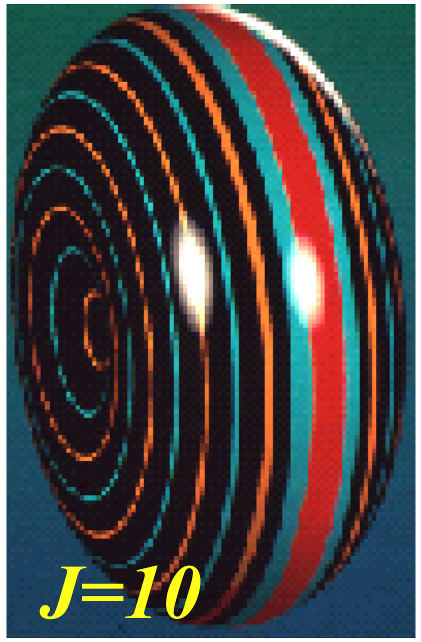
Symmetric rotor levels and RES plots

➡ *Asymmetric rotor levels and RES plots*

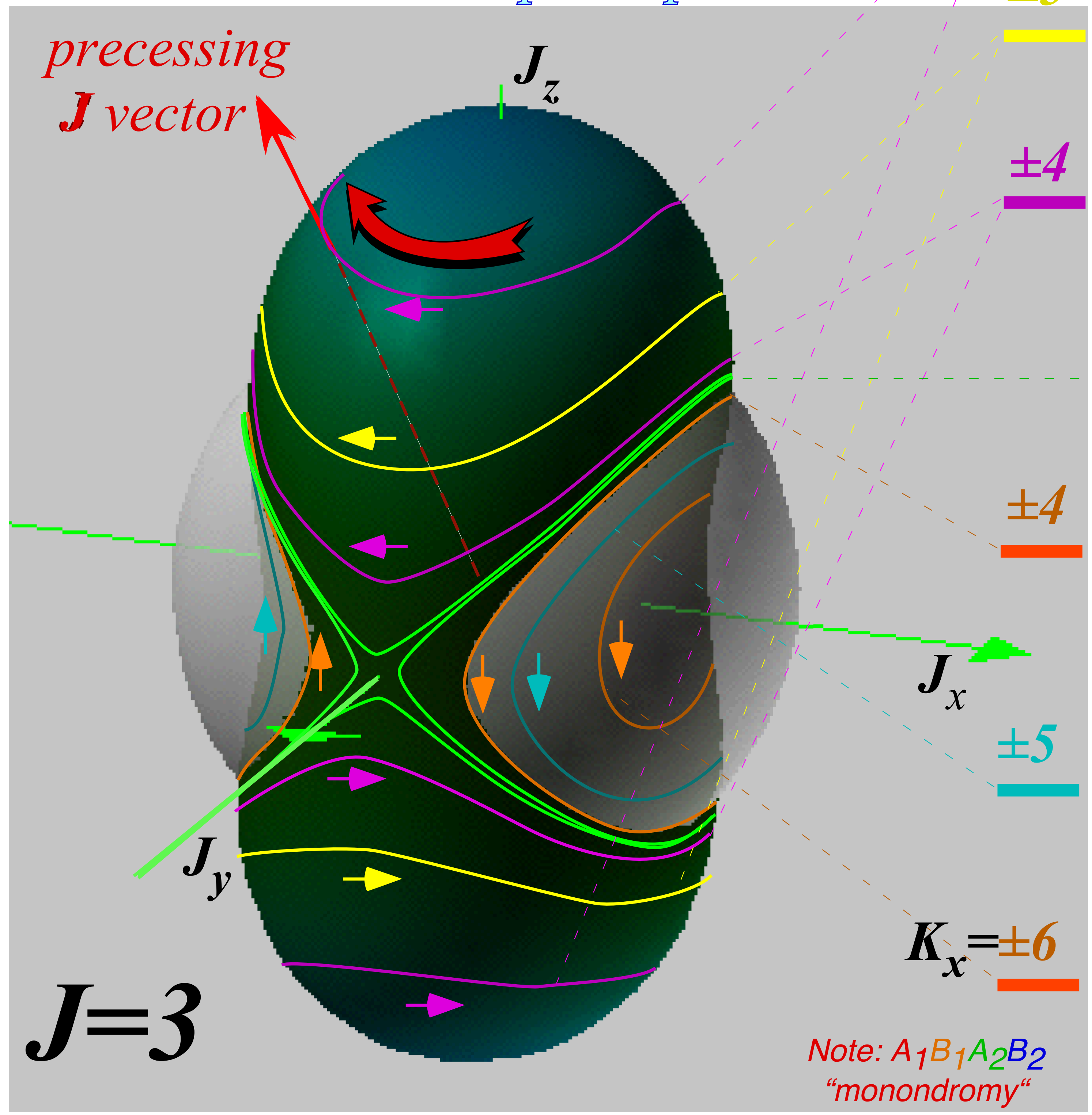
Spherical rotor levels and RES plots

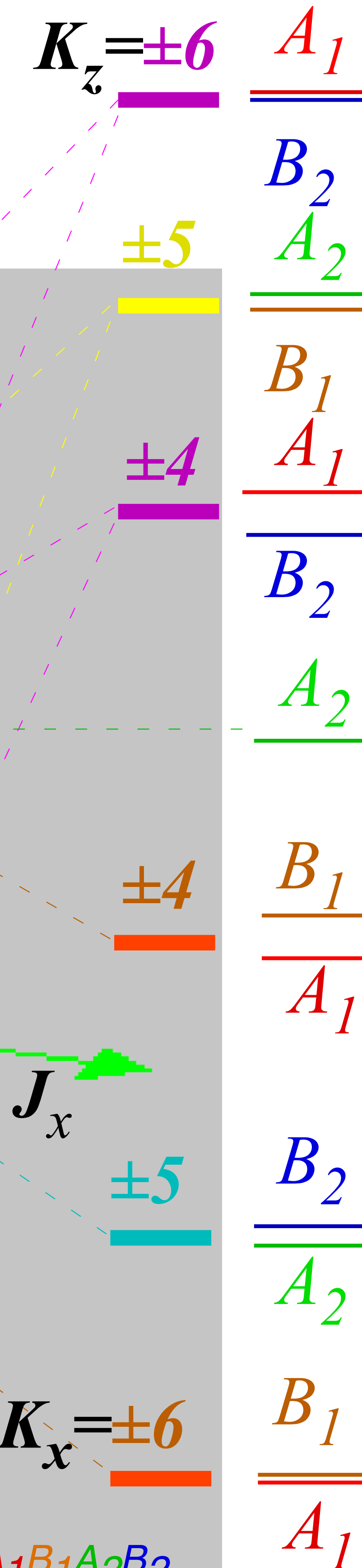
SF_6 spectral fine structure

CF_4 spectral fine structure

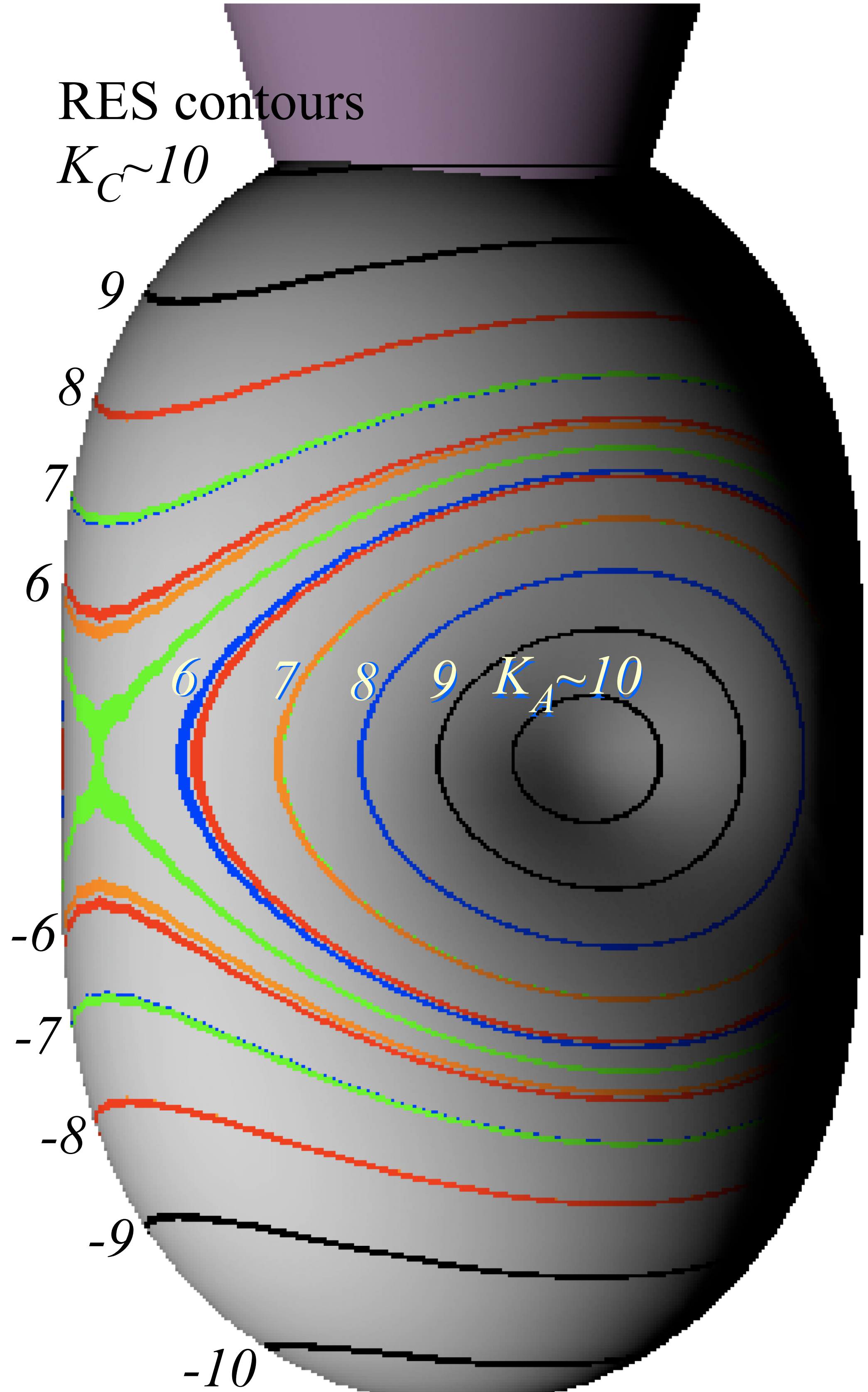


Asymmetric Top Eigensolutions Related to RE Surface and semi-classical J-phase paths



