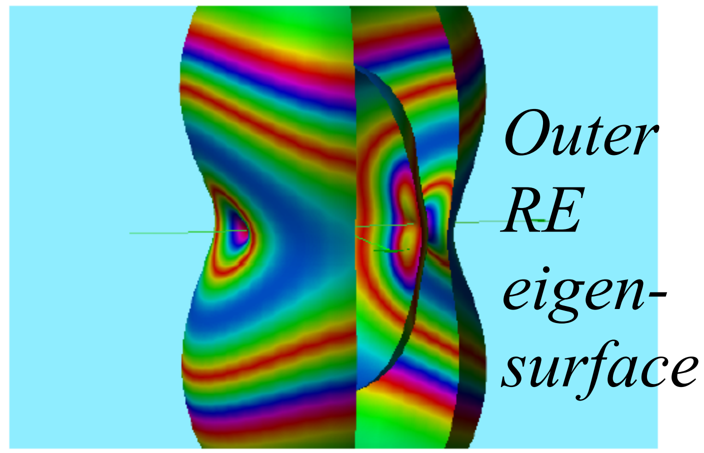
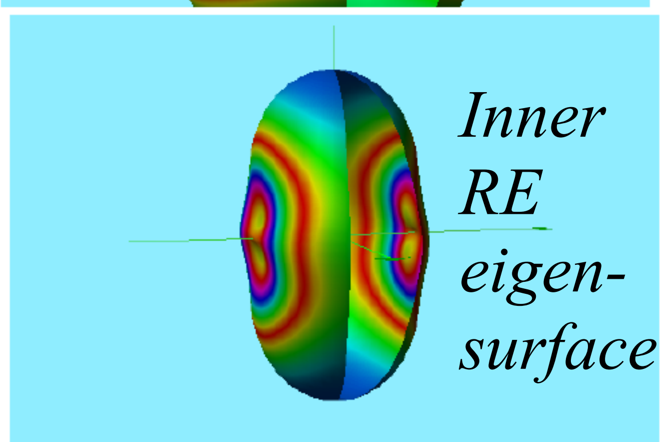
ROVIBRONIC PHASE PLOTS

II: MULTI-SURFACE ROTATIONAL ENEGRY ANISOTROPY FOR INTERNAL ROTOR MOLECULES AND ROTATIONAL JAHN-TELLER-RENNER ANALOGS





Bill Harter , Justin Mitchell - University of Arkansas

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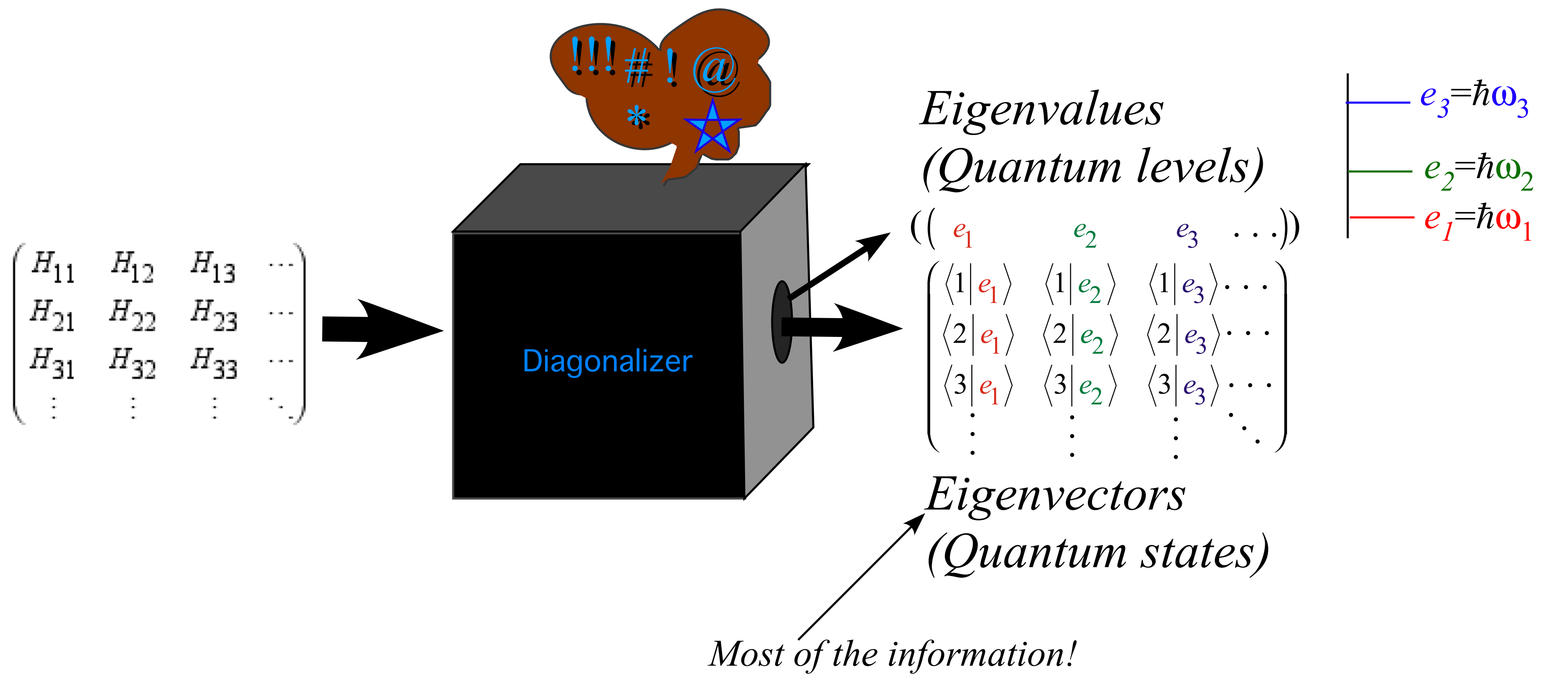
Matrix Diagonalization:
The **BLACK BOX** *of quantum physics, chemistry, and spectroscopy*



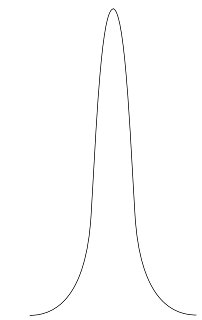
$$\begin{pmatrix} H_{11} & H_{12} & H_{13} & \cdots \\ H_{21} & H_{22} & H_{23} & \cdots \\ H_{31} & H_{32} & H_{33} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

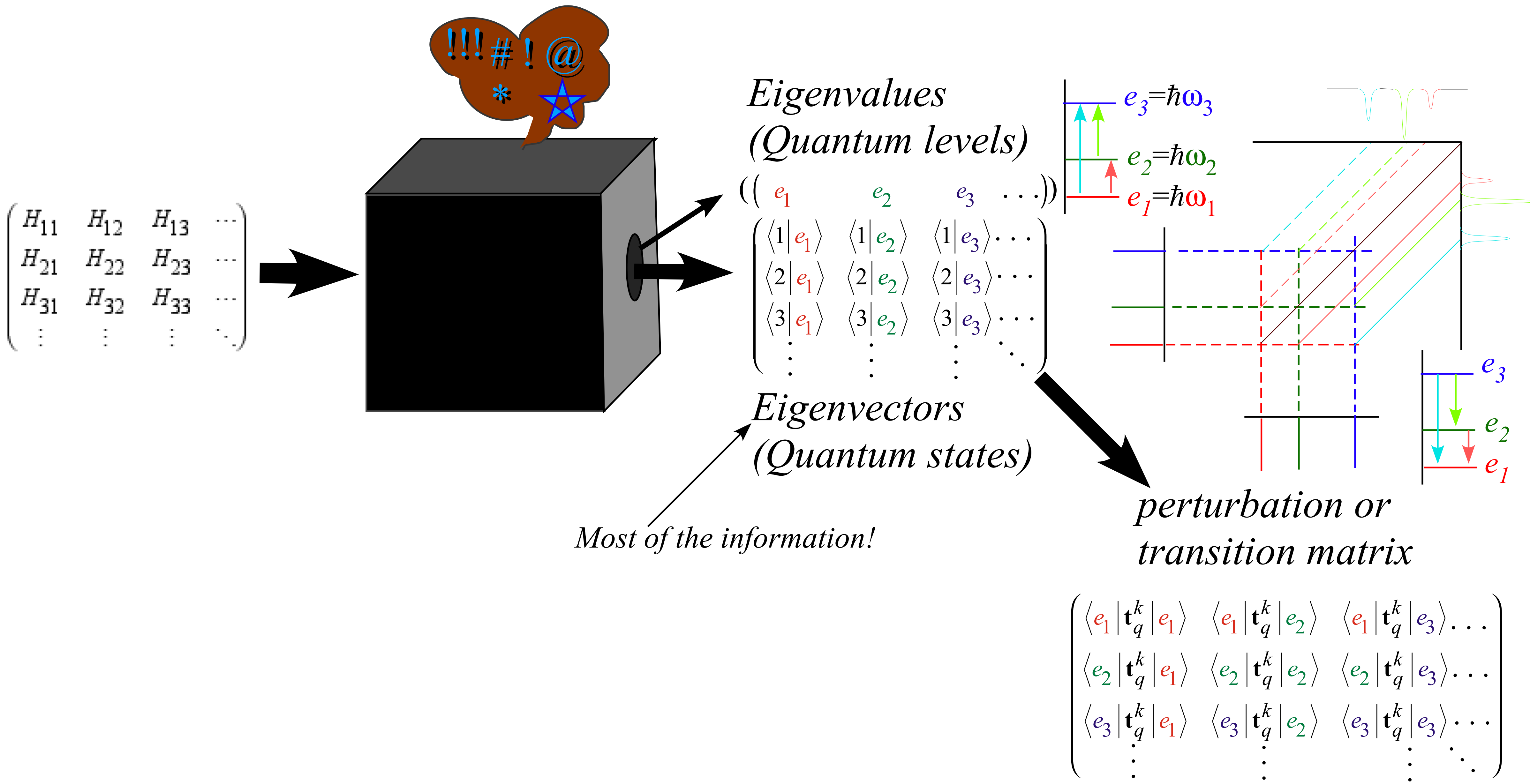
$$((\ e_1 \quad e_2 \quad e_3 \quad \ldots))$$

$$\begin{pmatrix} \langle 1|e_1\rangle & \langle 1|e_2\rangle & \langle 1|e_3\rangle & \cdots \\ \langle 2|e_1\rangle & \langle 2|e_2\rangle & \langle 2|e_3\rangle & \cdots \\ \langle 3|e_1\rangle & \langle 3|e_2\rangle & \langle 3|e_3\rangle & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

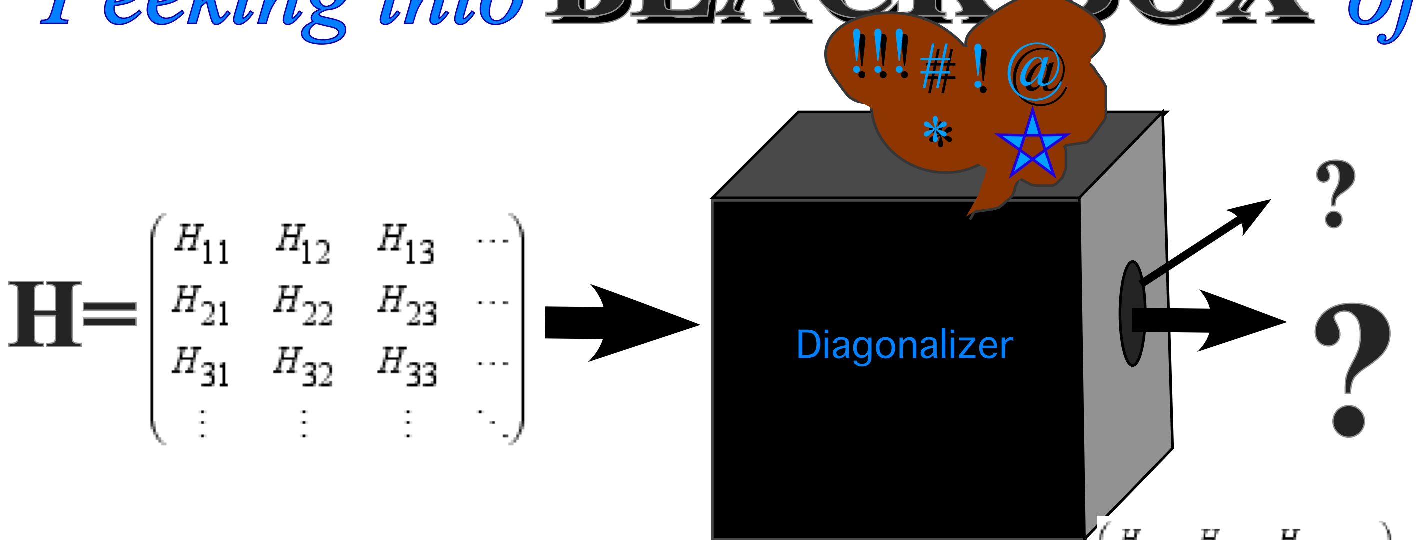
Matrix Diagonalization

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





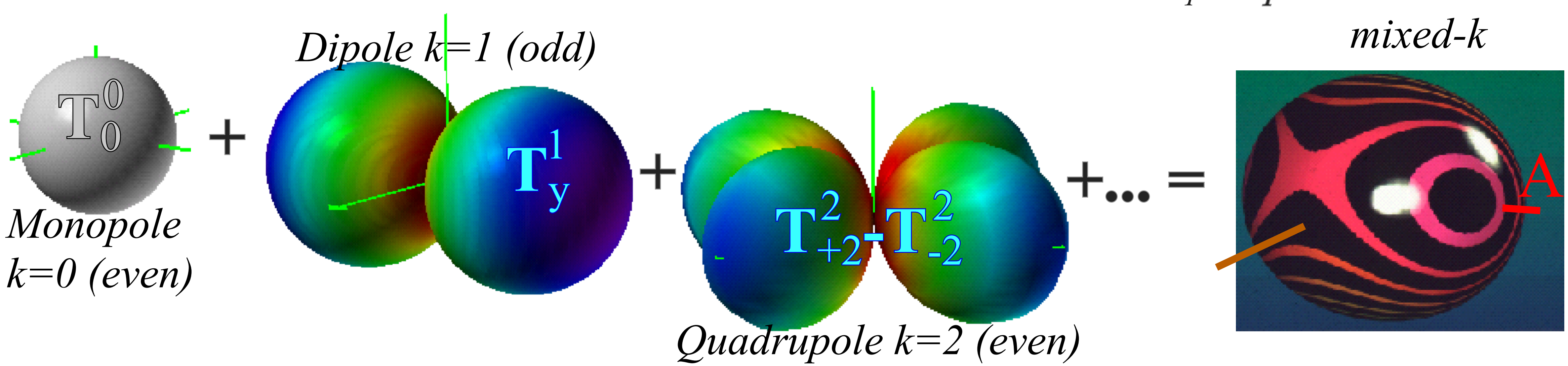
Peeking into **BLACK BOX** *of matrix diagonalization:*



