Dynamics of localized angular momentum and multi-surface rotational energy anisotropy: internal-rotor molecules and spin symmetry conversion effects

William G. Harter and Justin C. Mitchell
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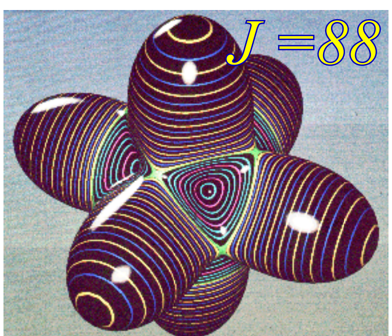
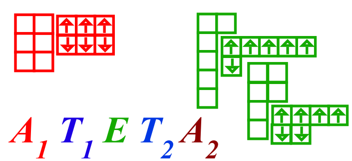
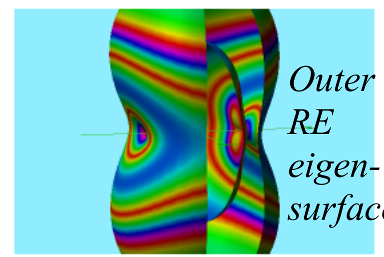
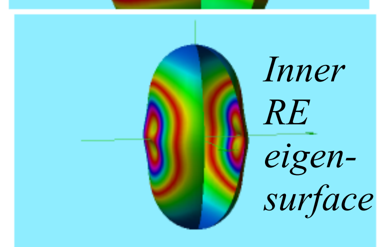








CONSERVATION OF ROVIBRONIC SPECIES - Two Views:

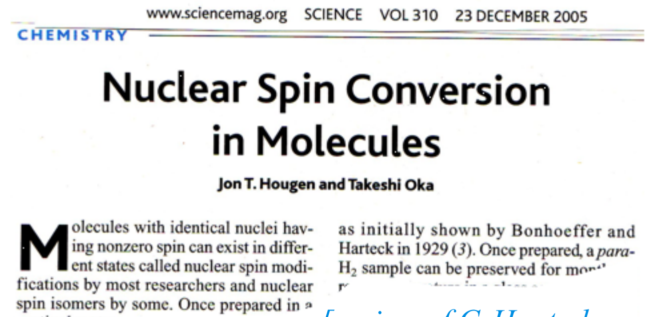
Old *versus* ***New (1978- 2005)***

(1939, 1945, and 1966)

"...transitions between...species (A_1,..E,..T_2..)
...are **very strictly forbidden**..."

...for diatomic molecules...I p. 150
...for D_2 asymmetric tops...II p.468
...for D_n symmetric tops...II p.415
...for O-T_d spherical tops...II p.441-453

...during transitions involving...
...rotational states,...III p.246
...vibrational states,... " "
... electronic states,... " "
... collisional states... " "


www.sciencemag.org SCIENCE VOL 310 23 DECEMBER 2005

CHEMISTRY

Nuclear Spin Conversion in Molecules

Jon T. Hougen and Takeshi Oka

Molecules with identical nuclei having nonzero spin can exist in different states called nuclear spin modifications by most researchers and nuclear spin isomers by some. Once prepared in a ... as initially shown by Bonhoeffer and Harteck in 1929 (3). Once prepared, a *para*-H_2 sample can be preserved for mon...

[review of C_2H_4 study: Sun, Takagi, Matsushima, Science ***310****, 1938(2005)]*

Strictly *versus* **NOT!**

Conservation and preservation?

No Way! *versus* **WAY!**

Conversion, perversion or transition?

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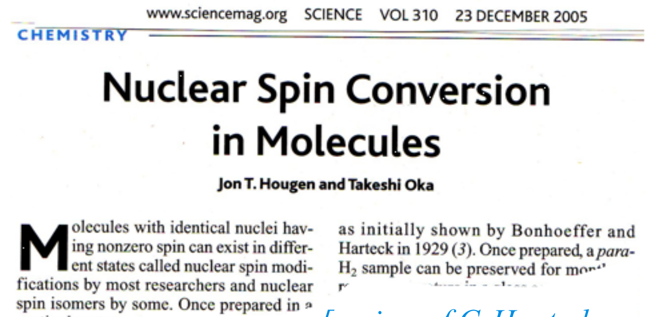

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Conservation and preservation?

To conserve vs. To convert

To preserve vs. To pervert

No Way! *versus* **WAY!**

Conversion, perversion or transition?

Widespread and extreme mixing of species (perversion)
reported in CF4, SiF_4 and SF_6 :

Ch. Borde, Phys. Rev. ***A20****,254(1978)(expt.)*
Harter, Phys. Rev. ***A24****,192 (1981)(theory)*

HOW CONSERVED IS ROVIBRONIC-SPIN SYMMETRY?

What preserves it? *versus* ***What mixes it up?***

No Way!

WAY!

and...

What is it?

SPIN SYMMETRY correlation has a new name...

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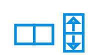
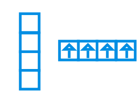
and...

What is it?

SPIN SYMMETRY correlation has a new name...

it's now called ENTANGLEMENT!





Herzberg's terms:
"..Overall ...symmetry..."

Better terms:
..Under-all ... or internal symmetry...spin frame..... "Bare" rotor

(From an overall "Coupled" state we SUBTRACT *vibronic "Activity" to get underlying "Bare" rotor.)*

HOW CONSERVED IS ROVIBRONIC-SPIN SYMMETRY?

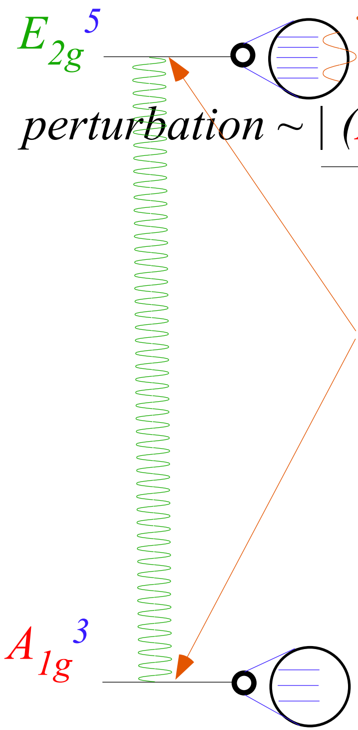
What preserves it? *versus* ***What messes it up?***

$A_{2u}{}^{1}$

No Way!