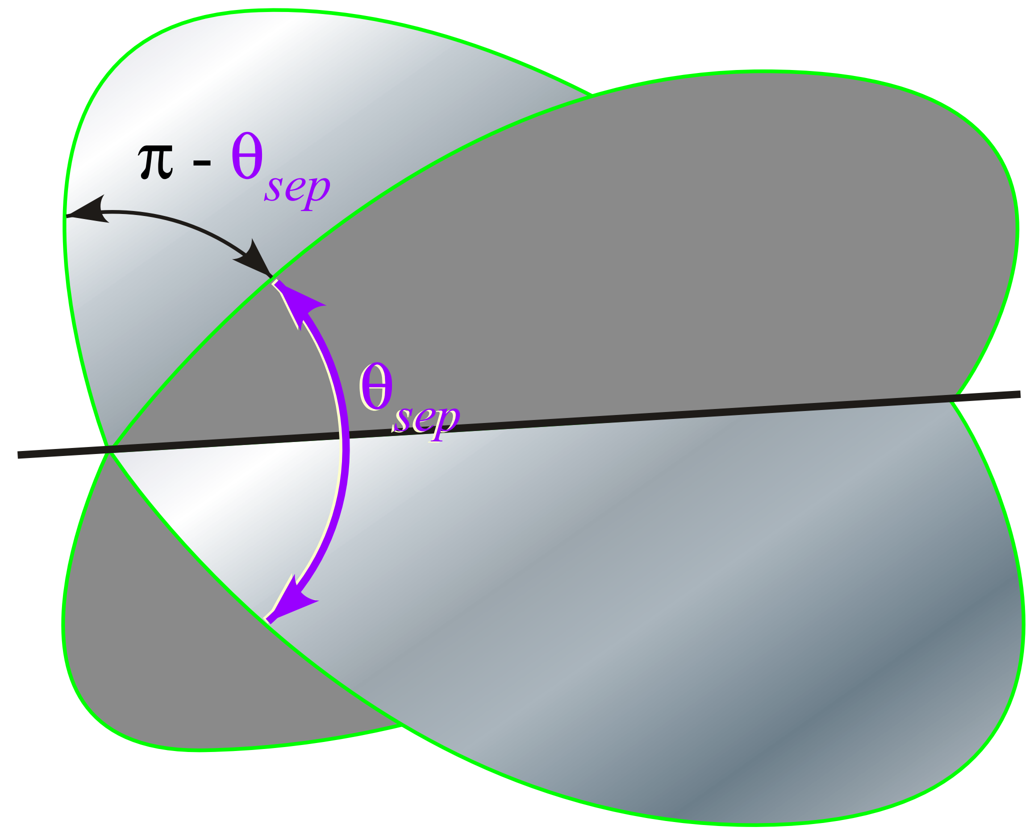


after QTforCA Unit 8. Ch. 25 Fig. 25.4.1



Separatrix circle pair
dihedral angle

$$\theta_{sep}=\text{atan}\left(\frac{A-B}{B-C}\right)$$



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

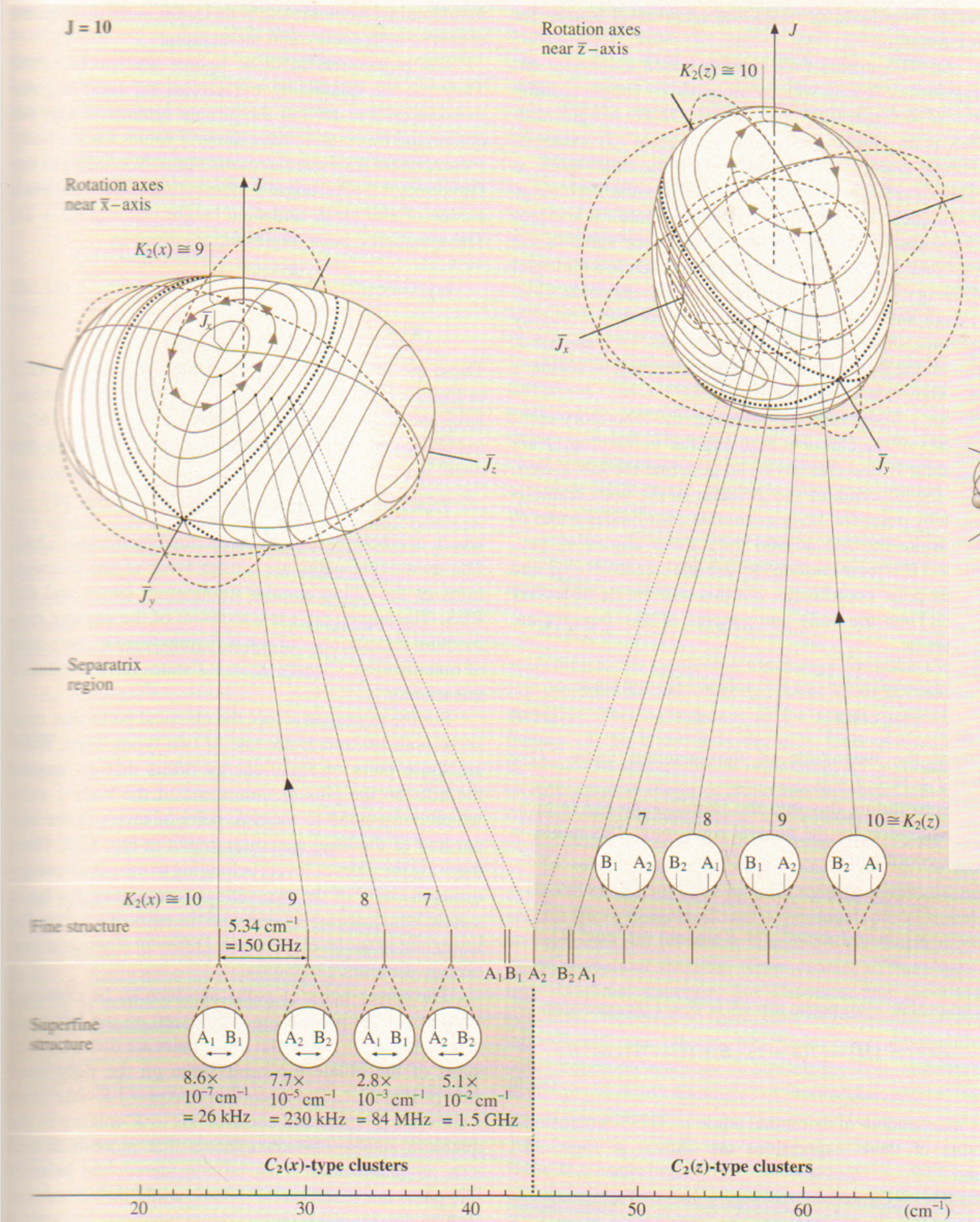
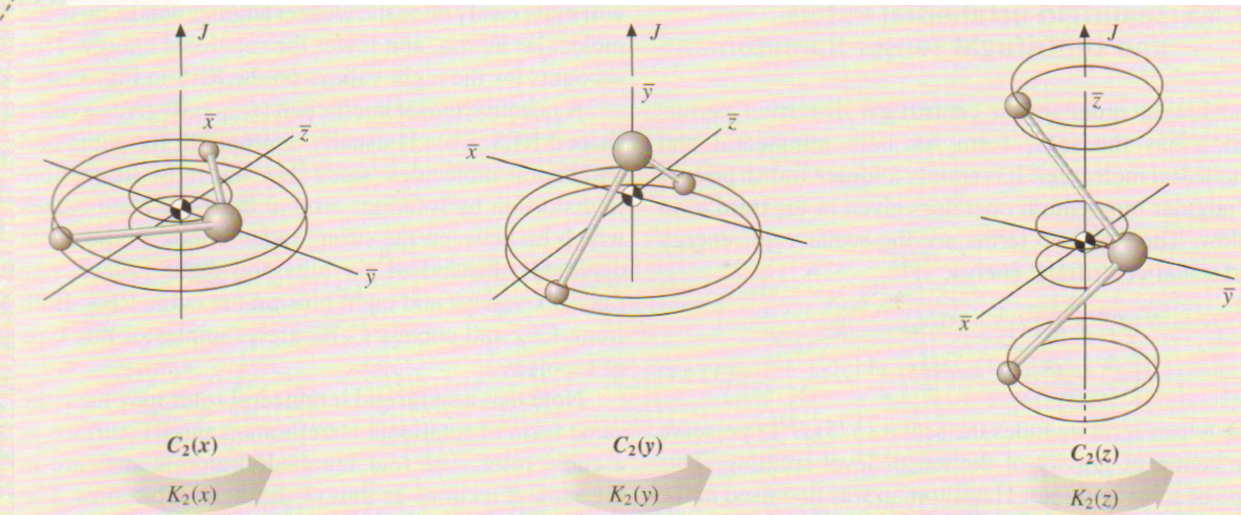


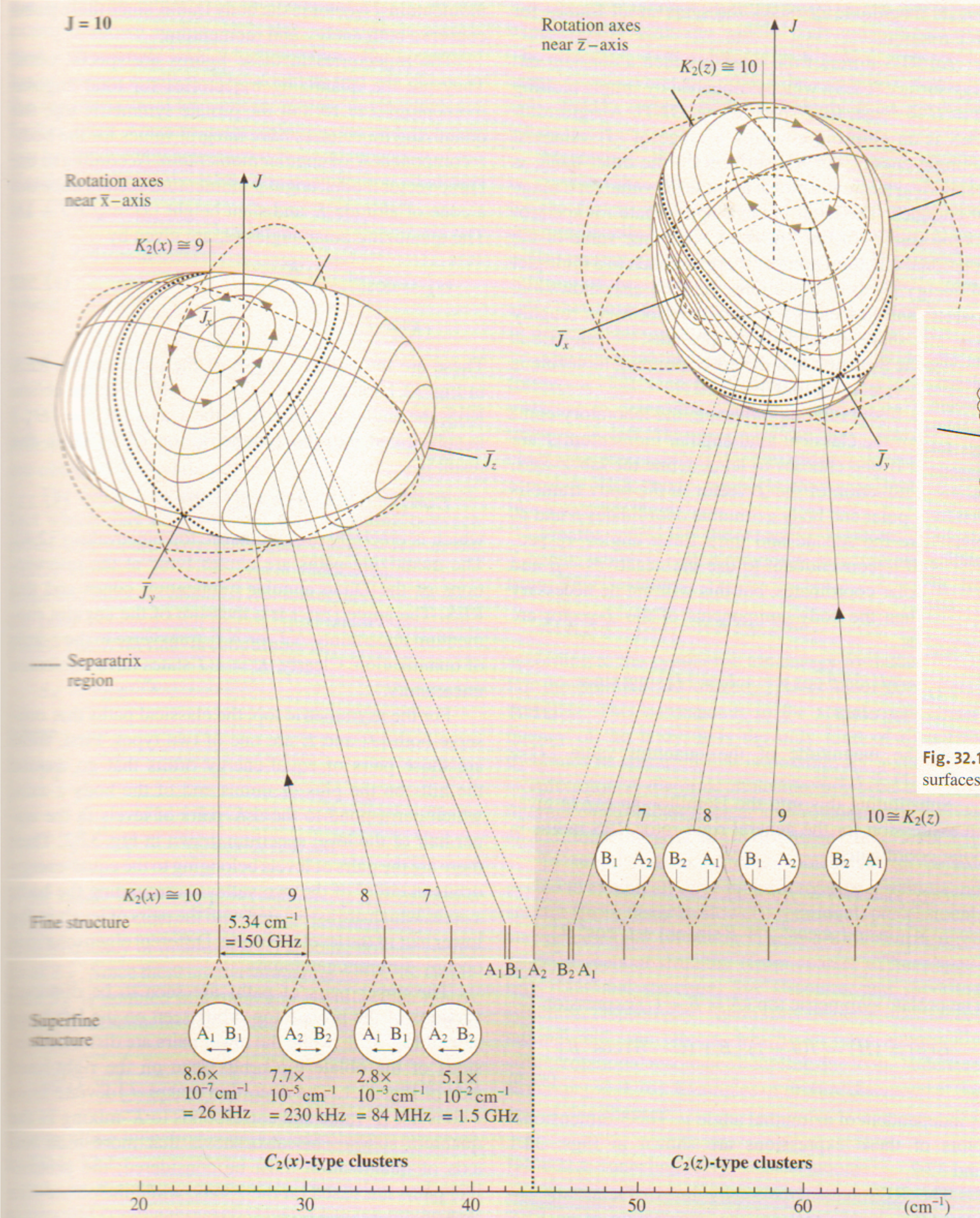
Fig. 32.2 $J = 10$ rotational energy surface and related level spectrum for an asymmetric rigid rotator ($A = 0.2$, $B = 0.4$, $C = 0.6\,\mathrm{cm}^{-1}$)



	O_2	I_2		O_2	I_2		O_2	I_2
A_1	❙	•	A_1	❙	•	A_1	❙	•
A_2	•	❙	A_2	❙	•	A_2	•	❙
B_1	❙	•	B_1	•	❙	B_1	•	❙
B_2	•	❙	B_2	•	❙	B_2	❙	•

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



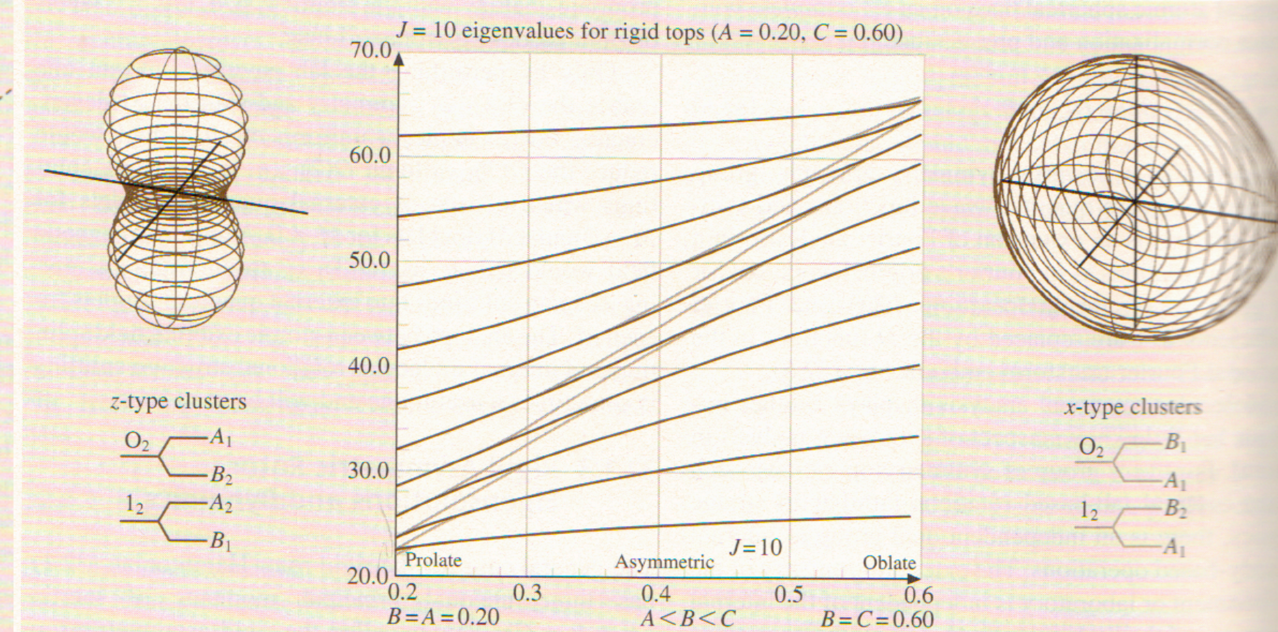
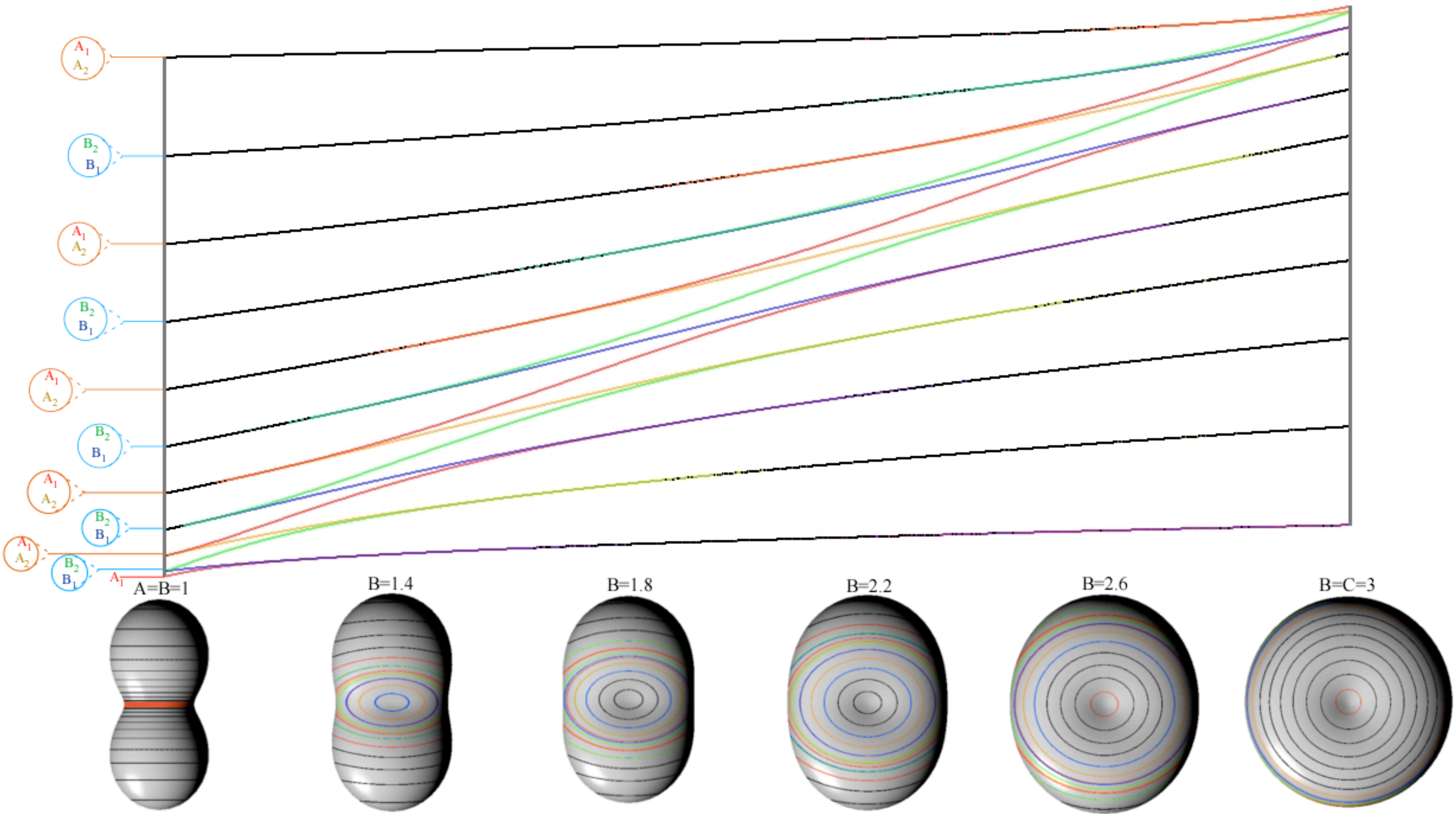