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 +..*

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



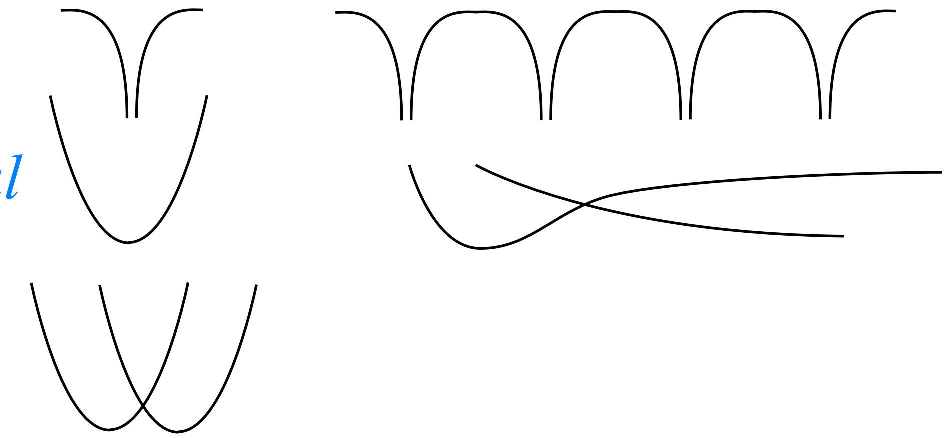
Some ways to picture AMO eigenstates

- *Potential Energy Surfaces (PES)*

  electronic

  vibrational

  vibronic

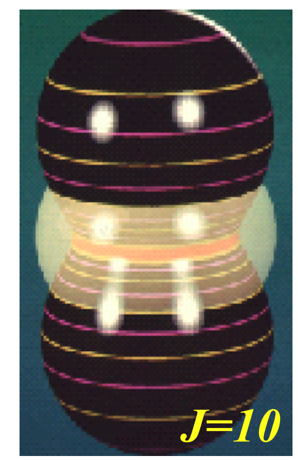


- *Rotational Energy Surfaces (RES)*

  pure rotational (centrifugal) effects

  rovibrational (centrifugal and Coriolis) effects

  rovibronic (centrifugal, Coriolis, and Jahn-Teller) effects

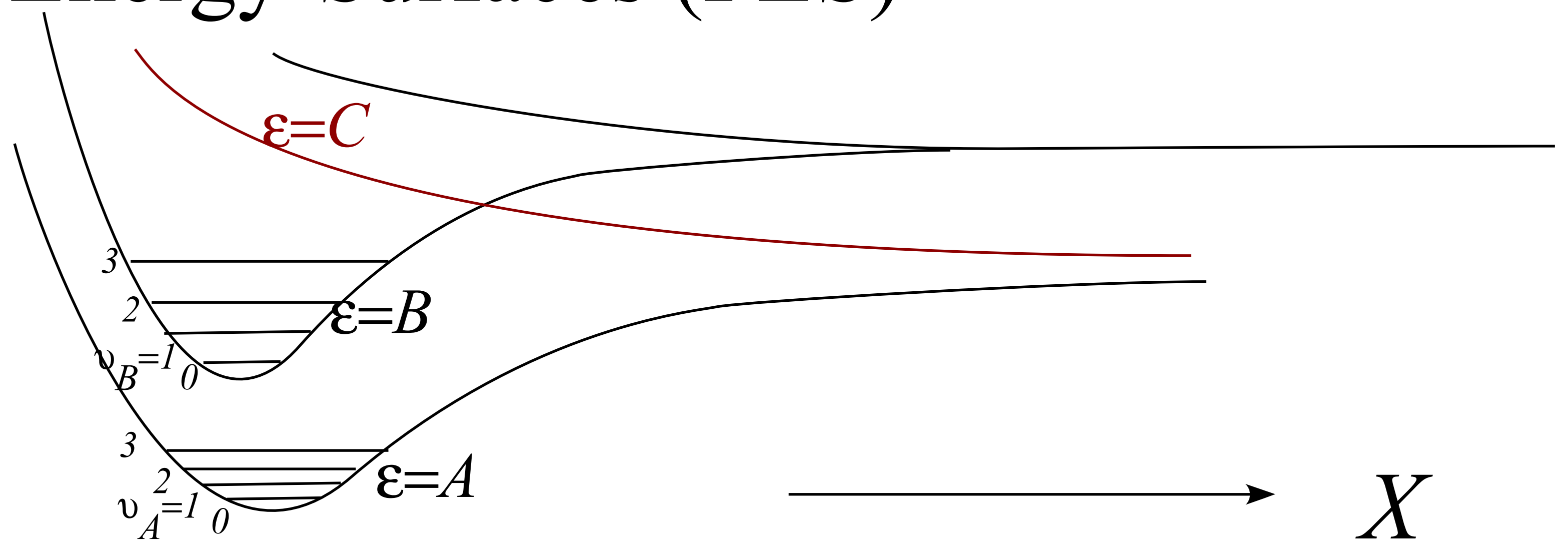


- *Generalized phase spaces*

  vibrational polyad sphere

  high energy pulse state space

Born-Oppenheimer-Approximate (BOA)
Potential-Energy-Surfaces (PES)



BOA-"Entangled" or correlated products:

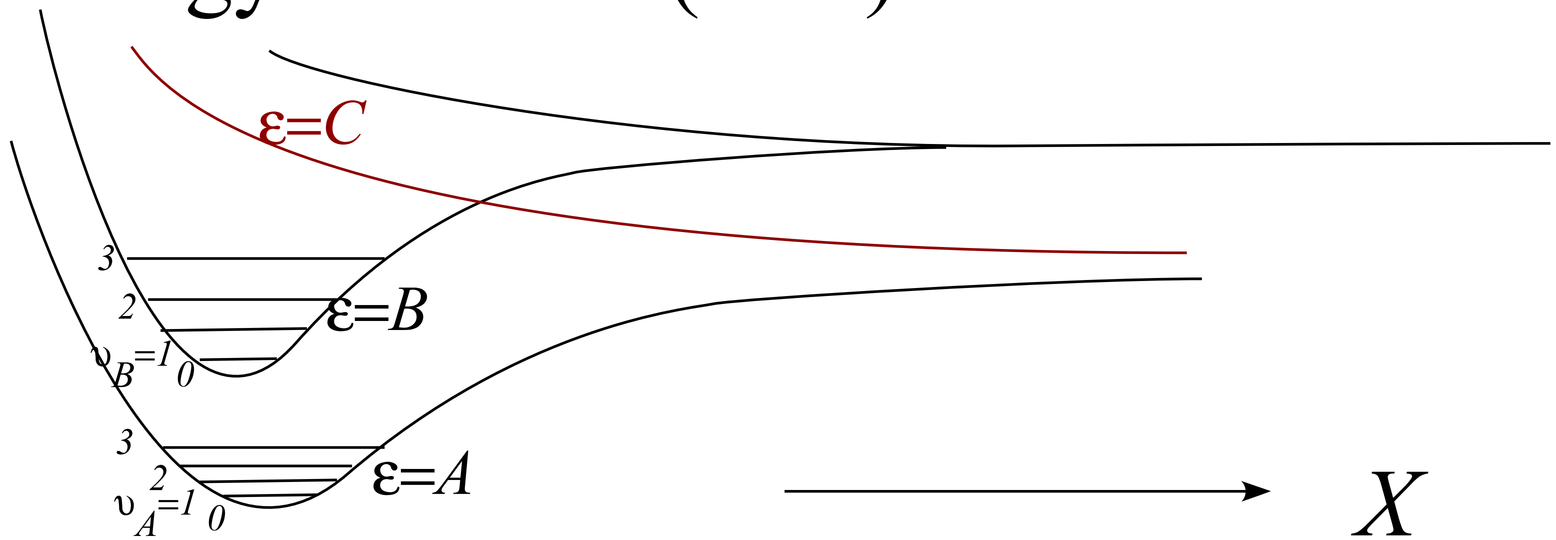
"FAST" stuff "SLOW"stuff

$$\Psi_{\upsilon(\varepsilon)}(x^{electron}\ldots X^{nuclei}\ldots) = \psi_{\varepsilon}(x(X\ldots)\ldots) \cdot \eta_{\upsilon(\varepsilon)}(X\ldots)$$

electron $x_{(X)}$-coordinates have adiabatic dependence on nuclear X-coordinates

nuclear υ_{ε}-quanta have adiabatic dependence on electron ε-quanta

Born-Oppenheimer-Approximate (BOA) Potential-Energy-Surfaces (PES)



BOA-“Entangled” or correlated products

“FAST” stuff “SLOW”stuff

$$\Psi_{\upsilon(\varepsilon)}(x^{electron}\ldots X^{nuclei}\ldots) = \psi_{\varepsilon}(x(X\ldots)\ldots) \cdot \eta_{\upsilon(\varepsilon)}(X\ldots)$$

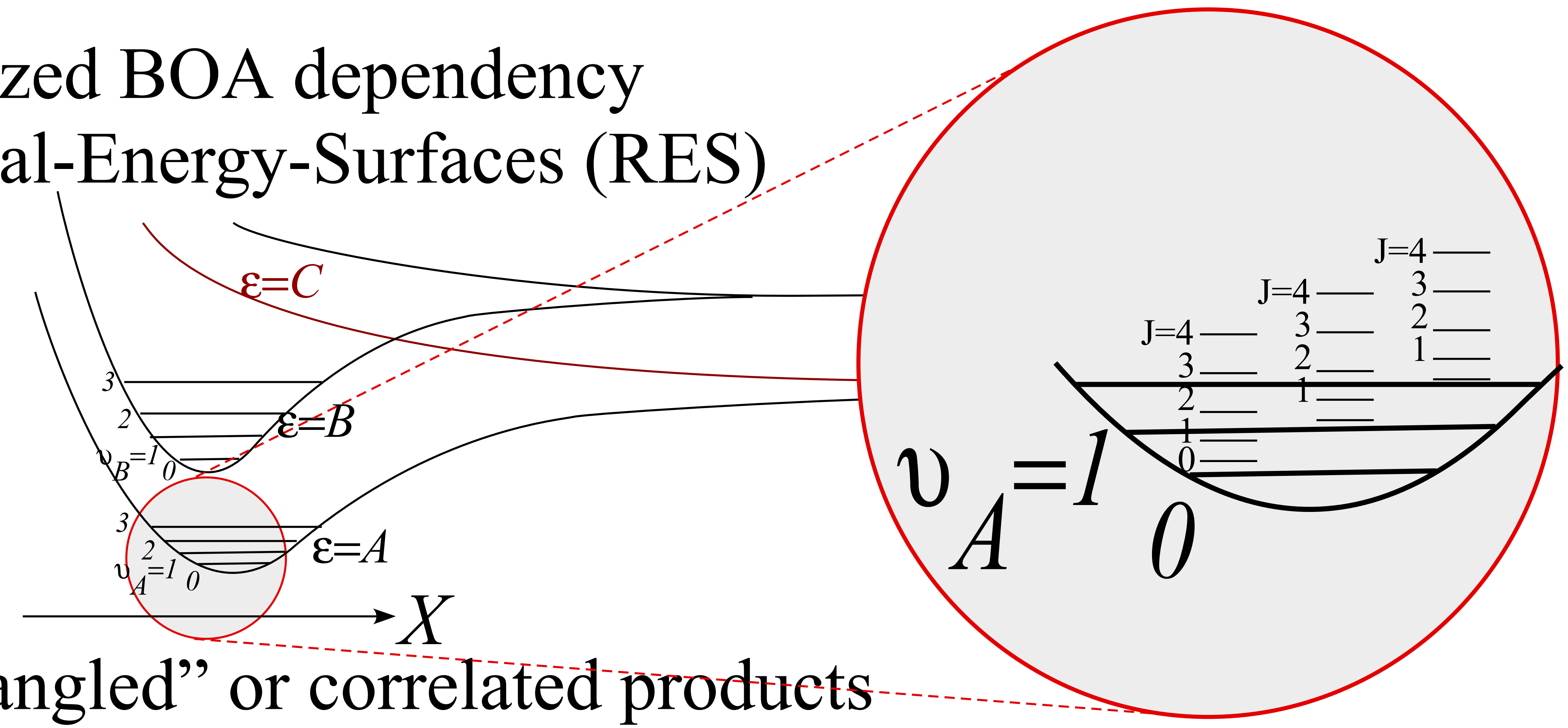
Compare BOA to <u>un</u>entangled state: $|\varepsilon\rangle|\eta\rangle=|\varepsilon,\eta\rangle$.

$$\psi_{\varepsilon}(x)\cdot\eta_{\upsilon}(X)=\langle x|\varepsilon\rangle\langle X|\eta\rangle=\langle x,X|\varepsilon,\eta\rangle$$

Simplest entangled state: $(|\varepsilon\rangle|\eta\rangle+|\varepsilon'\rangle|\eta'\rangle)/\sqrt{2}$ *(it only takes two to entangle)*

$$\psi_{\varepsilon}(x)\cdot\eta_{\upsilon}(X)+\psi_{\varepsilon'}(x)\cdot\eta_{\upsilon'}(X)=(\langle x|\varepsilon\rangle\langle X|\eta\rangle+\langle x|\varepsilon'\rangle\langle X|\eta'\rangle)/\sqrt{2}$$

Generalized BOA dependency
Rotational-Energy-Surfaces (RES)



BOA-"Entangled" or correlated products

"FAST" "SLOW" "SLOWER"

$$\Phi_{J[\upsilon(\varepsilon)]}(x^{elect.}\ldots Q^{vib.}\ldots\Theta^{rotate}) = \psi_\varepsilon(x_{(Q(\Theta)\ldots)}\ldots)\cdot\eta_{\upsilon(\varepsilon)}(Q_{(\Theta)}\ldots)\cdot\rho_{J[\upsilon(\varepsilon)]}(\Theta)$$

electron $x_{(Q(\Theta))}$-coords depend on vibration Q-coords and rotation Θ coords

vibe υ(ε)-quanta depend on electron ε-quanta

vibe $Q(\Theta)$-coords depend on rotation Θ-coords

rotation $J[\upsilon(\varepsilon)]$-quanta depend on vibe υ-quanta and electron ε-quanta

$$\Phi^{BOA}_{J[\upsilon(\varepsilon)]}(x^{vibronic},\Theta^{rotate}) = \psi_{\varepsilon}(x_{(\Theta)}) \cdot \rho_{J[\varepsilon]}(\Theta)$$

$$= \psi_{\varepsilon}(x_{(body)}) \cdot \rho_{J,M,K}(\alpha,\beta,\gamma)$$

Detailed model of BOA rotor entanglement

Using rotational symmetry analysis

$$= \psi^{\ell}_{\bar{\mu}}(\bar{x}) \cdot D^{J*}_{M,K=n+\bar{\mu}}(\alpha,\beta,\gamma)\sqrt{[J]}$$

bod-based vibronic factor

body-wave from lab-wave

$$\psi^{\ell}_{\bar{\mu}}(\bar{x}) = \psi^{\ell}_{\mu}(x) D^{\ell}_{\bar{\mu},\mu}(\alpha,\beta,\gamma)$$

sum $\mu = -J \ldots +J$

frame rotation

lab-wave from body-wave

$$\psi^{\ell}_{\mu}(x) = \psi^{\ell}_{\bar{\mu}}(\bar{x}) D^{\ell *}_{\mu,\bar{\mu}}(\alpha,\beta,\gamma)$$

sum $\bar{\mu} = -J \ldots +J$

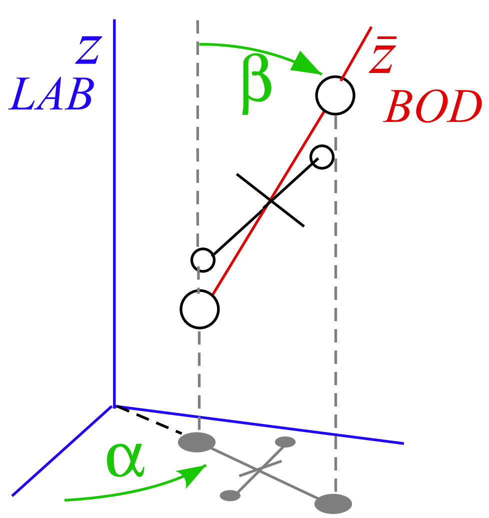
lab-based vibronic factor

"Hook-up" unentangled lab-based products: $\psi^{\ell}_{\mu}(x) \cdot D^{R*}_{m,n}(\alpha,\beta,\gamma)\sqrt{[R]}$

