Classical, semi-classical, and quantum dynamics of uni-axial and multi-axial floppy rotors

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(1st Half)

Ways to geometrically visualize single-rotor quantum states and dynamics

(2nd Half)

Ways to begin visualizing compound-rotor quantum states and dynamics

(Next talk)

Ways to begin computing compound-rotor states...

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

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

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

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

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

Asymmetric Top
(A≠B≠C)

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

Some 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?!?)

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

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

(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*

Some Approaches for Treating Rotor Hamiltonians (contd)

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

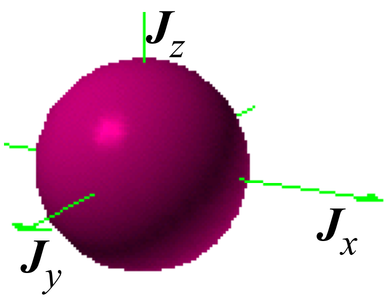
$$\left\langle \mathbf{T}_0^{(0)} \right\rangle = cY_0^0 = J(J+1)$$

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

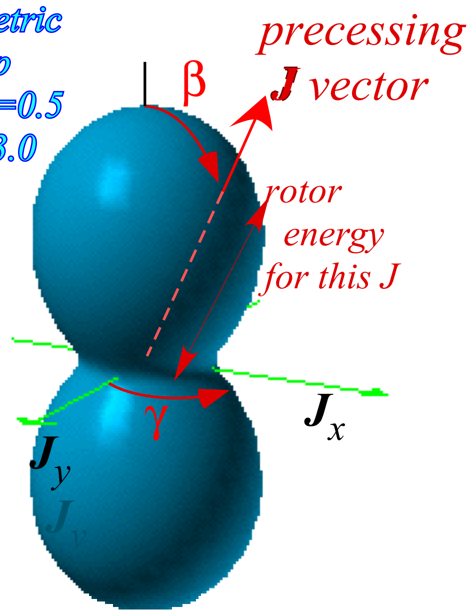
$$\left\langle 2\mathbf{T}_0^{(2)} \right\rangle = cY_0^2 = J(J+1)\left(3\cos^2\beta - 1\right)$$

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

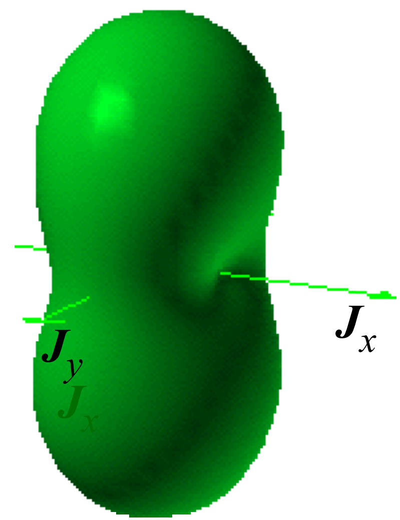
Spherical Top
A = B = C = 1.0



Symmetric Top
A = B = 0.5
C = 3.0



Asymmetric Top
A = 0.5
B = 1.5
C = 3.0



<u>*RE surface*</u>
Energy plotted radially
vs.
direction of J-vector
|for fixed magnitude |J

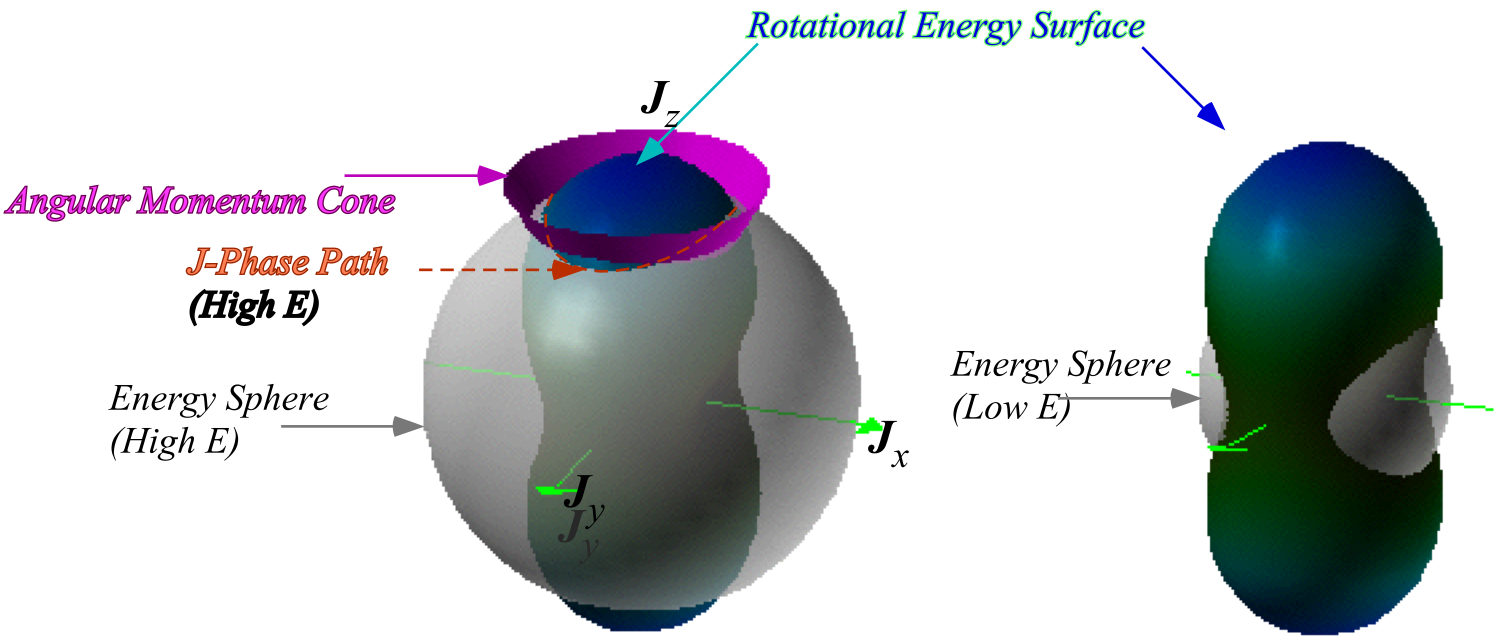
(S) Semiclassical Analysis

Uses

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

and

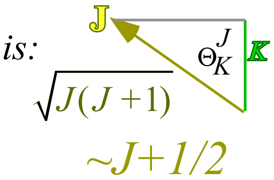
Quantum angular momentum cones



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

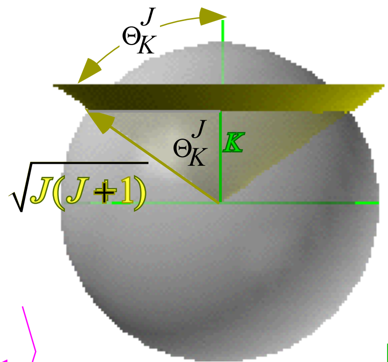
$$\mathbf{J}_z \left| \begin{matrix} J \\ K \end{matrix} \right\rangle = K \left| \begin{matrix} J \\ K \end{matrix} \right\rangle$$

