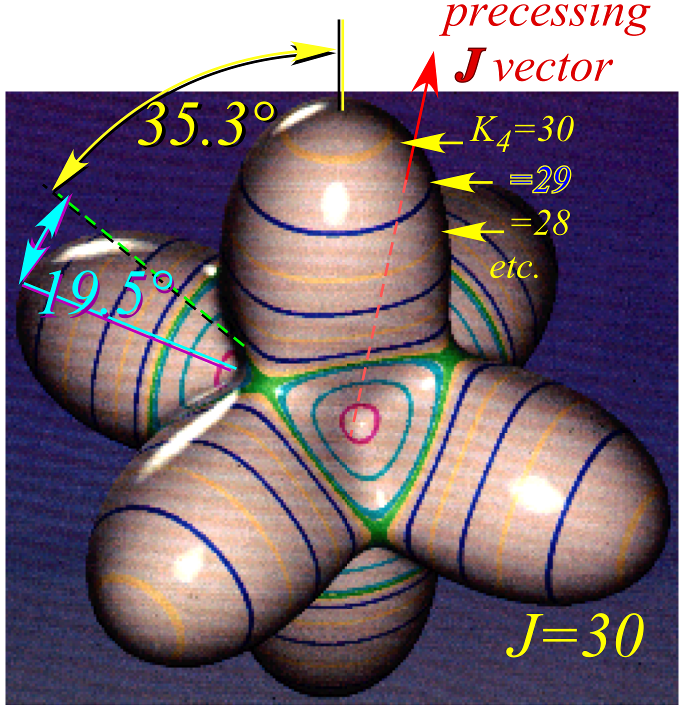
Rovibronic energy topography I.

Tensor eigenvalue structure and tunneling effects in low-symmetry species-clustering in high symmetry molecules.



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University of Arkansas

HARTER-Soft

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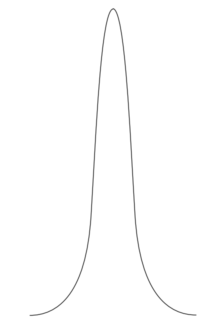
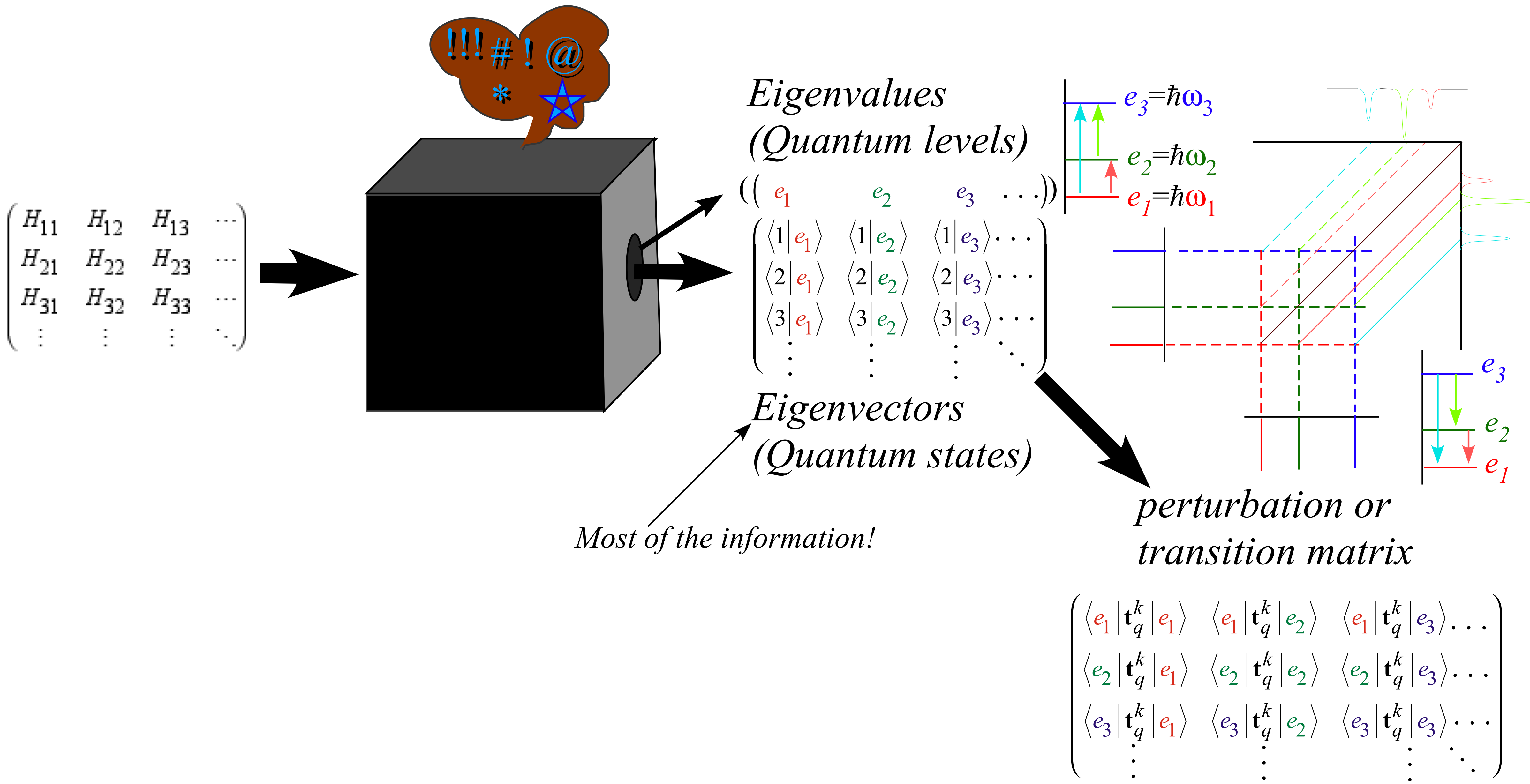
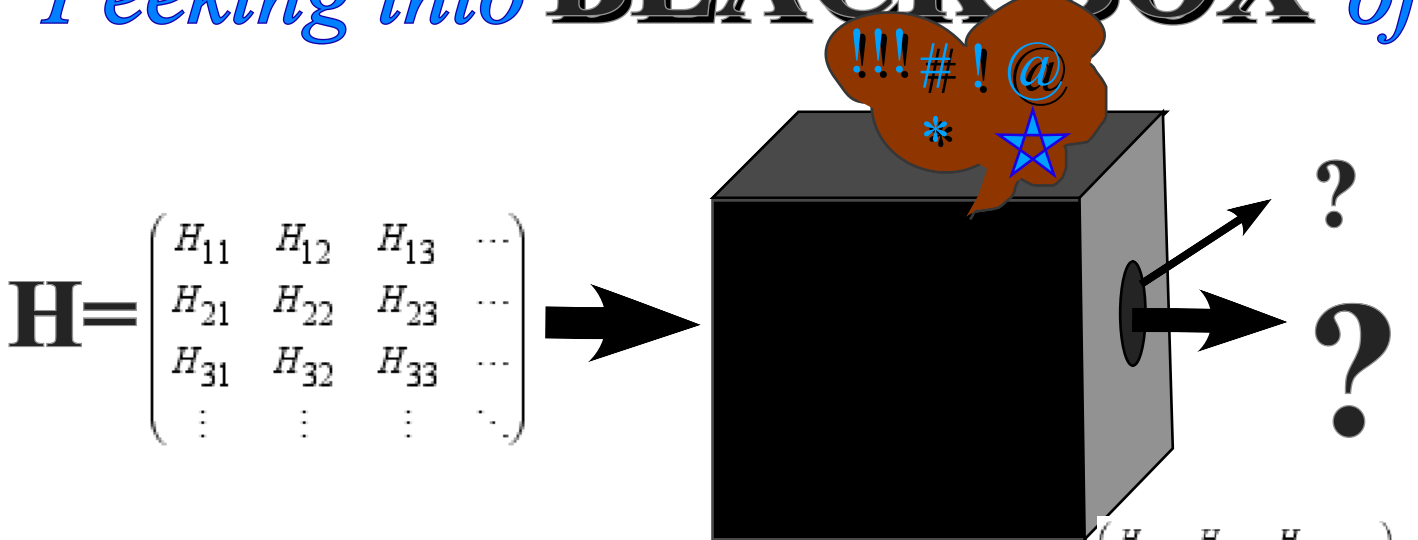
Matrix Diagonalization

The **BLACK BOX** *of quantum physics, chemistry, and spectroscopy*





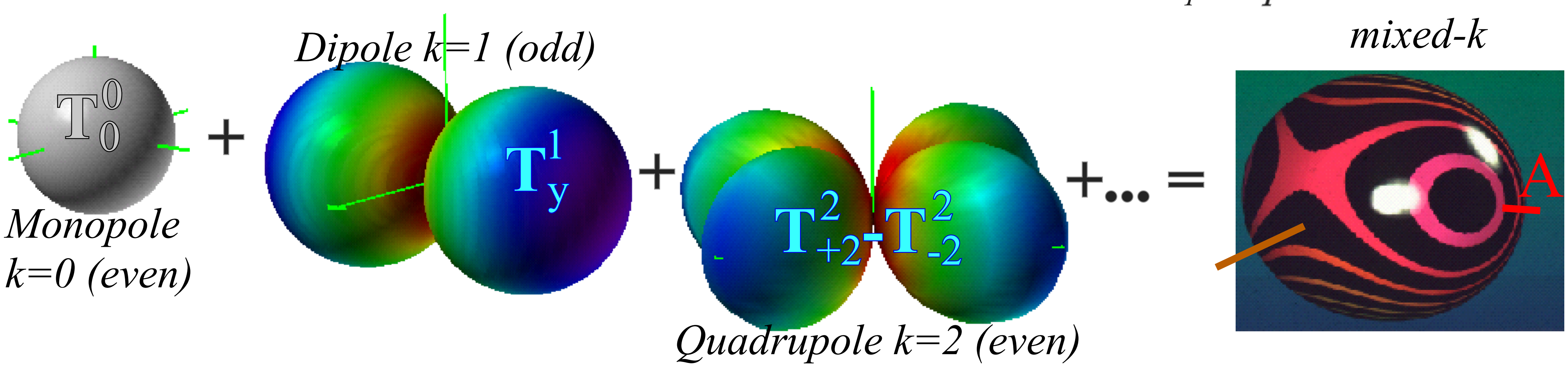
Peeking into **BLACK BOX** *of matrix diagonalization:*



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 +..*

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



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)

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)

$$\mathbf{u}^0_0=\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}\frac{1}{\sqrt{3}}$$

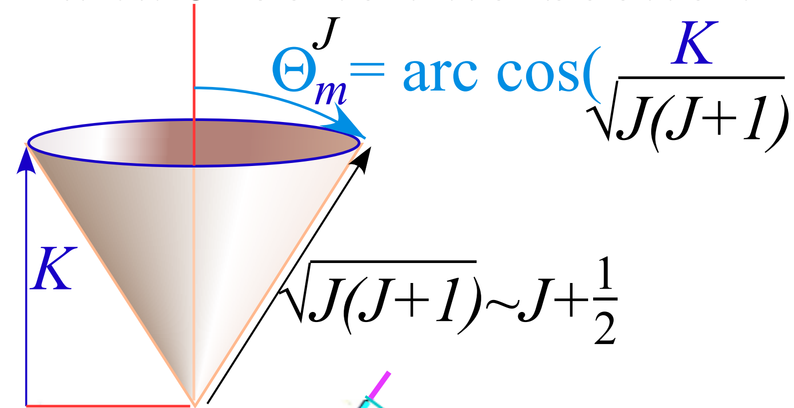
rank-0 (scalar)