(with Clebsch-Gordan $C^{\ell\ R\ J}_{\mu\ m\ M}$)

$$\Phi^{LAB_{hook\text{-}up}}_{J(\ell R)} = C^{\ell\ R\ J}_{\mu\ m M}\ \psi^{\ell}_{\mu}(x) \cdot D^{R*}_{m,n}(\alpha,\beta,\gamma)\sqrt{[R]}$$

sum $\mu = -J \ldots +J$ *with* $m = M - \mu$



Compare wave Products:

Lab "hook-up" *versus* "BOA-constricted bod"

$$\Phi^{BOA}_{J(\ell\bar{\mu})} = \psi^{\ell}_{\bar{\mu}}(\bar{x})\cdot D^{J*}_{MK}(\alpha,\beta,\gamma)\sqrt{[J]}$$

$$\Phi^{LAB_{hook\text{-}up}}_{J(\ell R)} = C^{\ell\ R\ J}_{\mu\ mM}\ \psi^{\ell}_{\mu}(x)\cdot D^{R*}_{m,n}(\alpha\beta\gamma)\sqrt{[R]}$$

sum $\mu=-J\ldots+J$ with $m=M-\mu$

$$\Phi^{LAB_{hook\text{-}up}}_{J(\ell R)} = C^{\ell\ R\ J}_{\mu\ mM}\ \psi^{\ell}_{\bar{\mu}}(\bar{x}) D^{\ell*}_{\mu,\bar{\mu}}(\alpha,\beta,\gamma)\cdot D^{R*}_{m,n}(\alpha\beta\gamma)\sqrt{[R]} = C^{\ell\ R\ J}_{\bar{\mu}\ nK}\psi^{\ell}_{\bar{\mu}}(x)\cdot D^{J*}_{MK}(\alpha\beta\gamma)\sqrt{[R]}$$

sum $\bar{\mu}=-J\ldots+J$; sum $\mu=-J\ldots+J$ with $m=M-\mu$; sum $\bar{\mu}=-J\ldots+J$

with: $K=\bar{\mu}+n$

$$\Phi^{LAB_{hook\text{-}up}}_{J(\ell R)} = C^{\ell\ R\ J}_{\bar{\mu}\ nK}\frac{\sqrt{[R]}}{\sqrt{[J]}}\ \Phi^{BOA}_{J(\ell\bar{\mu})}$$

sum $\bar{\mu}=-J\ldots+J$

This has form:

$$C^{\ell\ R\ J}_{\mu\ mM}\ D^{\ell*}_{\mu\bar{\mu}}(\alpha\beta\gamma)\cdot D^{R*}_{mn}(\alpha\beta\gamma) = C^{\ell\ R\ J}_{\bar{\mu}\ nK} D^{J*}_{MK}(\alpha\beta\gamma)$$

sum $\mu=-J\ldots J$ with $m=M-\mu$

with: $K=\bar{\mu}+n$

...that follows from well known coupling identity.

$$C^{\ell\ R\ J'}_{\mu\ mM}\ D^{\ell*}_{\mu\bar{\mu}}(\alpha\beta\gamma)\cdot D^{R*}_{mn}(\alpha\beta\gamma) C^{\ell\ R\ J}_{\bar{\mu}\ nK} = \delta^{JJ'}\ D^{J*}_{MK}(\alpha\beta\gamma)$$

sum $\mu=-J\ldots+J$ with $m=M-\mu$; sum $\bar{\mu}=-J\ldots+J$ with $n=K-\bar{\mu}$

$LAB_{hook\text{-}up}$	BOA_{bod}
state:	state:
sharp R	mixed R
mixed $\bar{\mu}$	sharp $\bar{\mu}$

BOTH HAVE...

sharp n	sharp n

An elementary "rovibronic species"

"...gyro in the suitcase"

Multiple-RE surfaces: Using semi-classical geometry...
Can we describe internal-rotor molecules and their spin symmetry?
Can we describe hyperfine spin dynamics?

The Simplest Cases:

Rigid top with one body fixed "Gyro" (one spin-1/2, one CH_3, ...)

Multiple-RE surfaces: Using semi-classical geometry...
Can we describe internal-rotor molecules and their spin symmetry?
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Rigid top with one body fixed "Gyro" (one spin-1/2, one CH_3, ...)

J. Chem. Phys. 101, 2710 (1994)

Rotational energy surfaces of molecules exhibiting internal rotation

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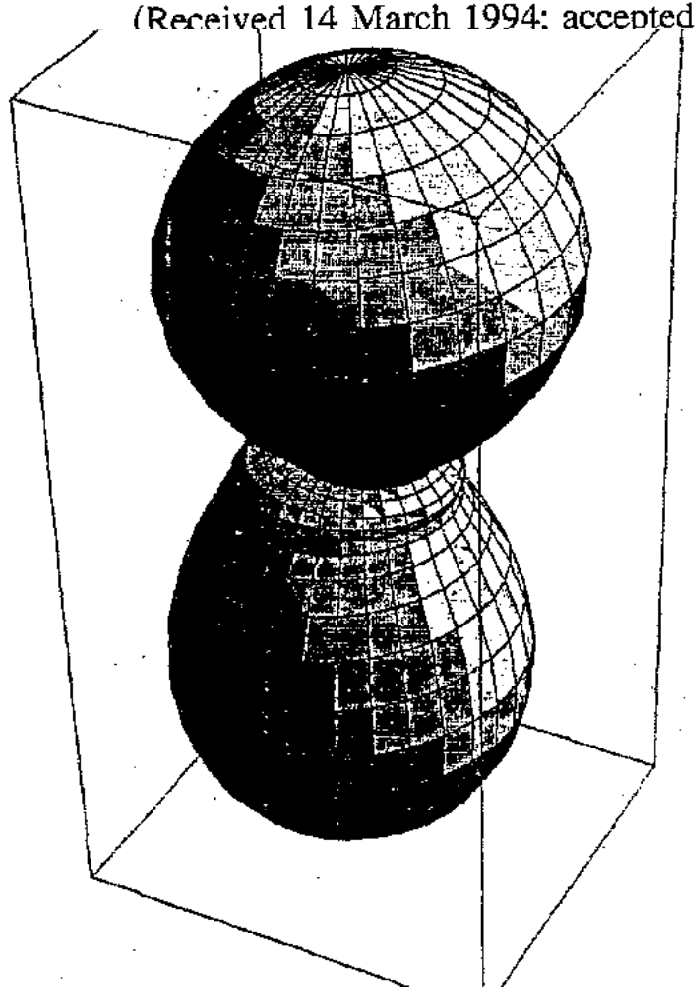
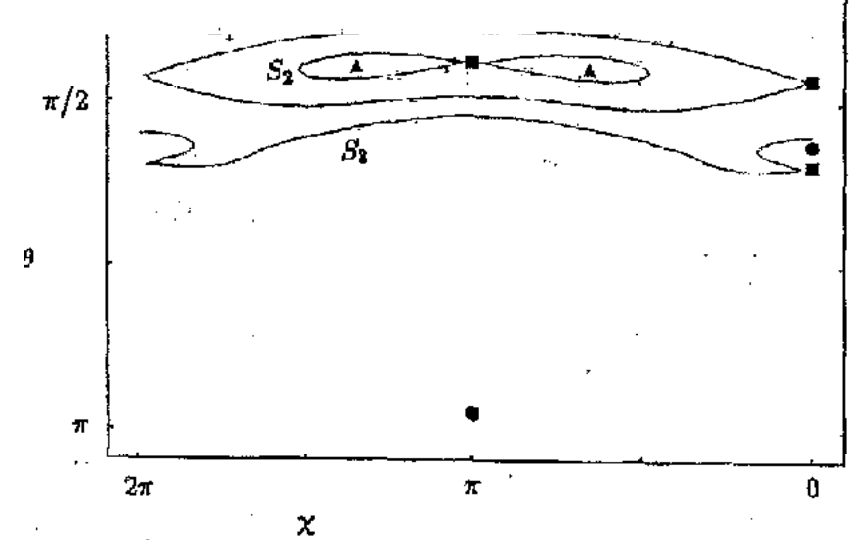
(Received 14 March 1994; accepted 28 April 1994)



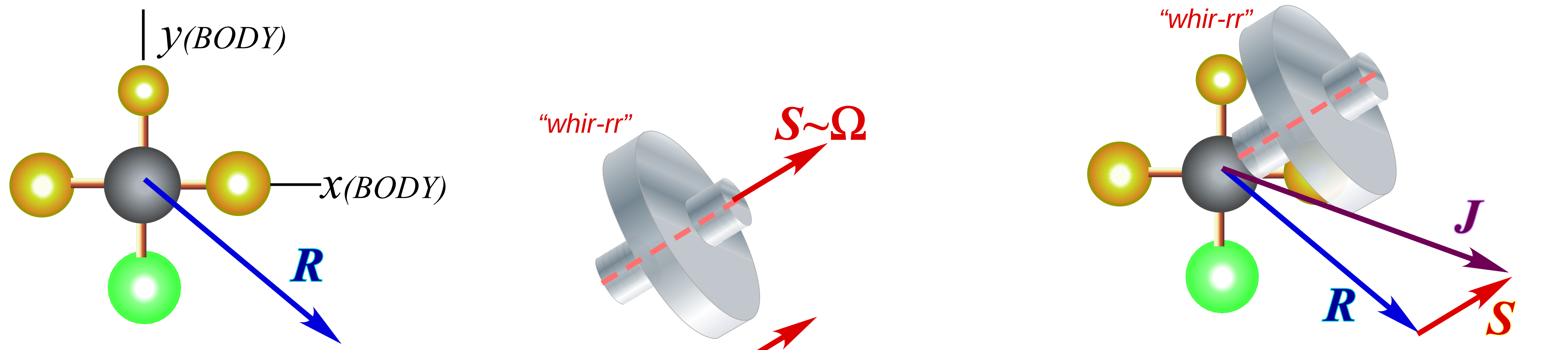
See also:

Hougen, Kleiner, and Ortigoso
JCP 96, 455 (1992)



One of the first Applications of
Multiple RES introduced in Comp.Phys.Rpt. 8,319(1988)

Problem: Mathematica graphic engines were not terrific!
(..and Los Alamos graphics was too $$expensive$$)



Rotor $\boldsymbol{R}$ **PLUS** ***"Gyro" Spin*** $\boldsymbol{S}$ **EQUALS** ***Compound Rotor*** $\boldsymbol{J}=\boldsymbol{R}+\boldsymbol{S}$

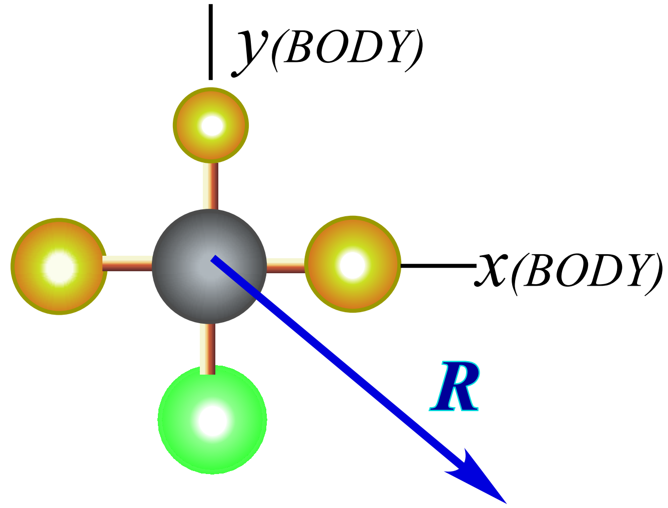
Compound Rotor Hamiltonian: *Rigid rotor with body-fixed "gyro"...*

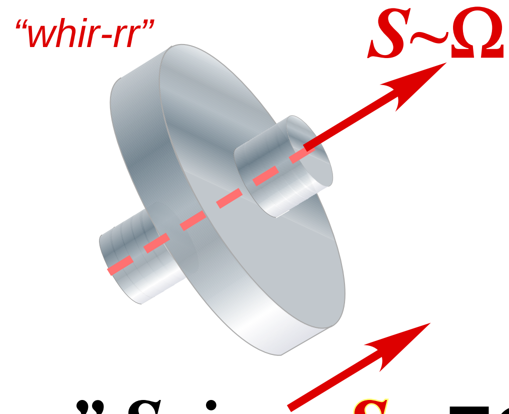
In general, this term is the difficult part...

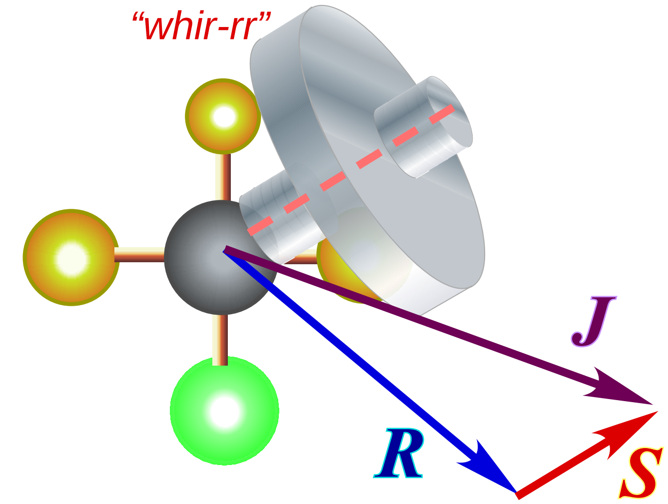
$$H=AR_x{}^2+BR_y{}^2+CR_z{}^2+\ldots+(\text{coupling or constraint})+\ldots+B_S S\cdot S$$

Zero-Interaction Potential 'Proximation (ZIPP)

...but suppose it's zero!
Constraints do <u>no</u> <u>work</u>.