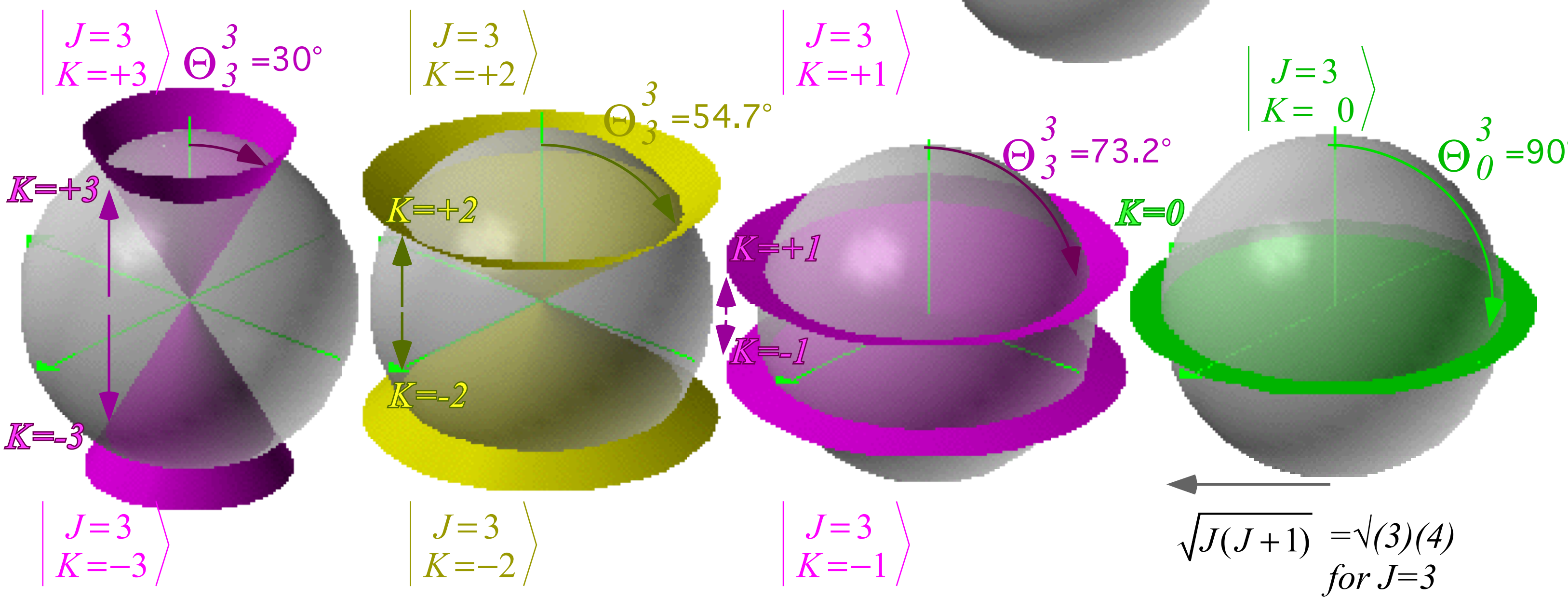
Interpreted "Literally" is:



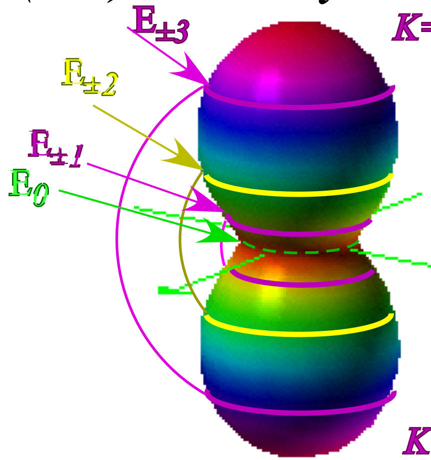
Quantum Angular Cone Uncertainty Angles

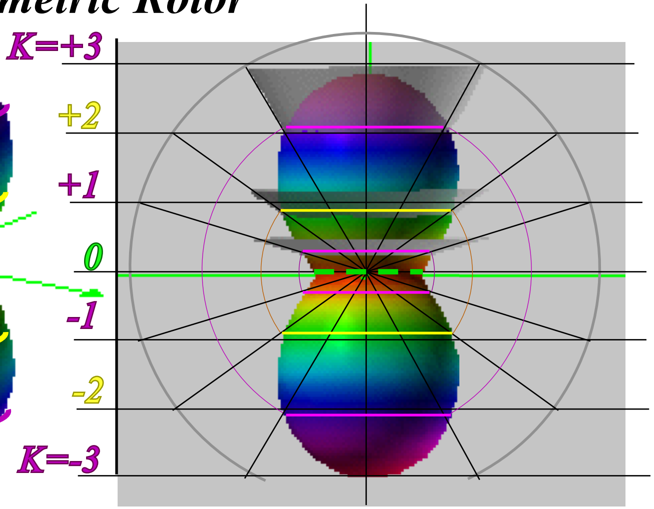
$$\cos \Theta_K^J = \frac{K}{\sqrt{J(J+1)}}$$

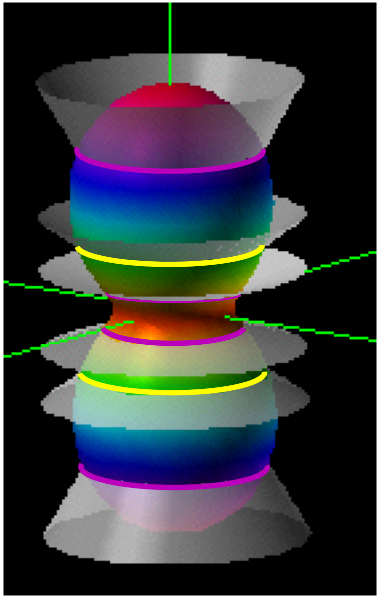




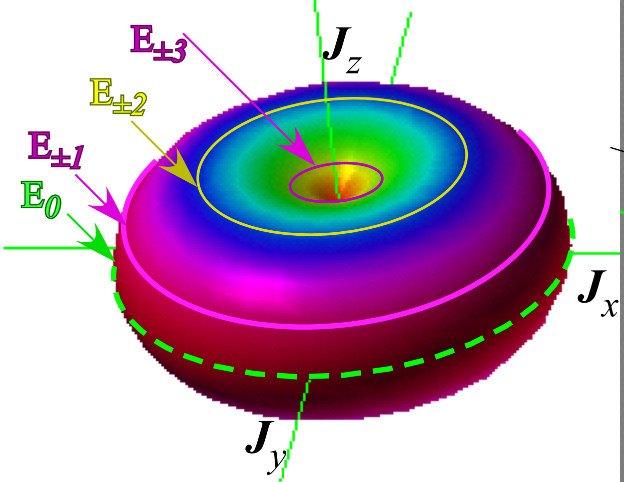
(S) Semiclassical J-Phase Paths for (J=3) Prolate Symmetric Rotor