Fig. 32.1 $J = 10$ eigenvalue plot for symmetric rigid rotors. ($A = 0.2$, $C = 0.6\,cm^{-1}$ $A < B < C$). Prolate and oblate RE surfaces are shown

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

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.4 p. 734

New geometric approach to rotational eigenstates and spectra

Introduction to Rotational Energy Surfaces (RES) and multipole tensor expansion

Rank-2 tensors from D^2-matrix

Building Hamiltonian $\mathbf{H} = A\mathbf{J}_x^2 + B\mathbf{J}_y^2 + C\mathbf{J}_z^2$ *out of scalar and tensor operators*

Comparing quantum and semi-classical calculations

Symmetric rotor levels and RES plots

Asymmetric rotor levels and RES plots

➡ *Spherical rotor levels and RES plots*

SF_6 spectral fine structure

CF_4 spectral fine structure

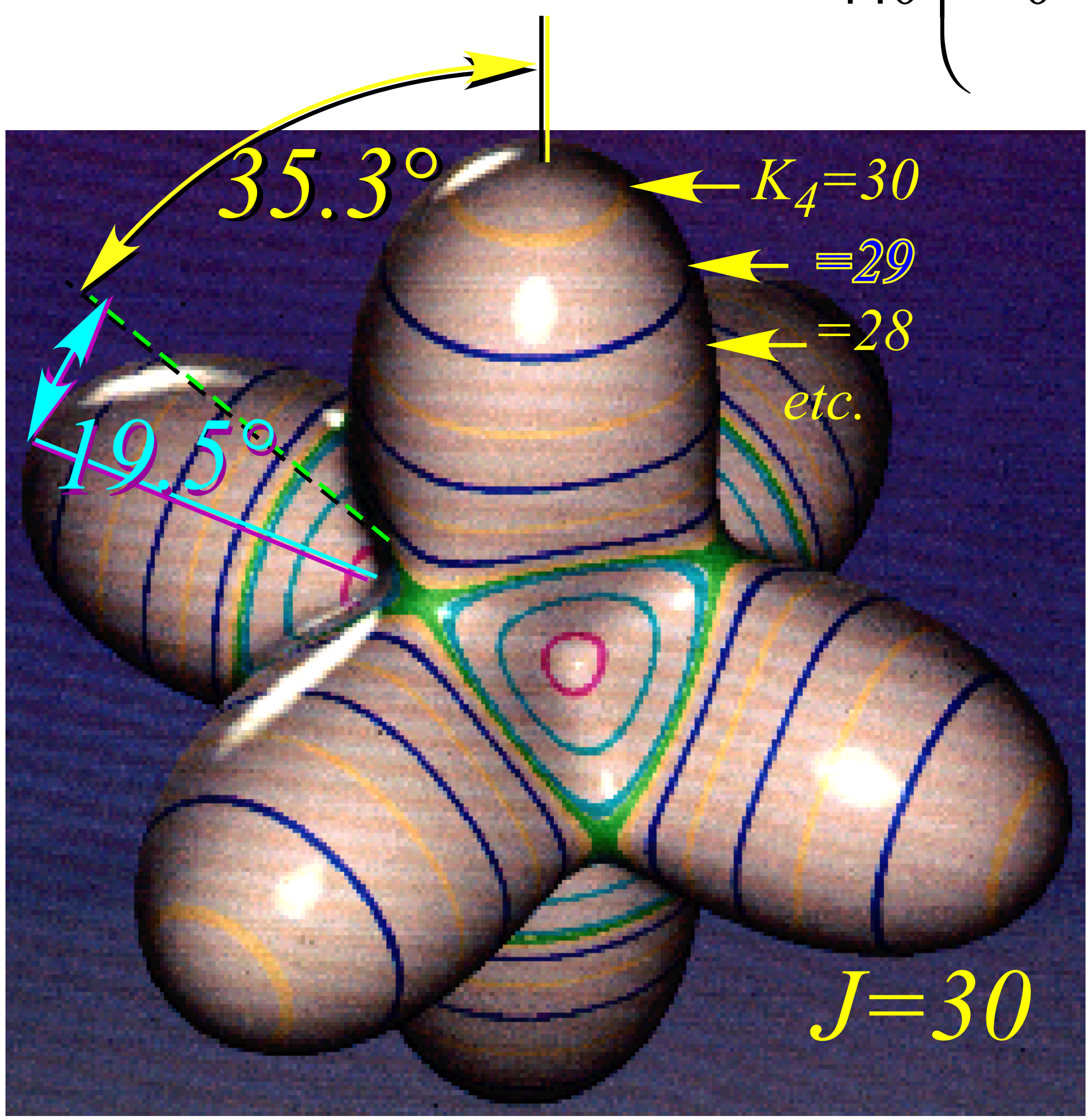
Semi Rigid Rotor Hamiltonian: *Centrifugal and Coriolis terms...*

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

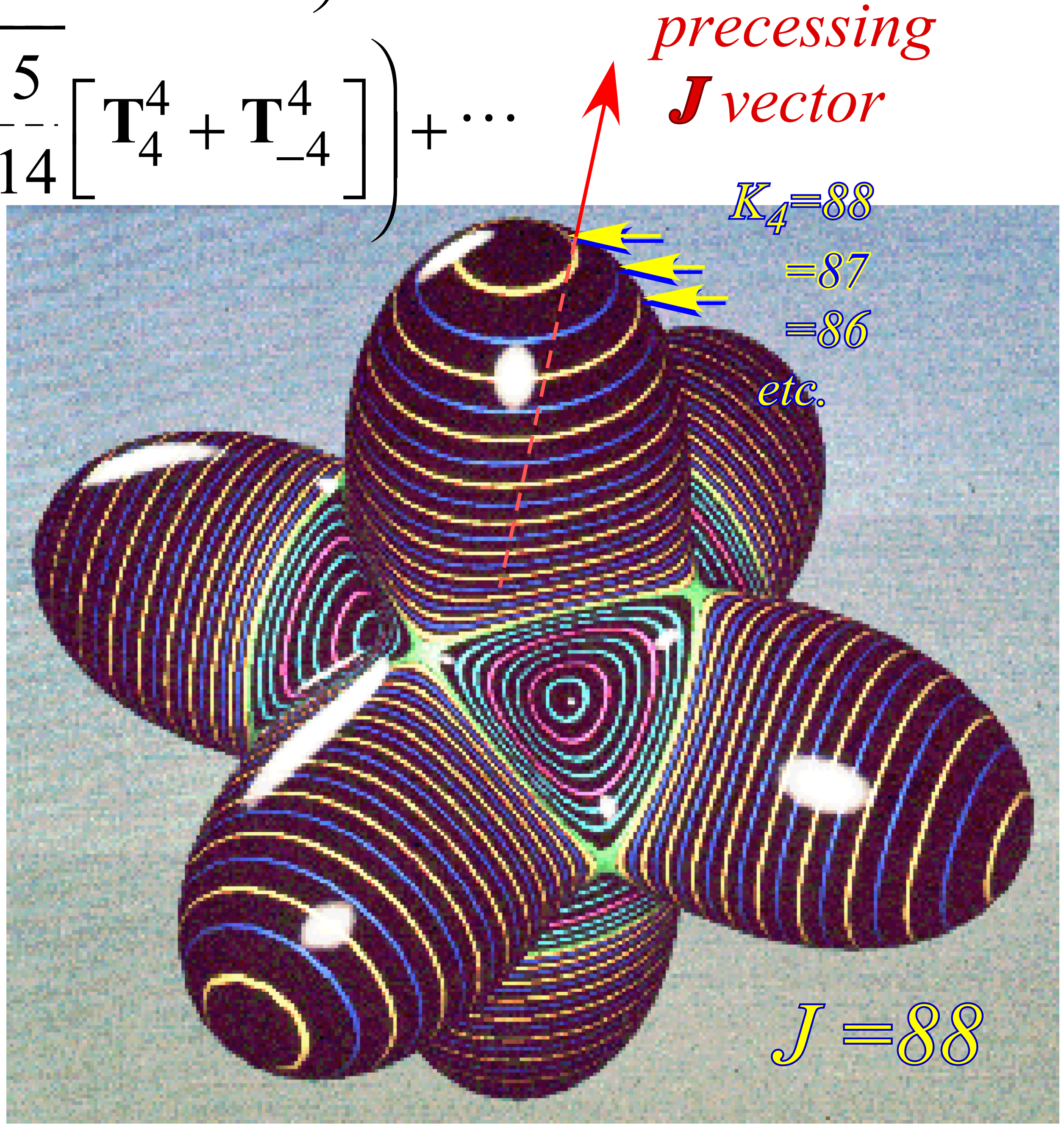
Semi Rigid O_h or T_d Spherical Top: *(Hecht Hamiltonian 1960)*