Mutually commuting diagonal operators

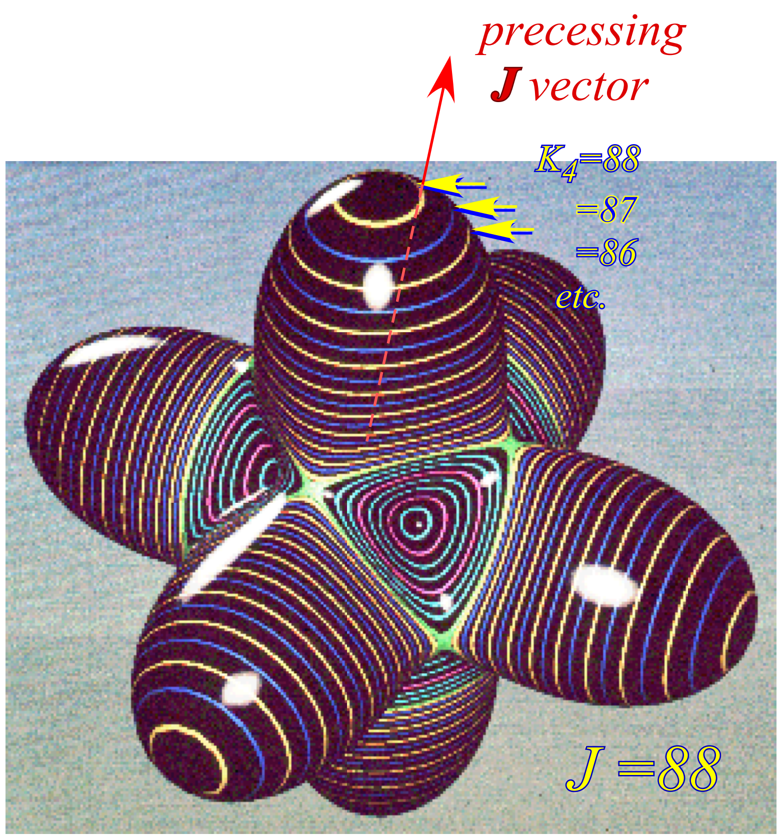
SF_6 Spectra of O_h Ro-vibronic Hamiltonian described by RE Tensor Topography and J-cone intersection

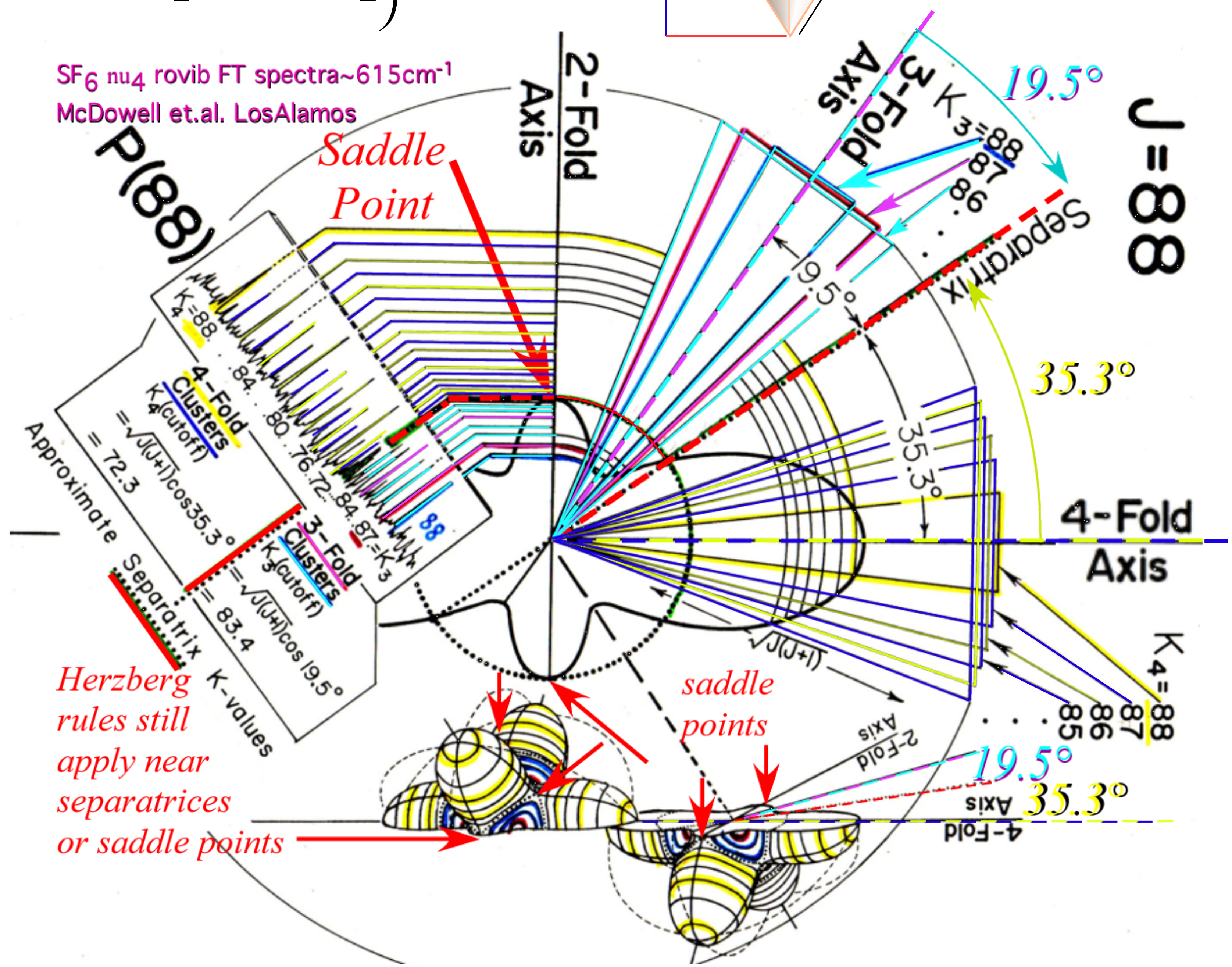
$$\mathbf{H} = B\left(\mathbf{J}_x^2 + \mathbf{J}_y^2 + \mathbf{J}_z^2\right) + t_{440}\left(\mathbf{J}_x^4 + \mathbf{J}_y^4 + \mathbf{J}_z^4 - \frac{3}{5}J^4\right) + \cdots$$

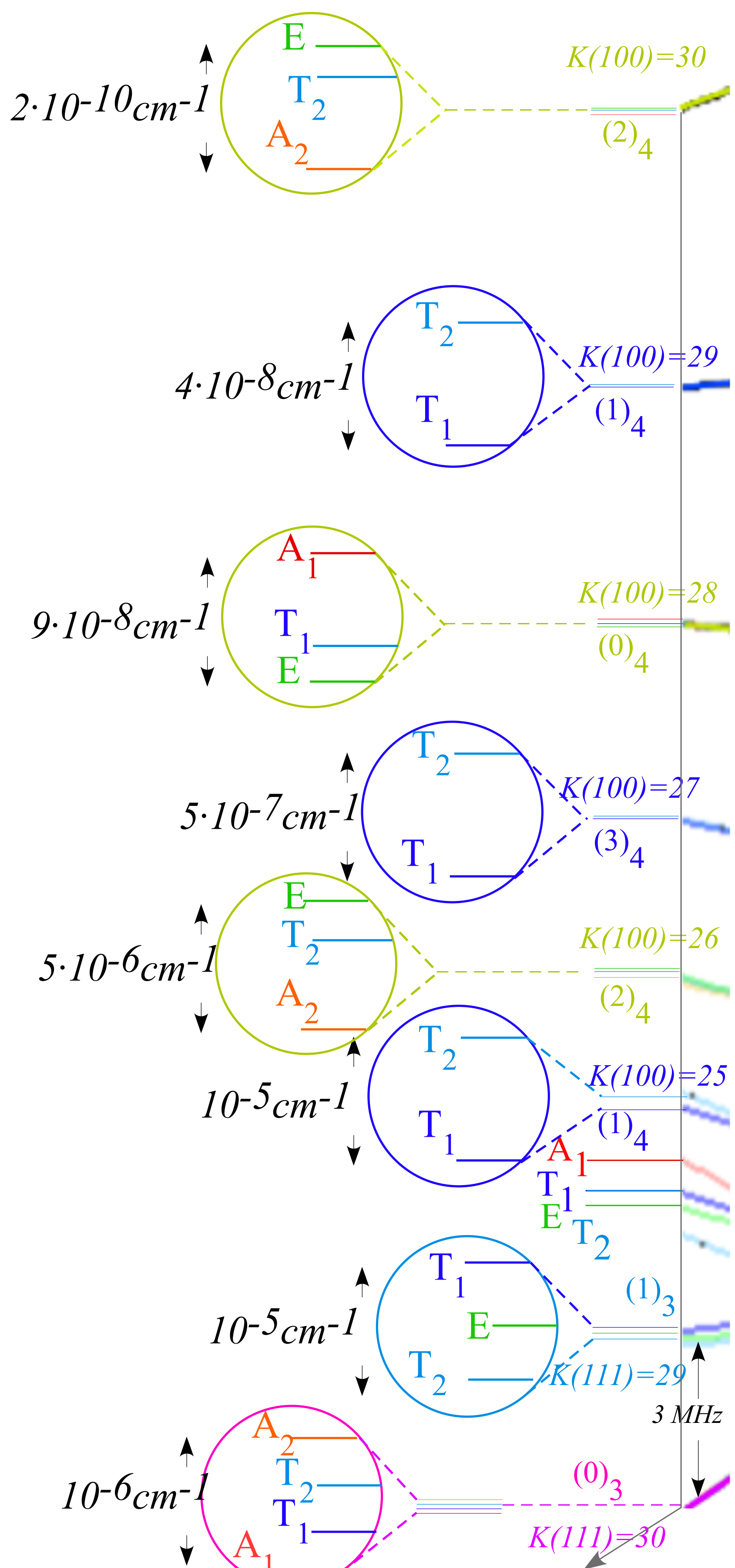
$$= \quad B\mathbf{J}^2 \quad + t_{440}\left(\mathbf{T}_0^4 + \sqrt{\frac{5}{14}}\left[\mathbf{T}_4^4 + \mathbf{T}_{-4}^4\right]\right) + \cdots$$