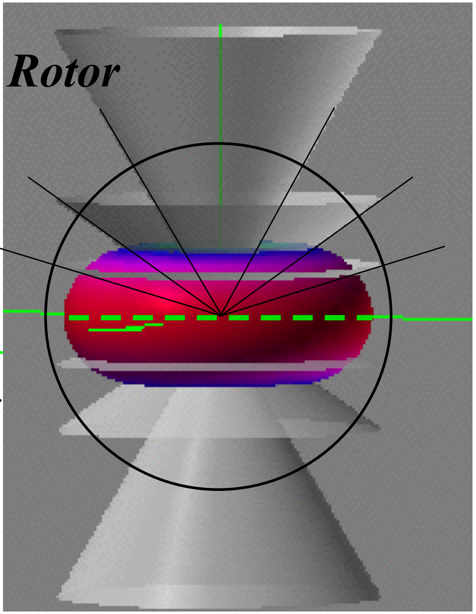


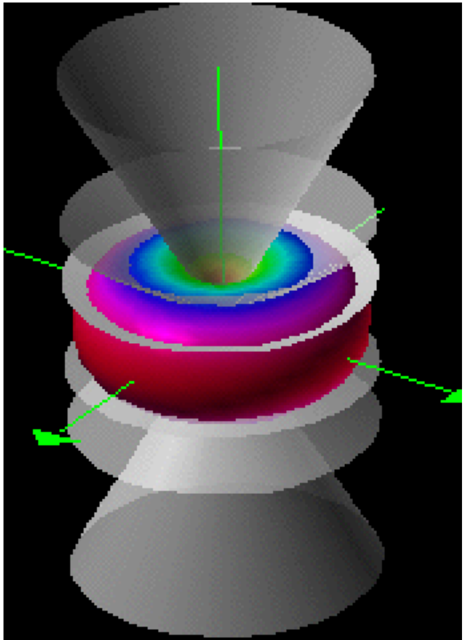




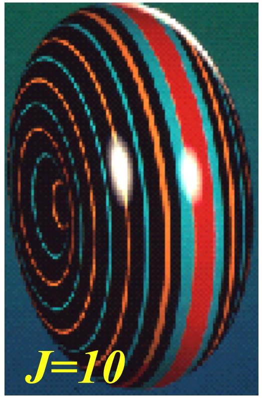
(J=3) Oblate Symmetric Rotor

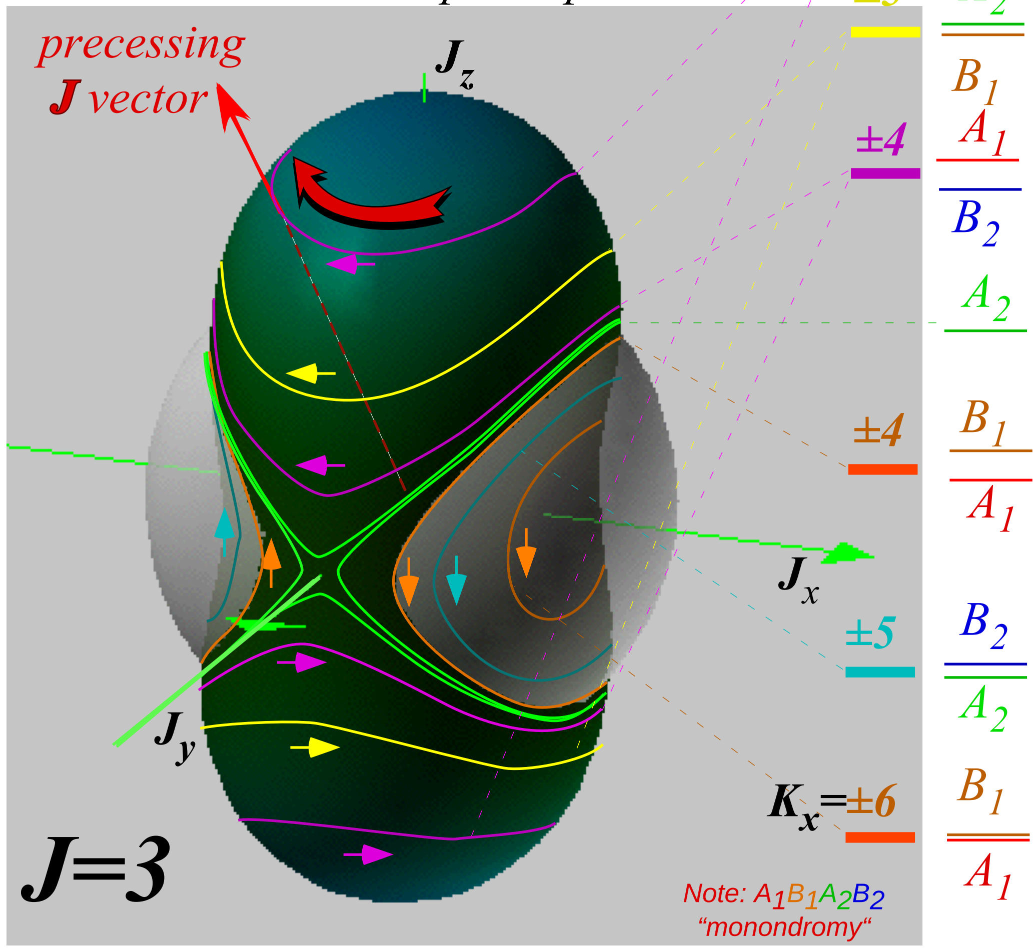




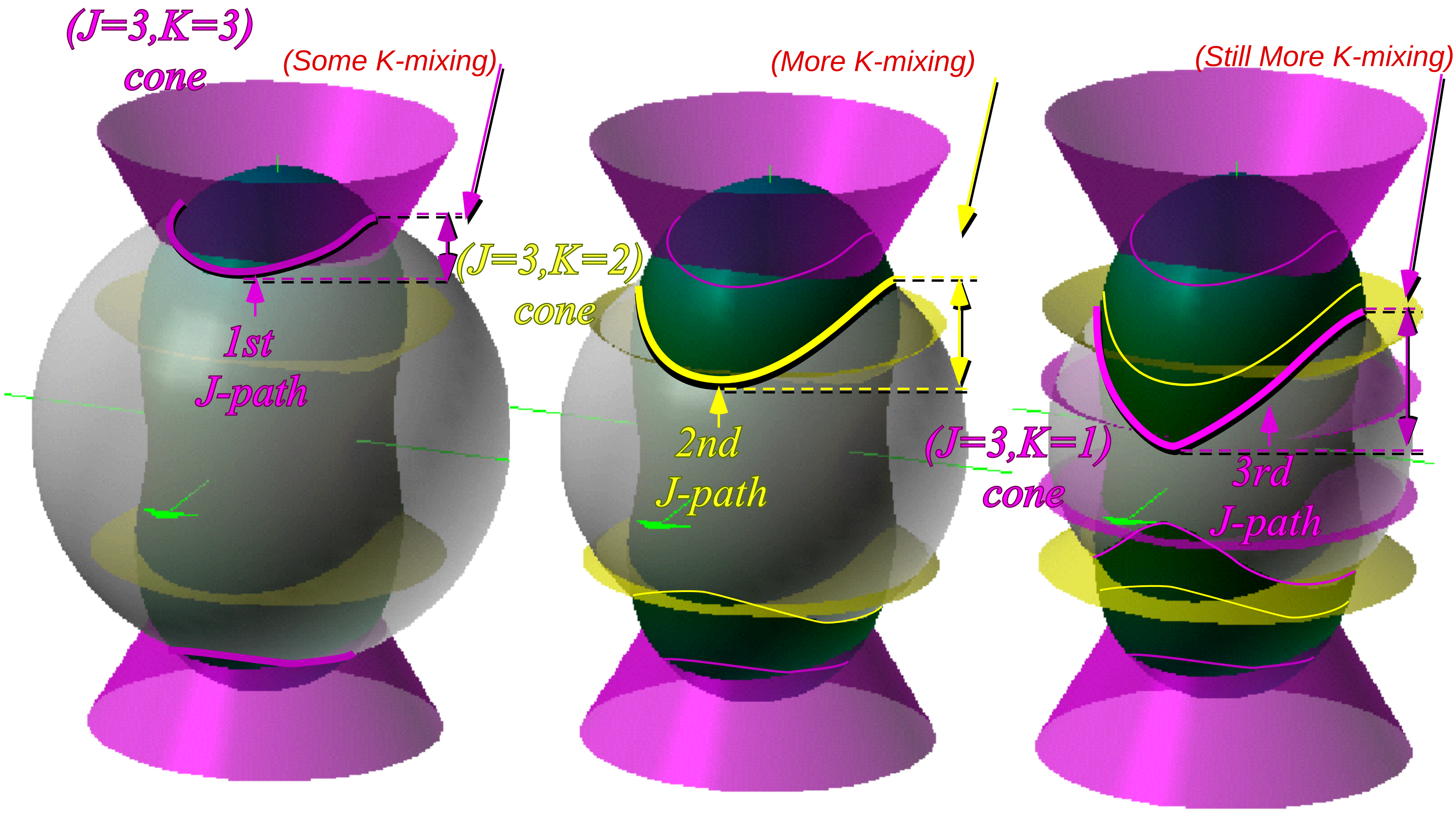


Asymmetric Top Eigensolutions Related to RE Surface and semi-classical J-phase paths





Asymmetric Top quantum ***J*** *phase paths deviate from (J,K)- cones at low J and K*
(This indicates more K-mixing in eigenstes)



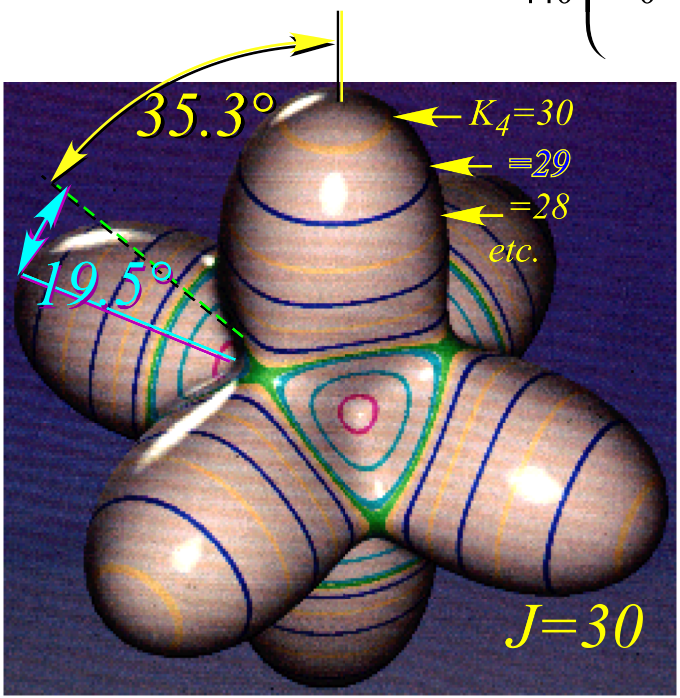
Semi Rigid Rotor Hamiltonian: *Centrifugal and Coriolis terms...*