...because nuclear moments...
...are so very slight..."

...too darn small (~kHz)...



$$perturbation \sim \frac{|\,(A_{1g}{}^{3}|\text{spin-rovib.}|E_{2g}{}^{5})\,|^{2}}{E_{A_{1g}{}^{3}} - E_{E_{2g}{}^{5}}}$$

...too darn big (*like* 10MHz)...

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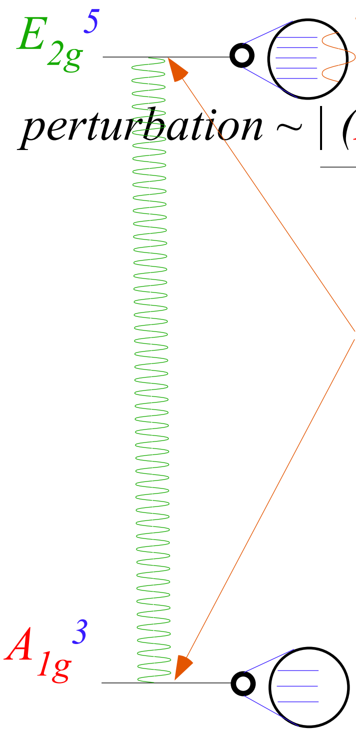

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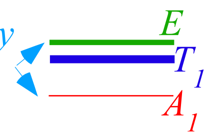
$$perturbation \sim \frac{|\,(A_{1g}{}^{3}|spin\text{-}rovib.|E_{2g}{}^{5})\,|^{2}}{E_{A_{1g}{}^{3}} - E_{E_{2g}{}^{5}}}$$

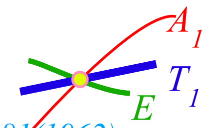
...too darn <u>big</u> (*like*10MHz)...

...exponentially tiny! (like 10^{-50}Hz)



WAY!

...because levels of different species are forced together by angular wave localization or "level-clustering" or (rarely) by "accidental" degeneracy.



<u>"Accidental" degeneracy</u>

Lea, Leask & Wolf JPCSol.23,1381(1962)

<u>Level-clustering</u>

Dorney and Watson JMS 42,135(1972)

Harter and Patterson PRL38,224(1977)

JCP 66,4872(1977)

<u>RE Surface precession vs. tunneling</u>

Harter and Patterson JMP 20,1453(1979)

JCP 80,4241(1984)

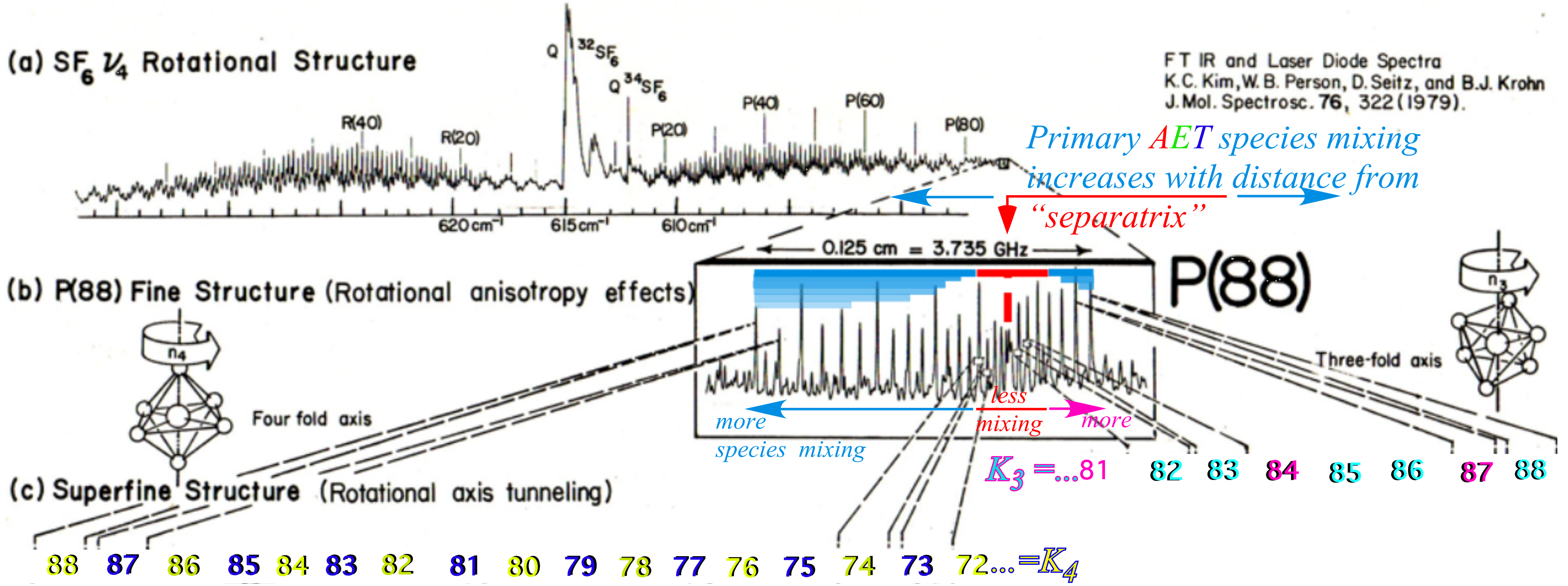
<u>RE Superhyperfine transitions</u>

Hyperfine effects may rule! A_1 T_1 E T_2 A_2 *get <u>seriously</u> mixed up.*

Harter,Patterson,and daPaixao, Rev.Mod.Phys. 50, 37(1978)