Rovibronic Energy (RE) Tensor Surface

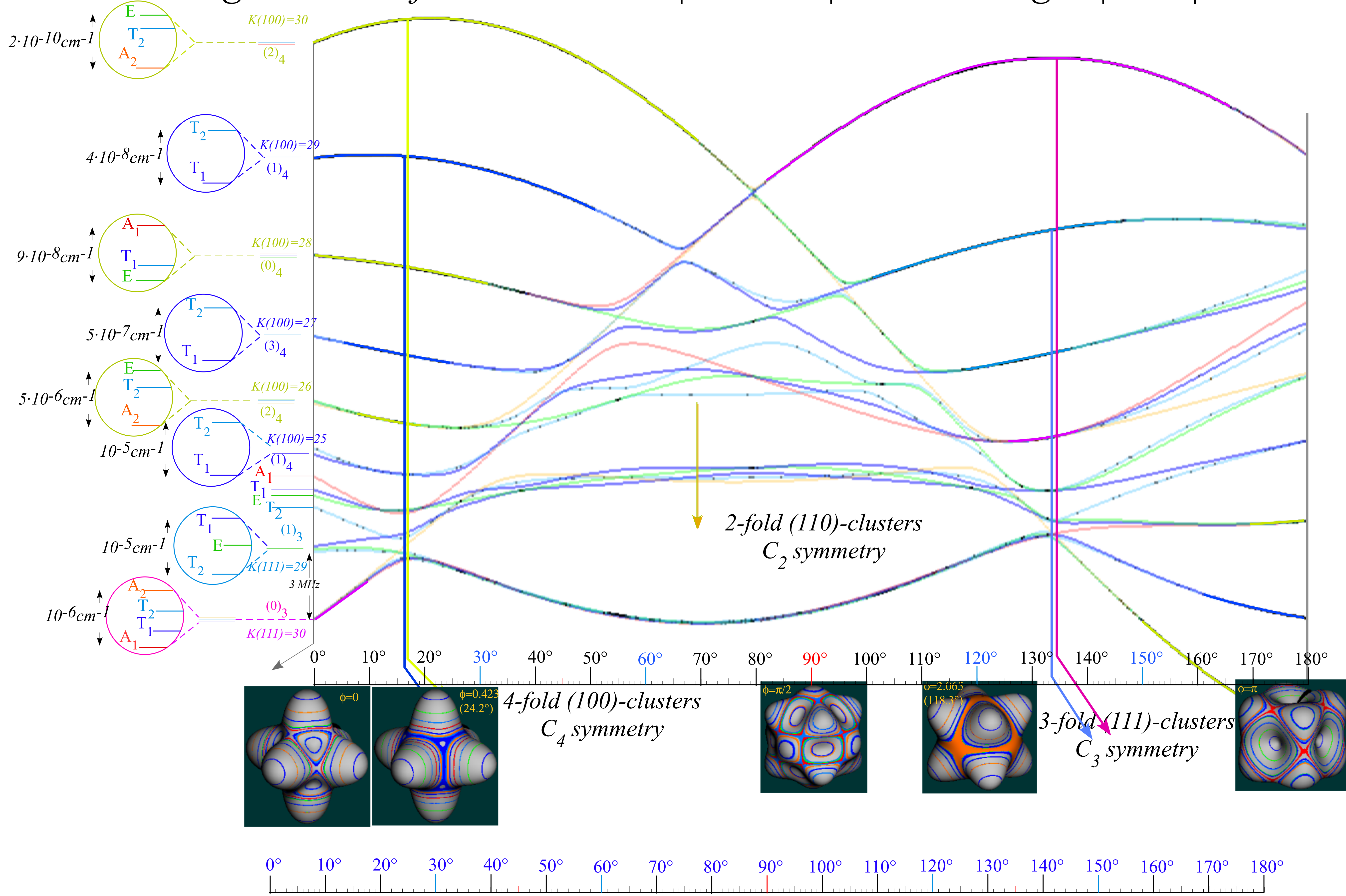




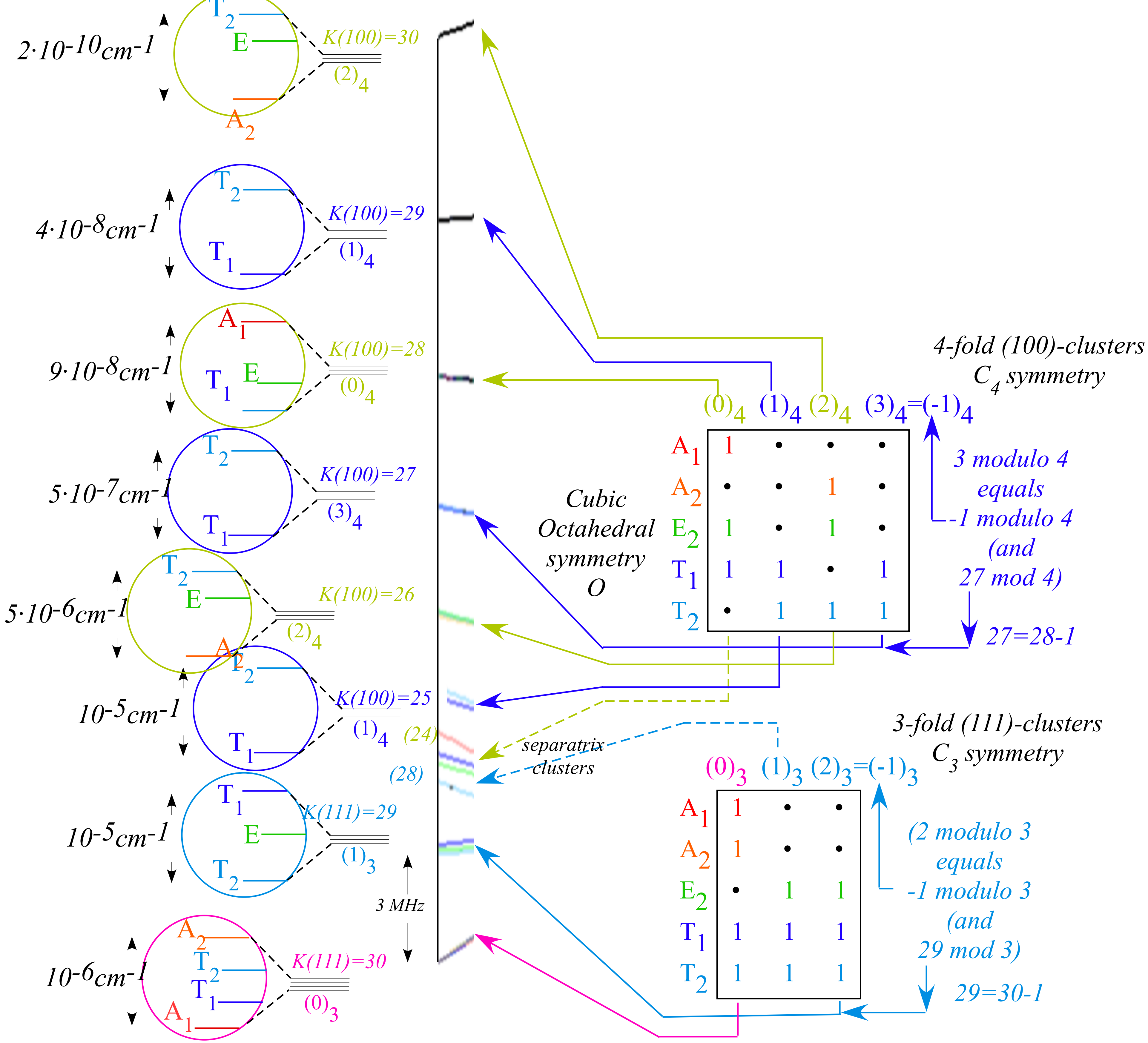


K(100)=30
(2)4
2·10-10cm-1
E
T2
A2
K(100)=29
(1)4
4·10-8cm-1
T2
T1
K(100)=28
(0)4
9·10-8cm-1
A1
T1
E
K(100)=27
(3)4
5·10-7cm-1
T2
T1
K(100)=26
(2)4
5·10-6cm-1
E
T2
A2
K(100)=25
(1)4
10-5cm-1
T2
T1
A1
T1
E
T2
(1)3
10-5cm-1
T1
E
T2
K(111)=29
3 MHz
(0)3
10-6cm-1
A2
T2
T1
A1
K(111)=30

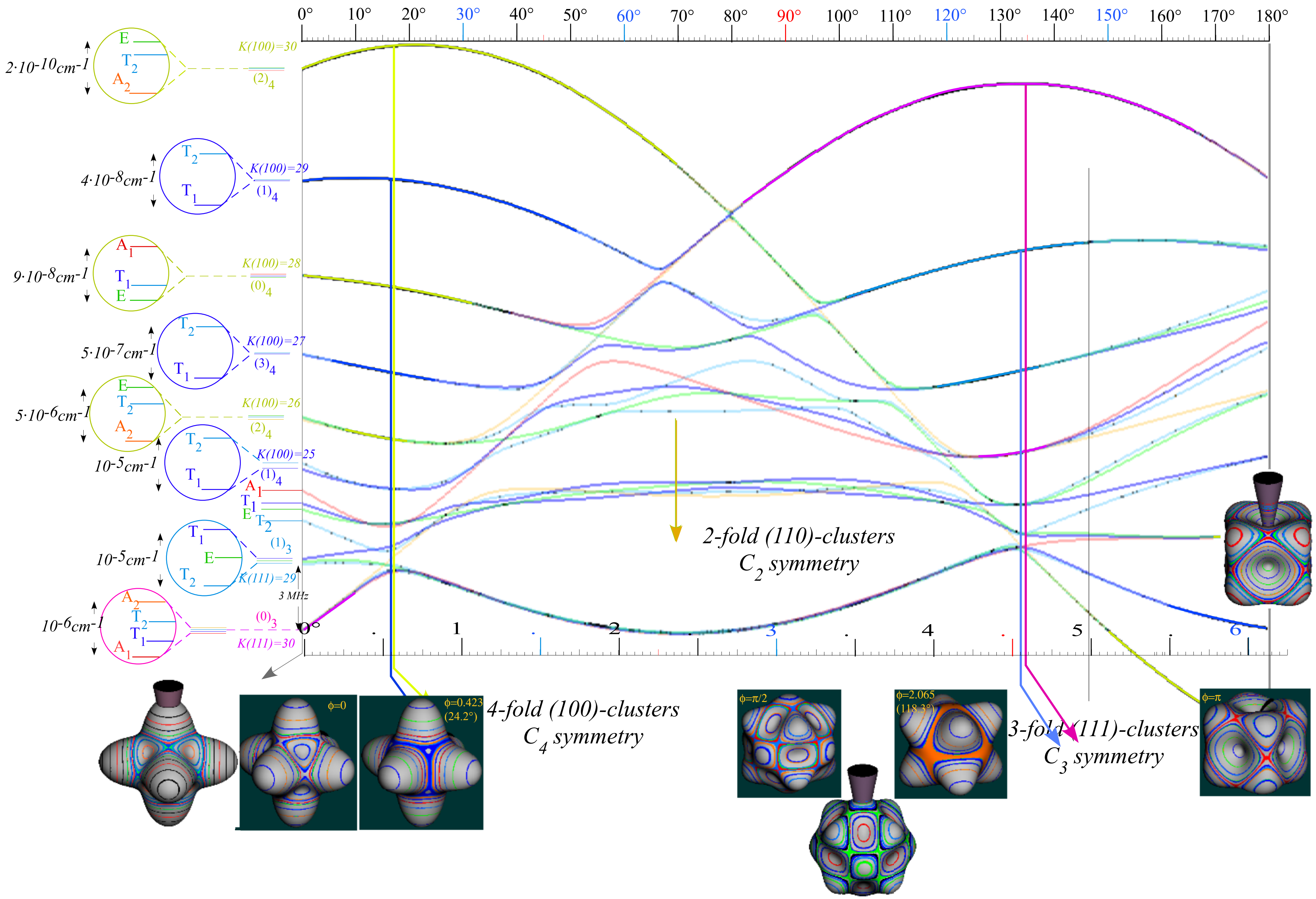
Eigenvalues of $\mathbf{H}=B\mathbf{J}^2+\cos\phi\,\mathbf{T}^{[4]}+\sin\phi\,\mathbf{T}^{[6]}$ *vs. mix angle* ϕ*:* $0<\phi<$