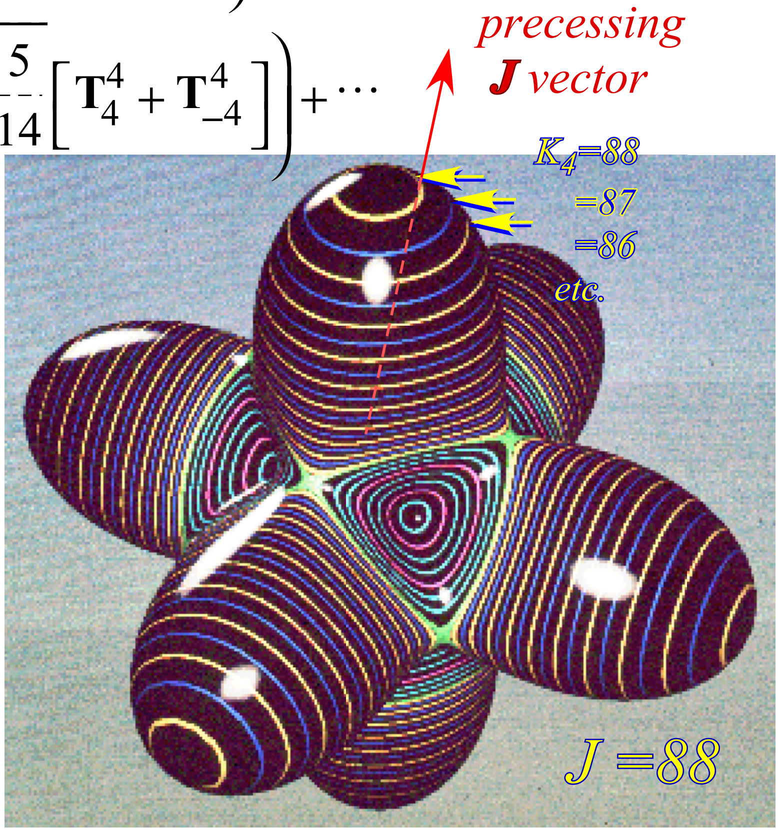
$$\mathbf{H} = A\mathbf{J}_x^2 + B\mathbf{J}_y^2 + C\mathbf{J}_z^2 + t_{xxxx}\mathbf{J}_x^4 + t_{xxyy}\mathbf{J}_x^2\mathbf{J}_y^2 + \cdots$$

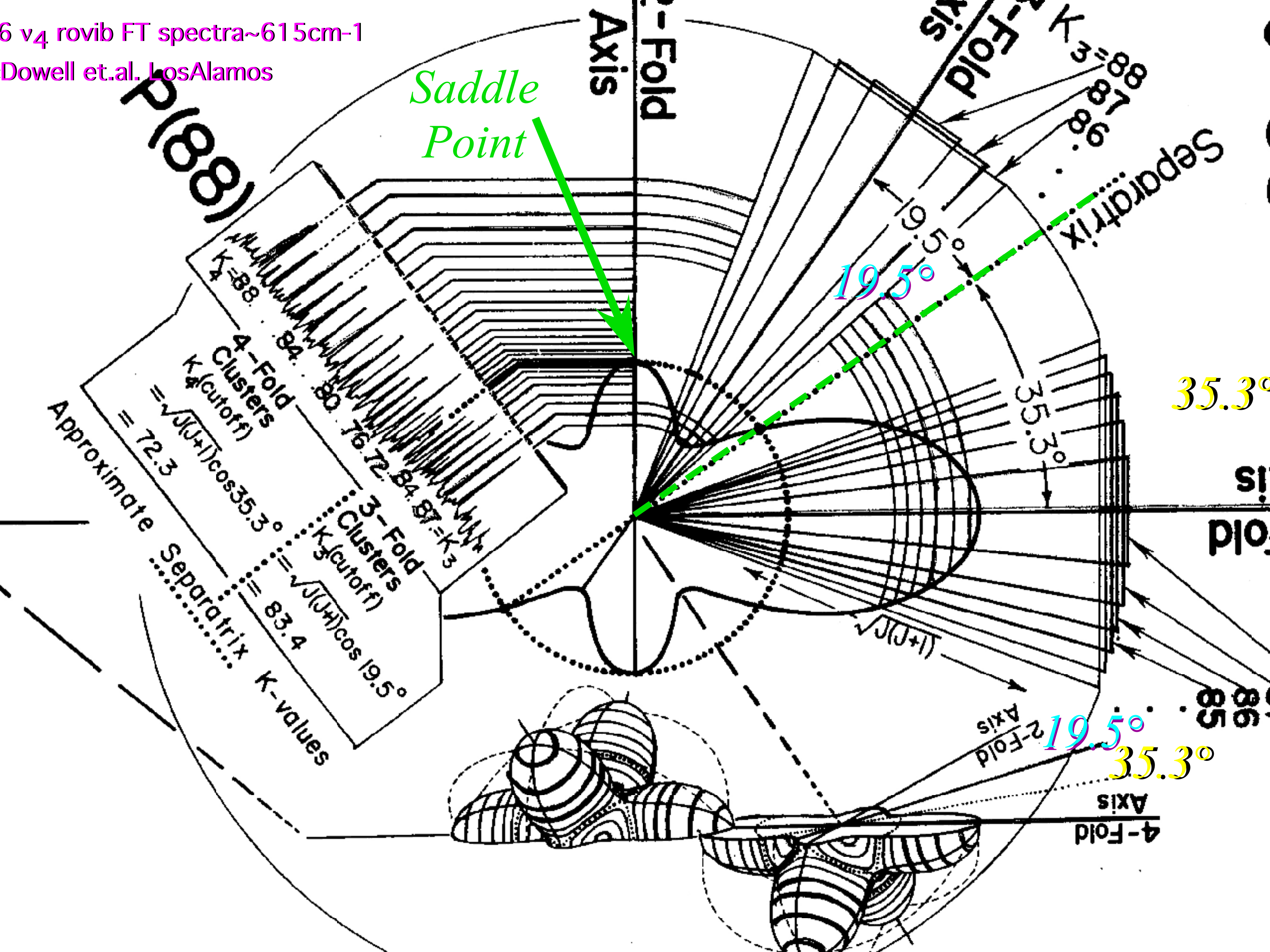
Semi Rigid O_h or T_d Spherical Top: *(Hecht Hamiltonian 1960)*

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

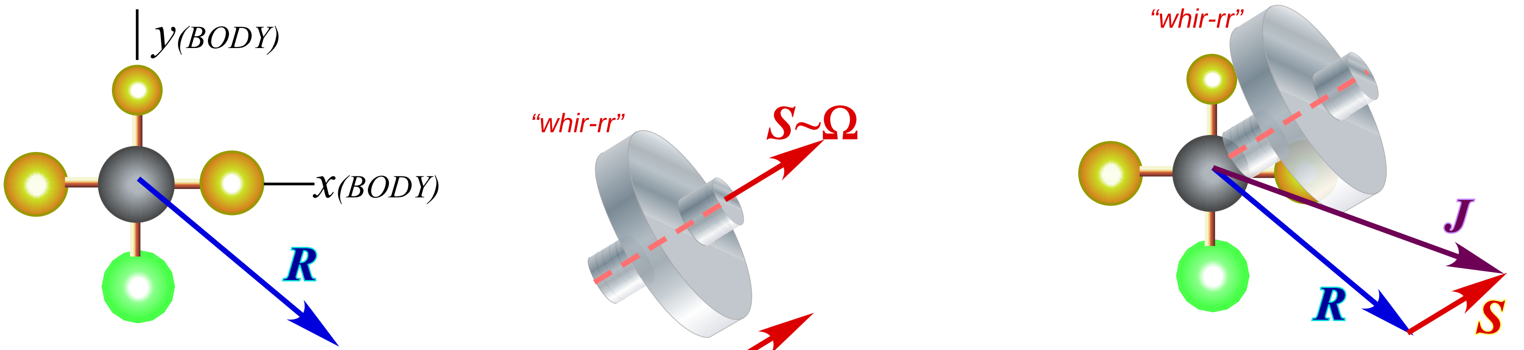
$$= B\mathbf{J}^2 + t_{440}\left(\mathbf{T}_0^4 + \sqrt{\frac{5}{14}}\left[\mathbf{T}_4^4 + \mathbf{T}_{-4}^4\right]\right) + \cdots$$