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

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

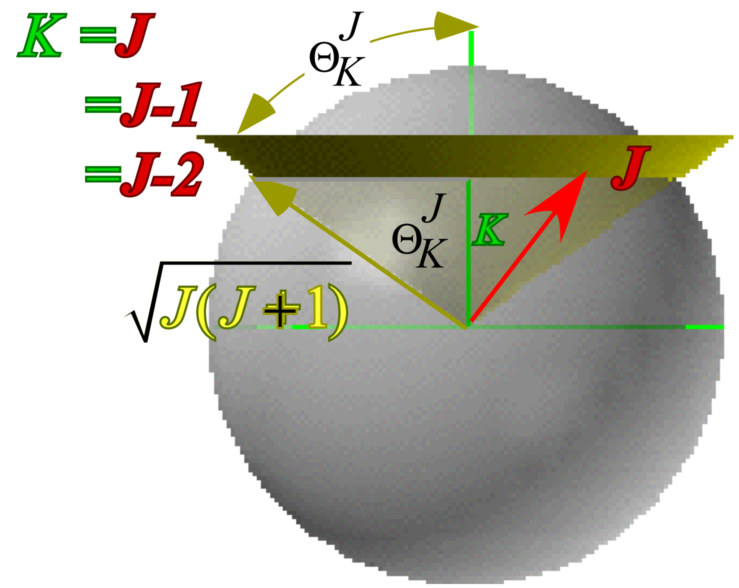


after QTforCA Unit 8. Ch. 25 Fig. 25.4.5



Finding Hamiltonian Eigensolutions by Geometry using Uncertainty Cone Angles

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

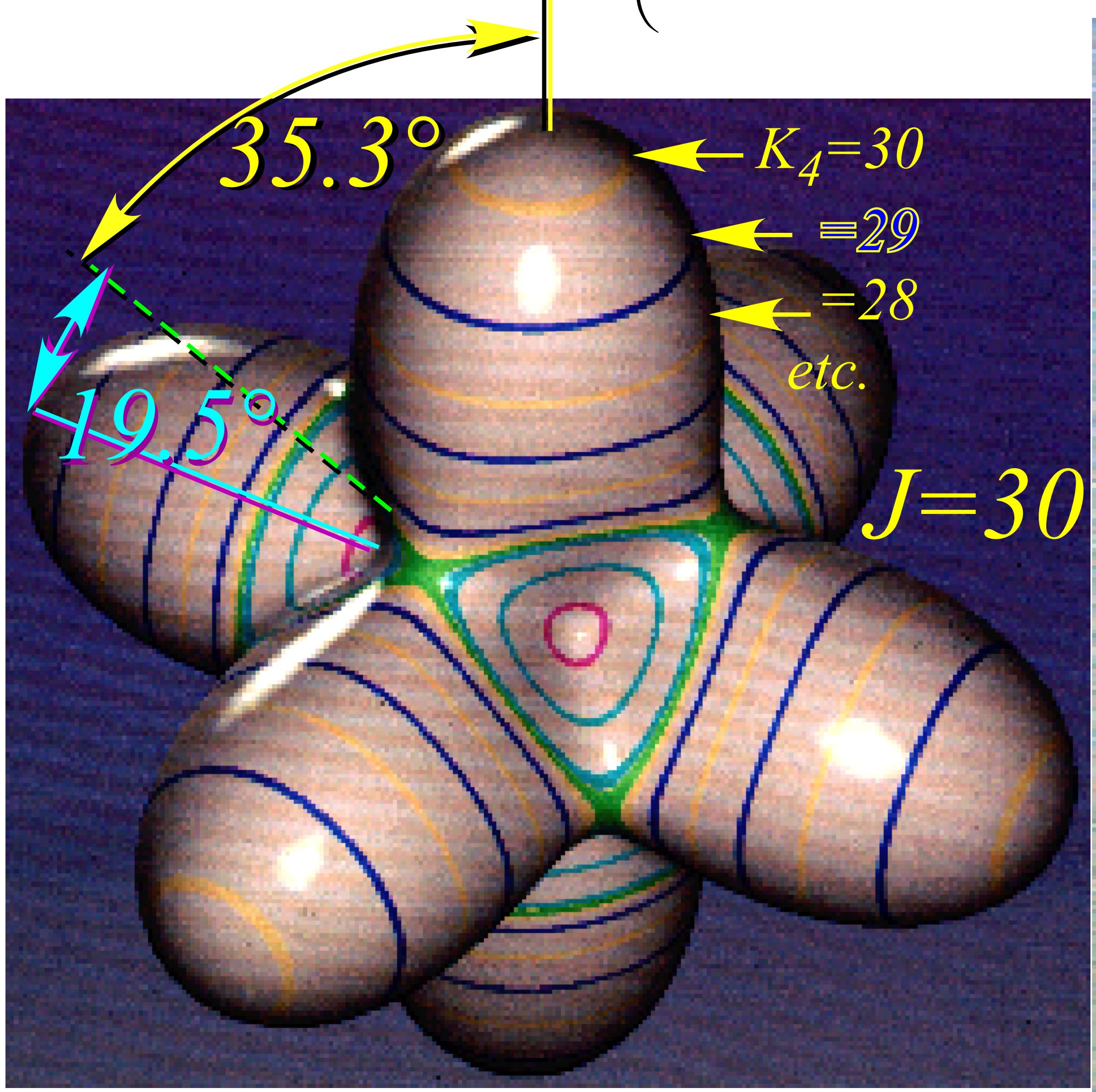


J cone intersects J=88 RE surface to give approx. K=J, J-1, J-2... energy levels

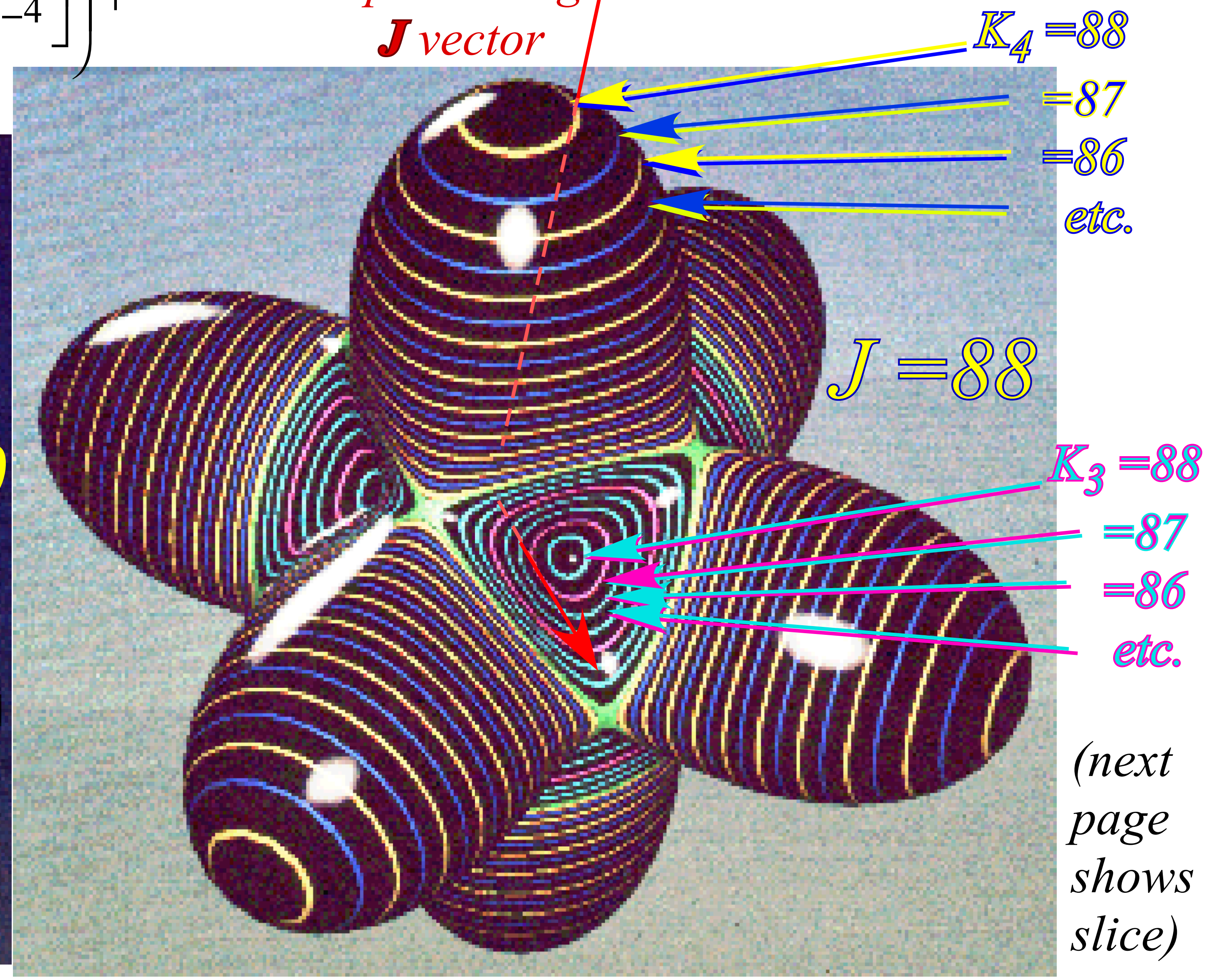
O_h or T_d Spherical Top: *(Hecht Ro-vib Hamiltonian 1960)*

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

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

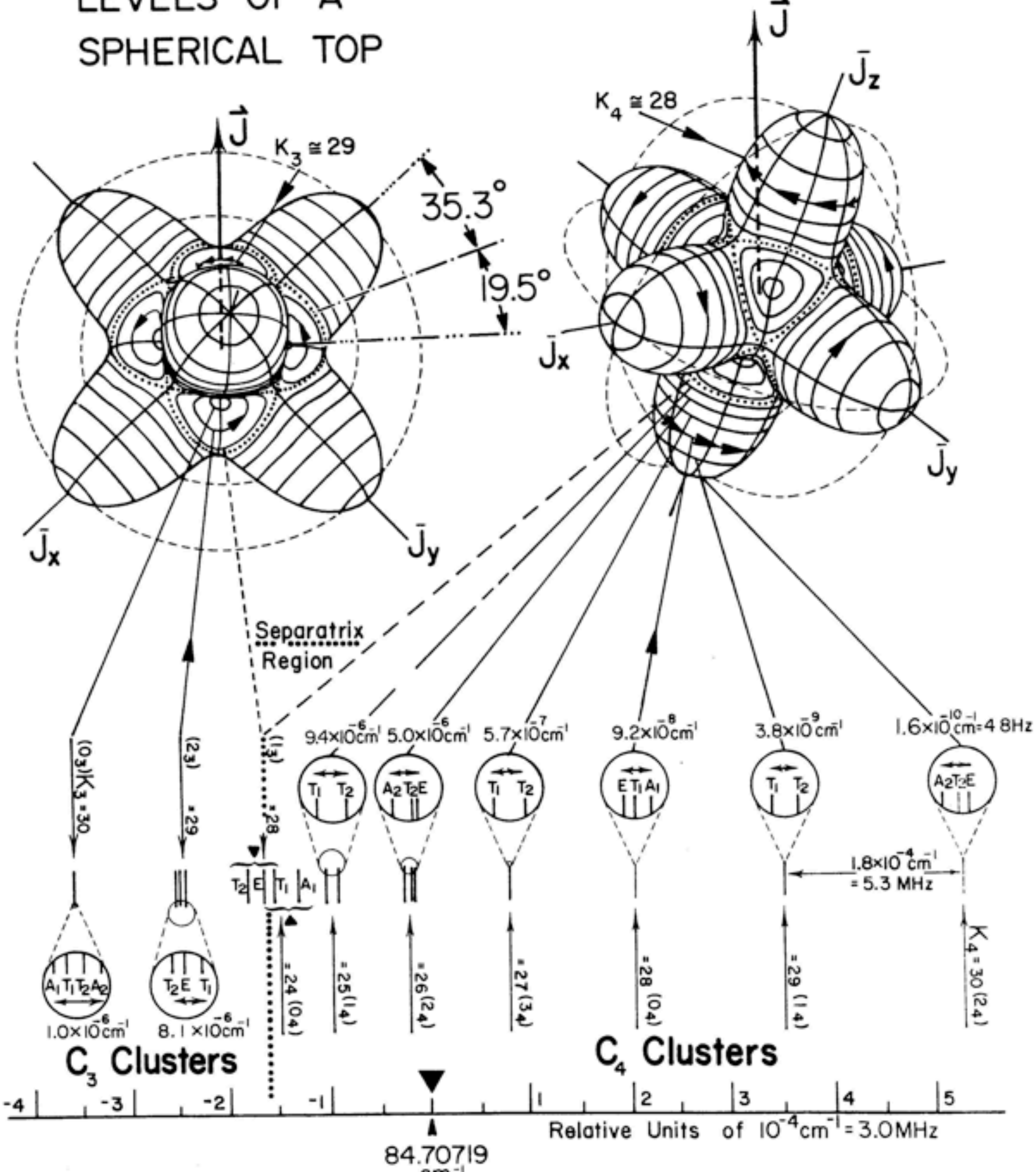


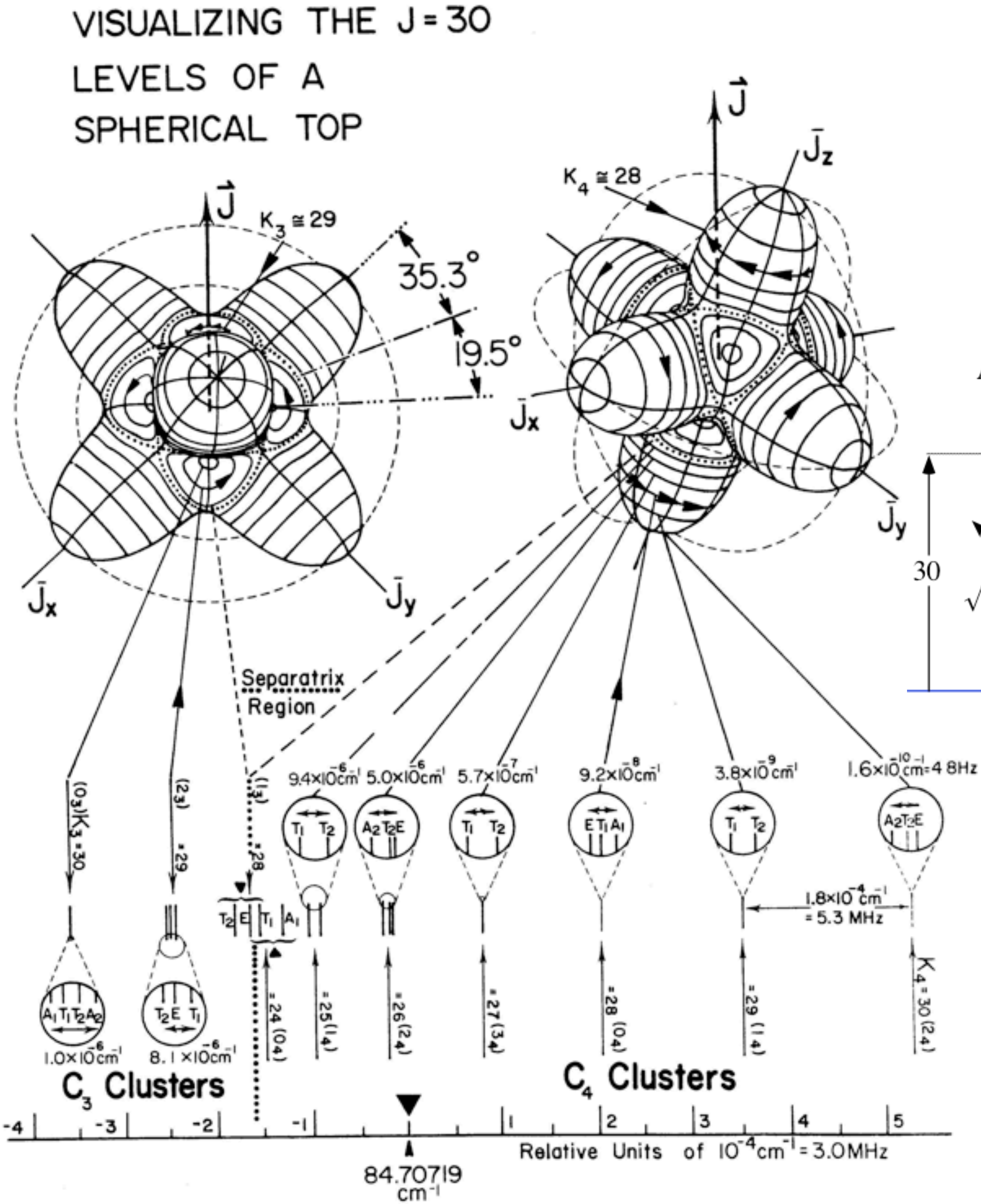
RE Surface topo-lines track precessing semi-classical J vector

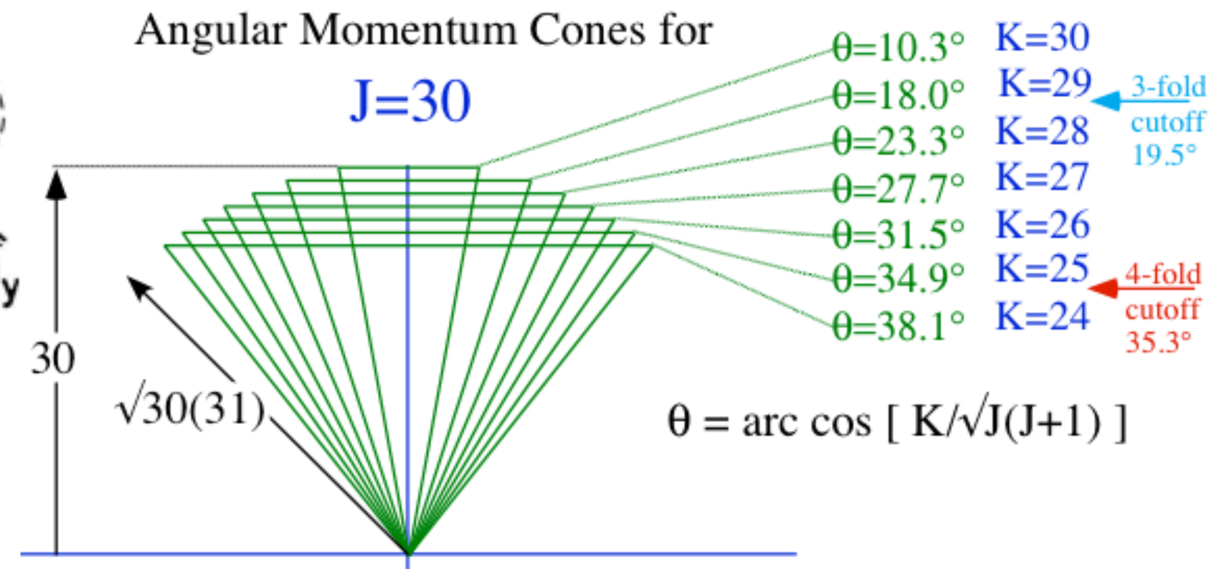


(next page shows slice)