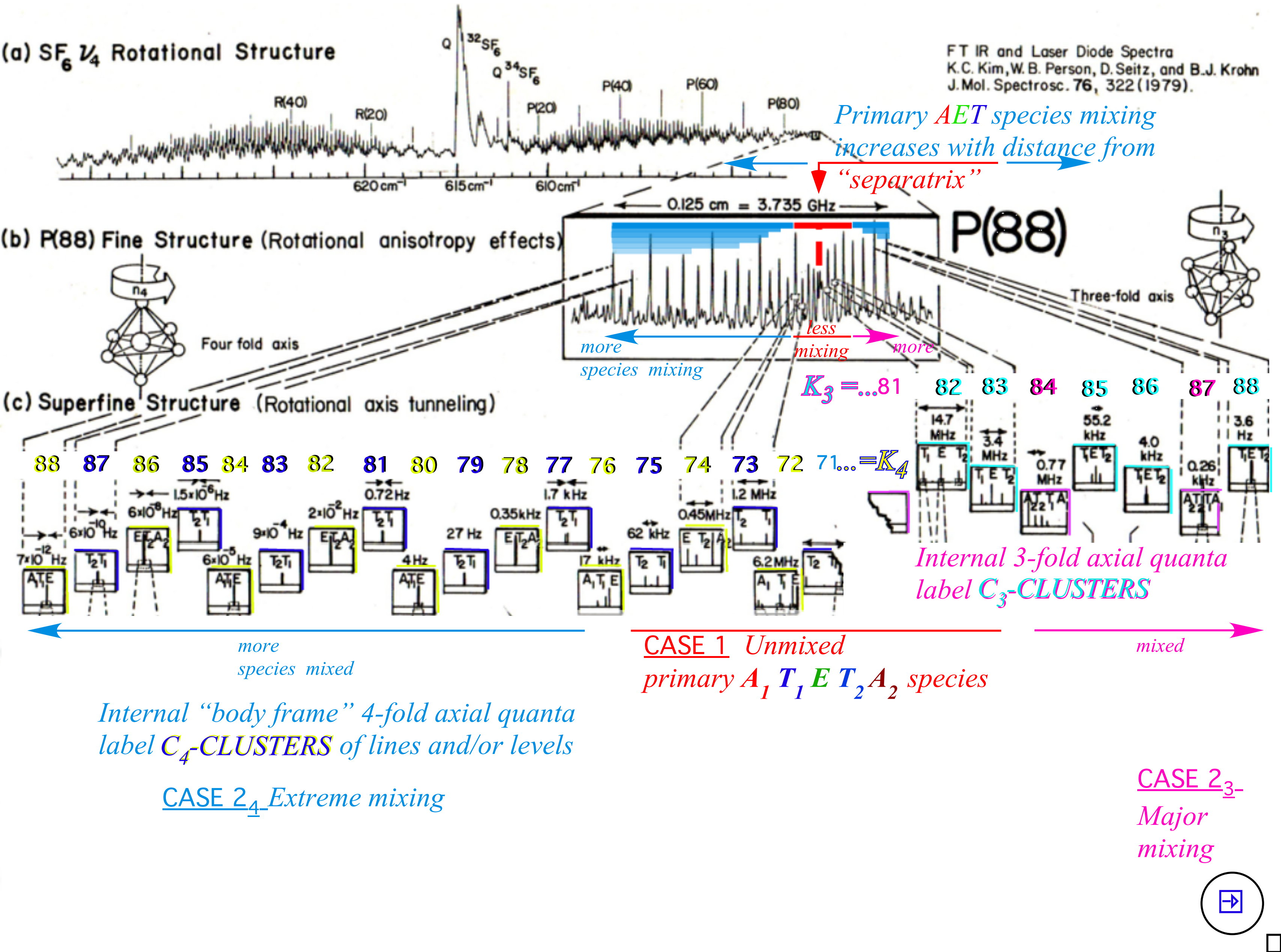
Harter and Patterson, Phys. Rev. A19,2277(1979) (CF_4)