***Rotor* R** **PLUS *"Gyro" Spin* S** **EQUALS** ***Compound Rotor* J= R+S**

Compound Rotor Hamiltonian: *Rigid rotor with body-fixed "gyro"...*

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$$H = AR_x{}^2 + BR_y{}^2 + CR_z{}^2 + \ldots + (\text{coupling or constraint}) + \ldots + B_S S\cdot S$$

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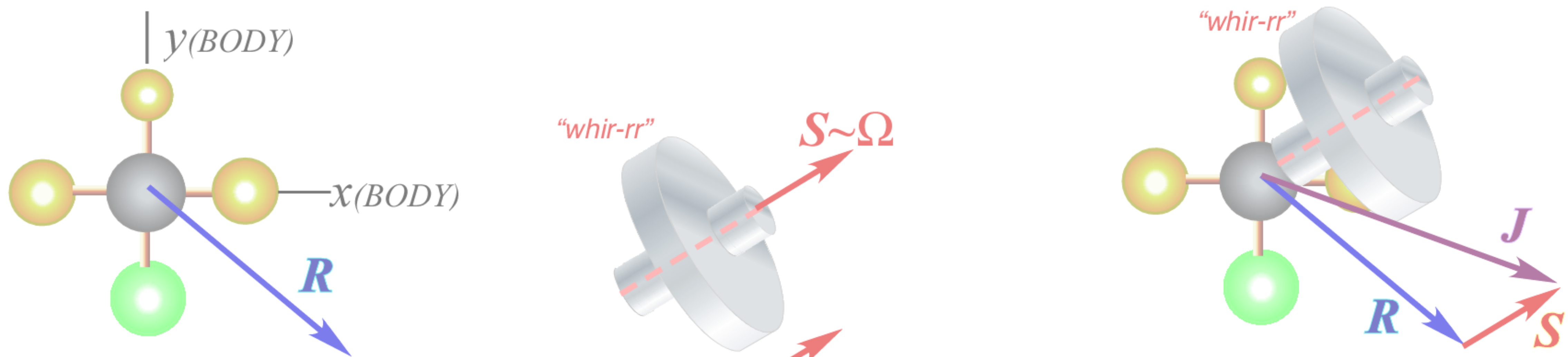
Zero-Interaction Potential 'Proximation (ZIPP)

(ZIPPed)

Let: $\mathbf{R} = \mathbf{J} - \mathbf{S}$ *and consider non-constant terms* *(ignore gyro S terms that are constant)*

$$H = A(J_x - S_x)^2 + B(J_y - S_y)^2 + C(J_z - S_z)^2 + \ldots + 0 \text{ (for constraint)} + \ldots + (\text{constant BS terms})$$



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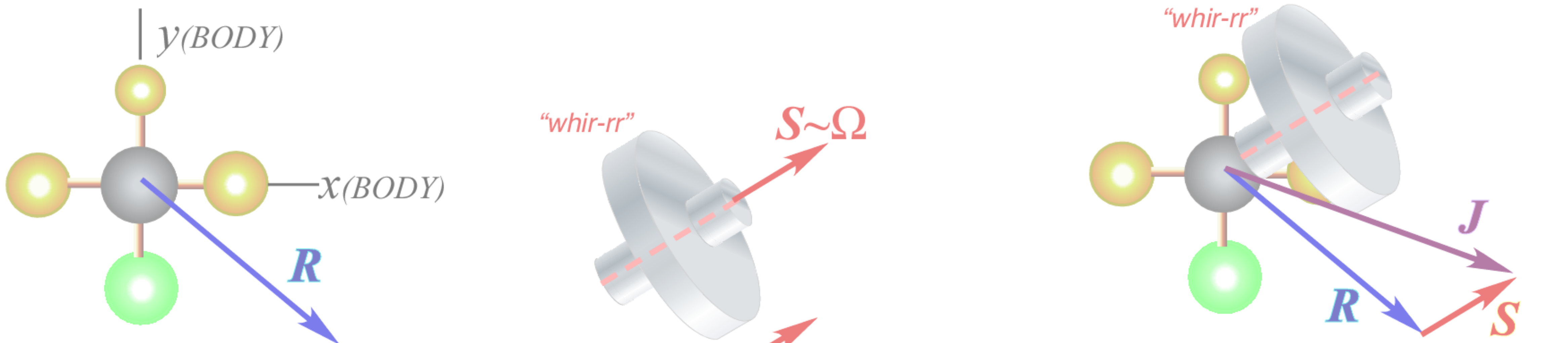
$$H = AJ_x^2 + BJ_y^2 + CJ_z^2 + \ldots - 2AJ_xS_x - 2BJ_yS_y - 2CJ_zS_z + \ldots + (\text{more constant terms})$$

"Coriolis effect" subtracts linear or 1st-order $\mathbf{J}_m$ *or* $\mathbf{T}^1_m$ *terms for gyro-rotor H*



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$$H=AJ_x{}^2+BJ_y{}^2+CJ_z{}^2+\ldots-2AJ_xS_x-2BJ_yS_y-2CJ_zS_z+\ldots+(\text{more constant terms})$$

"Coriolis effect" subtracts linear or 1st-order $\mathbf{J}_m$ *or* $\mathbf{T}^1{}_m$ *terms for gyro-rotor H*

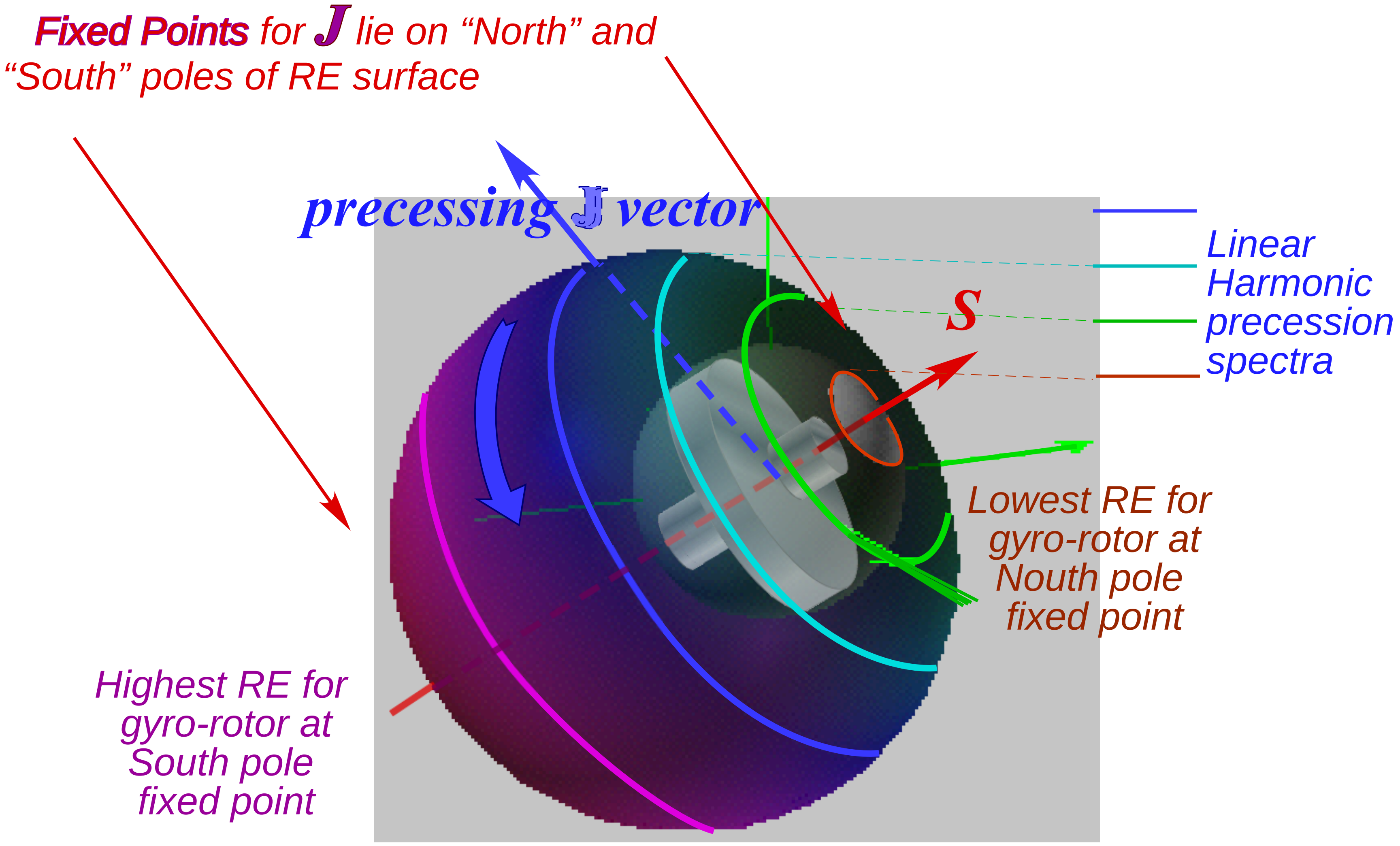
$B\boldsymbol{R}^2$ *to* $B(\boldsymbol{J}-\boldsymbol{S})^2$ *is analogous to* $\boldsymbol{p}^2/2M$ *to* $(\boldsymbol{p}-e\boldsymbol{A})^2/2M$ *gauge-transformation*

...$\boldsymbol{J}\bullet\boldsymbol{S}$ *is analogous to* $e\boldsymbol{p}\bullet\boldsymbol{A}$

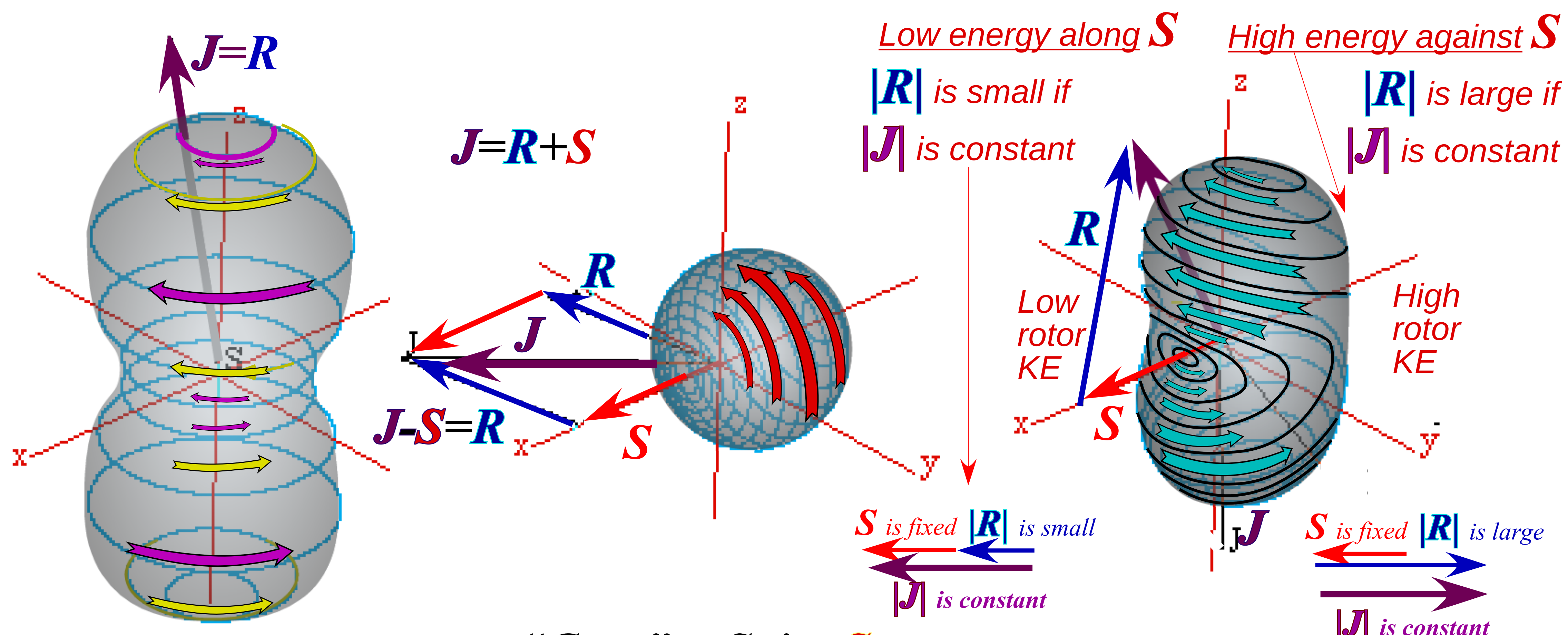
RE Surface for1st-order $\mathbf{J}_m$ *or* $\mathbf{T}^1{}_m$ *term is a cardioid displaced in J-direction*

Energy sphere intersections are concentric circular precession paths

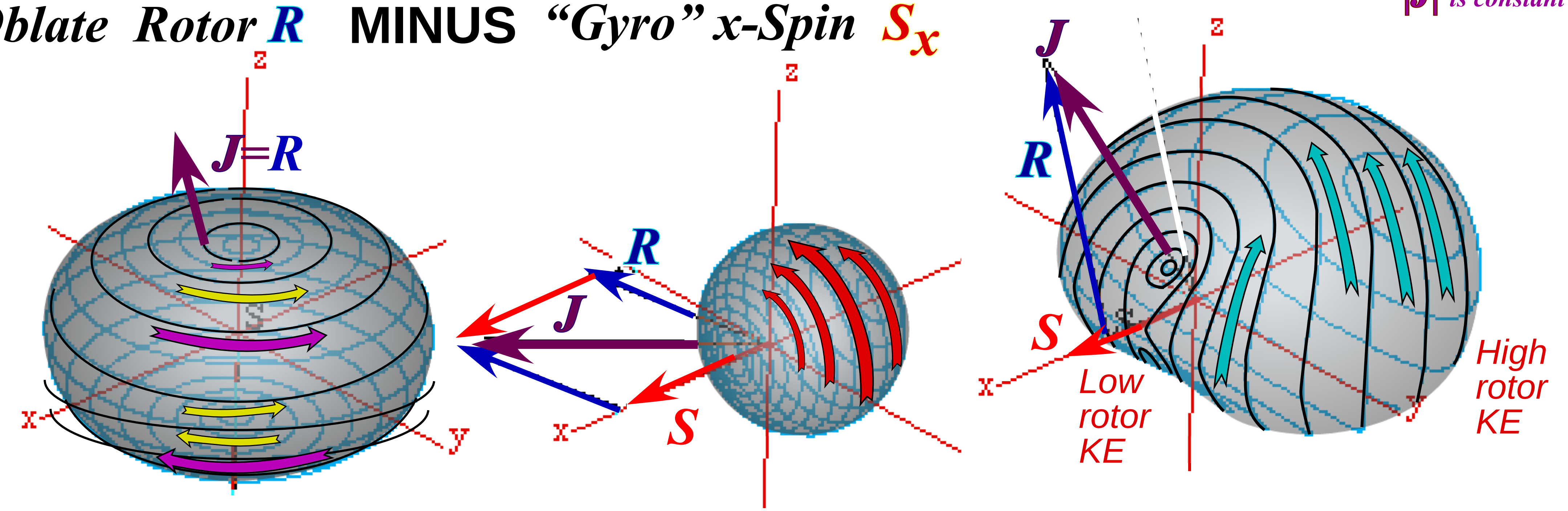
All paths precess with the same sense around gyro S-vector