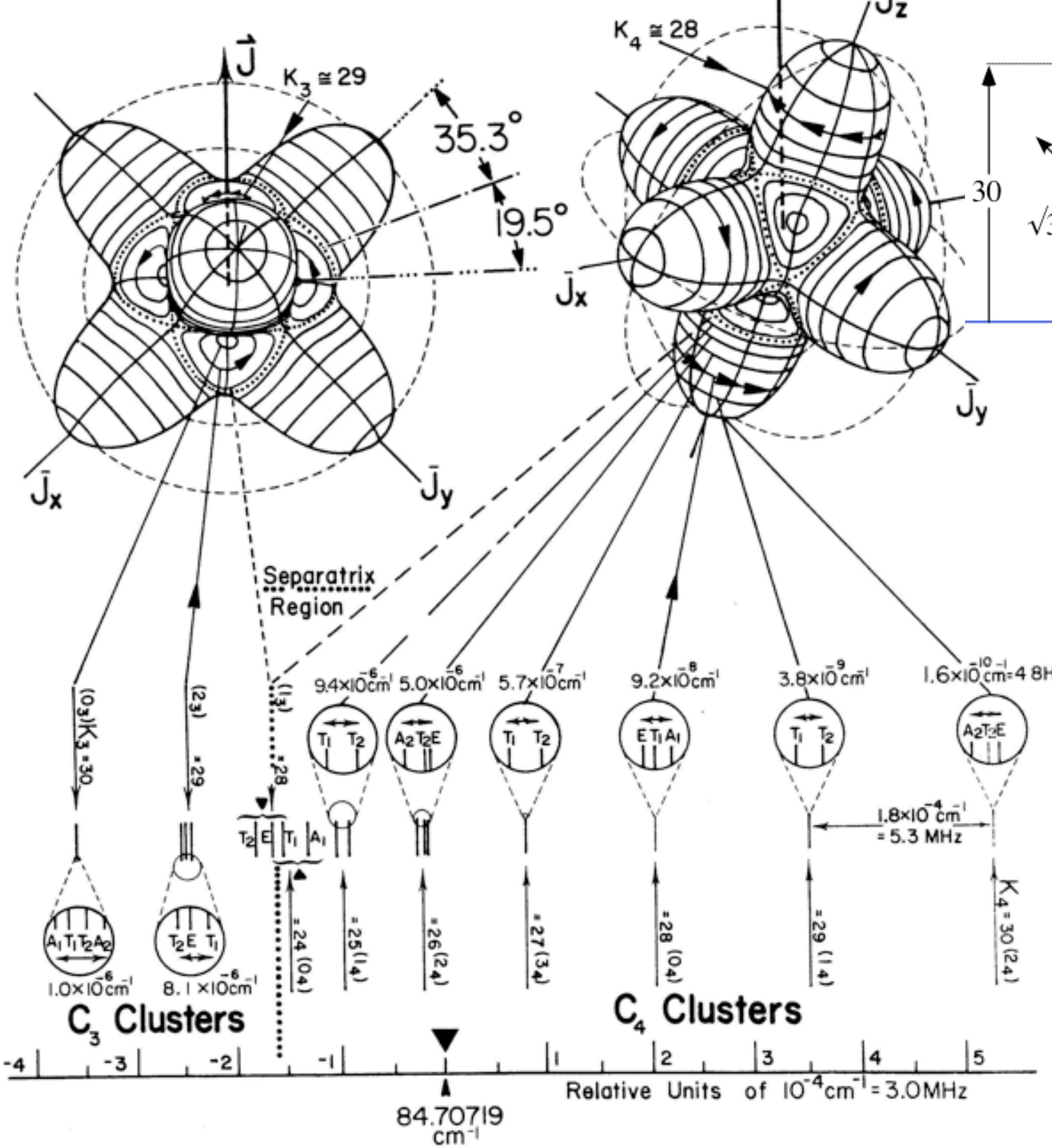
VISUALIZING THE J = 30 LEVELS OF A SPHERICAL TOP

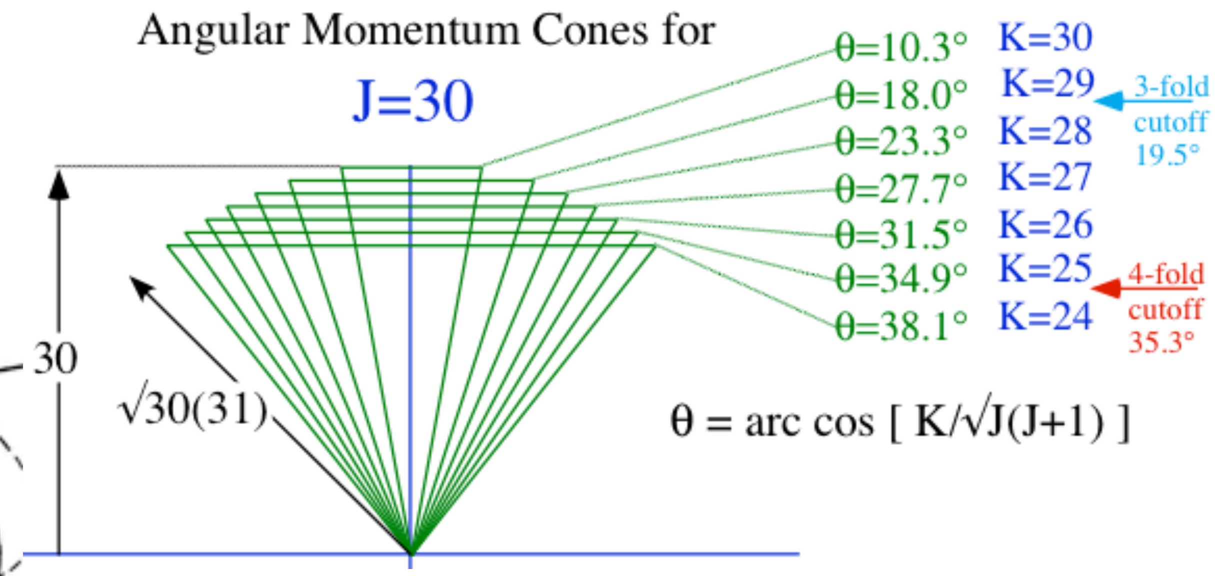


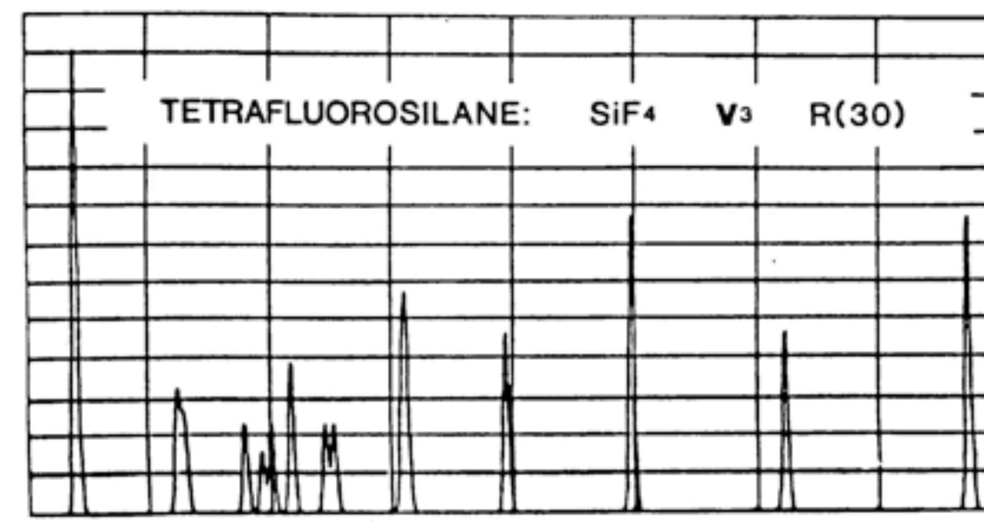

VISUALIZING THE J=30 LEVELS OF A SPHERICAL TOP
K3 ≅ 29
K4 ≅ 28
35.3°
19.5°
Separatrix Region
C3 Clusters
C4 Clusters
Relative Units of 10-4cm-1 = 3.0MHz
84.70719 cm-1

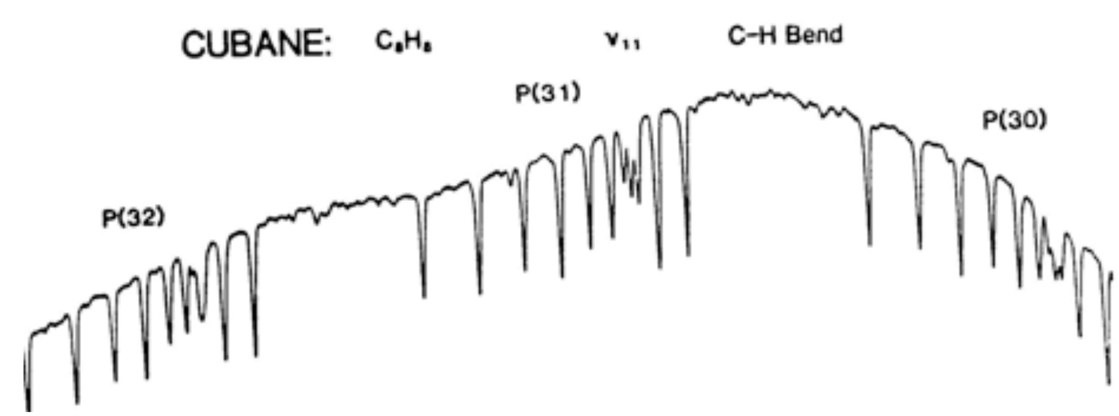

Angular Momentum Cones for
J=30
θ=10.3° K=30
θ=18.0° K=29
θ=23.3° K=28
θ=27.7° K=27
θ=31.5° K=26
θ=34.9° K=25
θ=38.1° K=24
3-fold cutoff 19.5°
4-fold cutoff 35.3°
30
√30(31)
θ = arc cos [K/√J(J+1)]

VISUALIZING THE J = 30 LEVELS OF A SPHERICAL TOP



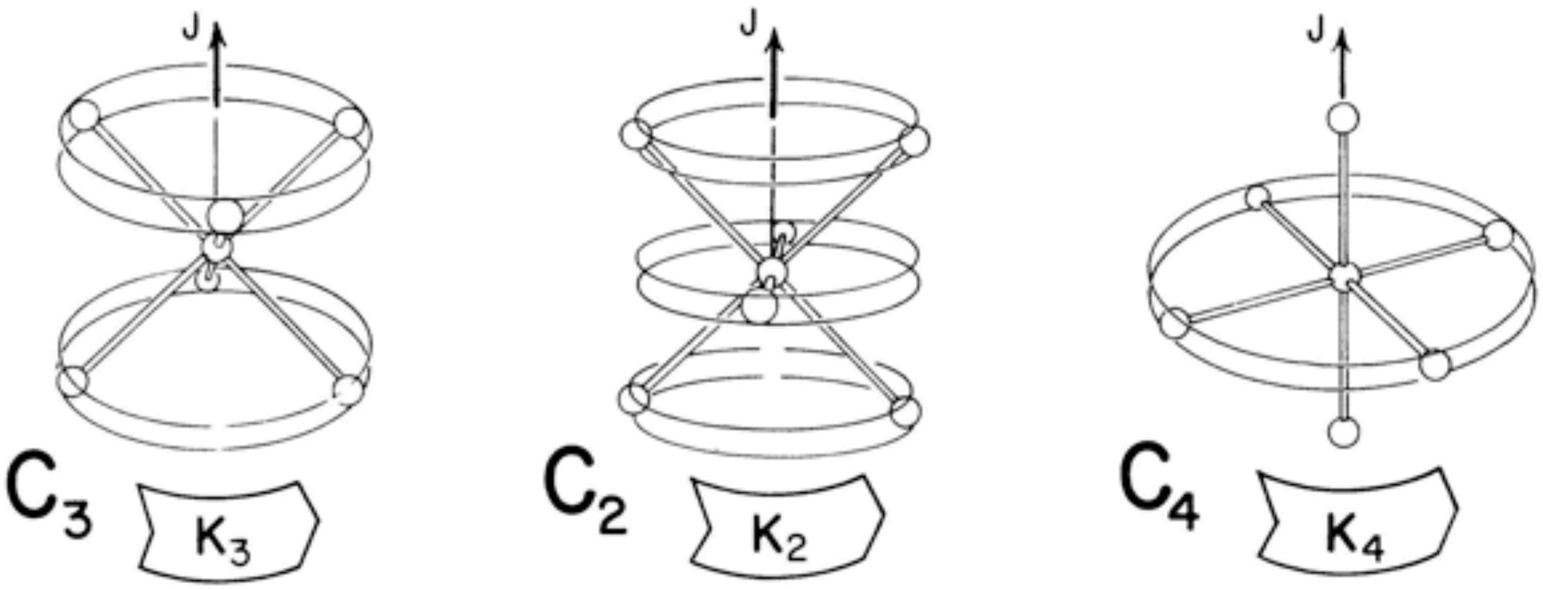






Previous page: QTforCA Unit 8. Ch. 25 Fig. 25.4.9

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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Spherical rotor levels and RES plots