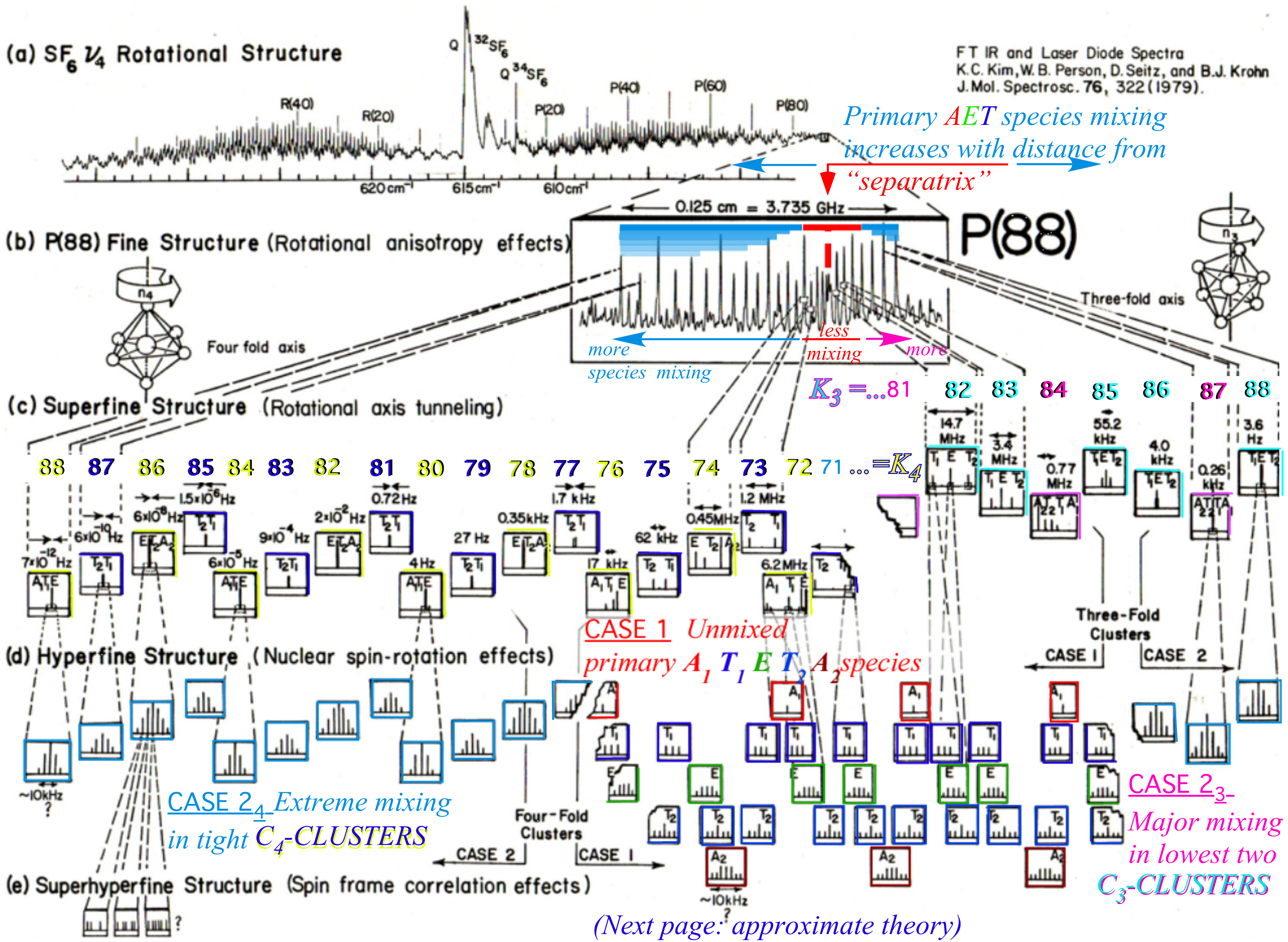
Harter, Phys. Rev. A24,192-262(1981) (SF_6)



Internal 3-fold axial quanta label C_3-CLUSTERS

Internal "body frame" 4-fold axial quanta label C_4-CLUSTERS of lines and/or levels


(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).
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
Primary AET species mixing increases with distance from "separatrix"
(b) P(88) Fine Structure (Rotational anisotropy effects)
0.125 cm = 3.735 GHz
P(88)
Four fold axis
Three-fold axis
more species mixing
less mixing
more
(c) Superfine Structure (Rotational axis tunneling)
K3 = ...81 82 83 84 85 86 87 88
14.7 MHz
3.4 MHz
0.77 MHz
55.2 kHz
4.0 kHz
0.26 kHz
3.6 Hz
88 87 86 85 84 83 82 81 80 79 78 77 76 75 74 73 72 71... = K4
7×10-12 Hz
6×10-10 Hz
6×10-8 Hz
1.5×10-6 Hz
6×10-5 Hz
9×10-4 Hz
2×10-2 Hz
0.72 Hz
4 Hz
27 Hz
0.35 kHz
1.7 kHz
17 kHz
62 kHz
0.45 MHz
1.2 MHz
6.2 MHz
Internal 3-fold axial quanta label C3-CLUSTERS
more species mixed
CASE 1 Unmixed primary A1 T1 E T2 A2 species
mixed
Internal "body frame" 4-fold axial quanta label C4-CLUSTERS of lines and/or levels
CASE 24 Extreme mixing
CASE 23 - Major mixing



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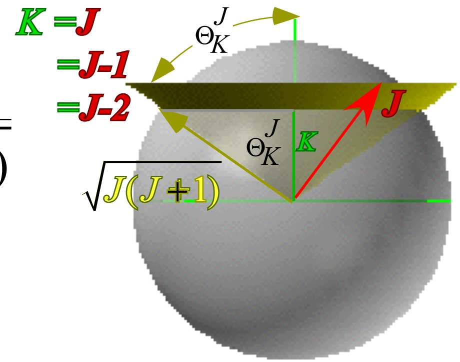
K3 =...81 82 83 84 85 86 87 88
88 87 86 85 84 83 82 81 80 79 78 77 76 75 74 73 72 71 ...=K4
Three-Fold Clusters
CASE 1 CASE 2
CASE 1 Unmixed primary A1 T1 E T2 A2 species
(d) Hyperfine Structure (Nuclear spin-rotation effects)
CASE 24 Extreme mixing in tight C4-CLUSTERS
Four-Fold Clusters
CASE 2 CASE 1
CASE 23 Major mixing in lowest two C3-CLUSTERS
(e) Superhyperfine Structure (Spin frame correlation effects)
(Next page: approximate theory)