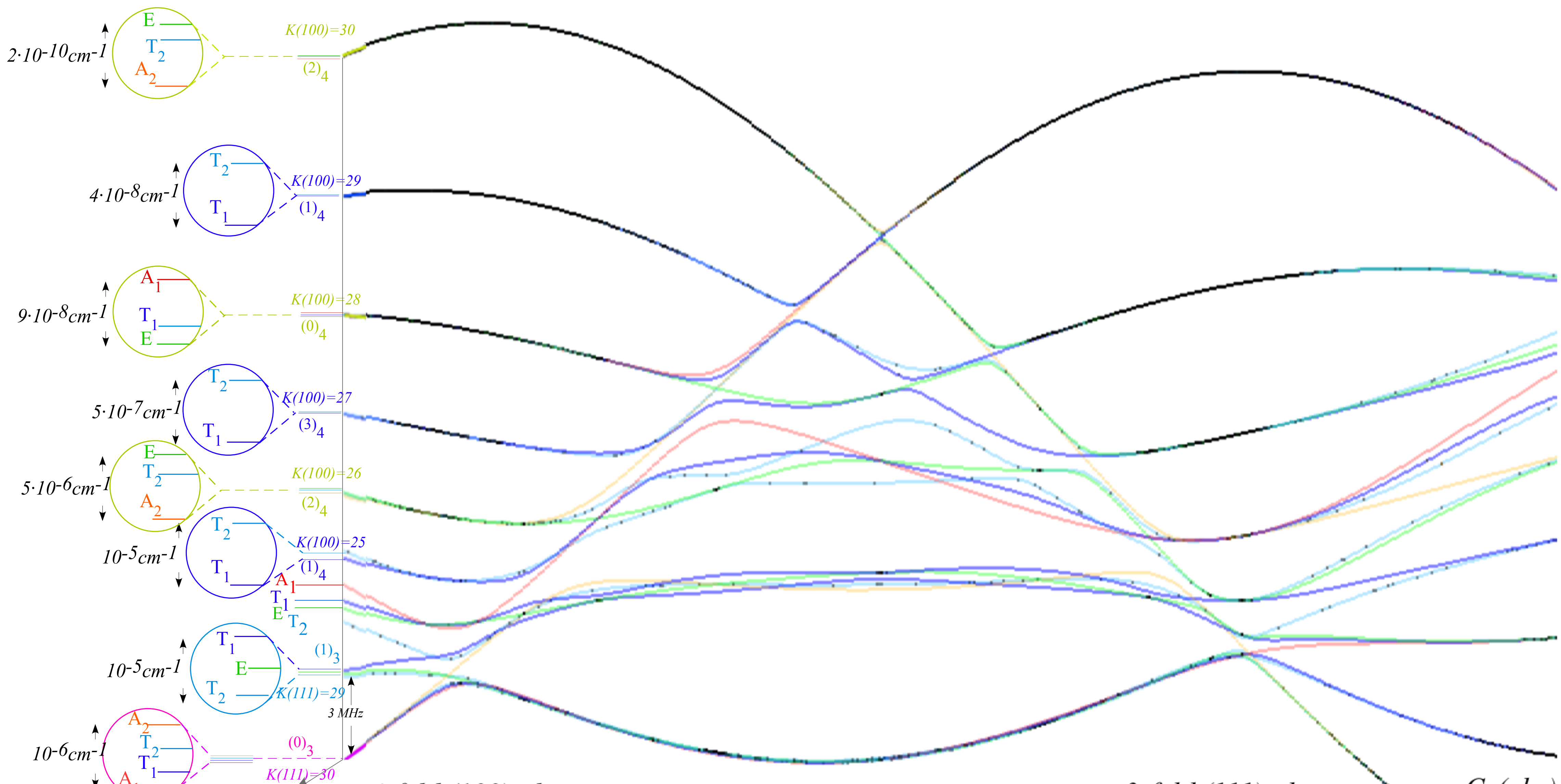
J=30 Eigenvalues of $\mathbf{H}=B\mathbf{J}^2+T^{[4]}$



Eigenvalues of $\mathbf{H}=BJ^2+\cos\phi\,\mathbf{T}^{[4]}+\sin\phi\,\mathbf{T}^{[6]}$ *vs. mix angle* ϕ*: 0<*ϕ*<*



Eigenvalues of $H=BJ^2+\cos(\phi)T^{[4]}+\sin(\phi)T^{[6]}$ vs. Parameter ϕ: $0<\phi<$



4-fold (100)-clusters C_4 symmetry	$(0)_4$	$(1)_4$	$(2)_4$	$(3)_4$
A_1	1	•	•	•
A_2	•	•	1	•
E_2	1	•	1	•
T_1	1	1	•	1
T_2	•	1	1	1

Cubic Octahedral symmetry O

2-fold (110)-clusters C_2 symmetry	$(0)_2$	$(1)_2$
A_1	1	•
A_2	•	1
E_2	1	1
T_1	1	2
T_2	2	1

3-fold (111)-clusters C_3 symmetry	$(0)_3$	$(1)_3$	$(2)_3$
A_1	1	•	•
A_2	1	•	•
E_2	•	1	1
T_1	1	1	1
T_2	1	1	1

$C_1(abc)$	$(0)_1$
A_1	1
A_2	1
E_2	2
T_1	3
T_2	3

Classical Legendre $P_k(\cos\theta)$

$$P_0 = 1$$
$$P_1(\cos\theta) = \cos\theta$$
$$P_2(\cos\theta) = -\frac{1}{2} + \frac{3}{2}\cos^2\theta$$
$$P_3(\cos\theta) = -\frac{3}{2}\cos\theta + \frac{5}{2}\cos^3\theta$$
$$P_4(\cos\theta) = \frac{3}{8} - \frac{30}{8}\cos^2\theta + \frac{35}{8}\cos^4\theta$$

Classical J-polynomials $|J|^k P_k(J_x, J_y, J_z)$

$$P_0 = 1$$
$$|J|^1 P_1(\cos\theta) = J_z$$
$$|J|^2 P_2(\cos\theta) = -\frac{1}{2}|J|^2 + \frac{3}{2}J_z^2$$
$$|J|^3 P_3(\cos\theta) = -\frac{3}{2}|J|^2 J_z + \frac{5}{2}J_z^3$$
$$|J|^4 P_4(\cos\theta) = \frac{3}{8}|J|^4 - \frac{30}{8}|J|^2 J_z^2 + \frac{35}{8}J_z^4$$

Compare classical with quantum

(Wigner-Racah $\mathbf{v}^k$ tensor eigenvalues)

$$\left\langle \mathbf{v}_0^k \right\rangle_m^J = \left\langle \begin{matrix} J \\ m \end{matrix} \middle| \mathbf{v}_0^k \middle| \begin{matrix} J \\ m \end{matrix} \right\rangle = (-1)^{J-m}\sqrt{[k]}\begin{pmatrix} k & J & J \\ 0 & m & -m \end{pmatrix} = (-1)^k \sqrt{\frac{[k]}{[J]}} C^{k\,J\,J}_{q\,m\,m}$$

$$\left\langle \mathbf{v}_0^0 \right\rangle_m^J = \frac{1}{\sqrt{2J+1}} \left[1 \right]$$

$$\left\langle \mathbf{v}_0^1 \right\rangle_m^J = \frac{2\sqrt{3}}{\sqrt{2J+2:0}} \left[m \right]$$

$$\left\langle \mathbf{v}_0^2 \right\rangle_m^J = \frac{2^2\sqrt{5}}{\sqrt{2J+3:-1}} \left[-\frac{1}{2}J(J+1) + \frac{3}{2}m^2 \right]$$

$$\left\langle \mathbf{v}_0^3 \right\rangle_m^J = \frac{2^3\sqrt{7}}{\sqrt{2J+4:-2}} \left[-\frac{3}{2}(J(J+1) - \frac{2}{3})m + \frac{5}{2}m^3 \right]$$

$$\left\langle \mathbf{v}_0^4 \right\rangle_m^J = \frac{2^4\sqrt{9}}{\sqrt{2J+5:-3}} \left[\frac{3}{8}(J+2:-1) - \frac{30}{8}(J(J+1) - \frac{5}{6})m^2 + \frac{35}{8}m^4 \right]$$

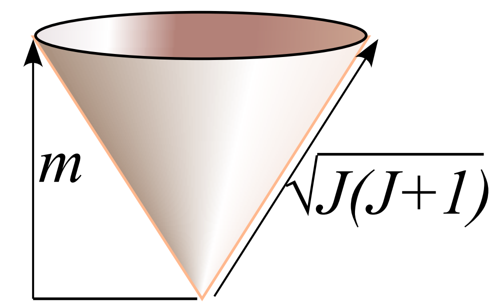
Semi-classical J-cone geometry of e-values

exact

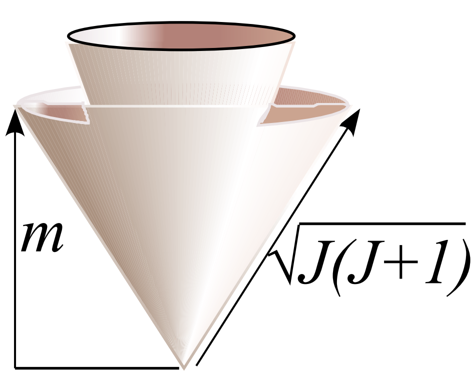
exact

approx.

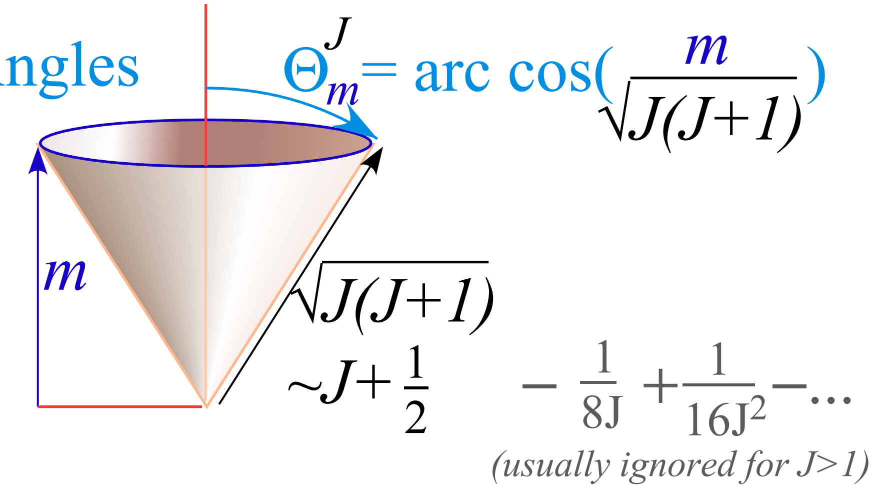
approx.