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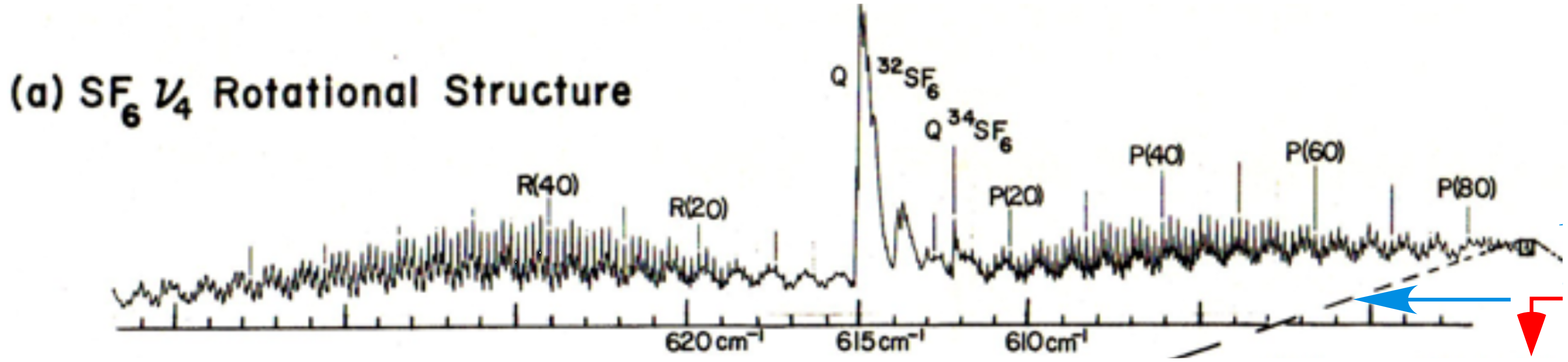
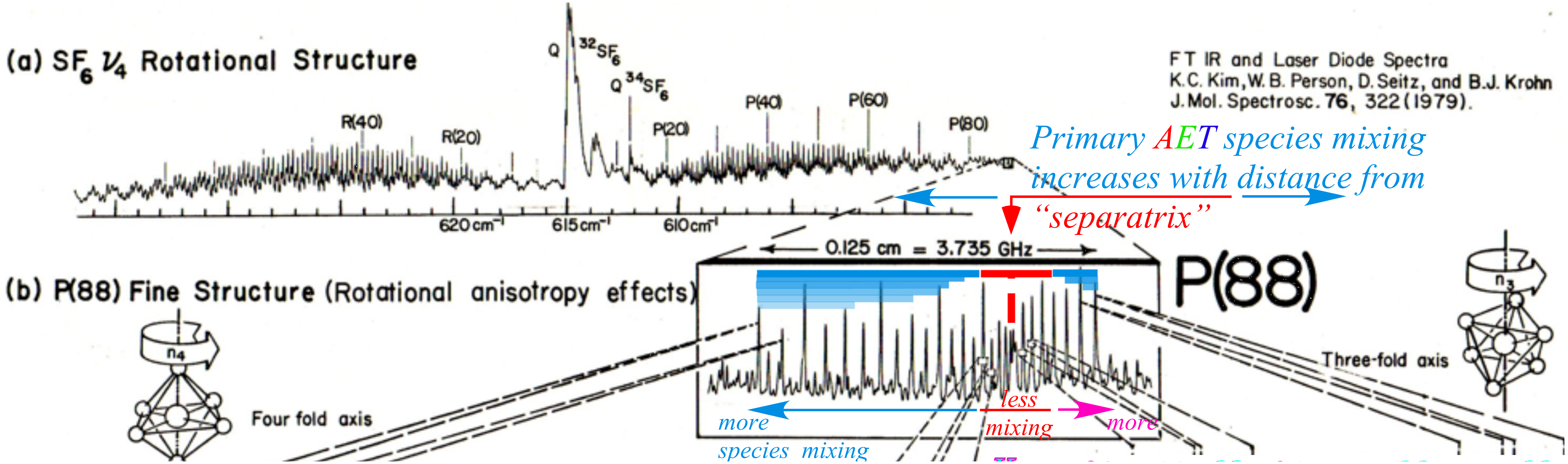
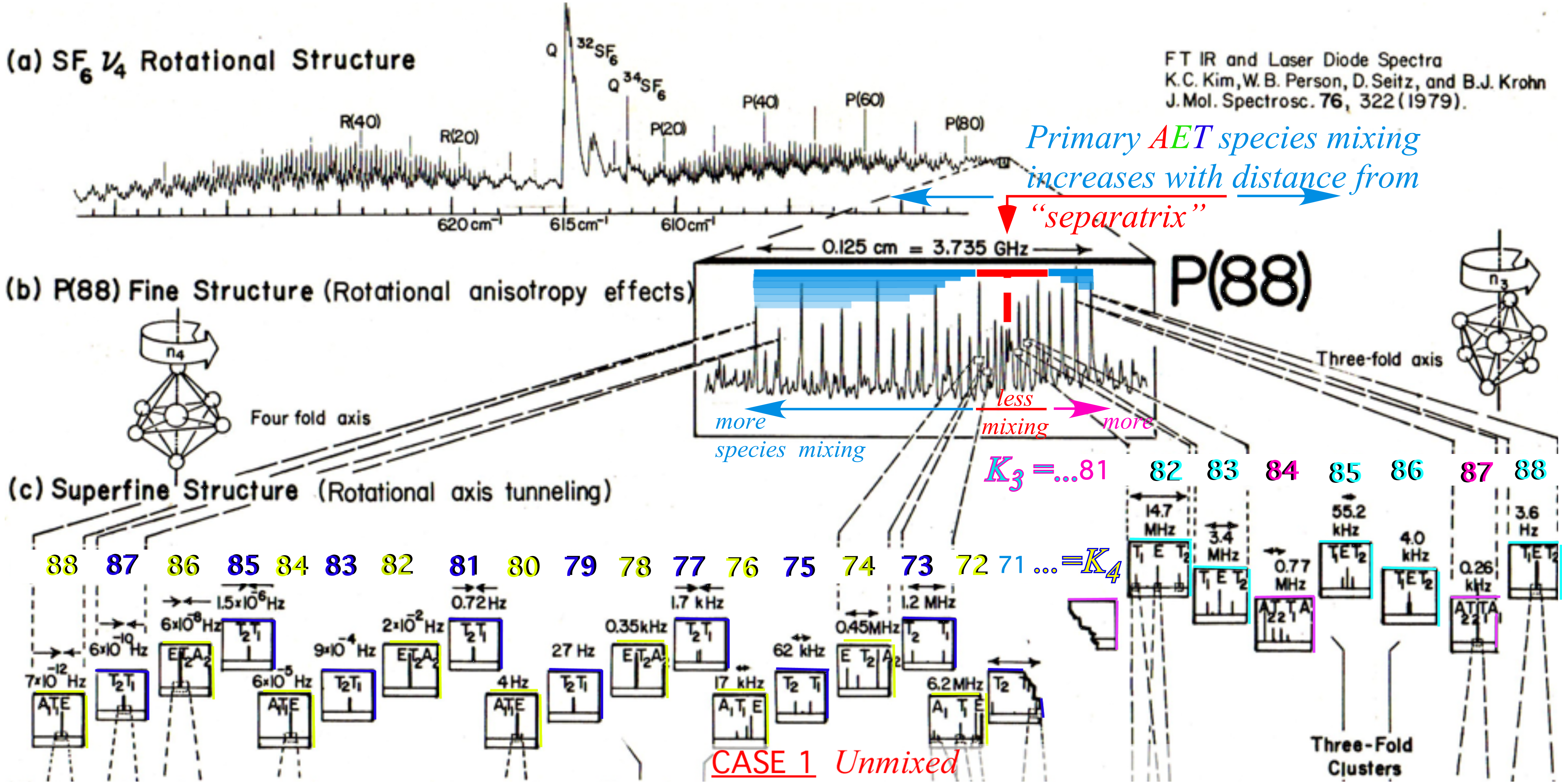
CF_4 spectral fine structure

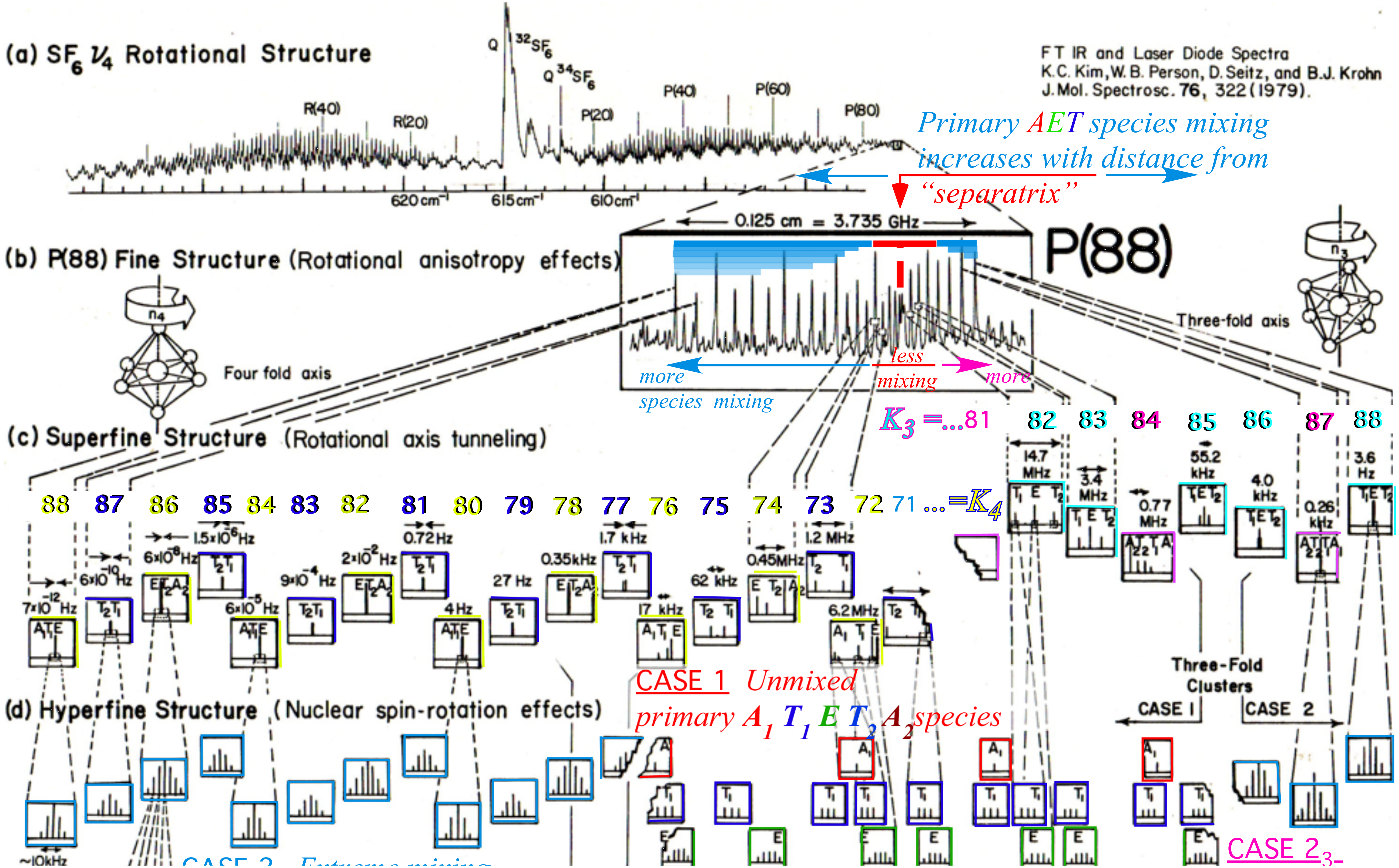


F T IR and Laser Diode Spectra
K.C. Kim, W. B. Person, D. Seitz, and B.J. Krohn
J. Mol. Spectrosc. **76**, 322 (1979).

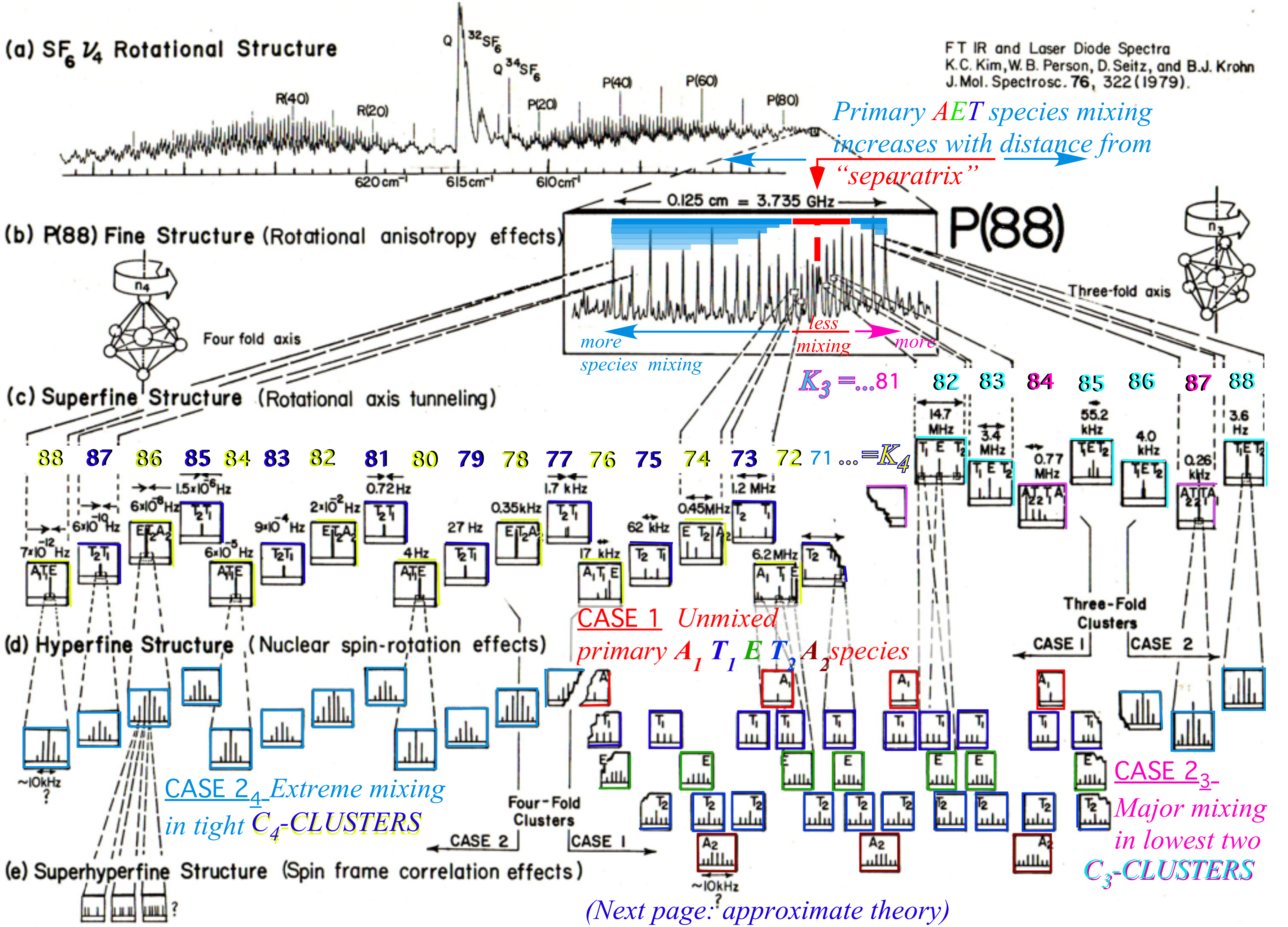

(a) SF6 ν4 Rotational Structure
Q
32SF6
Q 34SF6
R(40)
R(20)
P(20)
P(40)
P(60)
P(80)
620 cm-1
615 cm-1
610 cm-1
FT IR and Laser Diode Spectra
K.C. Kim, W.B. Person, D. Seitz, and B.J. Krohn
J. Mol. Spectrosc. 76, 322 (1979).
Primary AET species mixing
increases with distance from
"separatrix"
(b) P(88) 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
J. Mol. Spectrosc. 76, 322 (1979).
Primary AET species mixing increases with distance from "separatrix"
R(40)
R(20)
P(20)
P(40)
P(60)
P(80)
620 cm⁻¹
615 cm⁻¹
610 cm⁻¹
(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
Three-Fold Clusters
CASE 1 Unmixed



(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"
0.125 cm = 3.735 GHz
(b) P(88) Fine Structure (Rotational anisotropy effects)
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
(d) Hyperfine Structure (Nuclear spin-rotation effects)
CASE 1 Unmixed primary A1 T1 E T2 A2 species
Three-Fold Clusters
CASE 1
CASE 2
CASE 2
CASE 3 Extreme mixing