6 ν4 rovib FT spectra~615cm-1
Dowell et.al. LosAlamos
P(88)
Saddle Point
4-Fold Axis
2-Fold Axis
Separatrix
19.5°
35.3°
4-Fold Clusters
K4(cutoff) =√J(J+1)cos35.3° = 72.3
3-Fold Clusters
K3(cutoff) =√J(J+1)cos 19.5° = 83.4
Approximate Separatrix K-values
√J(J+1)



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"...*

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

(discussed in next talk)

Here constraint is rigid so <u>*body*</u> *components* (S_x, S_y, S_z) *are fixed* *("slippery gyro")*

ANALOGY: $p^2/2M$ becomes: $(p-eA)^2/2M$ in an em field

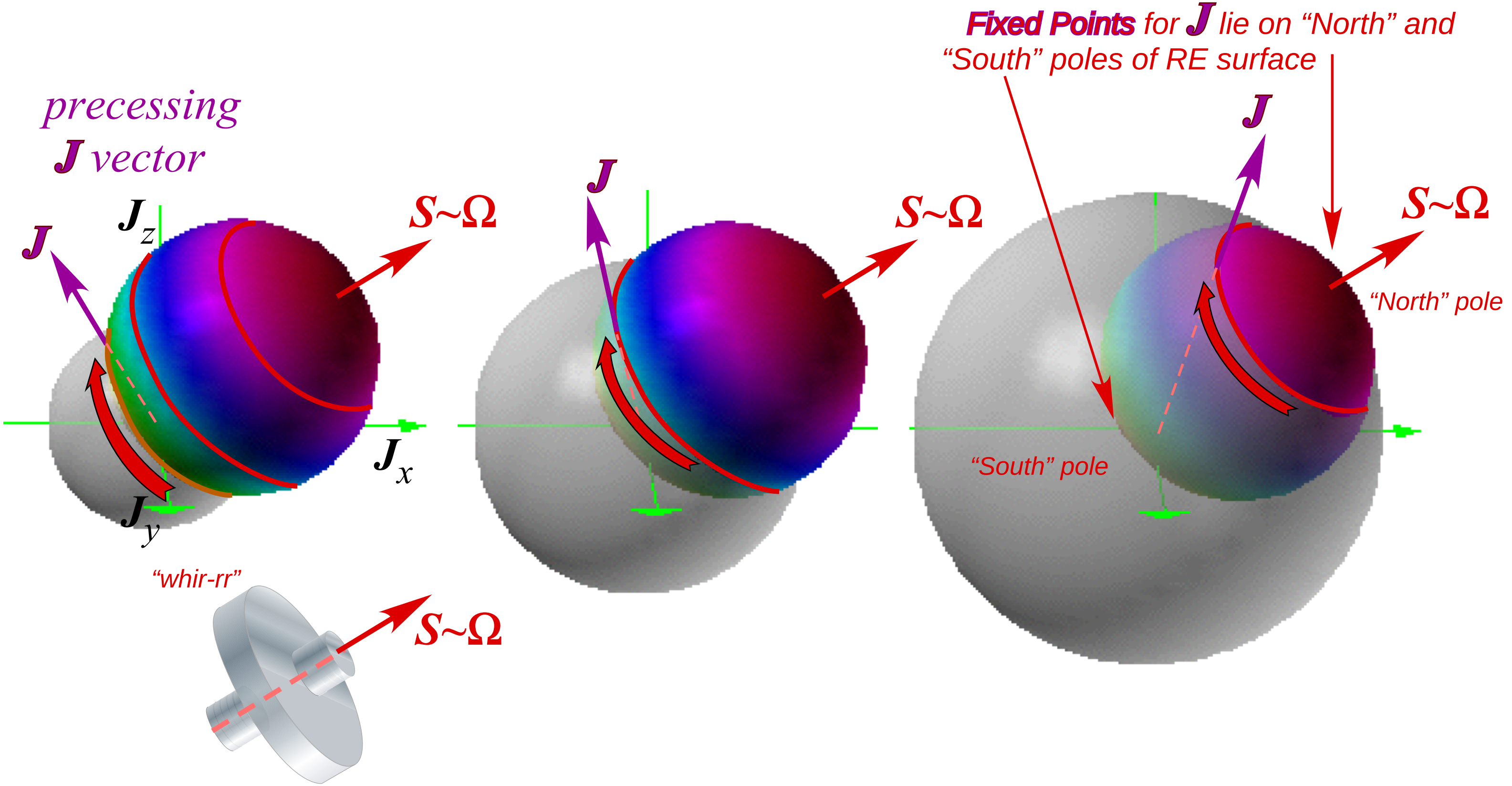
Let: $\boldsymbol{R}=\boldsymbol{J}-\boldsymbol{S}$ *and consider* <u>*non*</u>*-constant terms* *(ignore gyro S terms that are constant)*

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

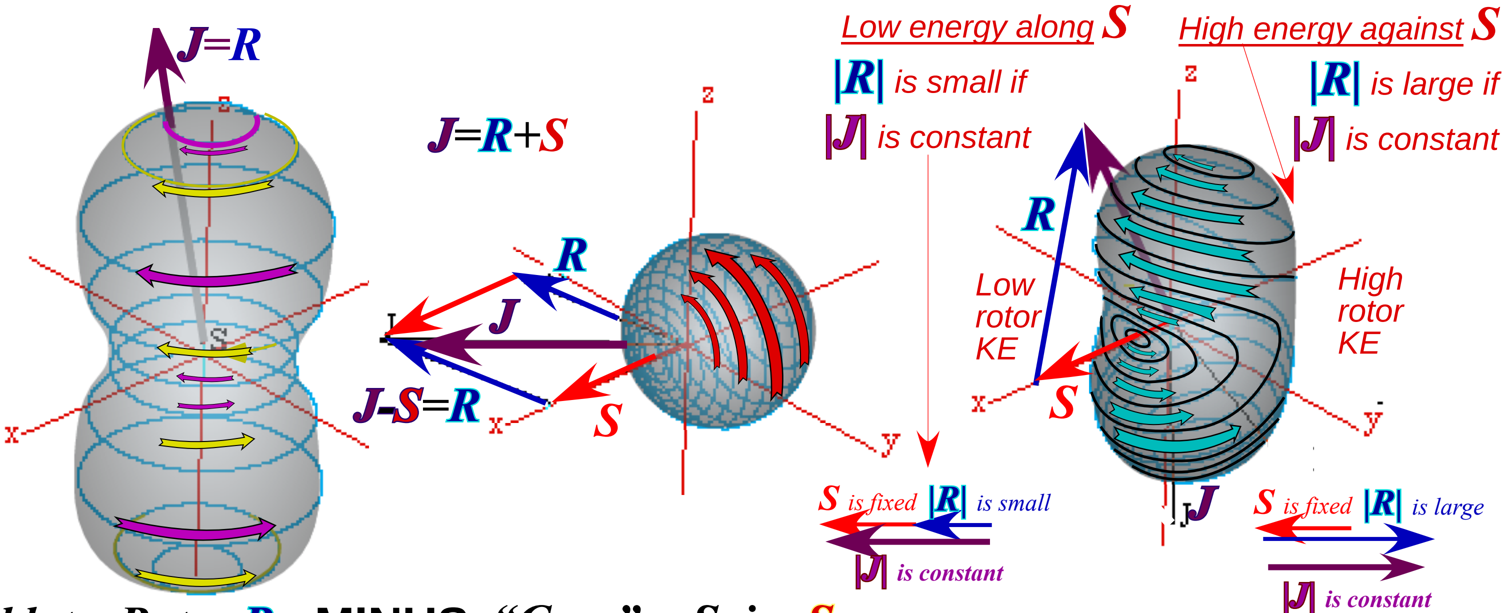
$$H=AJ_x^2+BJ_y^2+CJ_z^2+\ldots-2AJ_xS_x-2BJ_yS_y-2CJ_zS_z+\ldots+(\text{more constant terms})$$