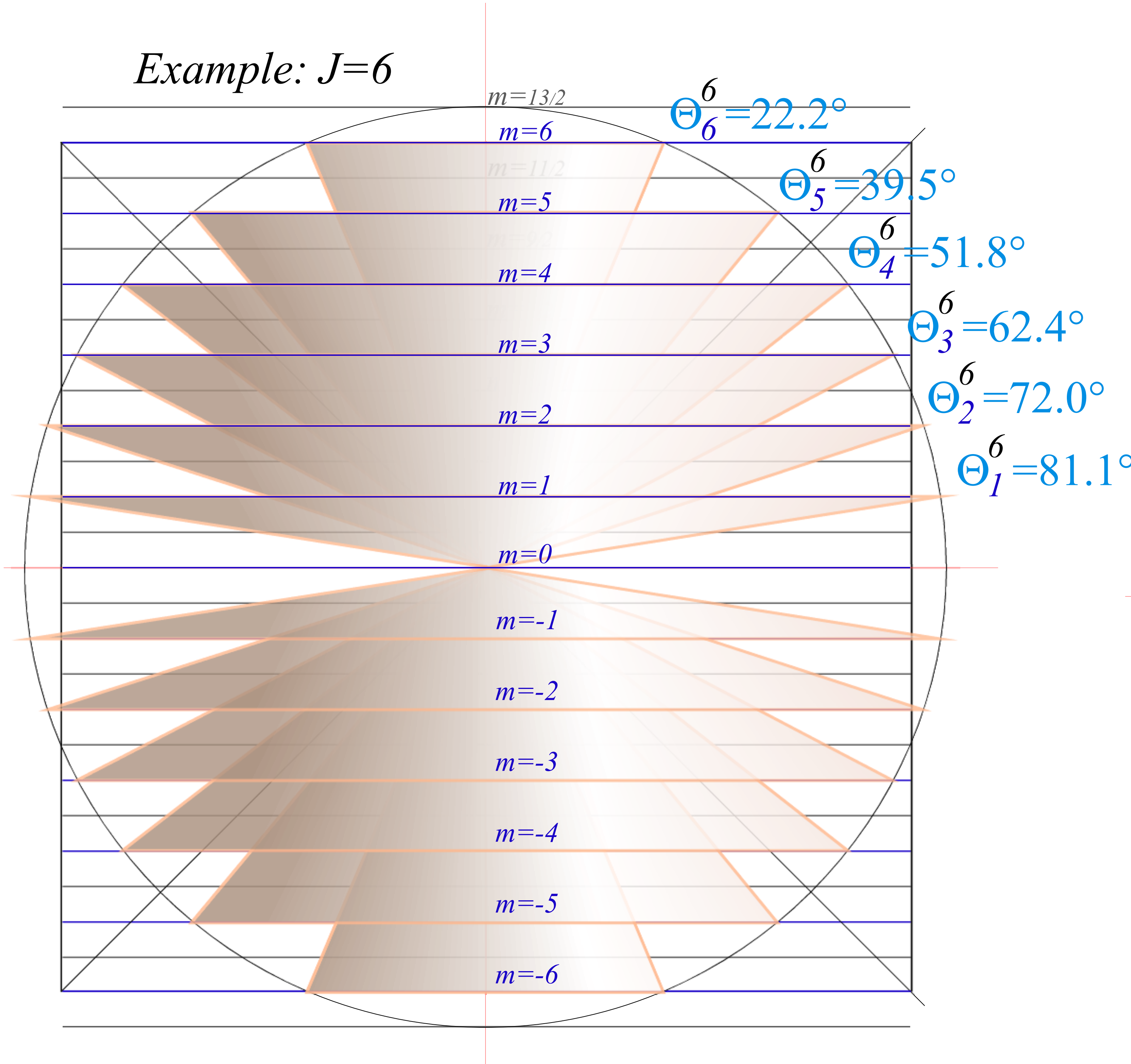


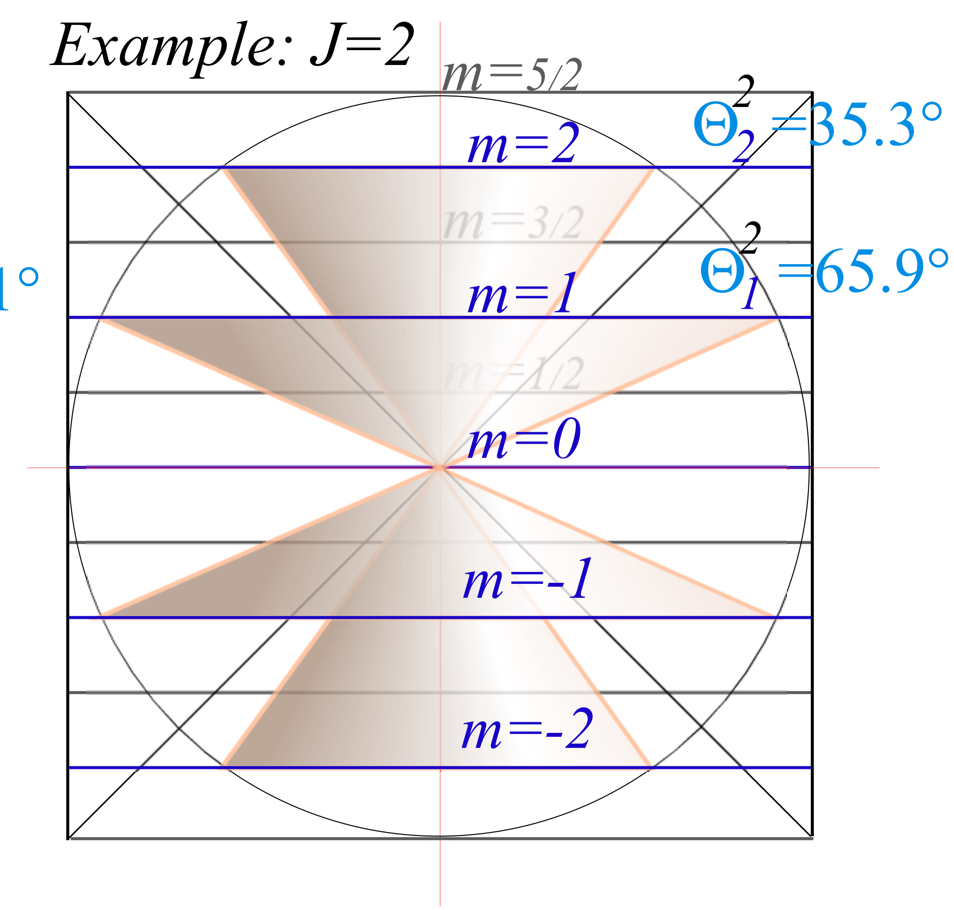
$$\left(= \frac{\sqrt{3}}{\sqrt{[J]}} \frac{m}{\sqrt{J(J+1)}} \right)$$