(a) SF_6 ν_4 Rotational Structure
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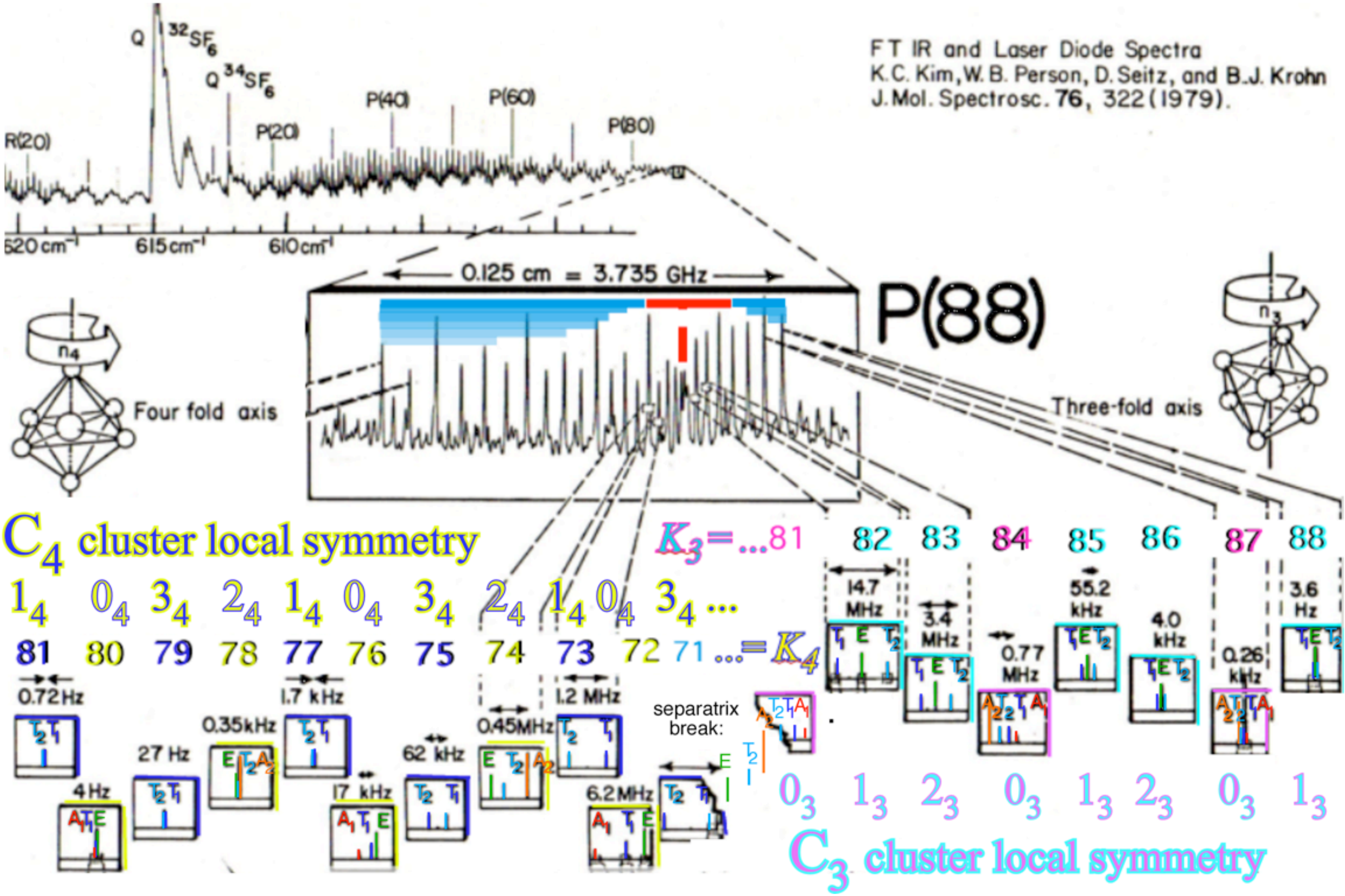
Four fold axis
Three-fold axis
more species mixing
less mixing
more
(c) Superfine Structure (Rotational axis tunneling)
K_3 =...81 82 83 84 85 86 87 88
88 87 86 85 84 83 82 81 80 79 78 77 76 75 74 73 72 71 ... $=K_4$
CASE 1 Unmixed primary A_1 T_1 E T_2 A_2 species
(d) Hyperfine Structure (Nuclear spin-rotation effects)
Three-Fold Clusters
CASE 1
CASE 2
CASE 2_4 Extreme mixing in tight C_4-CLUSTERS
Four-Fold Clusters
CASE 2
CASE 1
CASE 2_3 Major mixing in lowest two C_3-CLUSTERS
(e) Superhyperfine Structure (Spin frame correlation effects)
(Next page: approximate theory)

IR Spectra of SF6 ν₄ P(88)



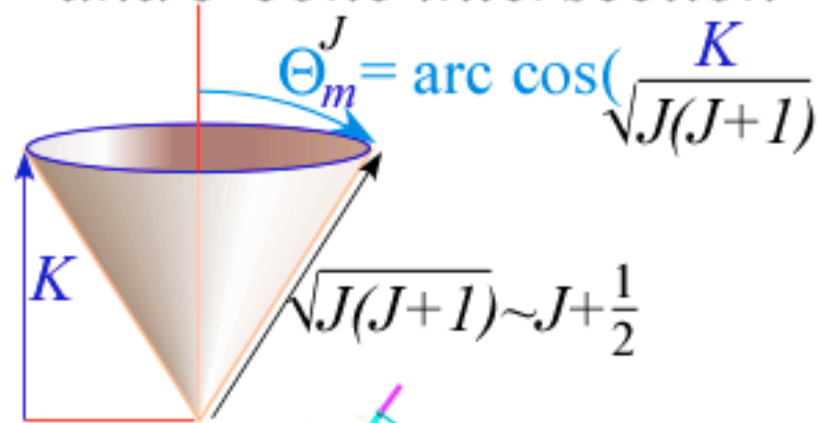
Int.J.Molecular Science 14.(2013) Fig.26 p. 783

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

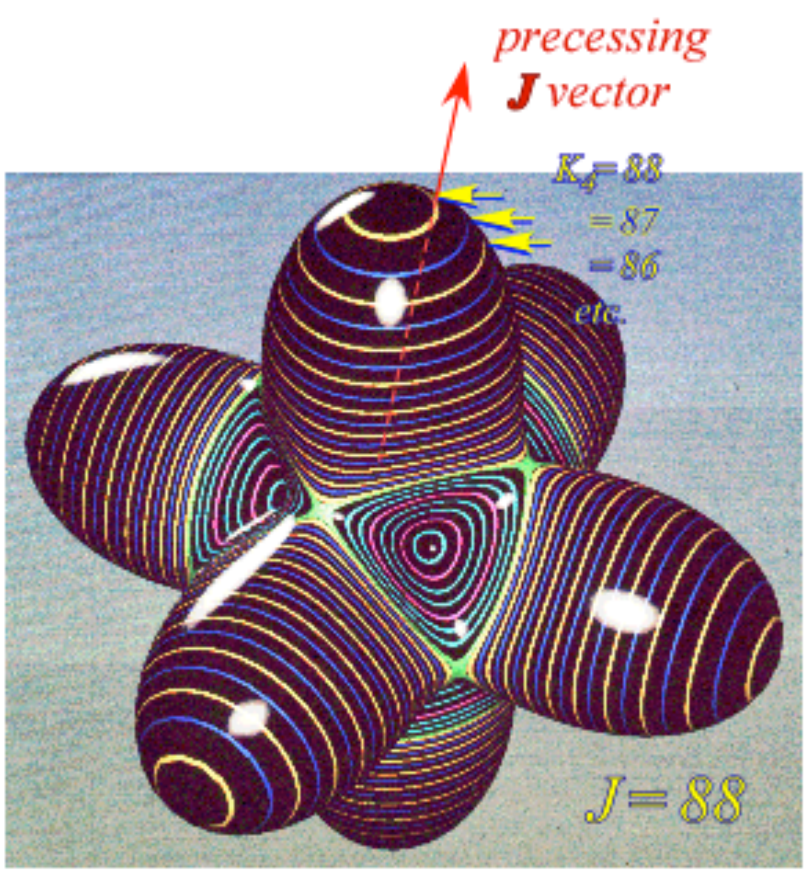
and J-cone intersection

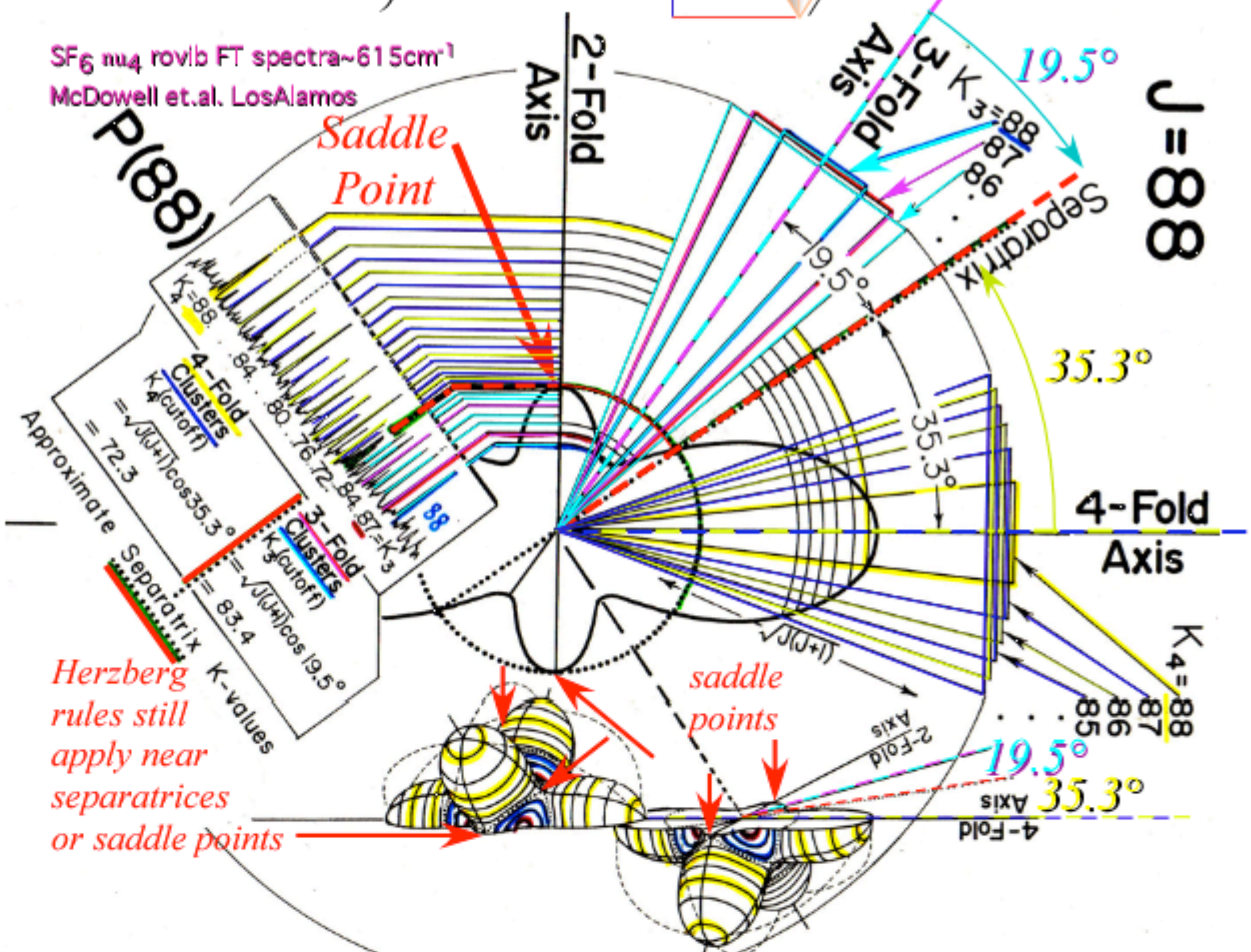
$$\mathbf{H} = B\left(\mathbf{J}_x^2 + \mathbf{J}_y^2 + \mathbf{J}_z^2\right) + t_{440}\left(\mathbf{J}_x^4 + \mathbf{J}_y^4 + \mathbf{J}_z^4 - \frac{3}{5}J^4\right) + \cdots$$

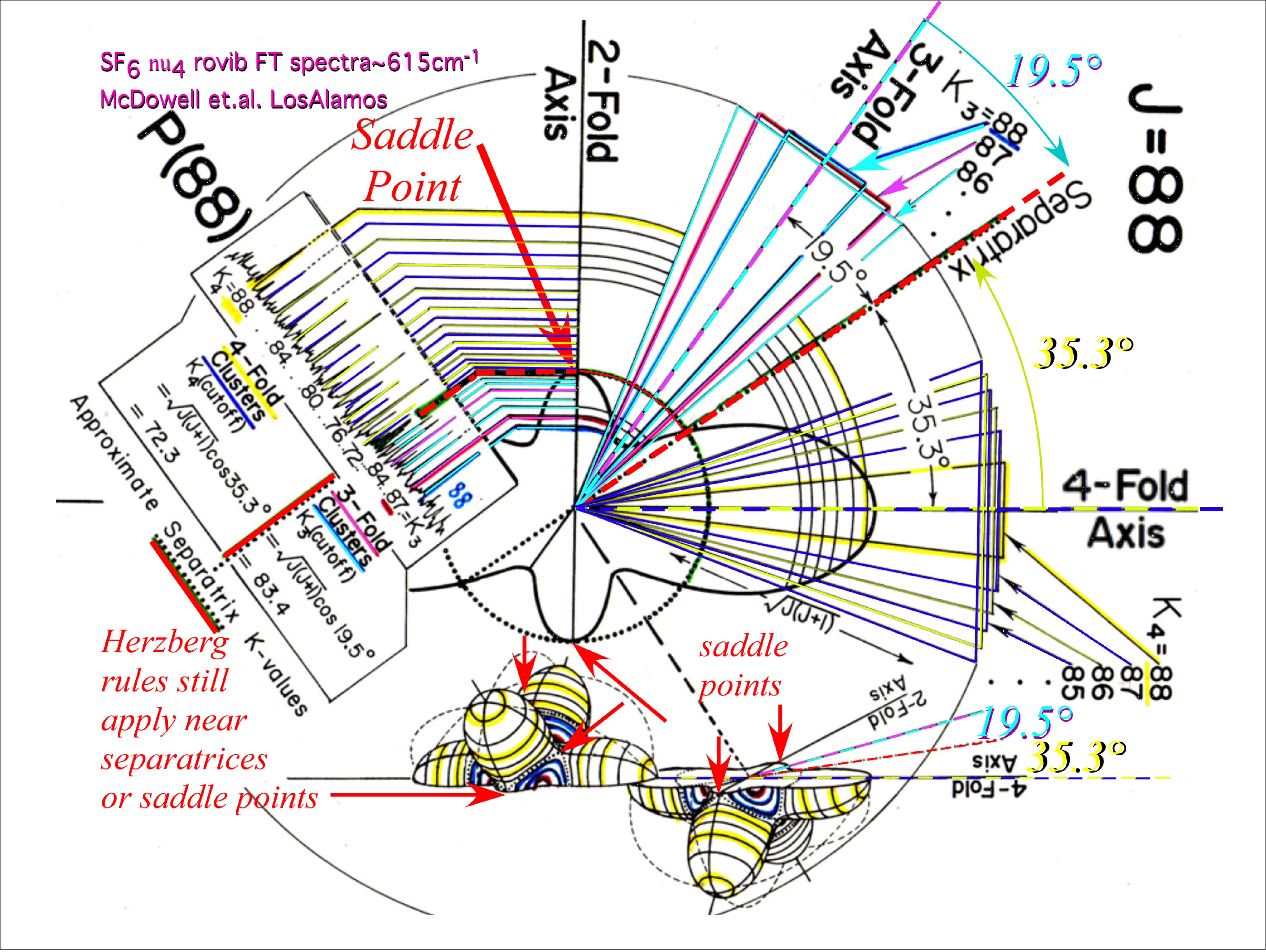
$$= \quad B\mathbf{J}^2 \quad + t_{440}\left(\mathbf{T}_0^4 + \sqrt{\frac{5}{14}}\left[\mathbf{T}_4^4 + \mathbf{T}_{-4}^4\right]\right) + \cdots$$