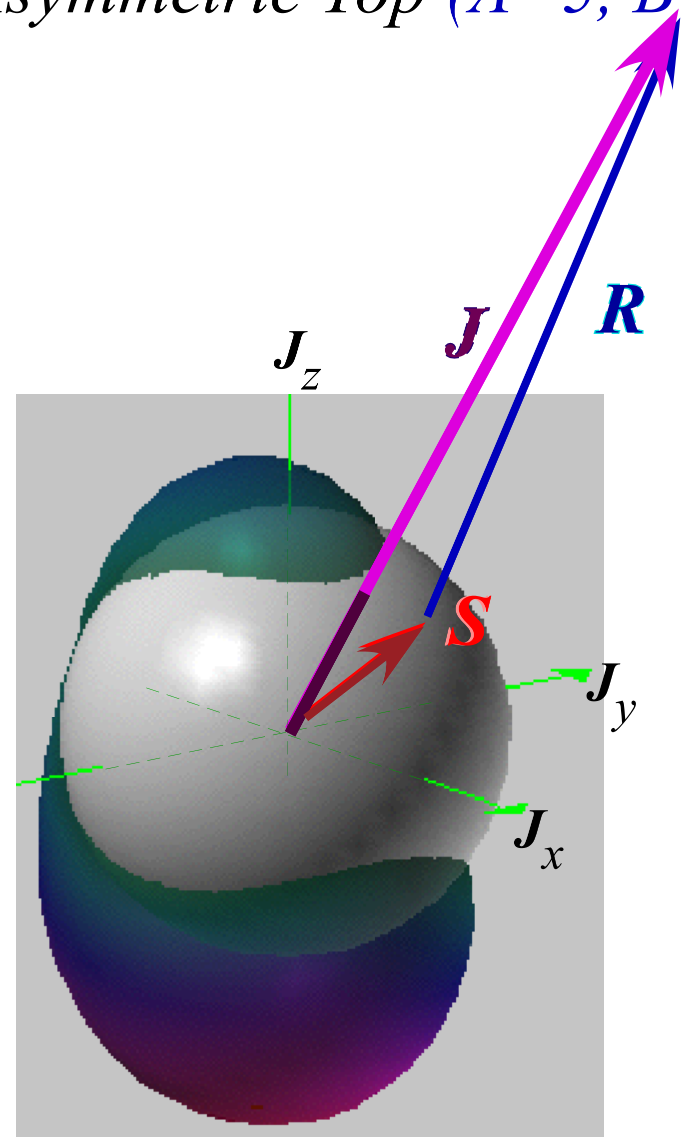
Prolate Rotor R MINUS *“Gyro” x-Spin* S_x



Oblate Rotor R MINUS *“Gyro” x-Spin* S_x

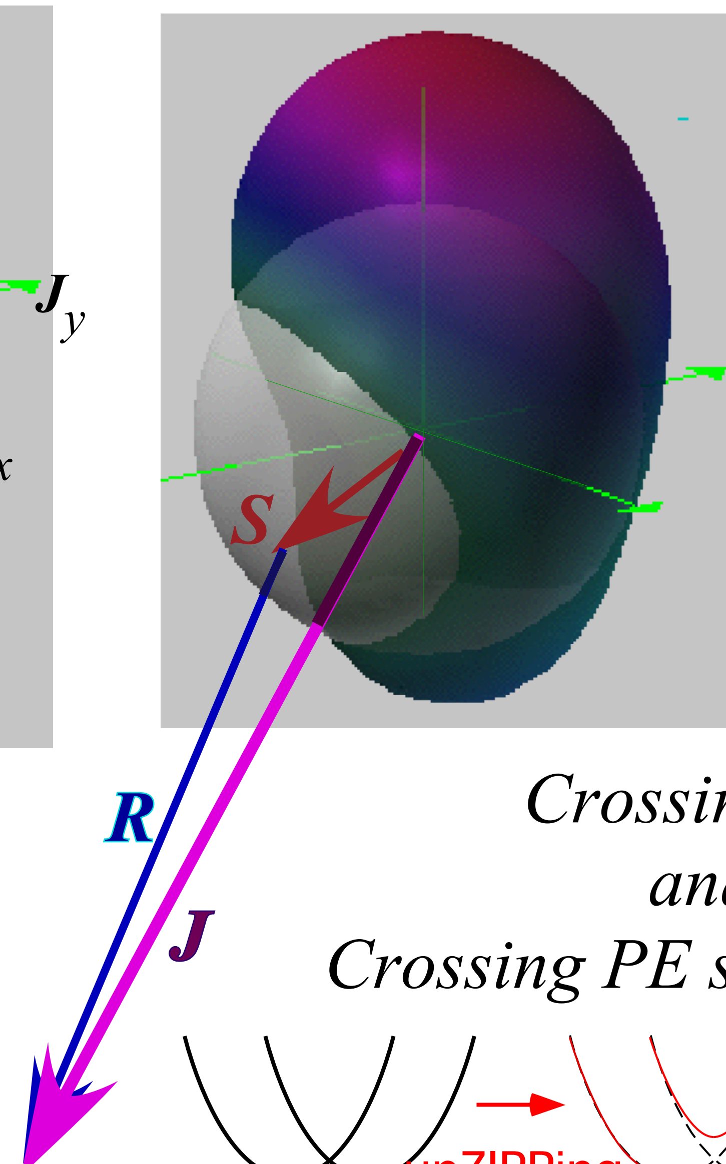


Spin gyro S=(1,1,1) attached (ZIPPed) to
Asymmetric Top (A=5, B=10, C=15)

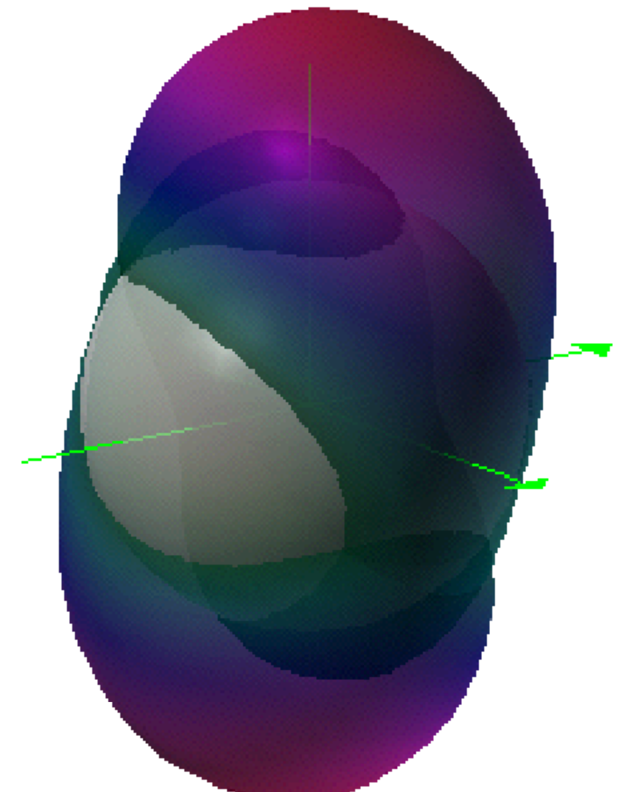


“Sherman” (The shark)

Time reversed
gyro -S=(-1,-1,-1)



The two together



Crossing RE surfaces
analogous to
Crossing PE surfaces (Jahn-Teller)

Two or more RE's beg to be unZIPPed. $\langle \mathbf{H} \rangle = \begin{pmatrix} Spin\text{-}up\ RE(\beta,\gamma) & Coupling(\beta,\gamma) \\ Coupling(\beta,\gamma)^* & Spin\text{-}down\ RE(\beta,\gamma) \end{pmatrix}$

Base RE surfaces are eigenvalues of matrix.

Classical RE

$$H=AJ_x{}^2+BJ_y{}^2+CJ_z{}^2+\ldots-2AJ_xS_x-2BJ_yS_y-2CJ_zS_z+\ldots+\textit{(more constant terms)}$$

Semi-Classical Spin-1/2 RE $\sigma_x=\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \sigma_y=\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \sigma_z=\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \mathbf{1}=\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$ *makes matrix*

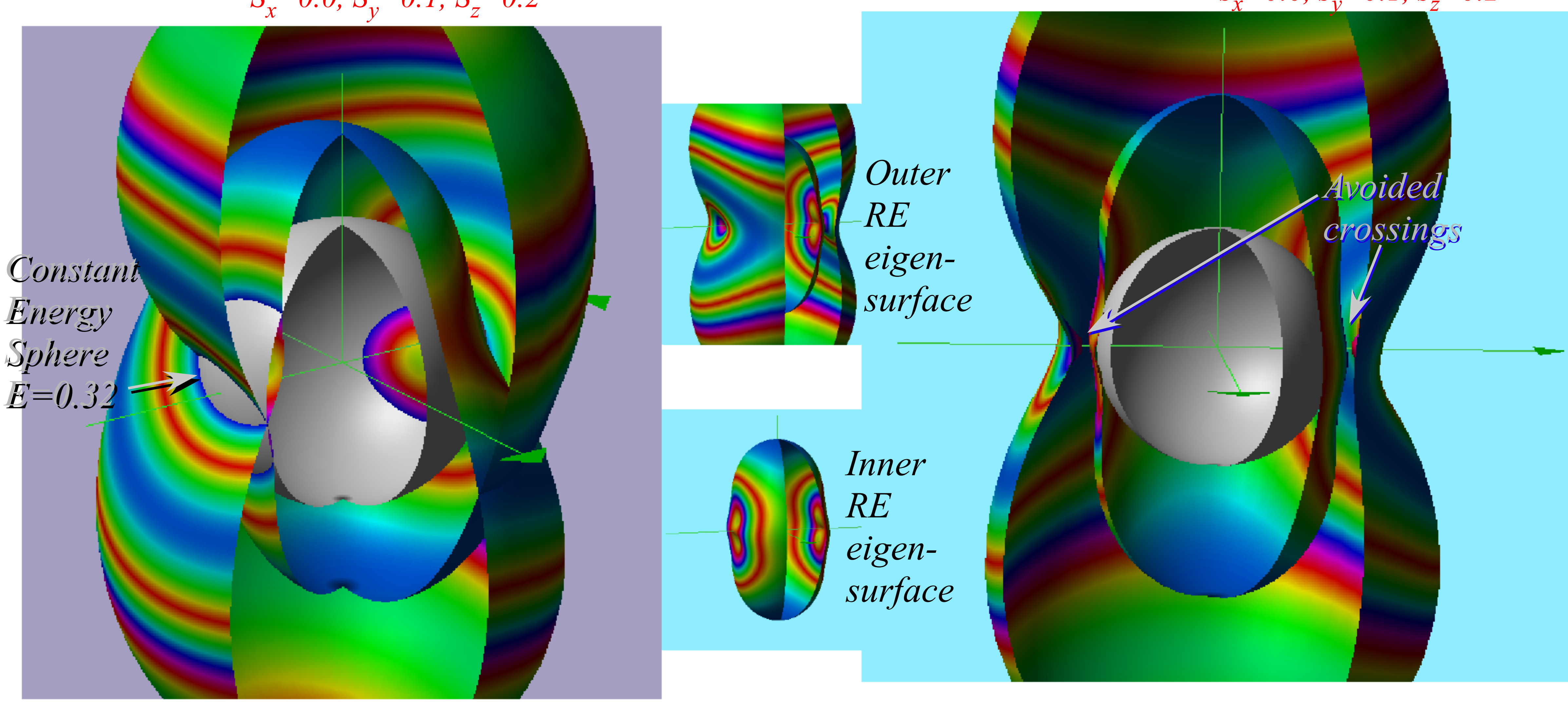
$$\mathbf{H}=(AJ_x{}^2+BJ_y{}^2+CJ_z{}^2)\mathbf{1}\ldots-AJ_xs_x\sigma_x\ -BJ_ys_y\sigma_y\ -CJ_zs_z\sigma_z+\ldots+\mathbf{1}\textit{(more constant terms)}$$

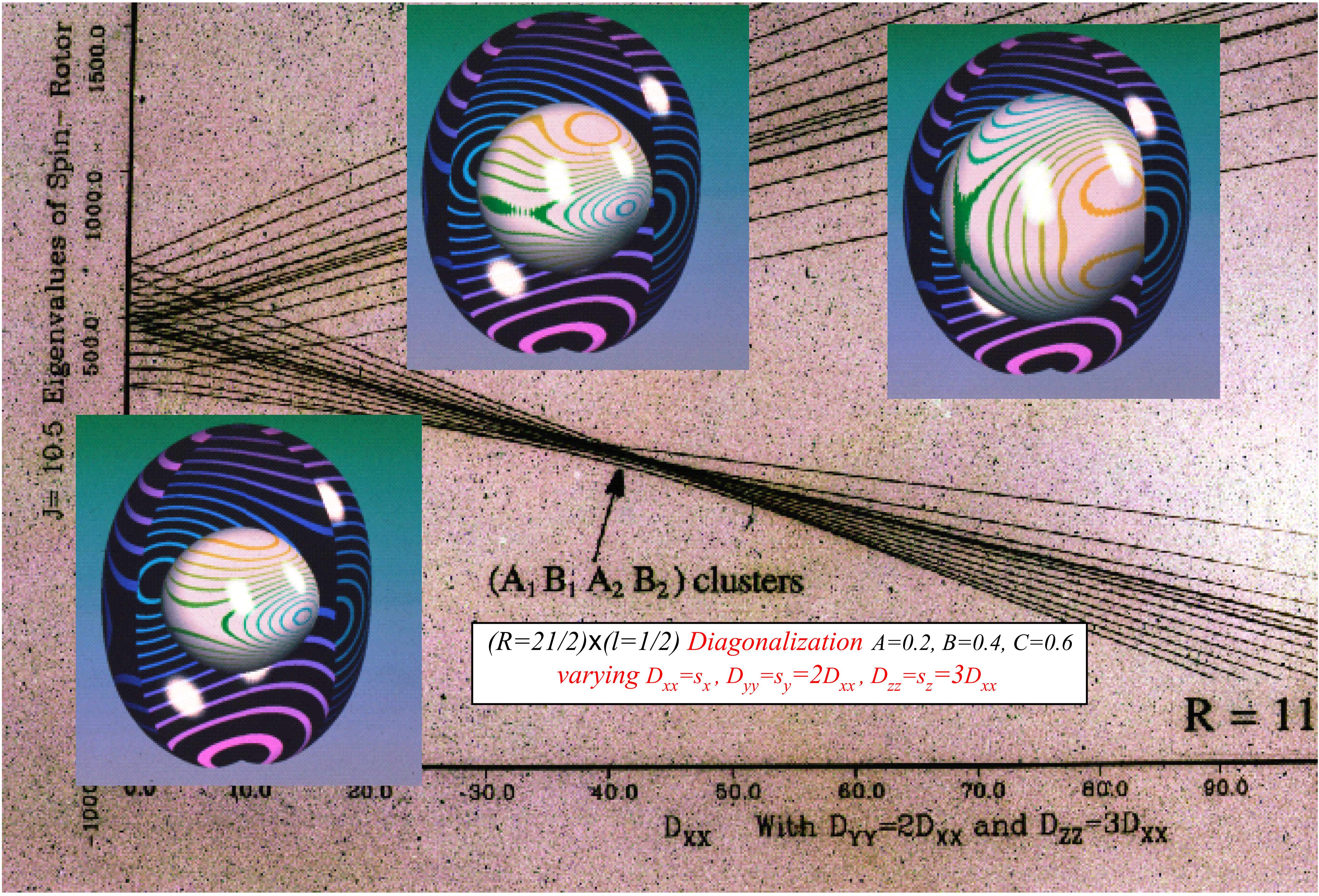
Classical ZIPP $A=0.2,\ B=0.8,\ C=1.4$

$S_x=0.0,\ S_y=0.1,\ S_z=0.2$

Semi-Classical spin-1/2 unZIPP $A=0.2,\ B=0.8,\ C=1.4$

$s_x=0.0,\ s_y=0.1,\ s_z=0.2$





J= 10.5 Eigenvalues of Spin- Rotor
1500.0
1000.0
500.0
-1000
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
D_{XX} With $D_{YY}=2D_{XX}$ and $D_{ZZ}=3D_{XX}$
$(A_1\ B_1\ A_2\ B_2)$ clusters
R = 11
(R=21/2)x(l=1/2) Diagonalization A=0.2, B=0.4, C=0.6
varying $D_{xx}=s_x$, $D_{yy}=s_y=2D_{xx}$, $D_{zz}=s_z=3D_{xx}$

Good news

Rotational energy surfaces (RES) may help visualize matrix eigensolutions in general, but rotational and vibrational-polyad states in particular.