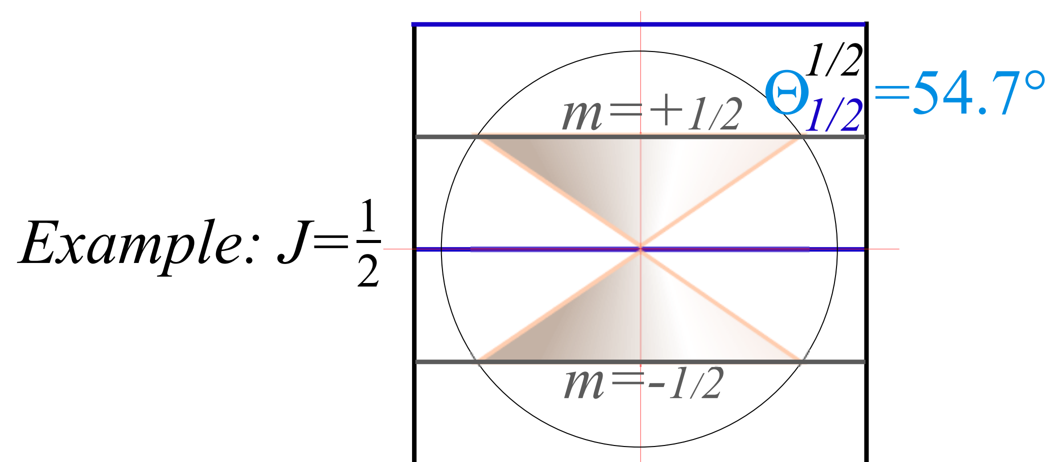


Angular Momentum Cones and Quantum Polar Angles

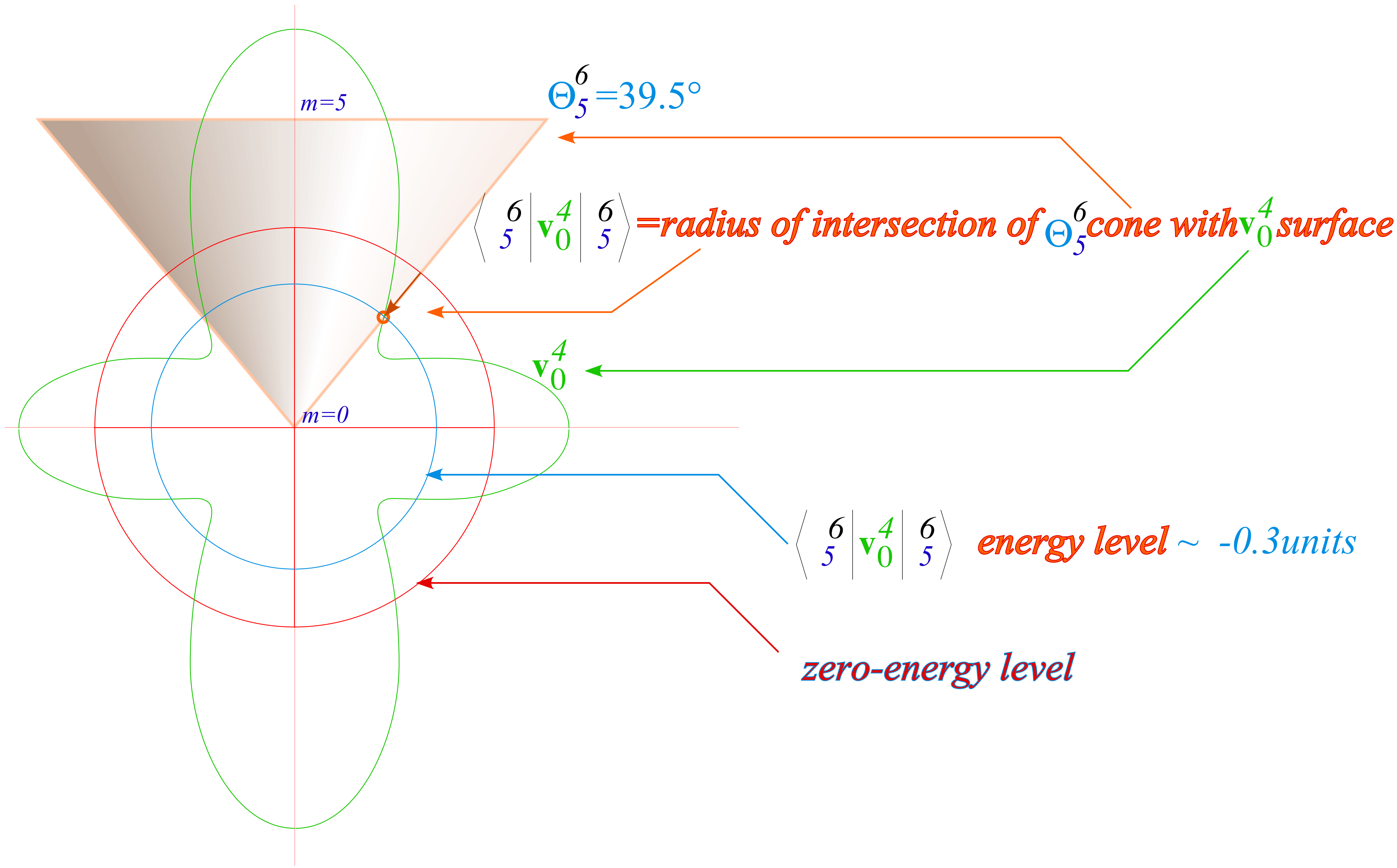


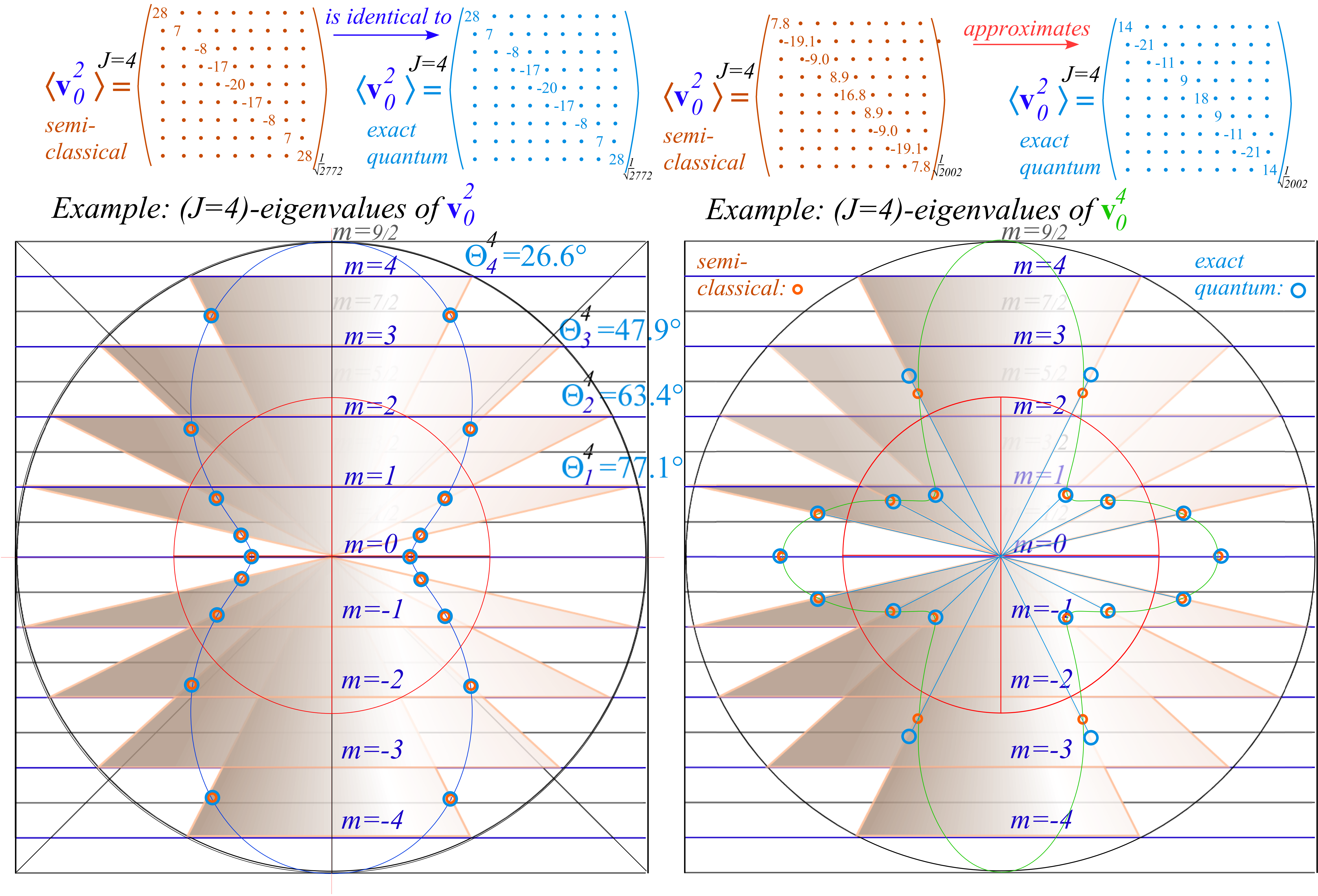






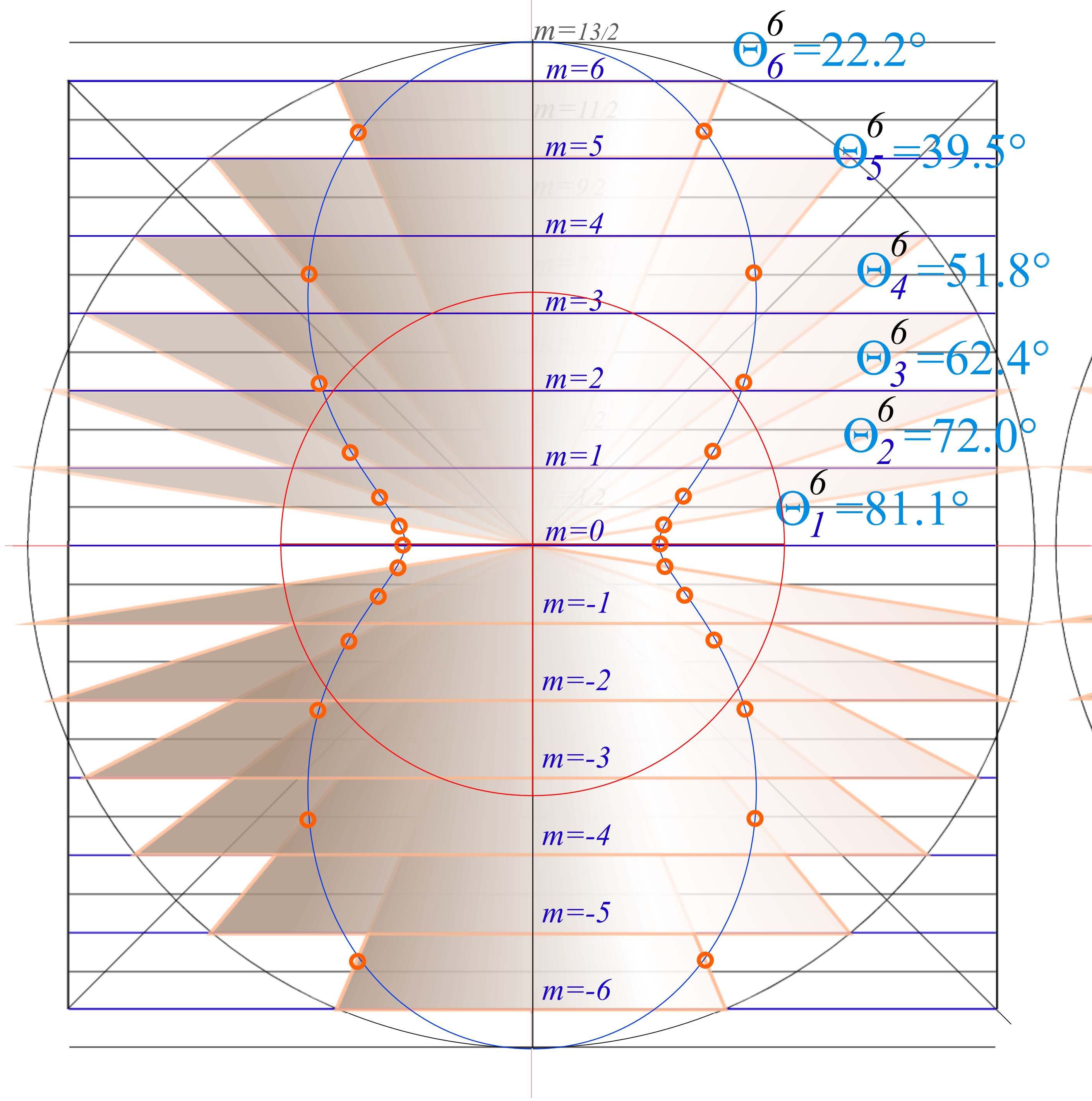
1^{st} semi-classical approximation of $\left\langle \mathbf{v}_0^k \right\rangle_m^J = \left\langle \begin{matrix} J \\ m \end{matrix} \middle| \mathbf{v}_0^k \middle| \begin{matrix} J \\ m \end{matrix} \right\rangle$ Example: $\left\langle \mathbf{v}_0^{k=4} \right\rangle_{m=5}^{J=6} = \left\langle \begin{matrix} 6 \\ 5 \end{matrix} \middle| \mathbf{v}_0^4 \middle| \begin{matrix} 6 \\ 5 \end{matrix} \right\rangle$