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

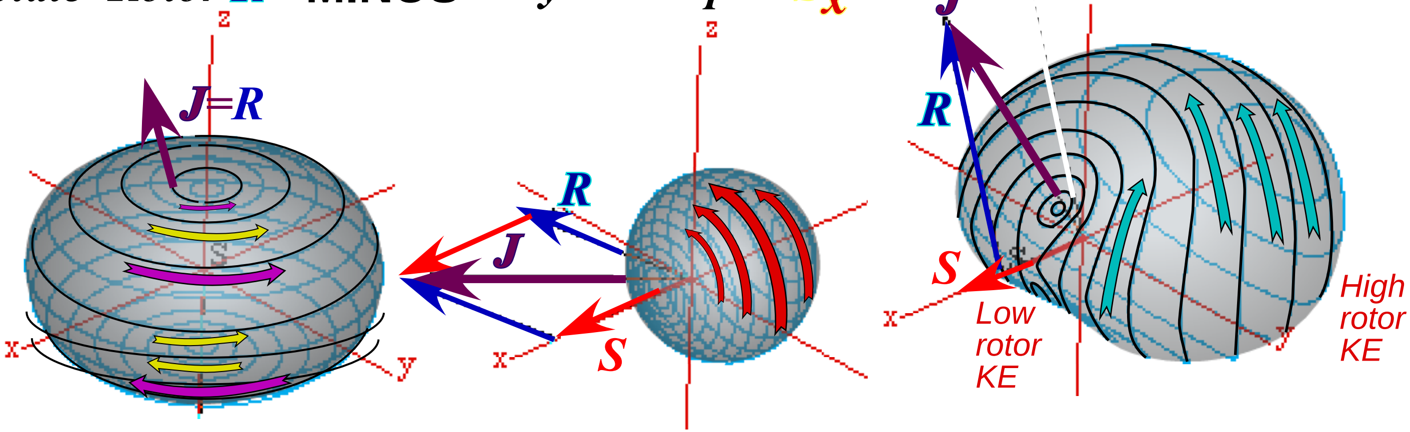
RE Surface for1st-order $\mathbf{J}_m$ *or* $\mathbf{T}^1{}_m$ *term is a sphere displaced in J-direction*
Energy sphere intersections are concentric circular precession paths
All paths precess with the same sense around gyro S-vector



Prolate Rotor ***R*** MINUS *"Gyro" x-Spin* S_x



Oblate Rotor ***R*** MINUS *"Gyro" x-Spin* S_x



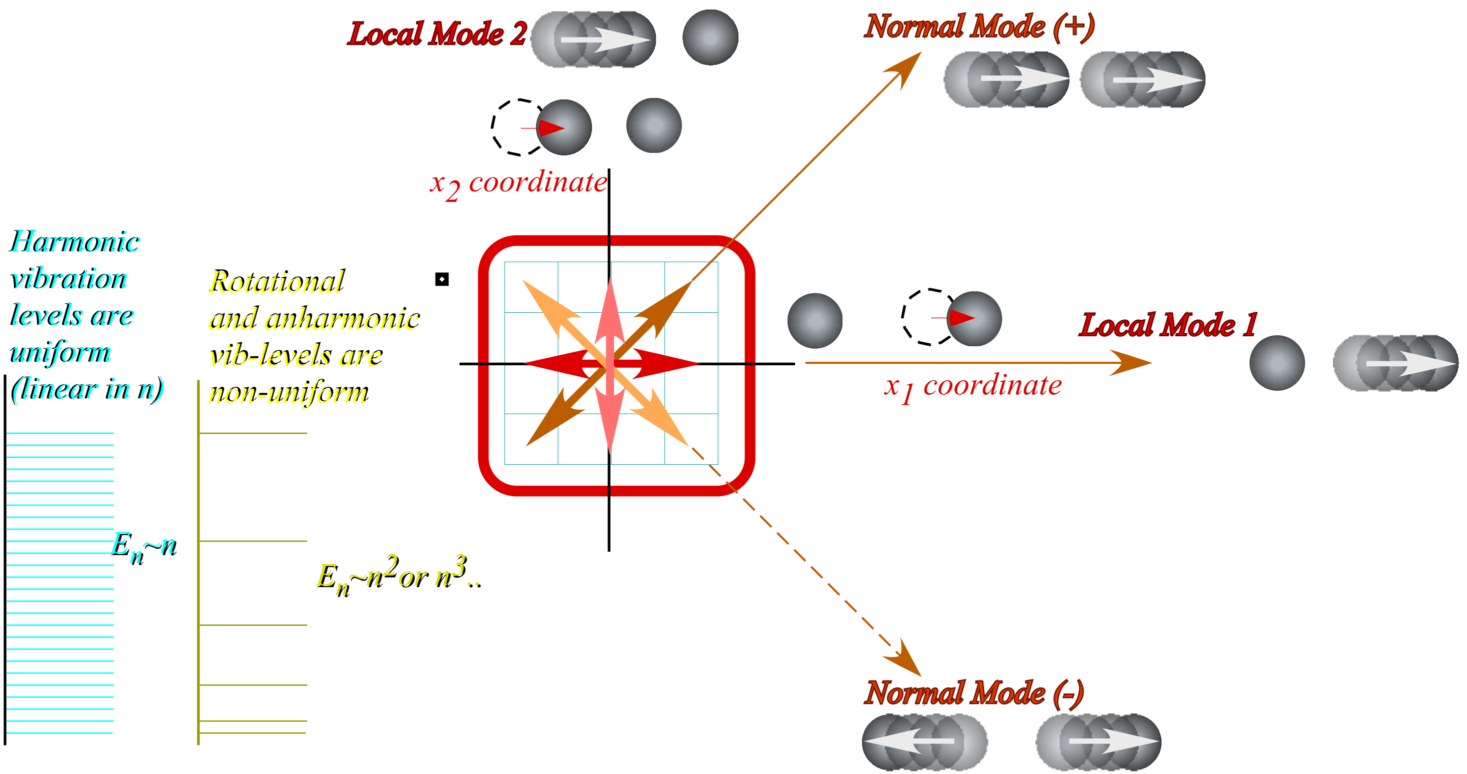
Recall Hamiltonian for 2D vibration has a (quasi-)spin theory, too

$$\mathbf{H} = \omega_0 \mathbf{1} + \Omega\left(\mathbf{a}^\dagger_{(+)}\mathbf{a}_{(+)} - \mathbf{a}^\dagger_{(-)}\mathbf{a}_{(-)}\right)/2 + \ldots + (anharmonic\ \mathbf{a}^\dagger_\mu \mathbf{a}_\nu \mathbf{a}^\dagger_\lambda \mathbf{a}_\kappa\ terms)$$

$$= \omega_0 \mathbf{1} + \Omega\ \mathbf{J}_x \qquad + \ldots + B\mathbf{J}_x^2 + C\mathbf{J}_y^2 + A\mathbf{J}_z^2 \ \ldots + a_{xy}\mathbf{J}_x\mathbf{J}_y +$$

1st-order $\mathbf{J}_m$ *or* $\mathbf{T}^1{}_m$ *term is harmonic part of* **H**