Good news

Rotational energy surfaces (RES) may help visualize matrix eigensolutions in general, but rotational and vibrational-polyad states in particular.

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Well, not every matrix! If your RES looks like a potato, you may be in trouble!

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Rotational energy surfaces (RES) may help visualize matrix eigensolutions in general, but rotational and vibrational-polyad states in particular.

Bad news

Well, not every matrix! If your RES looks like a potato, you may be in trouble!

Good news

RES can help expose new phenomena and suggest new experiments.

Bad news

That takes some thought and work. Let us know how you do.

Good news

Rotational energy surfaces (RES) may help visualize matrix eigensolutions in general, but rotational and vibrational-polyad states in particular.

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Well, not every matrix! If your RES looks like a potato, you may be in trouble!

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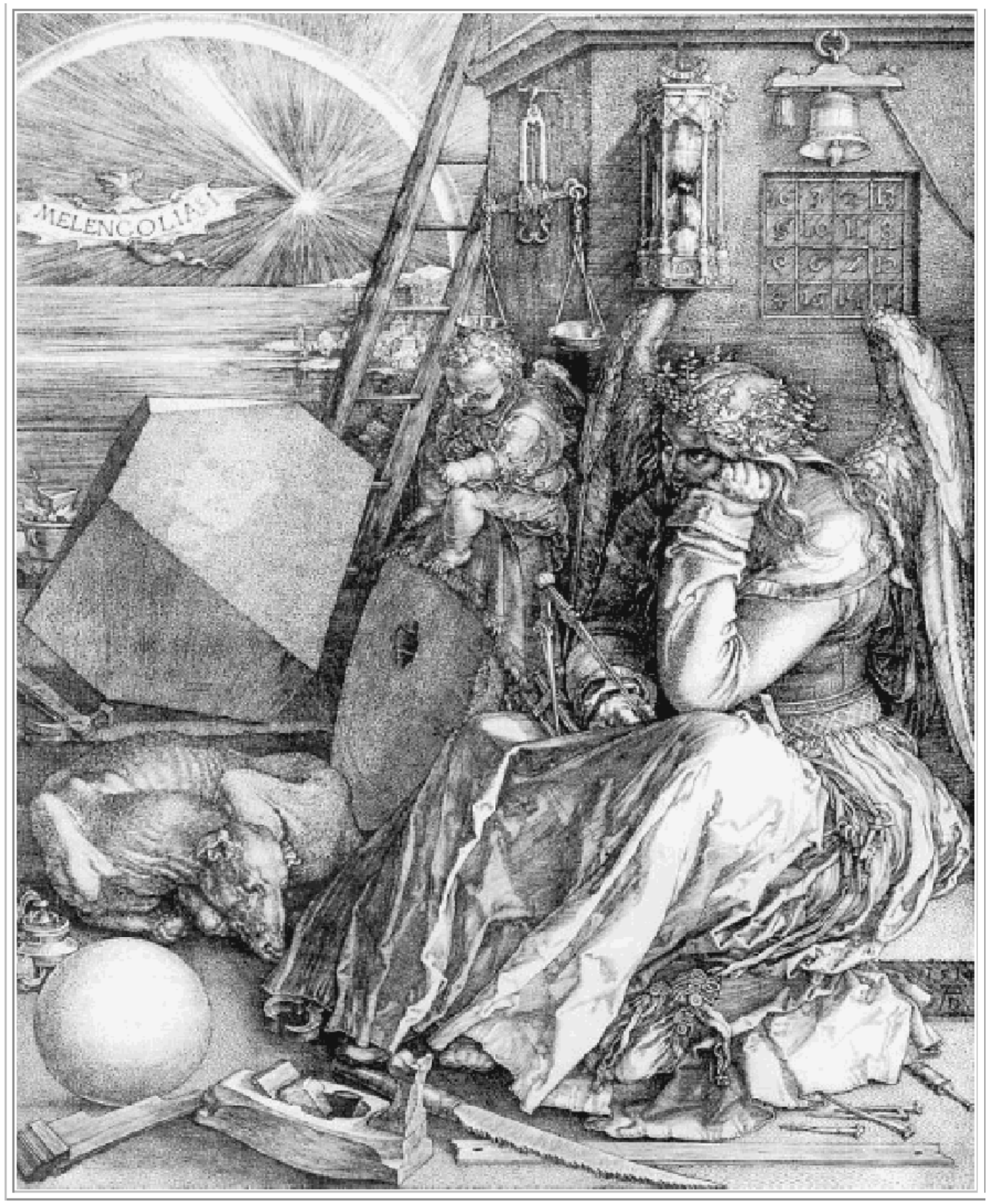
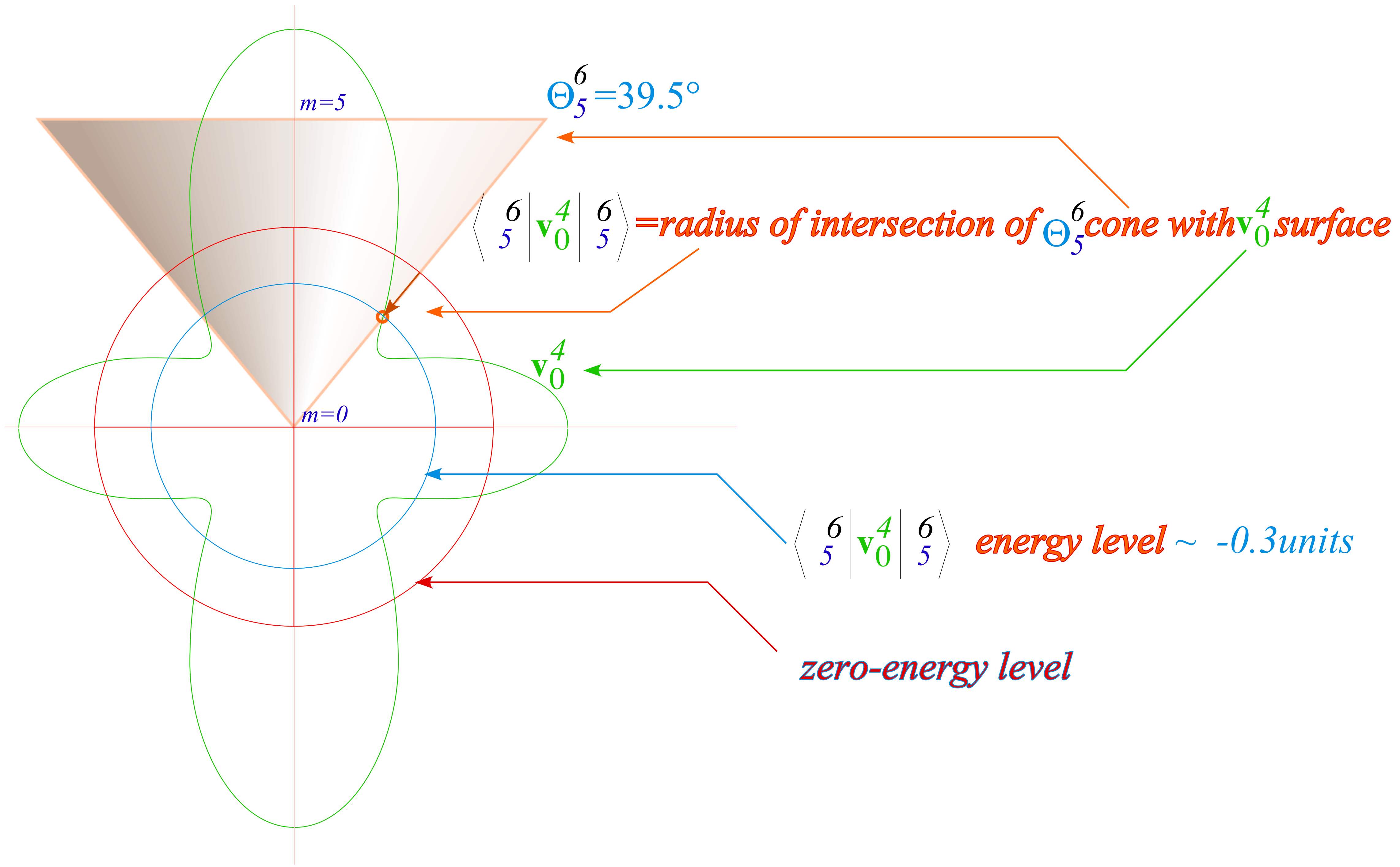
Don't count on it.

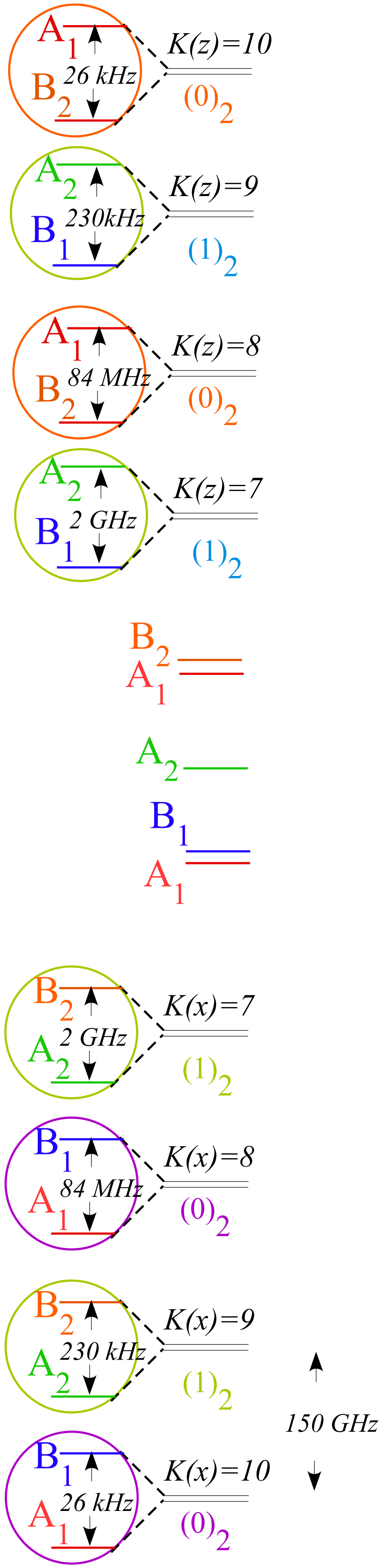


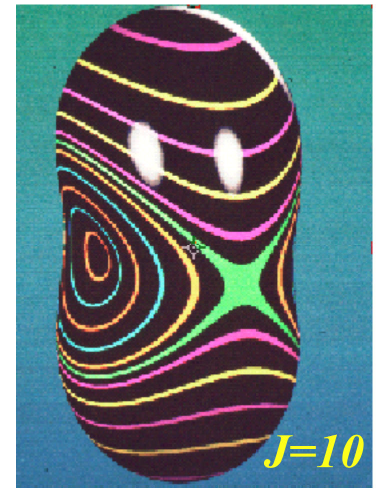
What's up, Doc?

Durer's "Melancholia"
1514

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



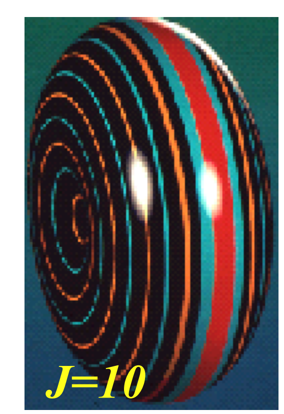




D_2 \ $C_2(x)$	$(0)_2$	$(1)_2$
A_1	1	•
A_2	•	1
B_1	1	•
B_2	•	1

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

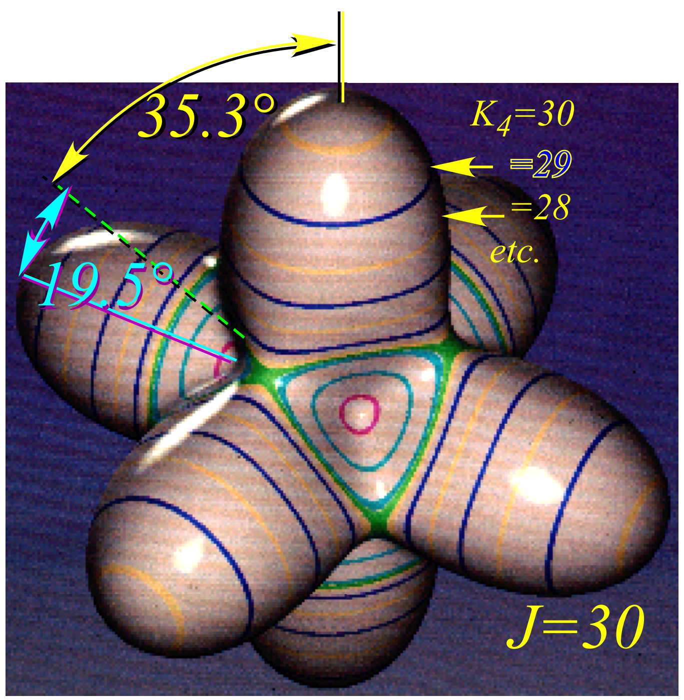
D_2 \ $C_2(z)$	$(0)_2$	$(1)_2$
A_1	1	•
A_2	•	1
B_1	•	1
B_2	1	•