Rovibronic Energy (RE) Tensor Surface







SF6 nu4 rovib FT spectra~615cm-1
McDowell et.al. LosAlamos
P(88)
Saddle Point
2-Fold Axis
3-Fold Axis
J=88
19.5°
K3=88
87
86
Separatrix
9.5°
35.3°
4-Fold Axis
K4=88
87
86
85
K4=88 .84..80..76..72..84..87=K3
88
4-Fold Clusters
K4(cutoff) = √J(J+1)cos35.3° = 72.3
3-Fold Clusters
K3(cutoff) = √J(J+1)cos19.5° = 83.4
Approximate Separatrix K-values
√J(J+1)
Herzberg rules still apply near separatrices or saddle points
saddle points
2-Fold Axis
4-Fold Axis
19.5°
35.3°

New geometric approach to rotational eigenstates and spectra

Introduction to Rotational Energy Surfaces (RES) and multipole tensor expansion

Rank-2 tensors from D^2-matrix

Building Hamiltonian $\mathbf{H} = A\mathbf{J}_x^{\ 2} + B\mathbf{J}_y^{\ 2} + C\mathbf{J}_z^{\ 2}$ *out of scalar and tensor operators*

Comparing quantum and semi-classical calculations

Symmetric rotor levels and RES plots

Asymmetric rotor levels and RES plots

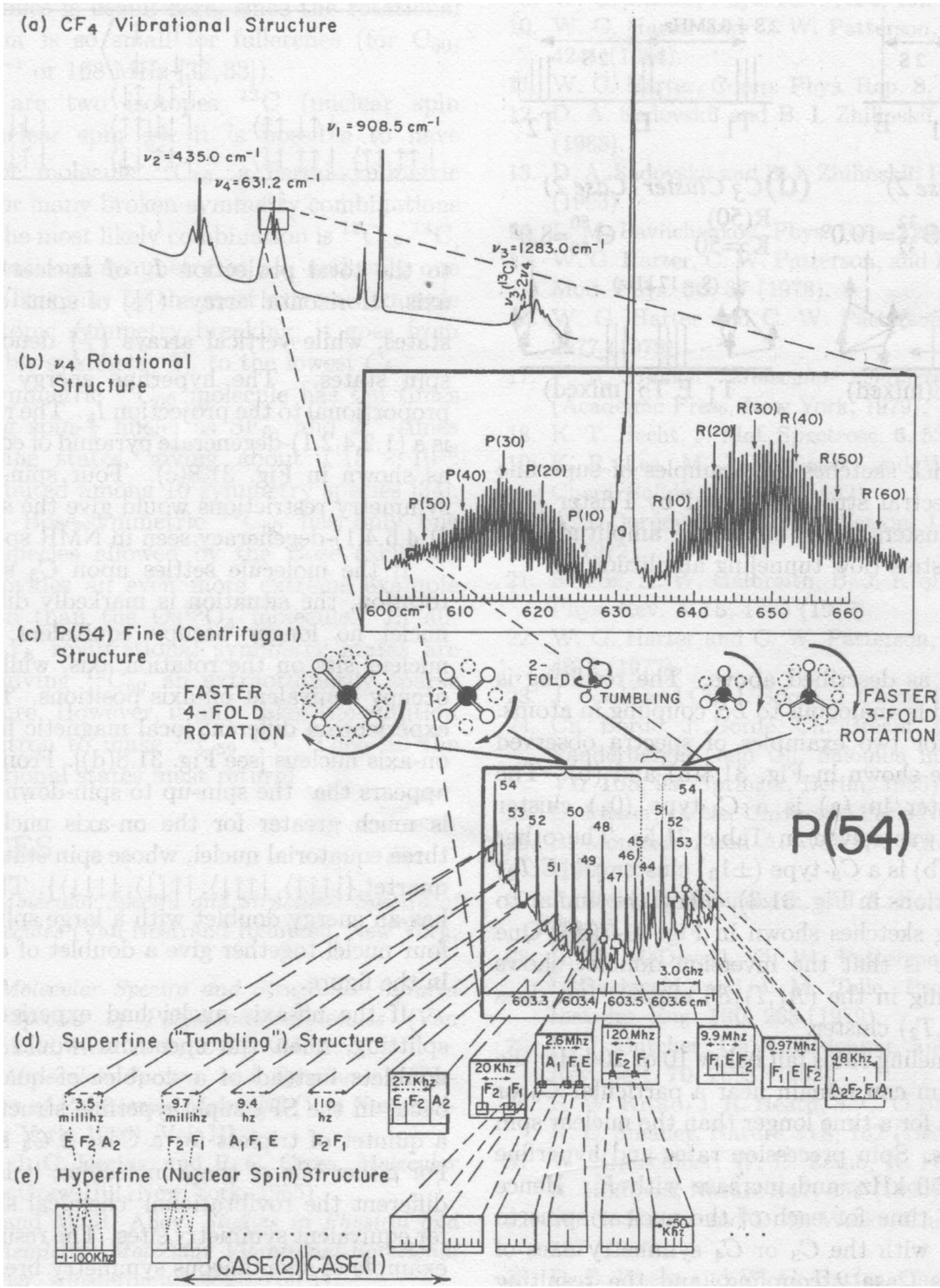
Spherical rotor levels and RES plots

SF_6 spectral fine structure

CF_4 spectral fine structure

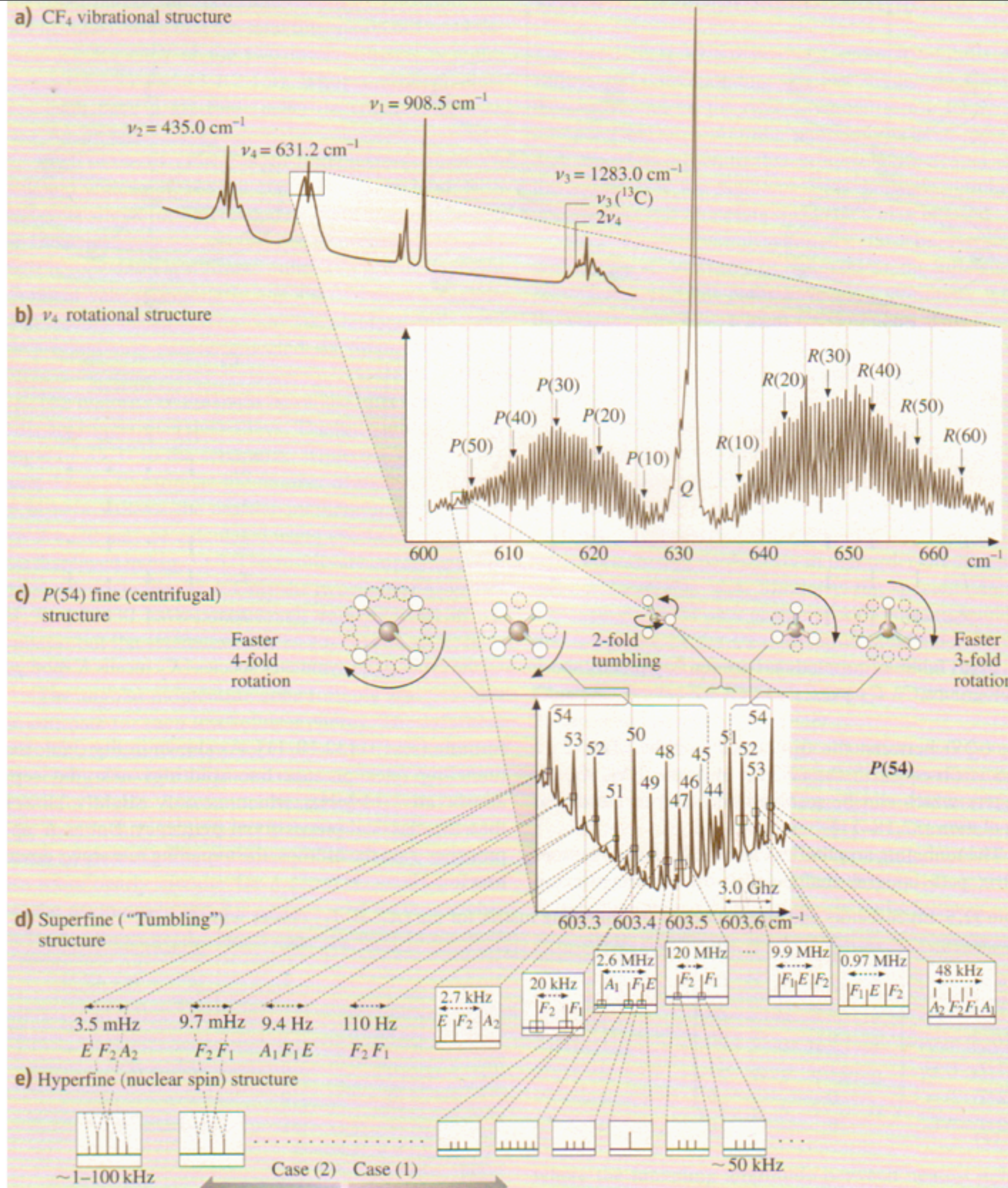
Example of frequency hierarchy for 16μm spectra of CF_4 (Freon-14)

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



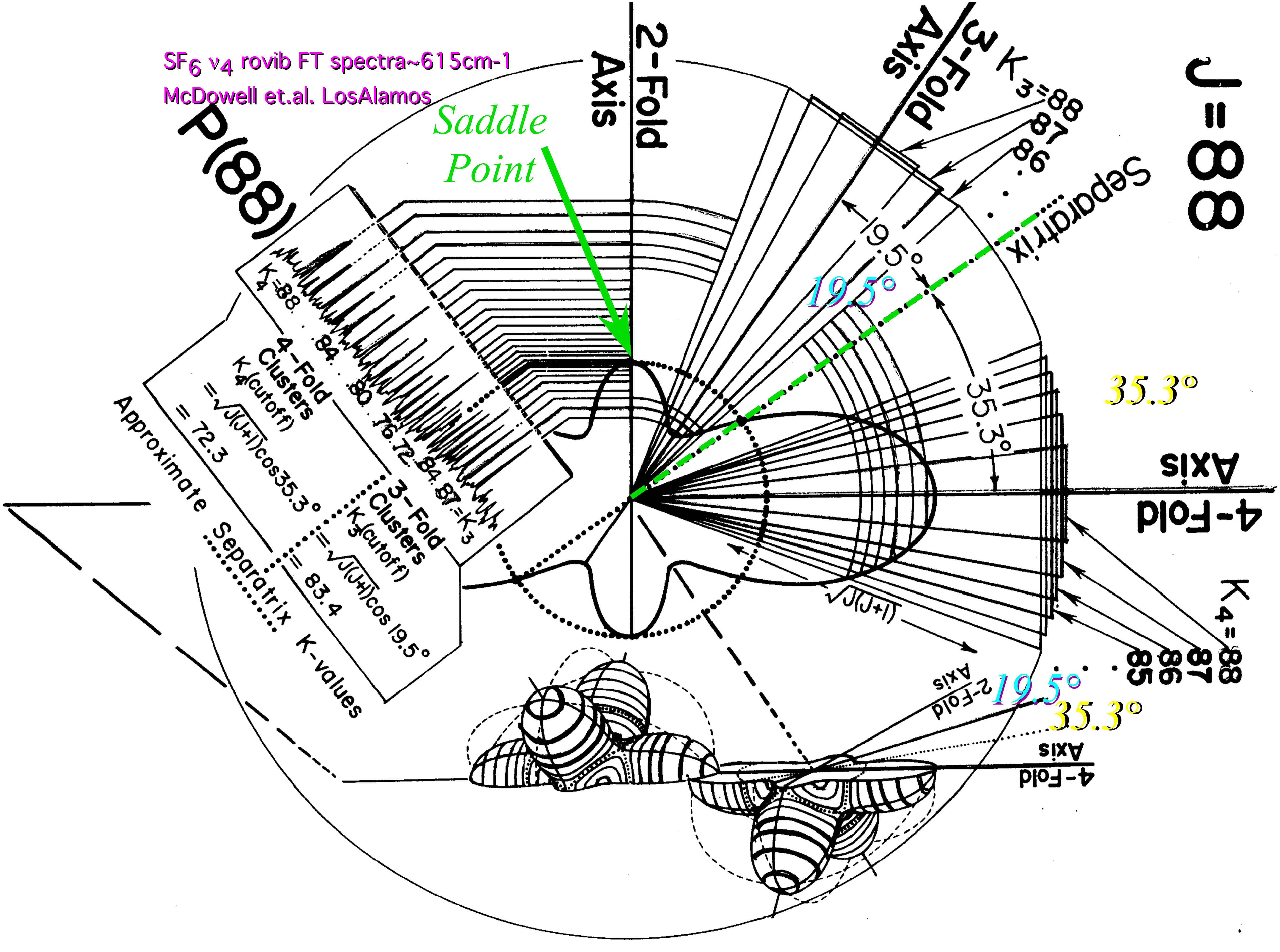
Example of frequency hierarchy for 16μm spectra of CF_4 (Freon-14)

W.G.Harter
Fig. 32.7
Springer Handbook of Atomic, Molecular, & Optical Physics
Gordon Drake Editor
(2005)



SF_6 ν_4 rovib FT spectra~615cm-1

McDowell et.al. LosAlamos



As of April 3, 2014

Links to the current Harter-Soft LearnIt web apps for Physics

Bold links have default redirect pages. *Italics* are not yet meant for production.Red: the final stages of testing.

List of *production* Harter-Soft Web Apps & Textbooks (For public)

Classical Mechanics with a Bang! - URL is "http://www.uark.edu/ua/modphys/markup/CMwBangWeb.html"
Quantum Theory for the Computer Age - URL is "http://www.uark.edu/ua/modphys/markup/QTCAWeb.html"
LearnIt Web Applications - URL is "http://www.uark.edu/ua/modphys/markup/LearnItWeb.html"

Individual web-apps for current classes:

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"
JerkIt - Production; URL is "http://www.uark.edu/ua/modphys/markup/JerkItWeb.html"
MolVibes - Production; URL is "http://www.uark.edu/ua/modphys/markup/MolVibesWeb.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"

The old relativity website (2005):
Relativity - Pirelli Entrant - Production; URL is "**http://www.uark.edu/ua/pirelli**" or "http://www.uark.edu/ua/pirelli/html/default.html"

Newer relativity web-apps currently being developed (2013-)
RelativIt Production; URL is "http://www.uark.edu/ua/modphys/markup/RelativItWeb.html"
RelaWavity Production; URL is "http://www.uark.edu/ua/modphys/markup/RelaWavityWeb.html"

Additional classical wep-apps:
Trebuchet Production; URL is "http://www.uark.edu/ua/modphys/markup/TrebuchetWeb.html"
WaveIt Production; URL is "http://www.uark.edu/ua/modphys/markup/WaveItWeb.html"

Link to master list of all Harter-Soft Web Apps & Textbooks (Prod, Testing, & Developement)

http://www.uark.edu/ua/modphys/testing/markup/Harter-SoftWebApps.html