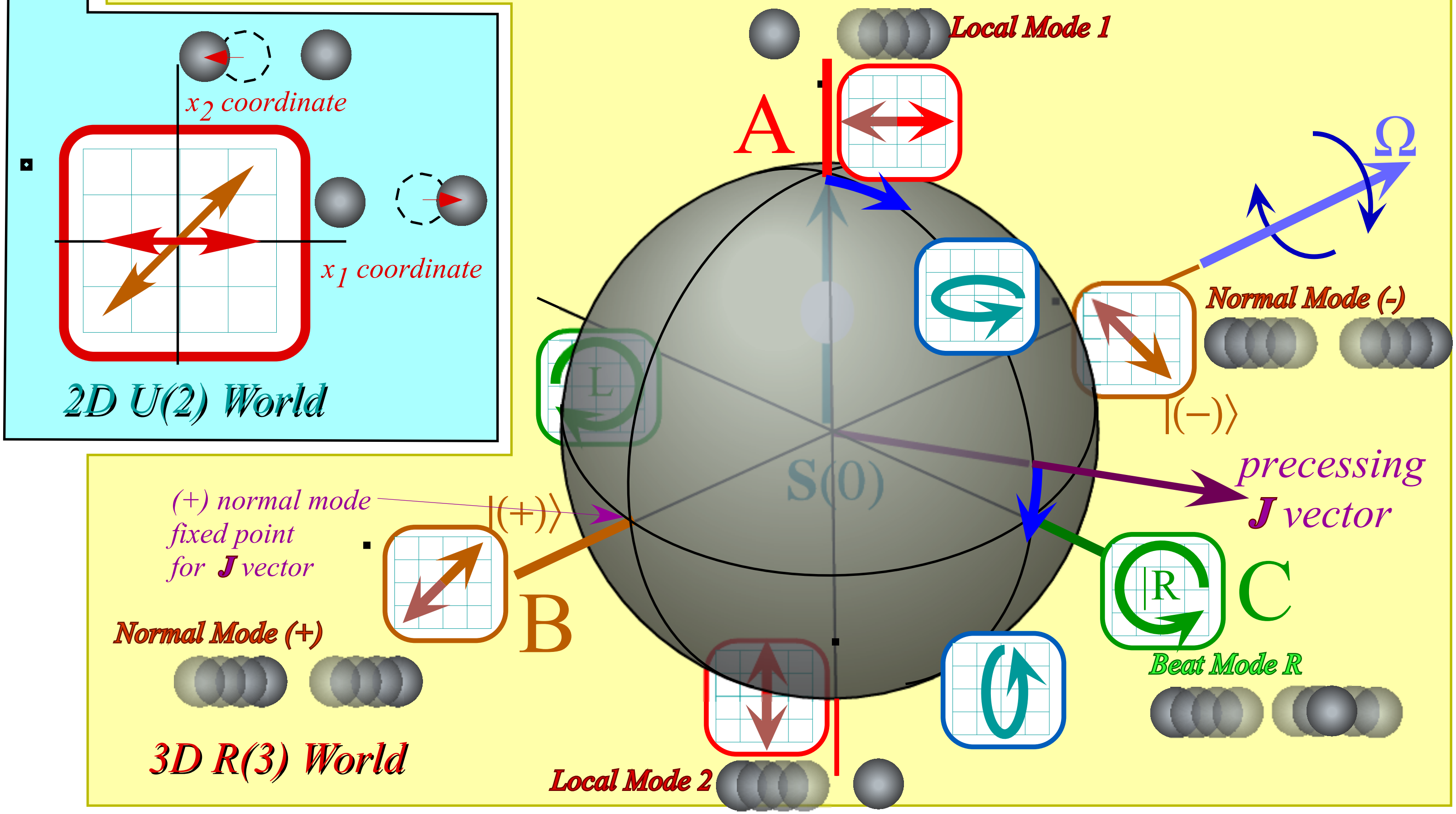
Higher-order $\mathbf{J}_m$ *or* $\mathbf{T}^1{}_m$ *terms are anharmonic parts of* **H**



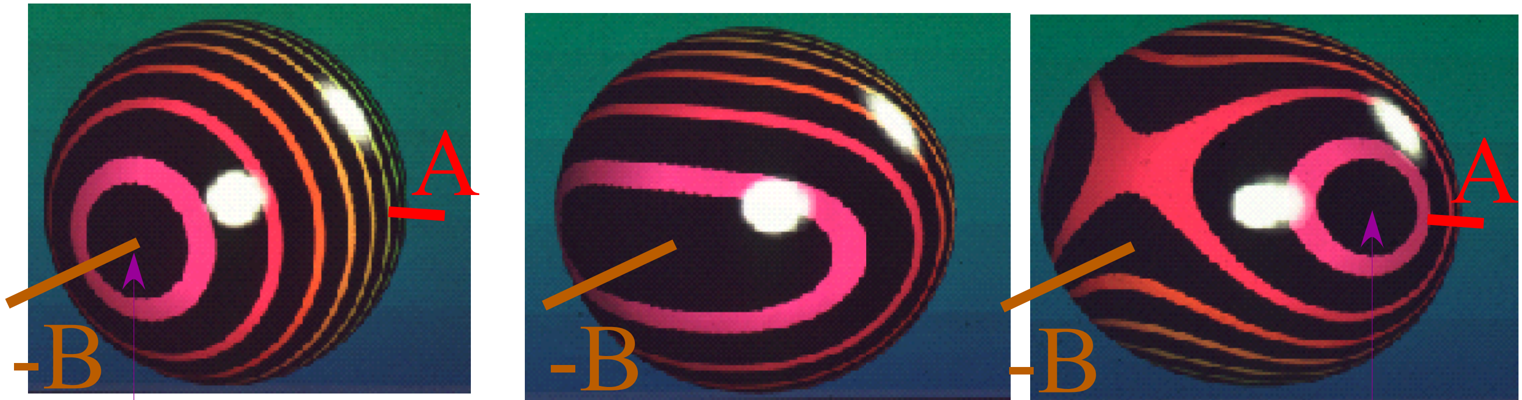
(contd) 2D vibration are related to 3D rotation of "quasi-spin" ***J***

$$\mathbf{H} = \omega_0 \mathbf{1} + \Omega\left(\mathbf{a}^{\dagger}_{(+)}\mathbf{a}_{(+)} - \mathbf{a}^{\dagger}_{(-)}\mathbf{a}_{(-)}\right)/2 + \ldots + (anharmonic\ \mathbf{a}_{\mu}^{\dagger}\mathbf{a}_{\nu}\mathbf{a}_{\lambda}^{\dagger}\mathbf{a}_{\kappa}\ terms)$$

$$\mathbf{H} = \omega_0 \mathbf{1} + \Omega\ \mathbf{J}_x + \ldots + B\mathbf{J}_x^2 + C\mathbf{J}_y^2 + A\mathbf{J}_z^2 \ldots + a_{xy}\mathbf{J}_x\mathbf{J}_y +$$

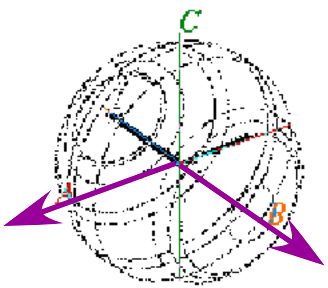


For higher J values, anharmonic terms grow to make stable local modes



*(+) normal mode fixed point for **J** vector*

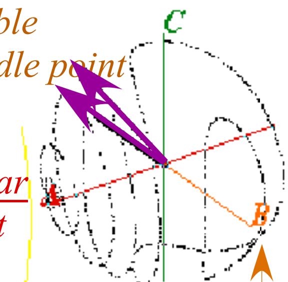
*(1) local mode fixed point for **J** vector*



±B-*axes are* ***J****-fixed points*

A-*axis is* *NOT* ***J****-fixed point*

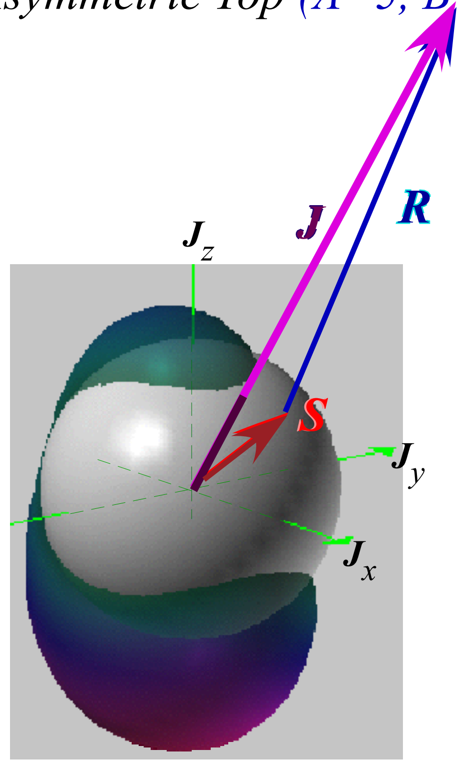
-B-*axis near unstable* ***J****-saddle point*