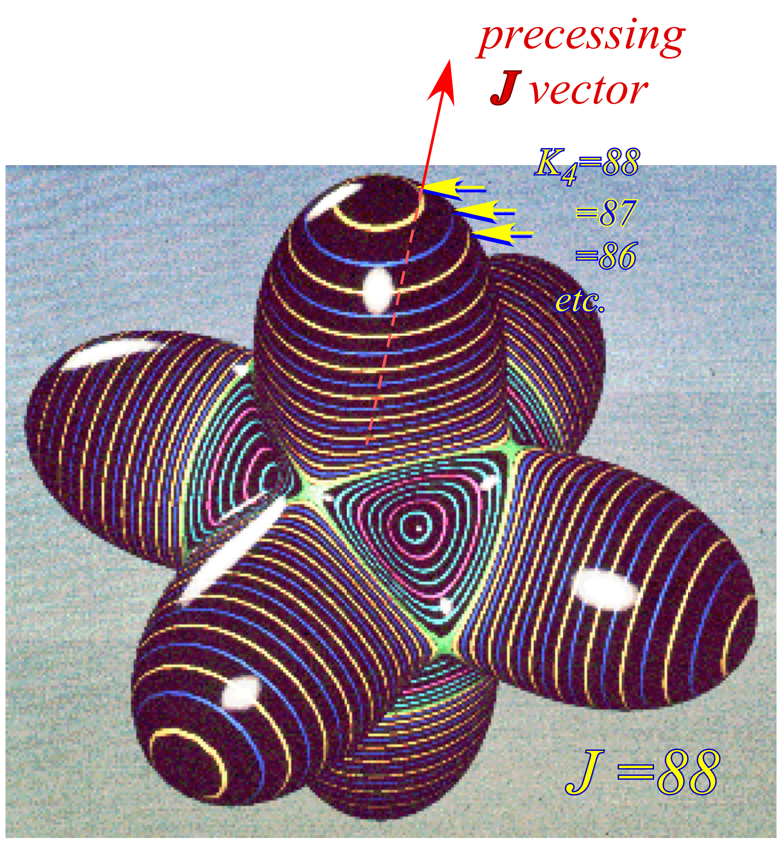


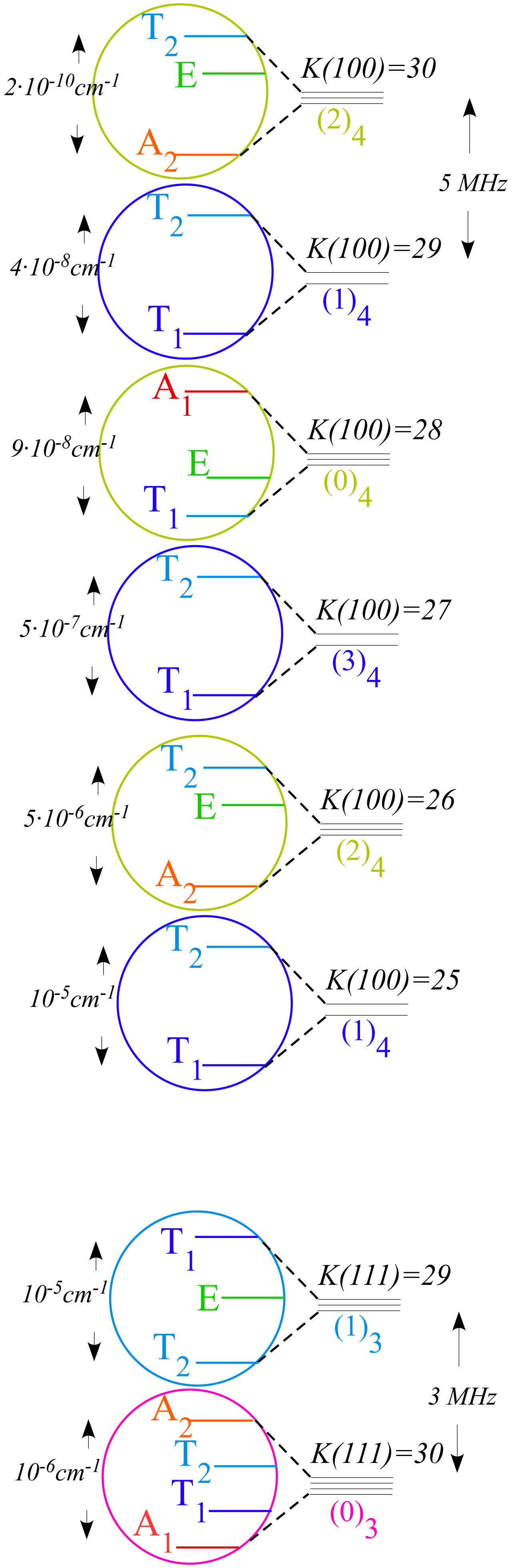
O_h or T_d Spherical Top: *(Hecht Ro-vib Hamiltonian 1960)*

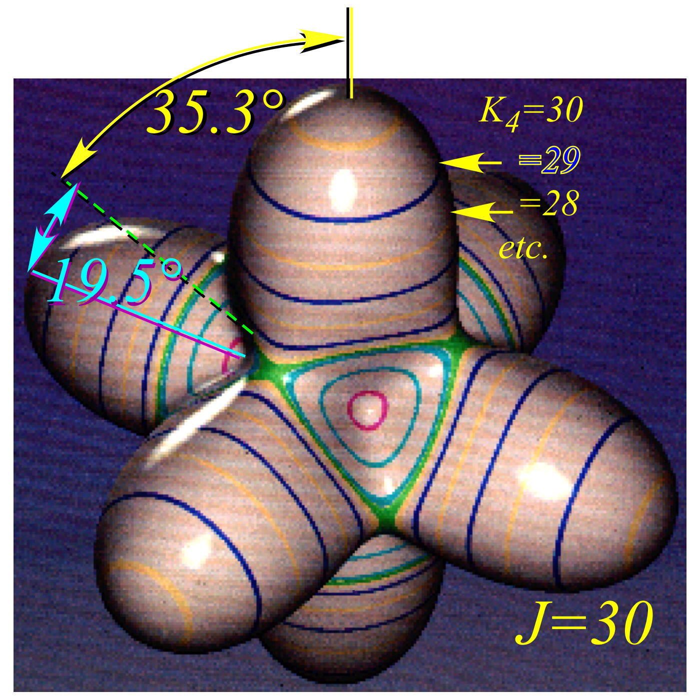
$$\mathbf{H} = B\left(\mathbf{J}_x^2 + \mathbf{J}_y^2 + \mathbf{J}_z^2\right) + t_{440}\left(\mathbf{J}_x^4 + \mathbf{J}_y^4 + \mathbf{J}_z^4 - \frac{3}{5}J^4\right) + \cdots$$

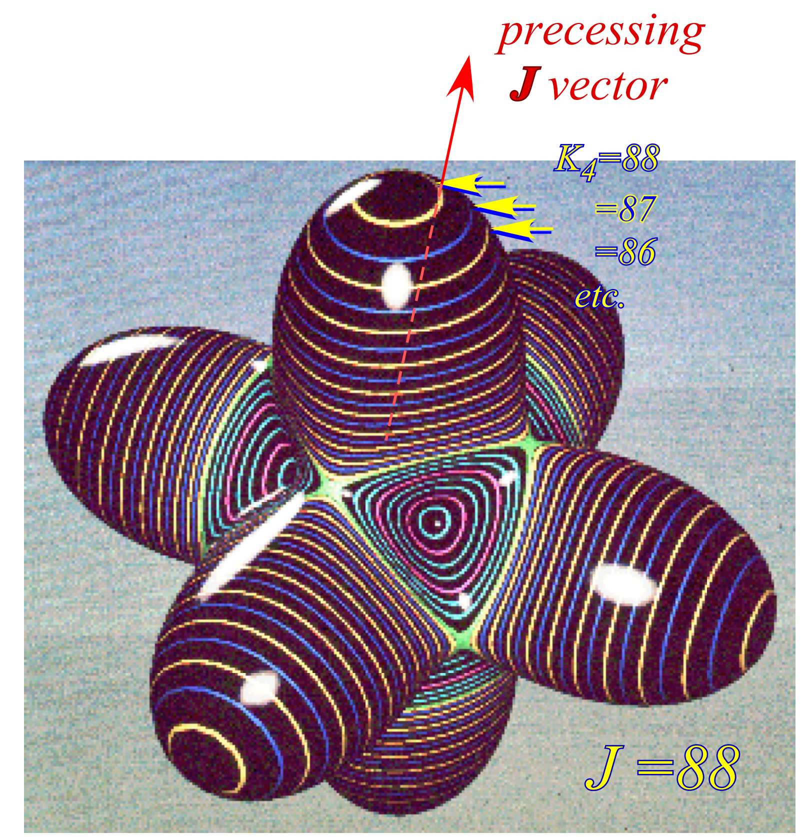
$$= B\mathbf{J}^2 + t_{440}\left(\mathbf{T}_0^4 + \sqrt{\frac{5}{14}}\left[\mathbf{T}_4^4 + \mathbf{T}_{-4}^4\right]\right) + \cdots$$









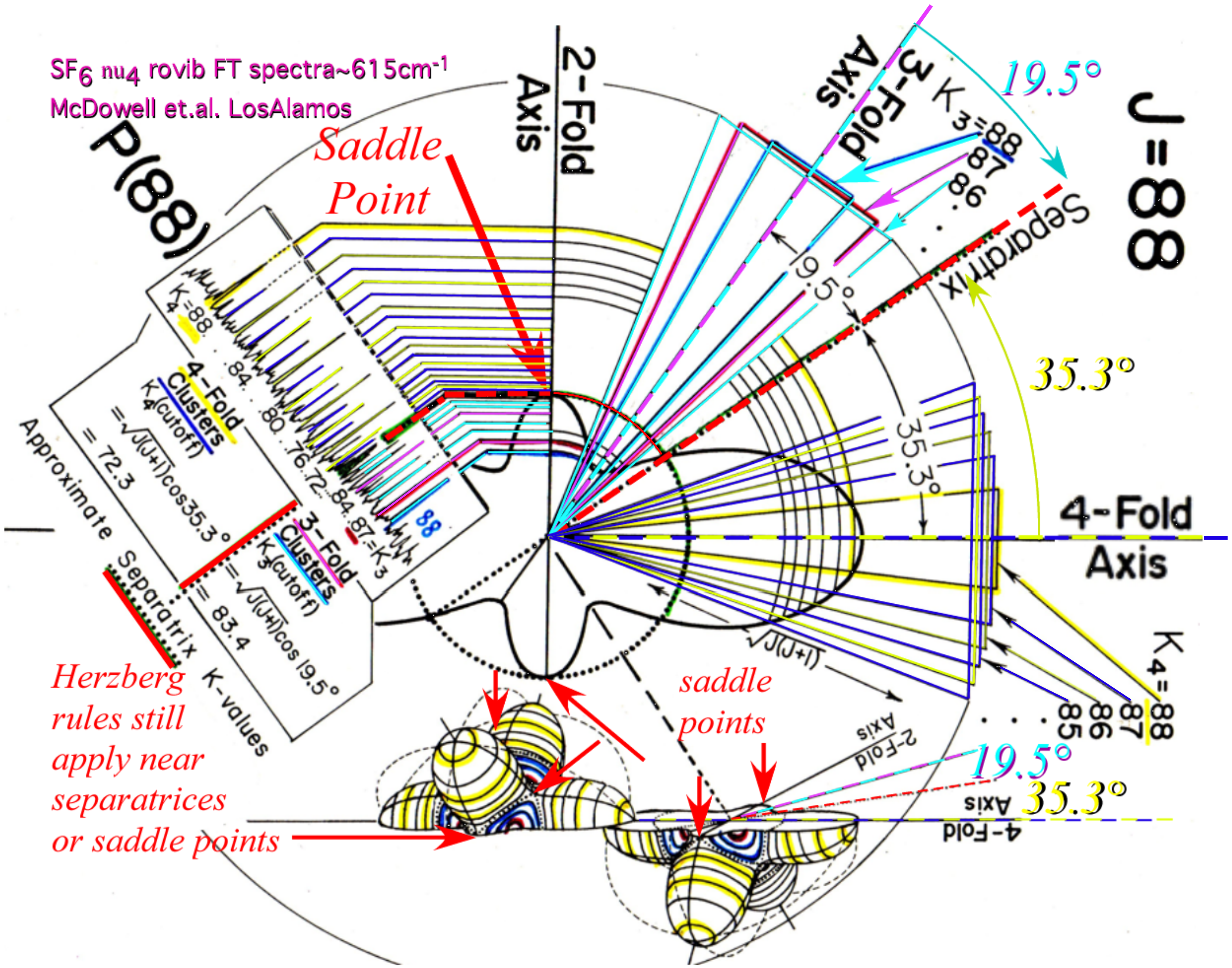


O \ $C_3(111)$	$(0)_3$	$(1)_3$	$(2)_3$
A_1	1	•	•
A_2	1	•	•
E_2	•	1	1
T_1	1	1	1
T_2	1	1	1

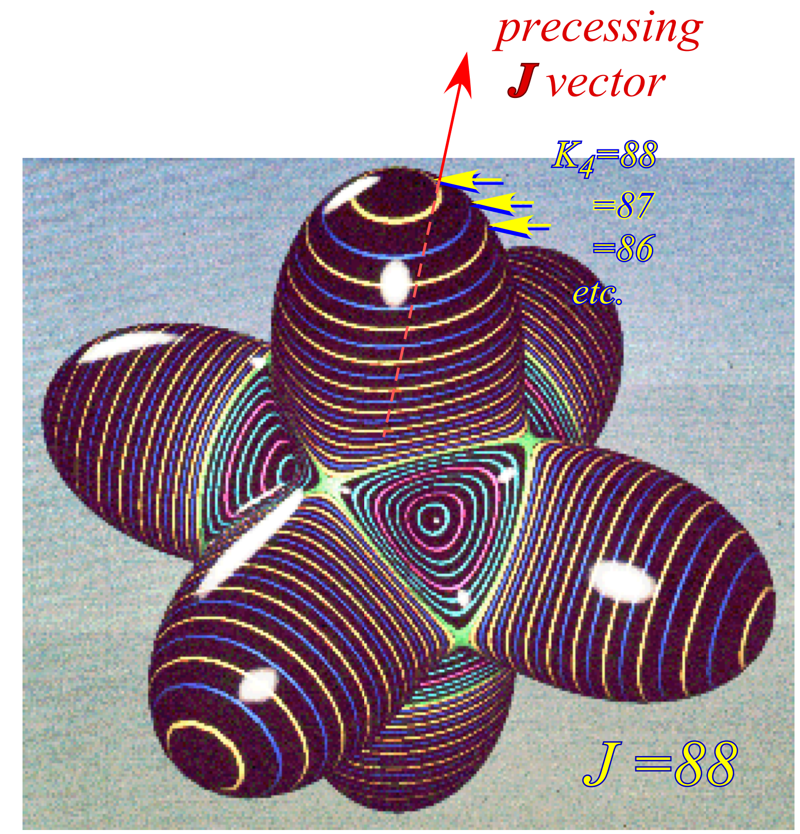
O \ $C_2(110)$	$(0)_2$	$(1)_2$
A_1	1	•
A_2	•	1
E_2	1	1
T_1	1	2
T_2	2	1