Finding Hamiltonian Eigensolutions by Geometry using Uncertainty Cone Angles

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

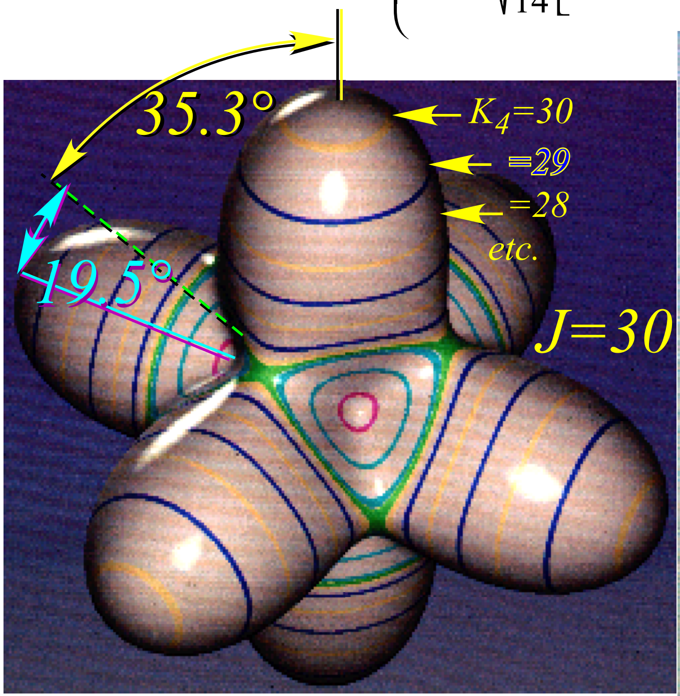


***J** cone intersects J=88 RE surface to give approx. K=J, J-1, J-2... energy levels*

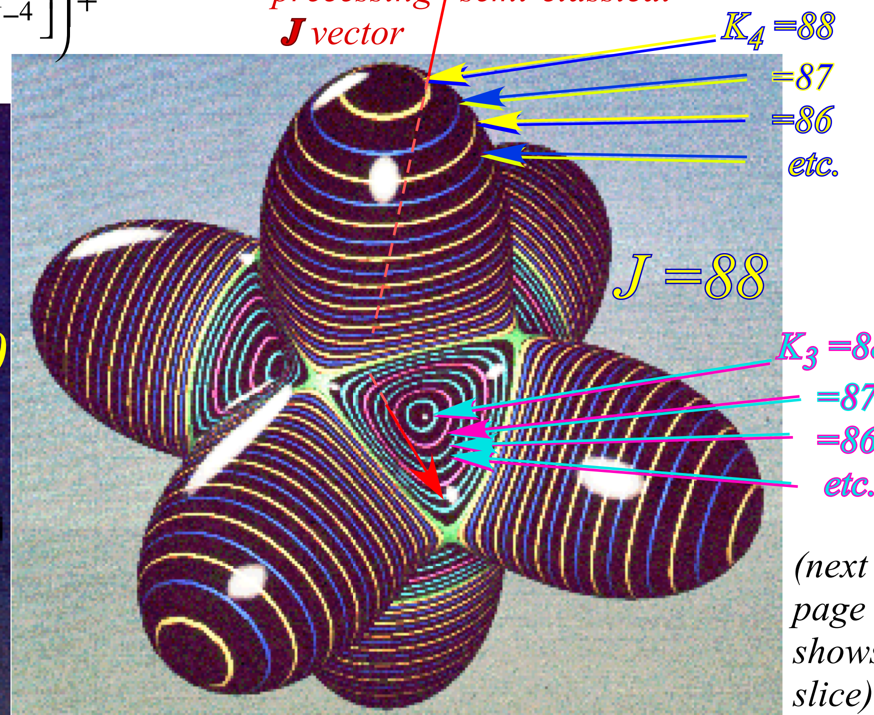
O_h or T_d Spherical Top: *(Hecht Ro-vib Hamiltonian 1960)*

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

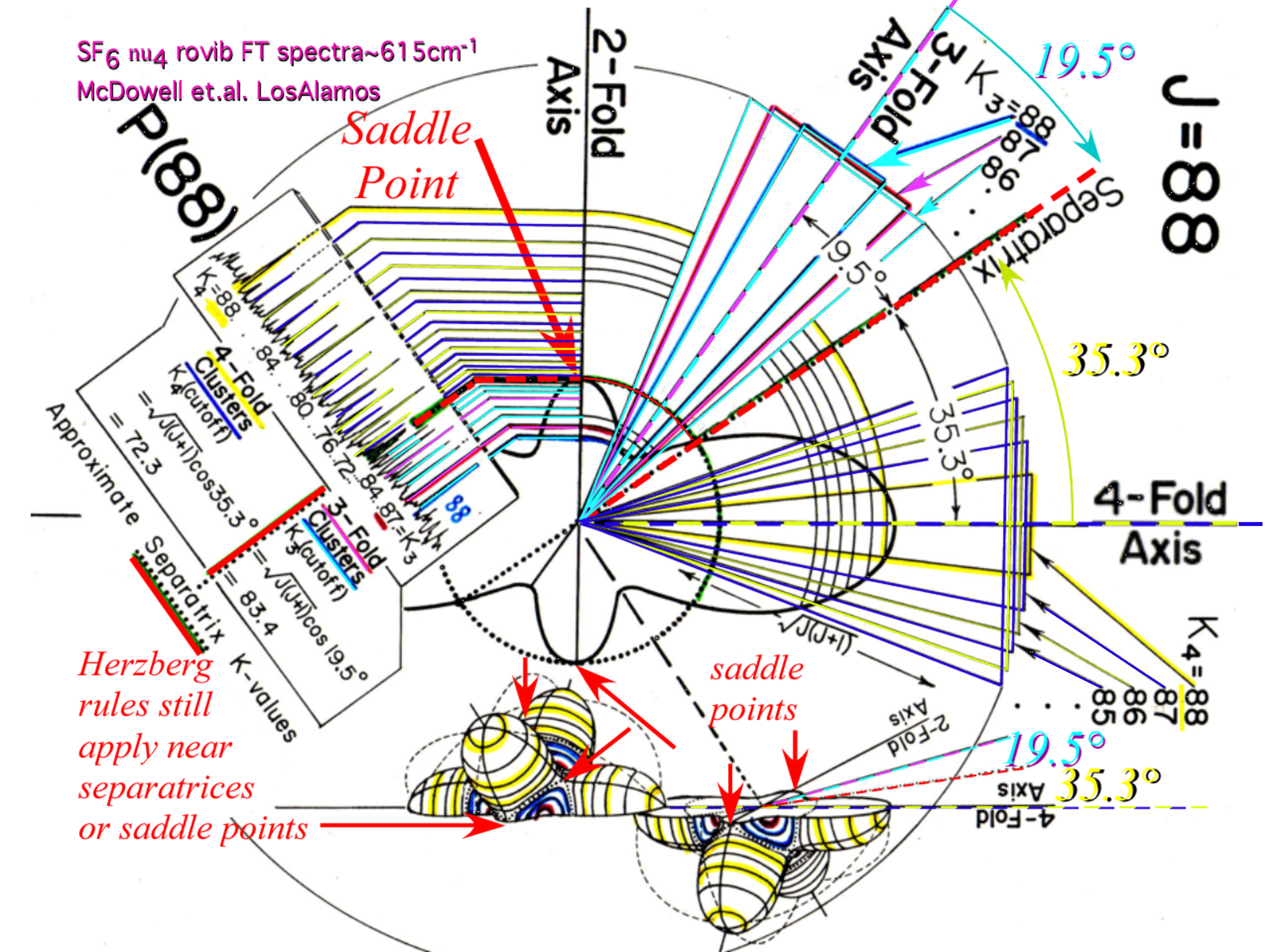
$$= \quad B\mathbf{J}^2 \quad + t_{440}\left(\mathbf{T}_0^4 + \sqrt{\frac{5}{14}}\left[\mathbf{T}_4^4 + \mathbf{T}_{-4}^4\right]\right) + \cdots$$