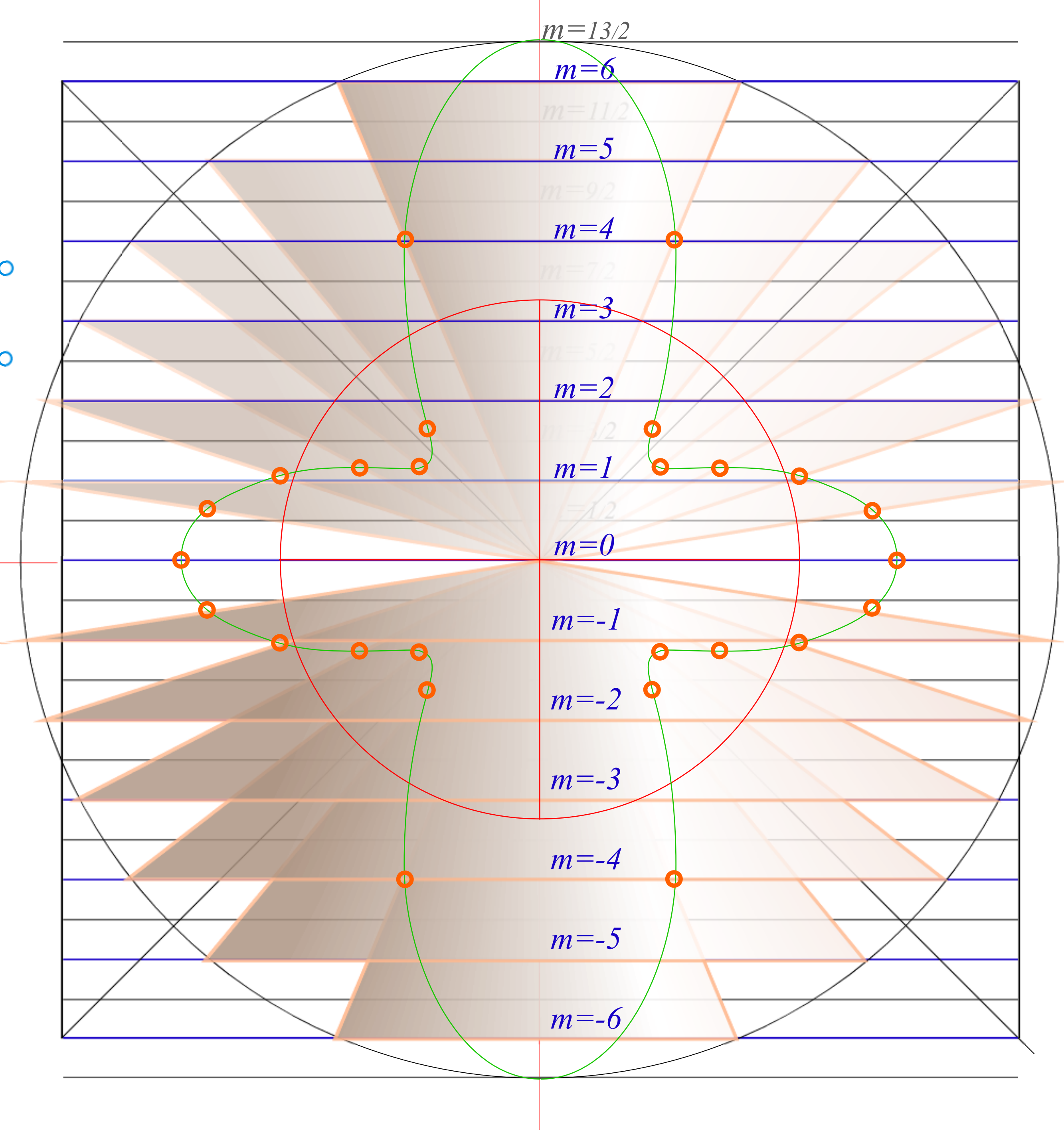


J=4
⟨v 2 0⟩ =
semi-classical
28 7 -8 -17 -20 -17 -8 7 28
1/√2772
is identical to
J=4
⟨v 2 0⟩ =
exact quantum
28 7 -8 -17 -20 -17 -8 7 28
1/√2772
J=4
⟨v 2 0⟩ =
semi-classical
7.8 -19.1 -9.0 8.9 16.8 8.9 -9.0 -19.1 7.8
1/√2002
approximates
J=4
⟨v 2 0⟩ =
exact quantum
14 -21 -11 9 18 9 -11 -21 14
1/√2002
Example: (J=4)-eigenvalues of v 2 0
Example: (J=4)-eigenvalues of v 4 0
m=9/2
m=4
m=7/2
m=3
m=5/2
m=2
m=1
m=0
m=-1
m=-2
m=-3
m=-4
Θ 4 4 =26.6°
Θ 4 3 =47.9°
Θ 4 2 =63.4°
Θ 4 1 =77.1°
m=9/2
semi-classical:
exact quantum:
m=4
m=7/2
m=3
m=5/2
m=2
m=1
m=0
m=-1
m=-2
m=-3
m=-4

Example: (J=6)-eigenvalues of $\mathbf{v}_0^2$



Example: (J=6)-eigenvalues of $\mathbf{v}_0^4$



Simple Rigid Rotor Hamiltonian...

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

...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)*

H= *B* **J**^{2}

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

Symmetric Top *(A=B≠C)*

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

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

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

Asymmetric Top *(A≠B≠C)*

H= *B* **J**^{2} +(2*C* -*A*- *B*)/3 $\mathbf{T}_0^{(2)}$ +(*A*- *B*)/√6($\mathbf{T}_2^{(2)}$ - $\mathbf{T}_{-2}^{(2)}$)

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* $Y_{q[\beta,\gamma]}^k$*)*

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

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

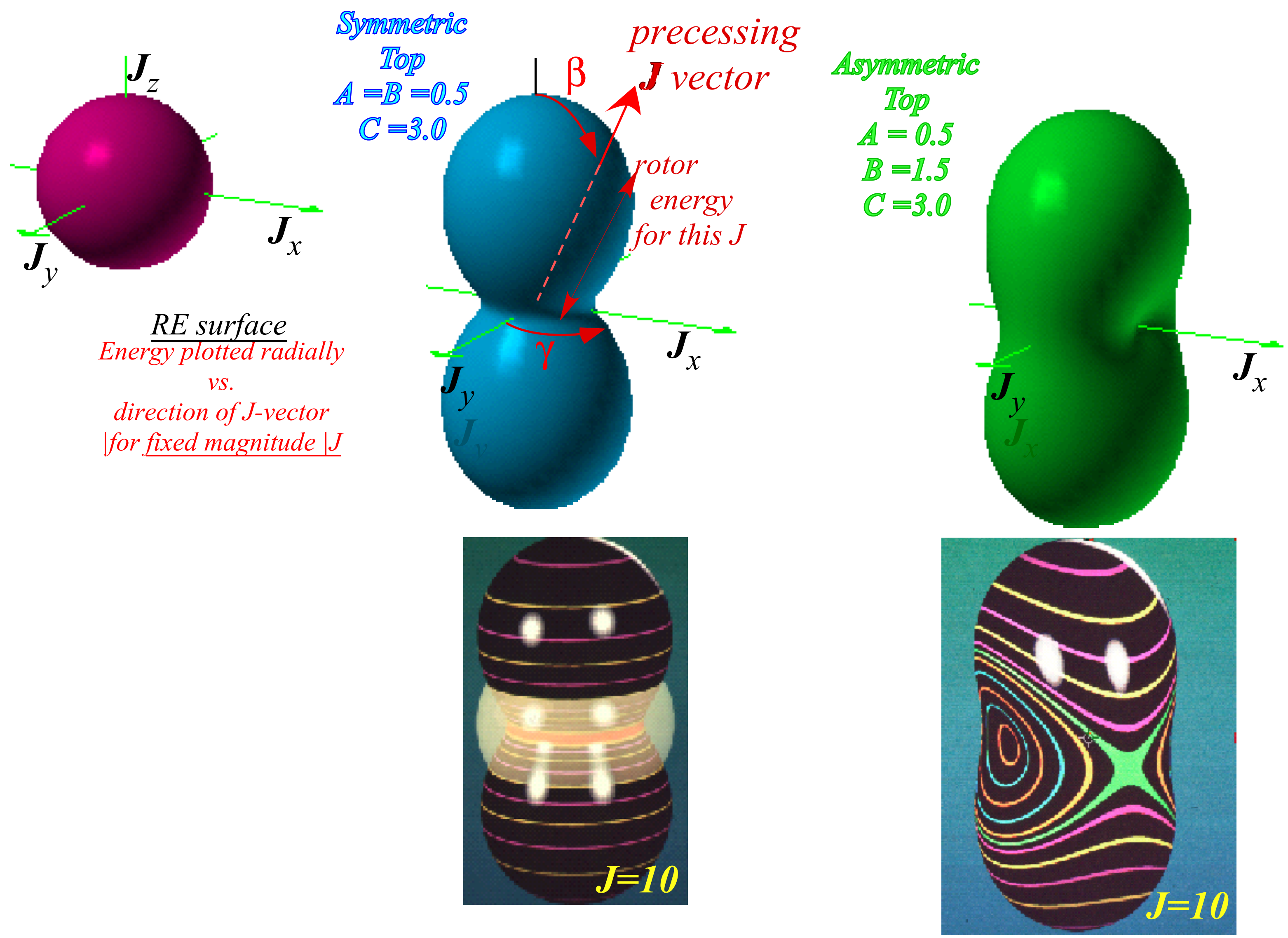
Classical RES Plot: *Rotational Energy (RE) surfaces and/or H-phase paths*

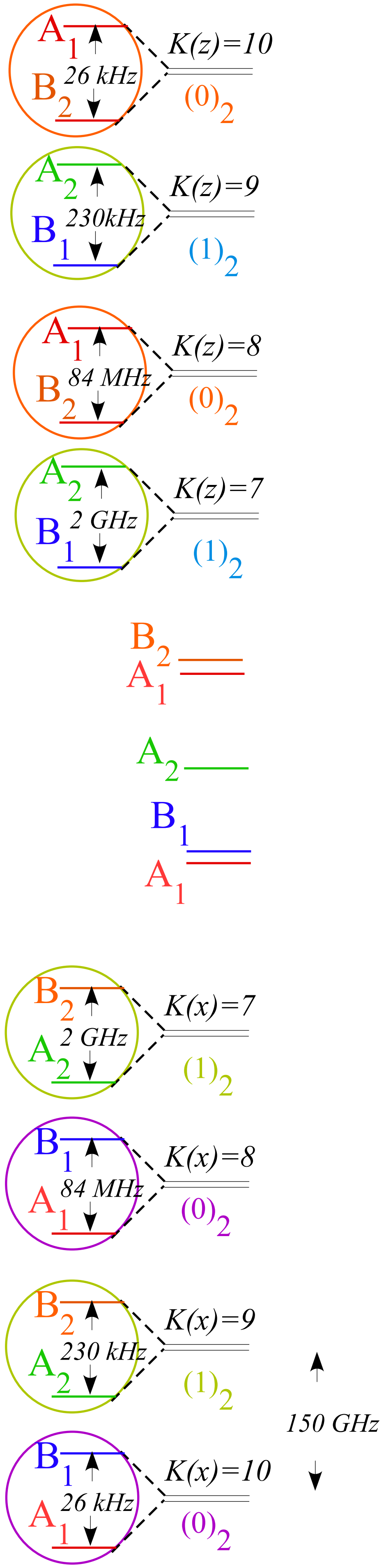
$$\left\langle \mathbf{T}^{(0)}_0 \right\rangle = cY^0_0 = J(J+1)$$

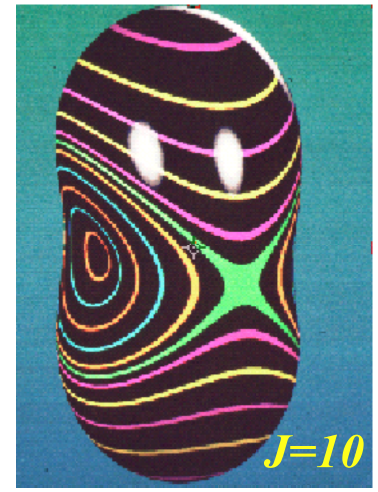
(tensor operator $\mathbf{T}^k_q$ *is replaced by spherical harmonic* $Y^k_{q[\beta,\gamma]}$*)*