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



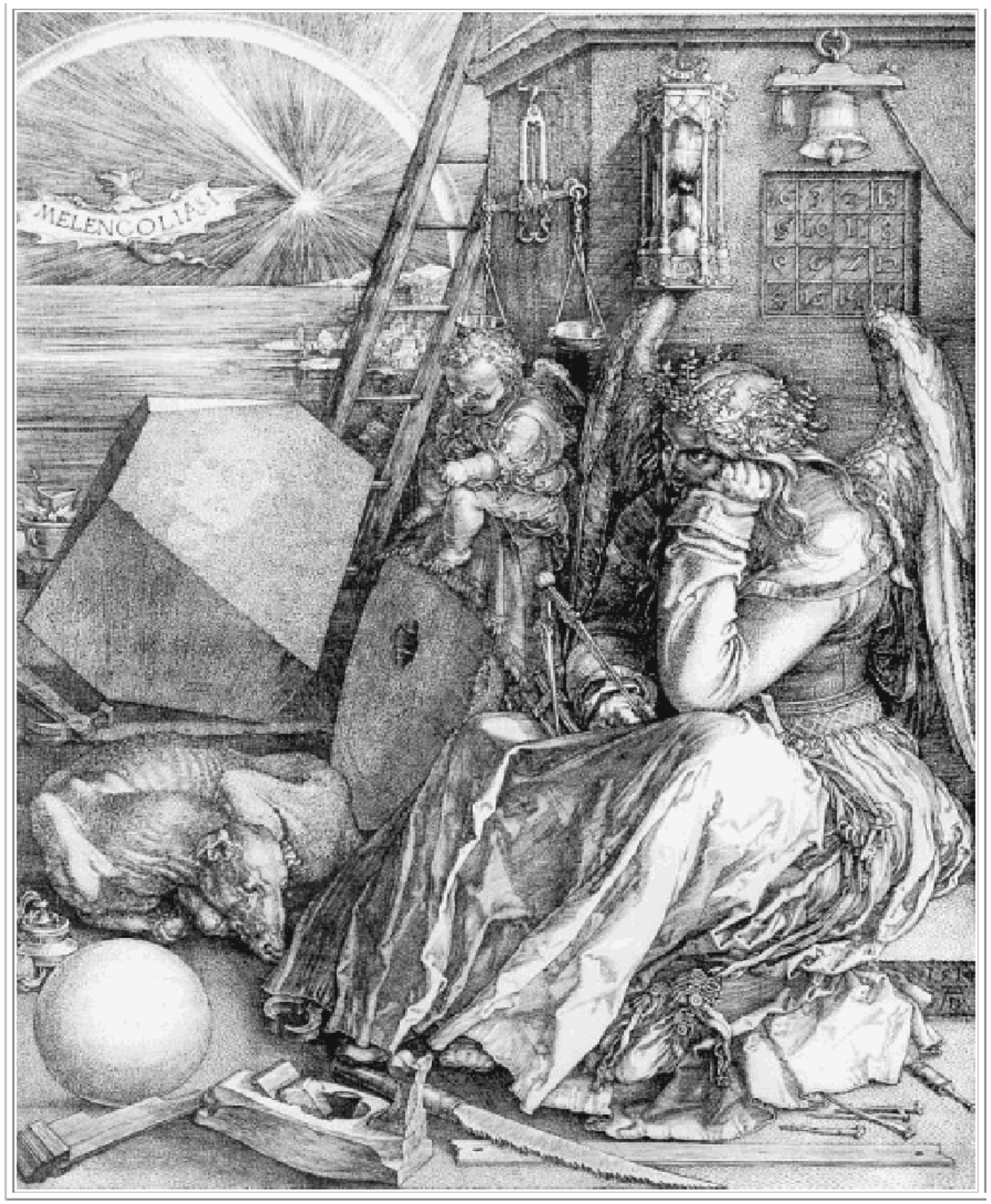
SF6 nu4 rovib FT spectra~615cm-1
McDowell et.al. LosAlamos
P(88)
Saddle Point
2-Fold Axis
3-Fold Axis
19.5°
J=88
Separatrix
35.3°
4-Fold Axis
4-Fold Clusters
3-Fold Clusters
Approximate Separatrix K-values
Herzberg rules still apply near separatrices or saddle points
saddle points



precessing
J vector
K4=88
=87
=86
etc.
J =88

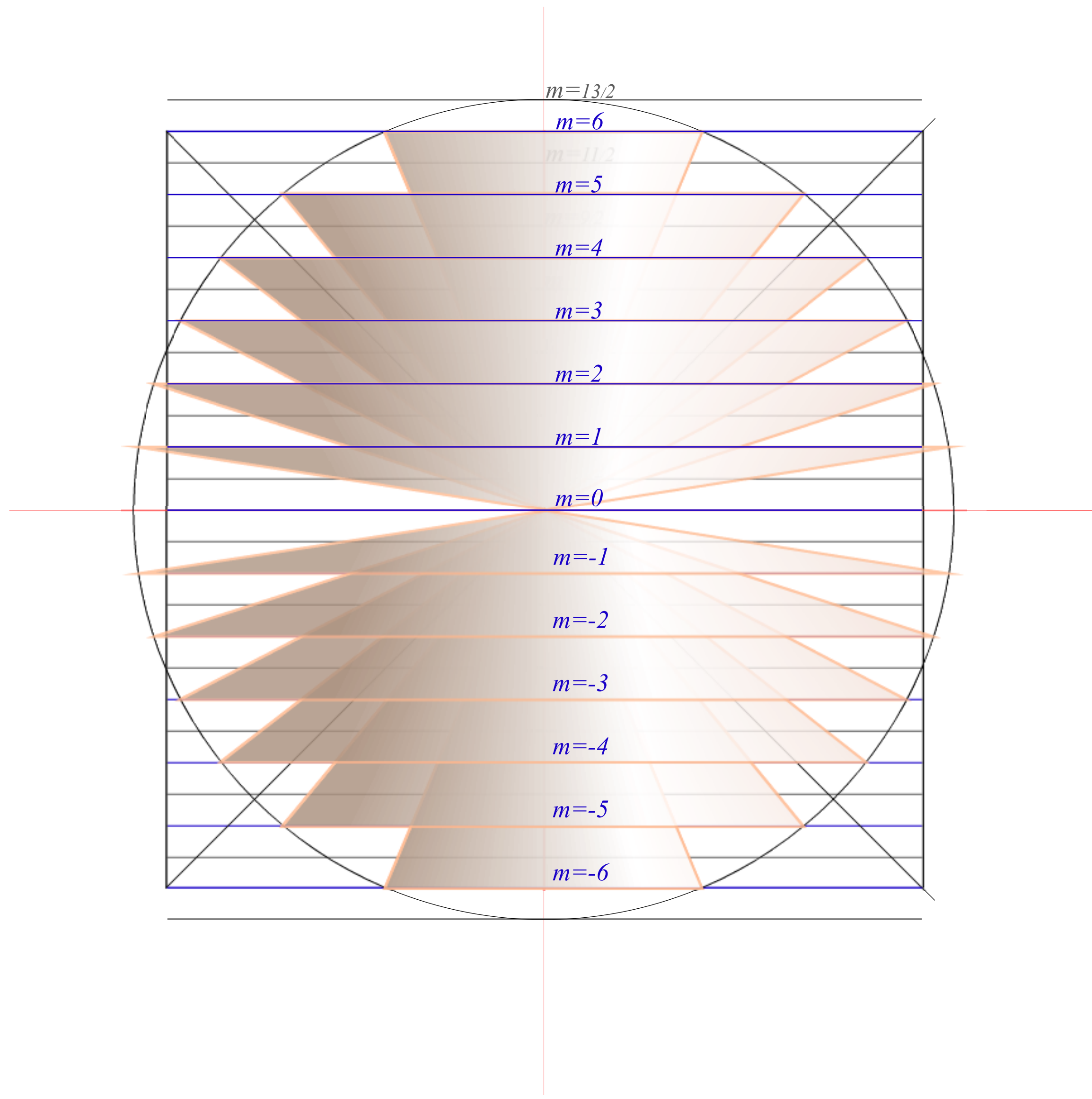
What reasoning can lead to!

(Why it is mostly in disfavor)

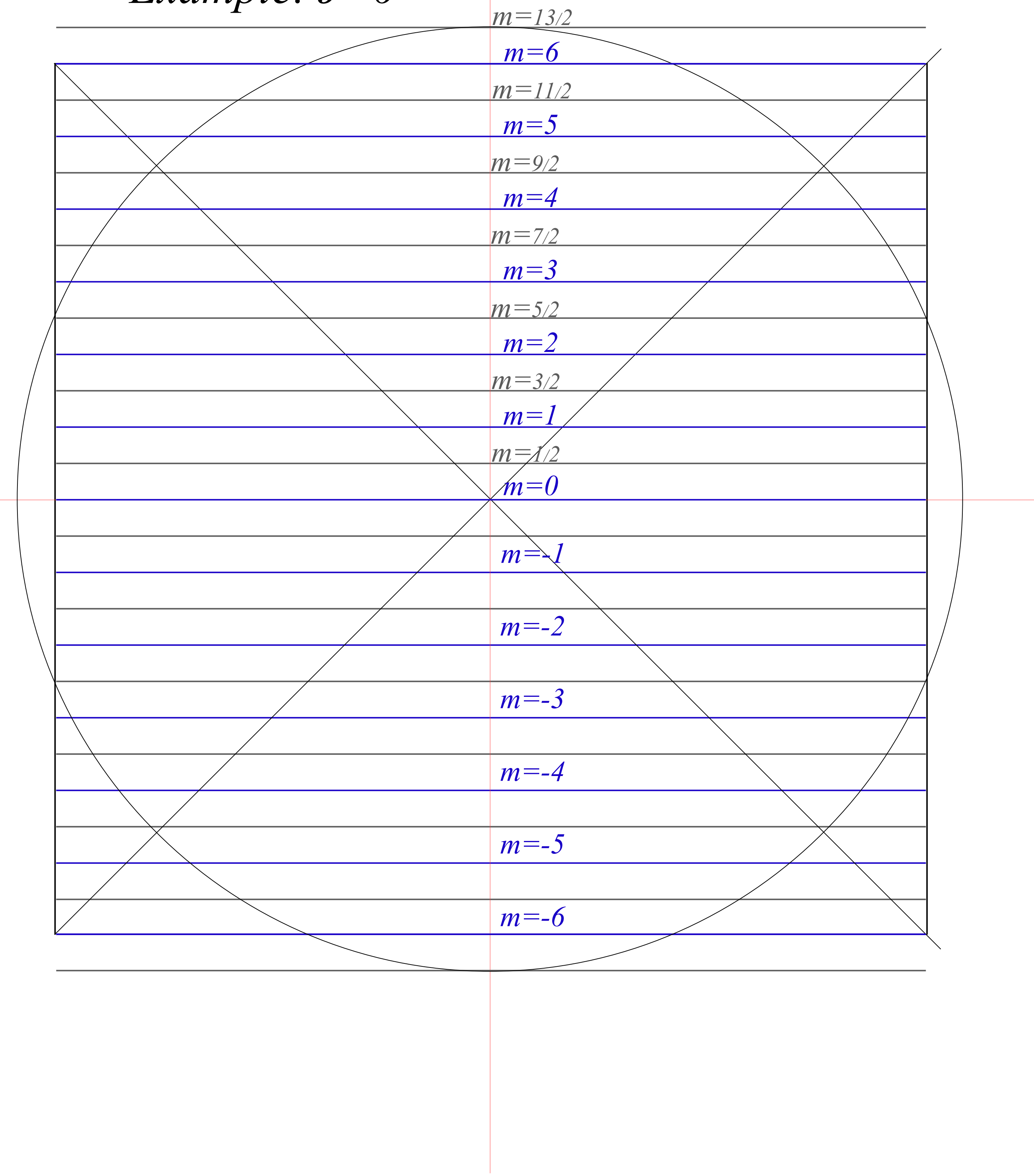


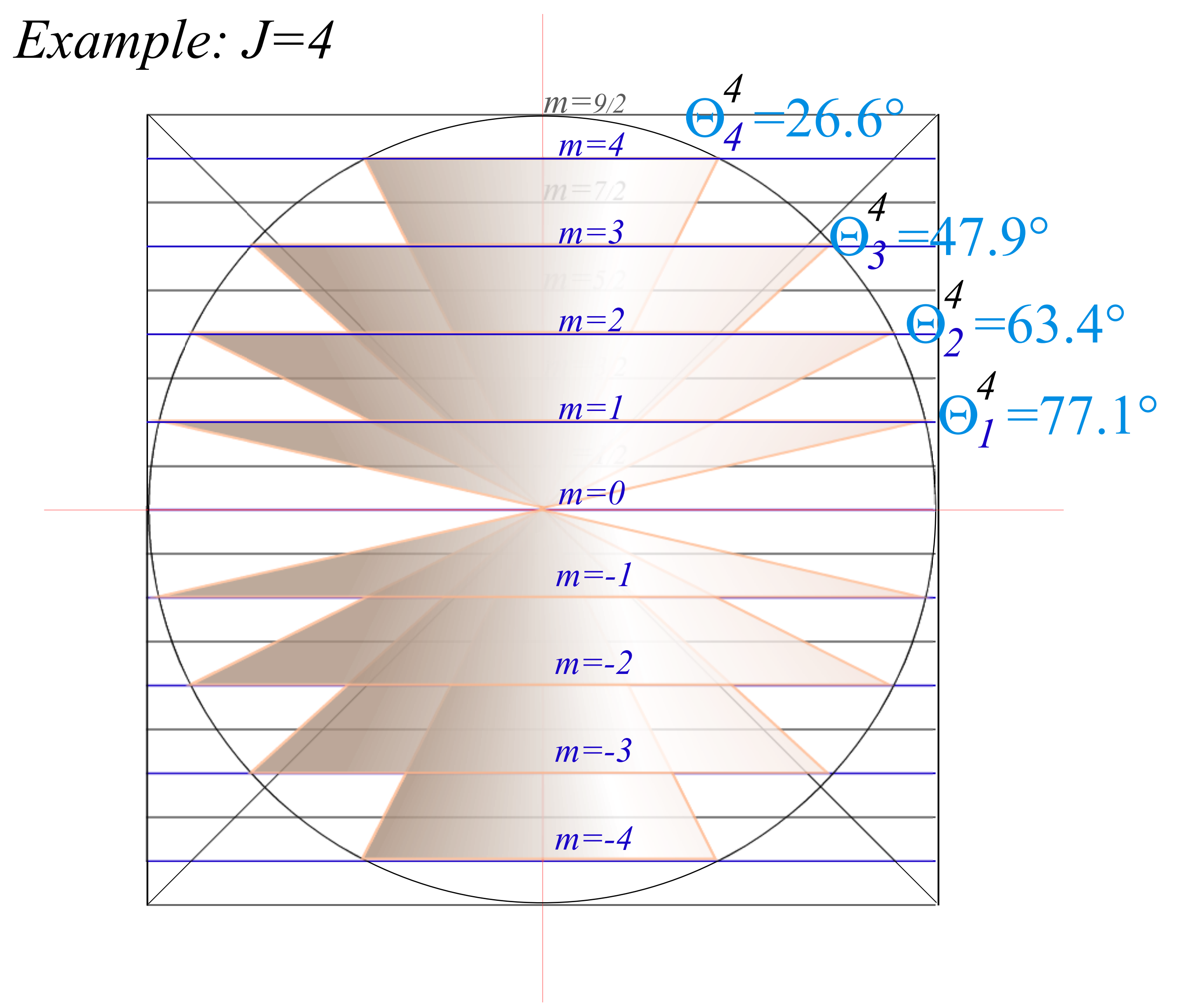
Durer's "Melancholia"
1514

It's not always the most comfortable occupation!


m=13/2
m=6
m=11/2
m=5
m=4
m=3
m=2
m=1
m=0
m=-1
m=-2
m=-3
m=-4
m=-5
m=-6

Example: J=6


m=13/2
m=6
m=11/2
m=5
m=9/2
m=4
m=7/2
m=3
m=5/2
m=2
m=3/2
m=1
m=1/2
m=0
m=-1
m=-2
m=-3
m=-4
m=-5
m=-6



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

Classical J-polynomials

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

Classical J-Polynomials

Classical J-Polynomials

C

Example: (J=6)-eigenvalues of $\mathbf{v}^{6}_{0}$