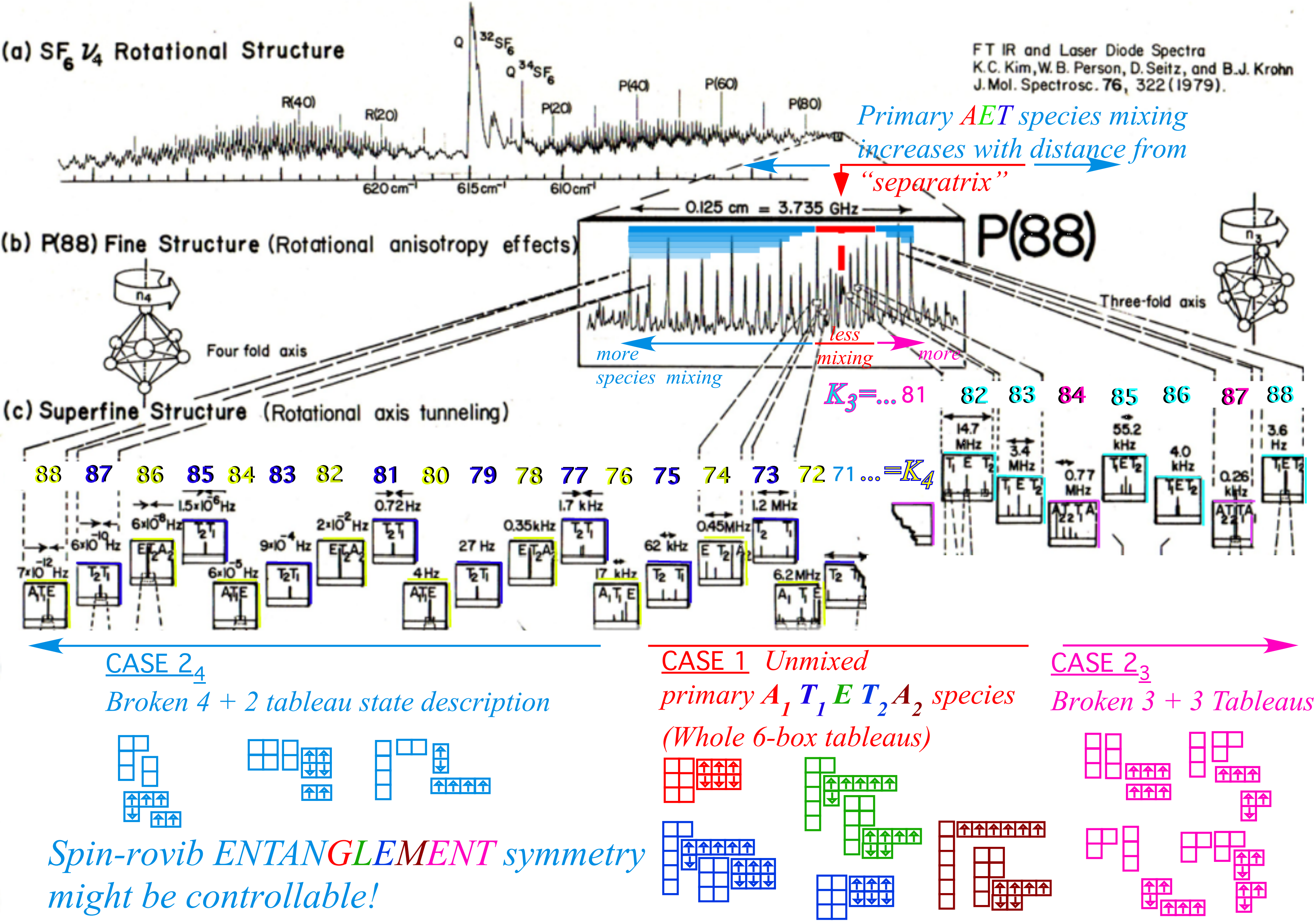
*RE Surface topo-lines track precessing semi-classical **J** vector*



(next page shows slice)



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
K3=88
87
86
Separatrix
35.3°
4-Fold Axis
K4=88
87
86
85
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)
Herzberg rules still apply near separatrices or saddle points
saddle points
2-Fold Axis
4-Fold Axis



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4 Hz
27 Hz
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1.7 kHz
17 kHz
62 kHz
0.45 MHz
1.2 MHz
6.2 MHz
CASE 24
Broken 4 + 2 tableau state description
CASE 1 Unmixed
primary A1 T1 E T2 A2 species
(Whole 6-box tableaus)
CASE 23
Broken 3 + 3 Tableaus
Spin-rovib ENTANGLEMENT symmetry
might be controllable!

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, ...)