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

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



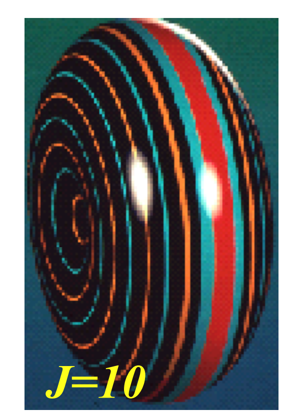




D_2 \ $C_2(x)$	$(0)_2$	$(1)_2$
A_1	1	•
A_2	•	1
B_1	1	•
B_2	•	1

D_2 \ $C_2(y)$	$(0)_2$	$(1)_2$
A_1	1	•
A_2	1	•
B_1	•	1
B_2	•	1

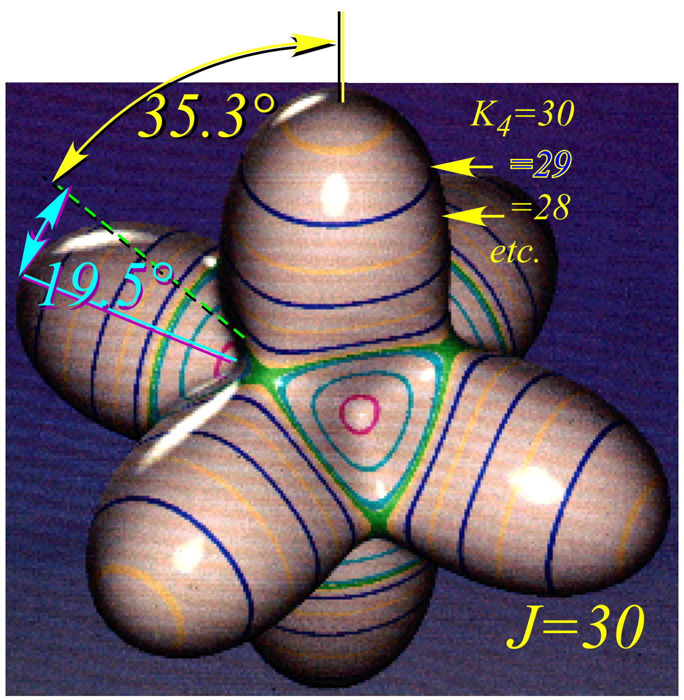
D_2 \ $C_2(z)$	$(0)_2$	$(1)_2$
A_1	1	•
A_2	•	1
B_1	•	1
B_2	1	•

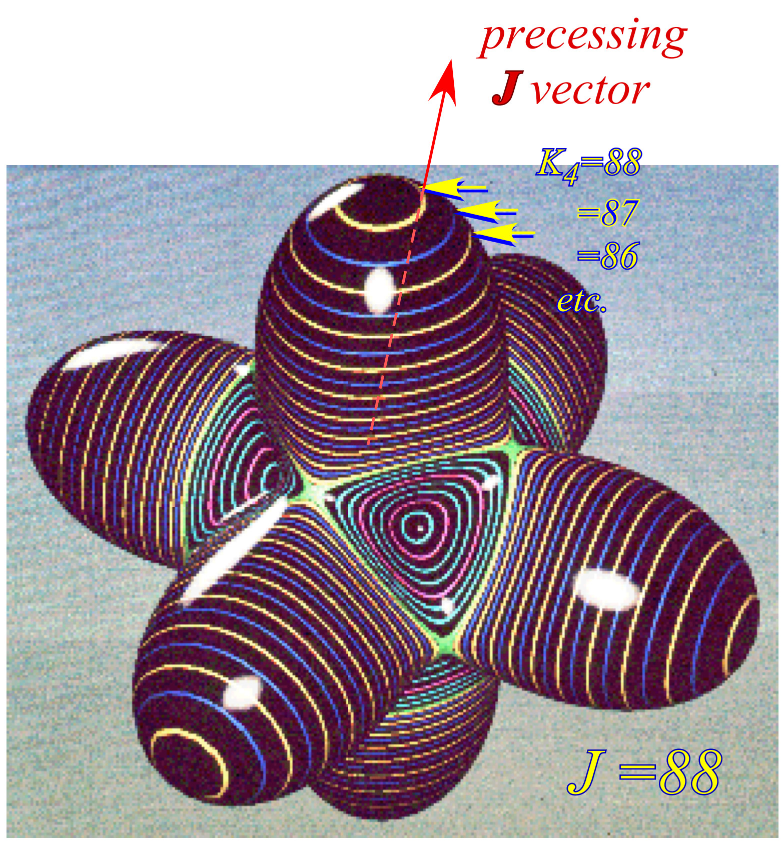


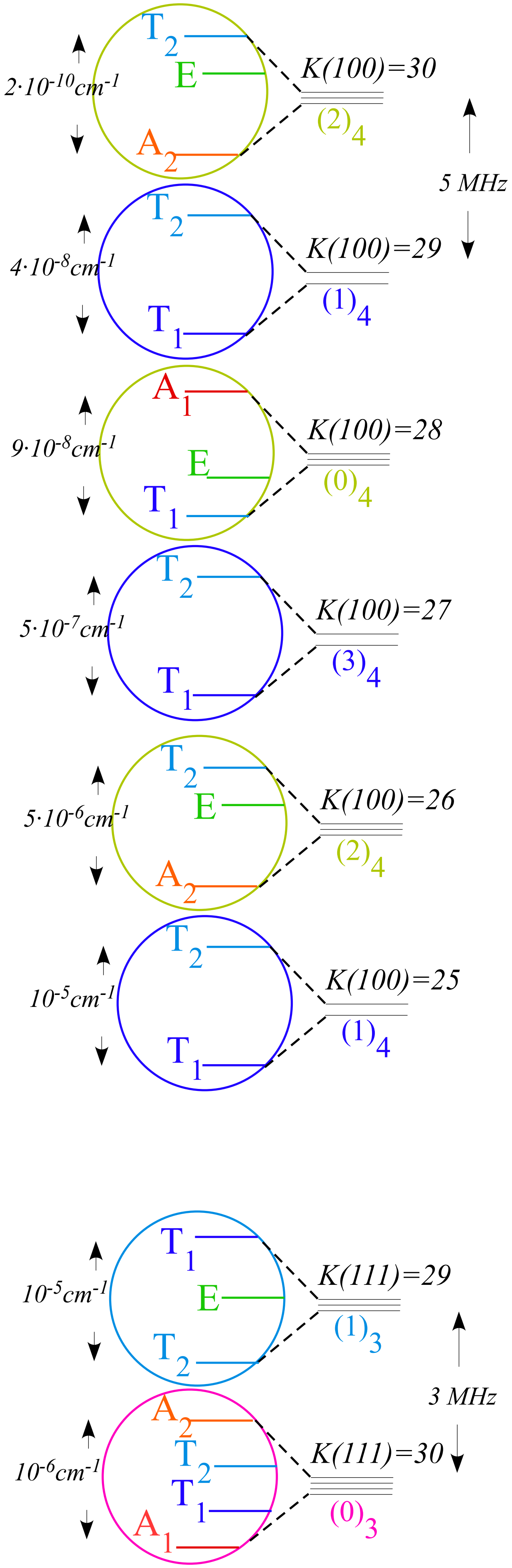
O_h or T_d Spherical Top: *(Hecht Ro-vib Hamiltonian 1960)*

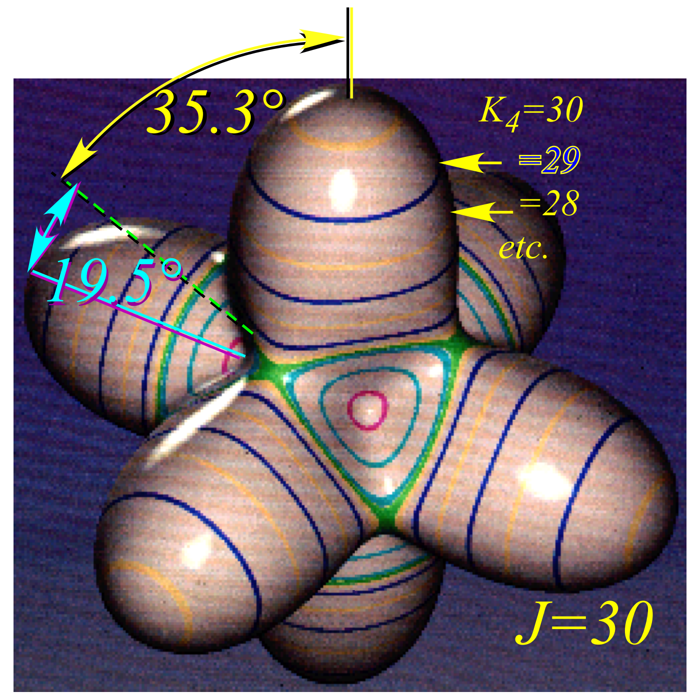
$$\mathbf{H} = B\left(\mathbf{J}_x^2 + \mathbf{J}_y^2 + \mathbf{J}_z^2\right) + t_{440}\left(\mathbf{J}_x^4 + \mathbf{J}_y^4 + \mathbf{J}_z^4 - \frac{3}{5}J^4\right) + \cdots$$

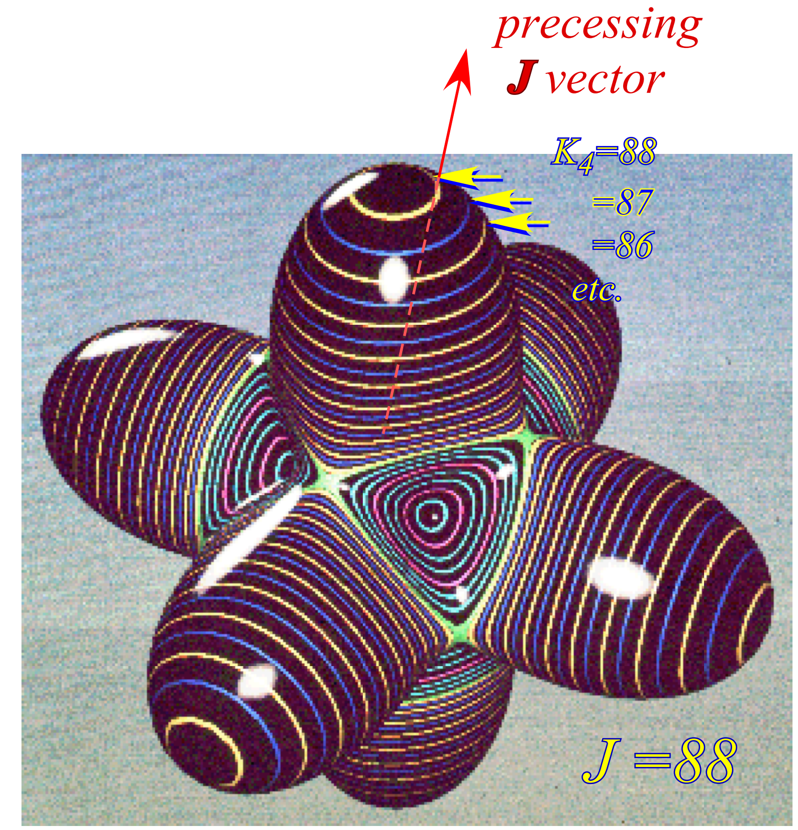
$$= \quad B\mathbf{J}^2 \quad + t_{440}\left(\mathbf{T}_0^4 + \sqrt{\frac{5}{14}}\left[\mathbf{T}_4^4 + \mathbf{T}_{-4}^4\right]\right) + \cdots$$











O \ $C_3(111)$	$(0)_3$	$(1)_3$	$(2)_3$
A_1	1	•	•
A_2	1	•	•
E_2	•	1	1
T_1	1	1	1
T_2	1	1	1

O \ $C_2(110)$	$(0)_2$	$(1)_2$
A_1	1	•
A_2	•	1
E_2	1	1
T_1	1	2
T_2	2	1

O \ $C_4(100)$	$(0)_4$	$(1)_4$	$(2)_4$	$(3)_4$
A_1	1	•	•	•
A_2	•	•	1	•
E_2	1	•	1	•
T_1	1	1	•	1
T_2	•	1	1	1

O \ $C_1(abc)$	$(0)_1$
A_1	1
A_2	1
E_2	2
T_1	3
T_2	3