A-*axis is near* ***J****-fixed point*

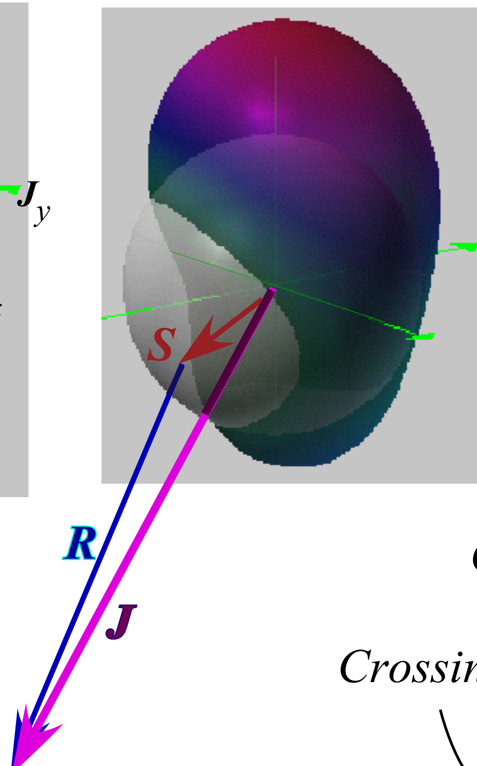
+B-*axis near stable* ***J****-fixed point*

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

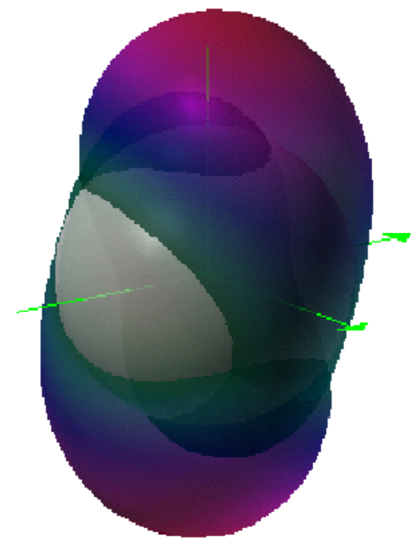


"Sherman" (The shark)
First appeared in a
1992 JCP article by
Hougan, Kleiner, and Ortigoso

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



The two together



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

(Pre) Conclusion
Rotational Energy (RE) surfaces: Past & Future

Two or more RE's beg for an interaction.
Here it's the coupling we "turned off" into a constraint.

$$\langle \mathbf{H} \rangle = \begin{pmatrix} \textit{Spin-up} \quad RE(\beta,\gamma) & \textit{Coupling}(\beta,\gamma) \\ \textit{Coupling}(\beta,\gamma)^{*} & \textit{Spin-down} \quad RE(\beta,\gamma) \end{pmatrix}$$

Base RE surfaces are eigensolutions of this matrix.
Combination RES depends on eigenvector chosen.

This opens worlds of interesting mechanics. (Both QM and CM)
Two (or more) surfaces imply an infinity of surfaces "between" them.

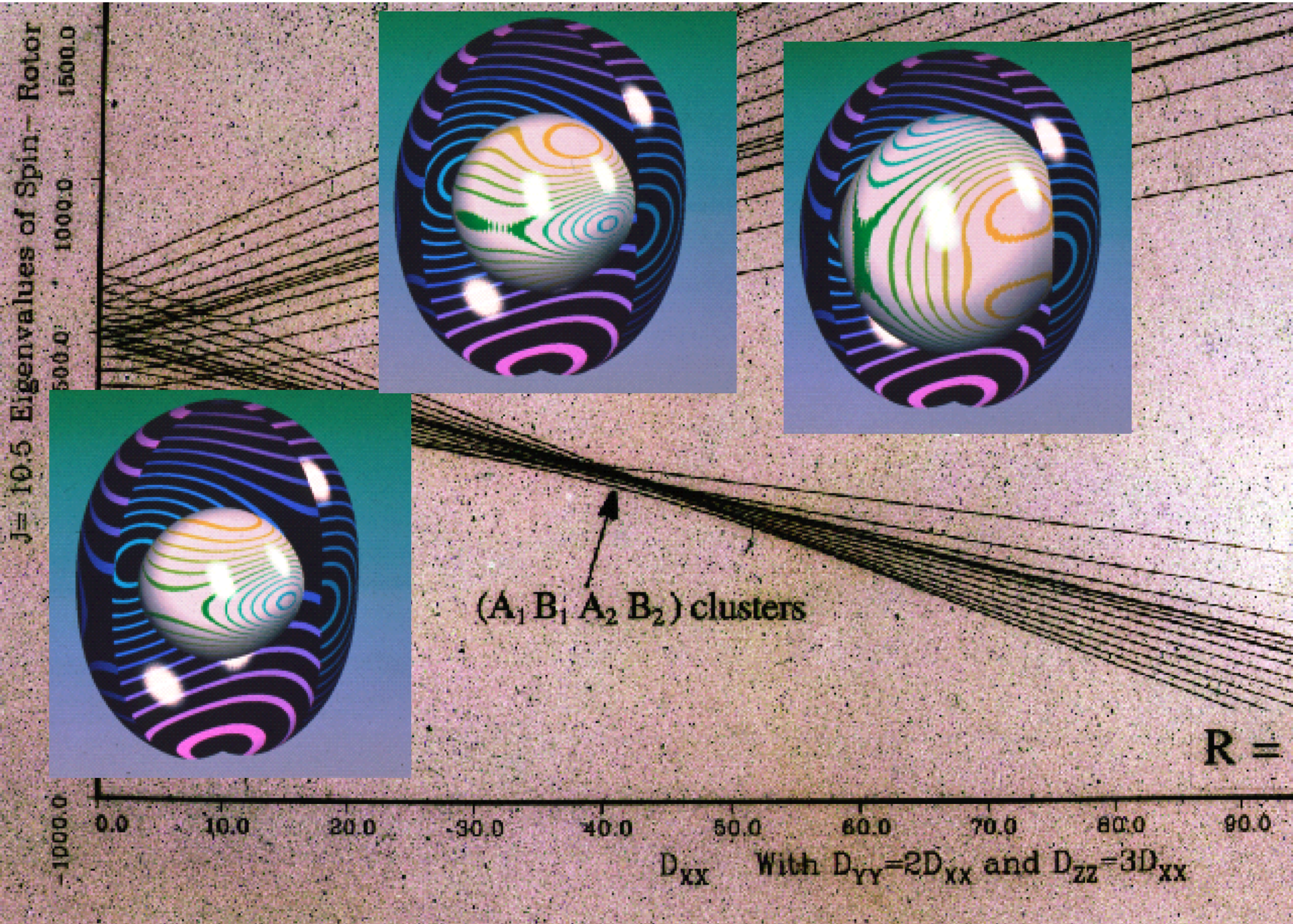
Intermediate surfaces not unique for each energy
("Tide" rises and falls, saddles open and close. Result: Chaotic trajectory)

(Recall that Born told Otto Stern that his spin experiment wouldn't show quantization.)

(Final) Conclusion
Rotational Energy (RE) surfaces help analyze rotor dynamics as do Potential Energy (PE) surfaces for vibration.

PE surfaces based on vibrational coordinates.
RE surfaces based on rovibrational phase space.
Can approximate quantum levels and spectra and also mixing and transitions.
RES have a variety of complementary surfaces:
Angular Velocity surfaces: (AVS) $\boldsymbol{\omega}\cdot\mathbf{I}\cdot\boldsymbol{\omega}=2E$ *(Poinsot ellipsoid)*
Angular Momentum surfaces: (AMS) $\mathbf{J}\cdot\mathbf{I}^{-1}\cdot\mathbf{J}=2E$ *(Landau ellipsoid)*

PE surfaces used since beginning of QM (Born 1926)
RE surfaces first used in 1976.



J= 10.5 Eigenvalues of Spin- Rotor
1500.0
1000.0
500.0
-1000.0
(A_1 B_1 A_2 B_2) clusters
R =
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}