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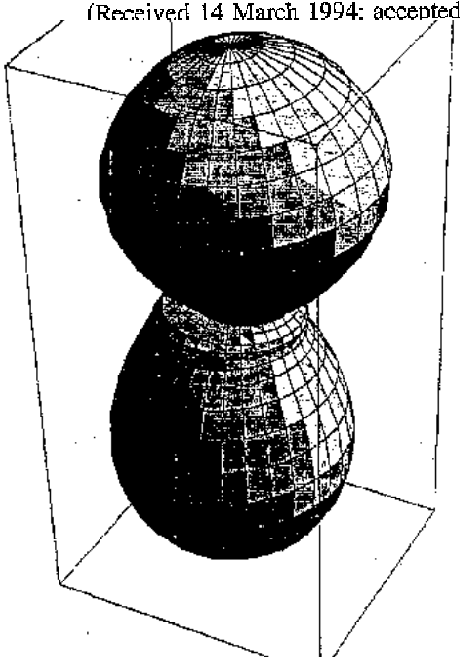
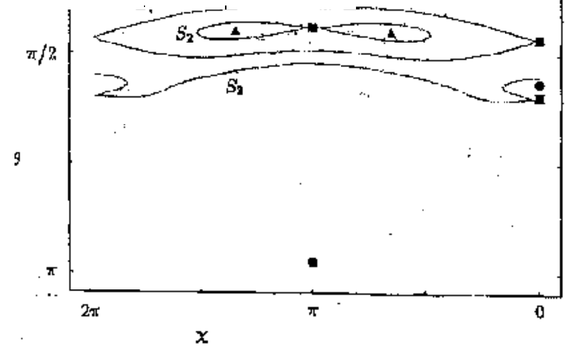
J. Chem. Phys. 101, 2710 (1994)

Rotational energy surfaces of molecules exhibiting internal rotation

Juan Ortigoso[a] and Jon T. Hougen
Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

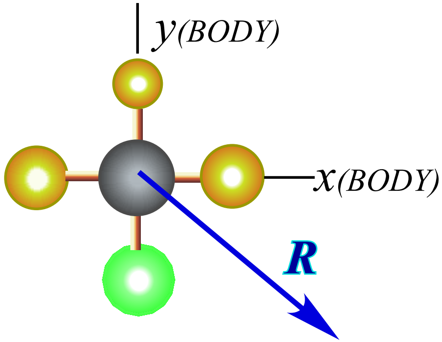
(Received 14 March 1994; accepted 28 April 1994)

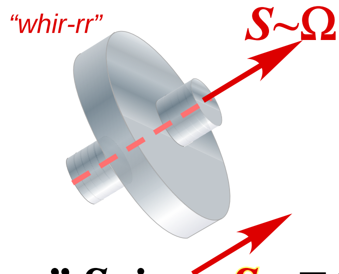


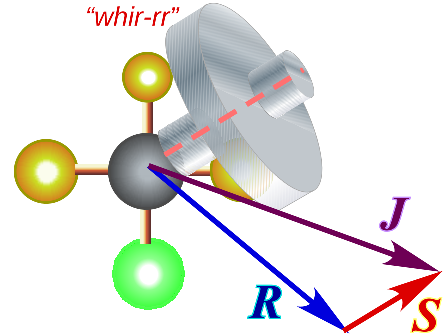


One of the first Applications of
Multiple RES introduced in Comp.Phys.Rpt. 8,319(1988)

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*** $\boldsymbol{J=R+S}$

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

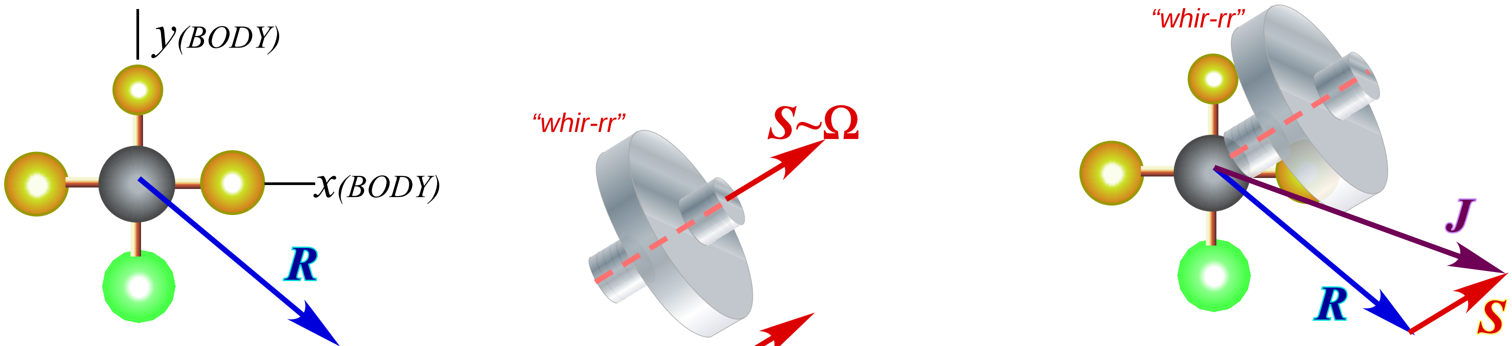
In general, this term is the difficult part...

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

Zero-Interaction Potential 'Proximation (ZIPP)

...but suppose it's zero!

Constraints do no work.



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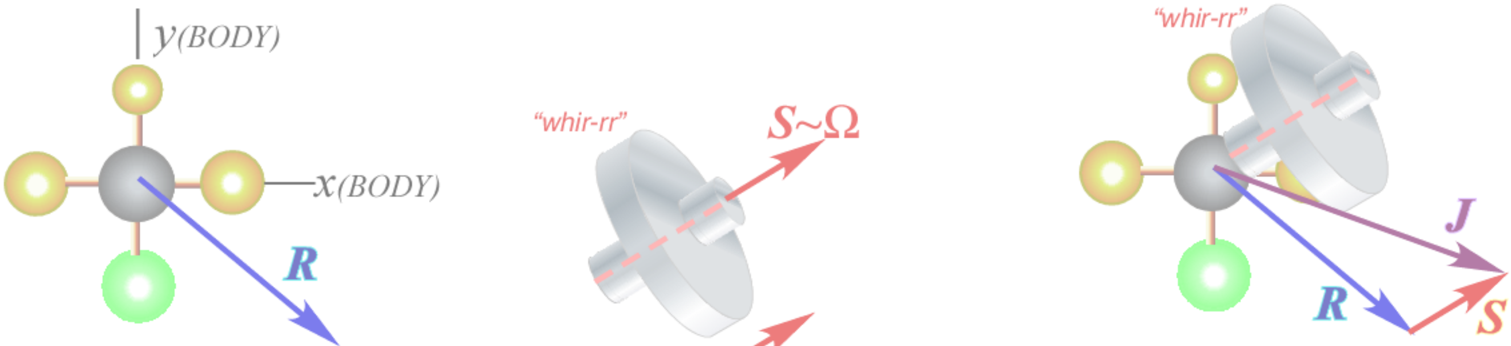
Zero-Interaction Potential 'Proximation (ZIPP)

(ZIPPed)

Let: $R = J - S$ *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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(ZIPPed)

(ignore gyro S terms that are constant)

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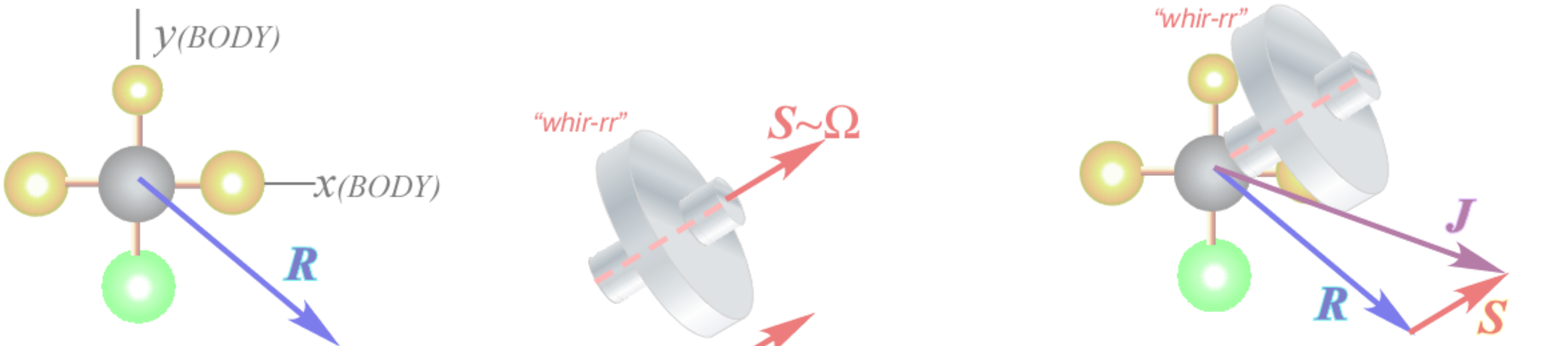
$$H = AJ_x^2 + BJ_y^2 + CJ_z^2 + \ldots - 2AJ_xS_x - 2BJ_yS_y - 2CJ_zS_z + \ldots + (\text{more constant terms})$$

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



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

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

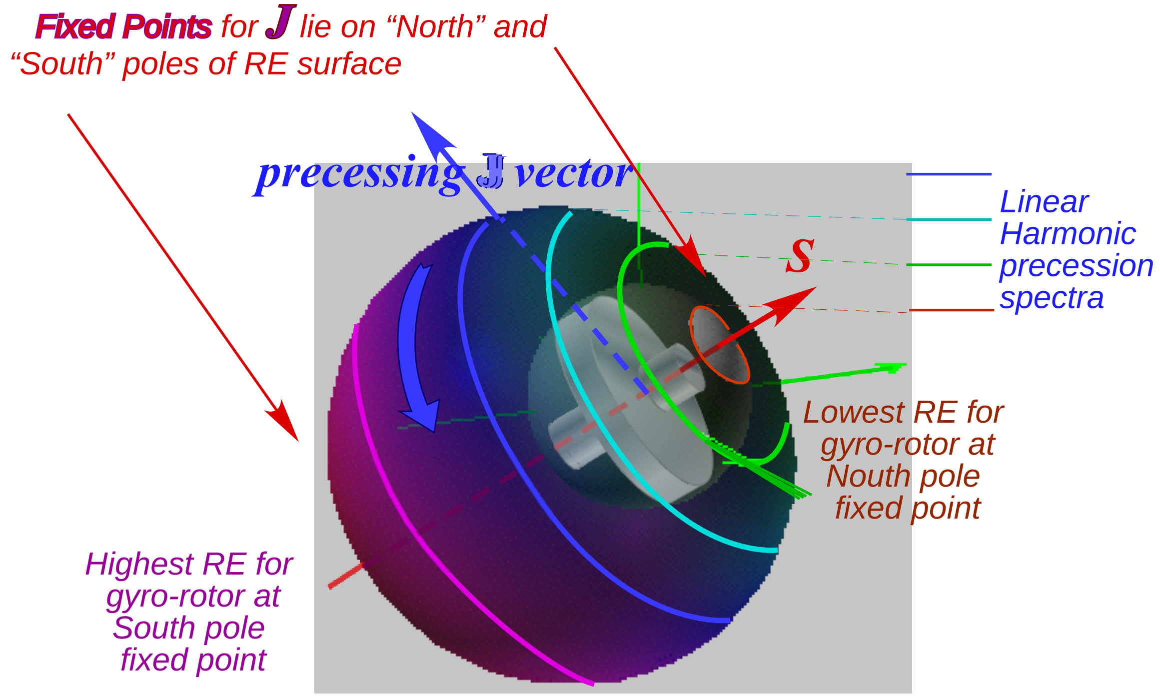
$B\boldsymbol{R}^2$ *to* $B(\boldsymbol{J}-\boldsymbol{S})^2$ *is analogous to* $\boldsymbol{p}^2/2M$ *to* $(\boldsymbol{p}-e\boldsymbol{A})^2/2M$ *gauge-transformation*

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

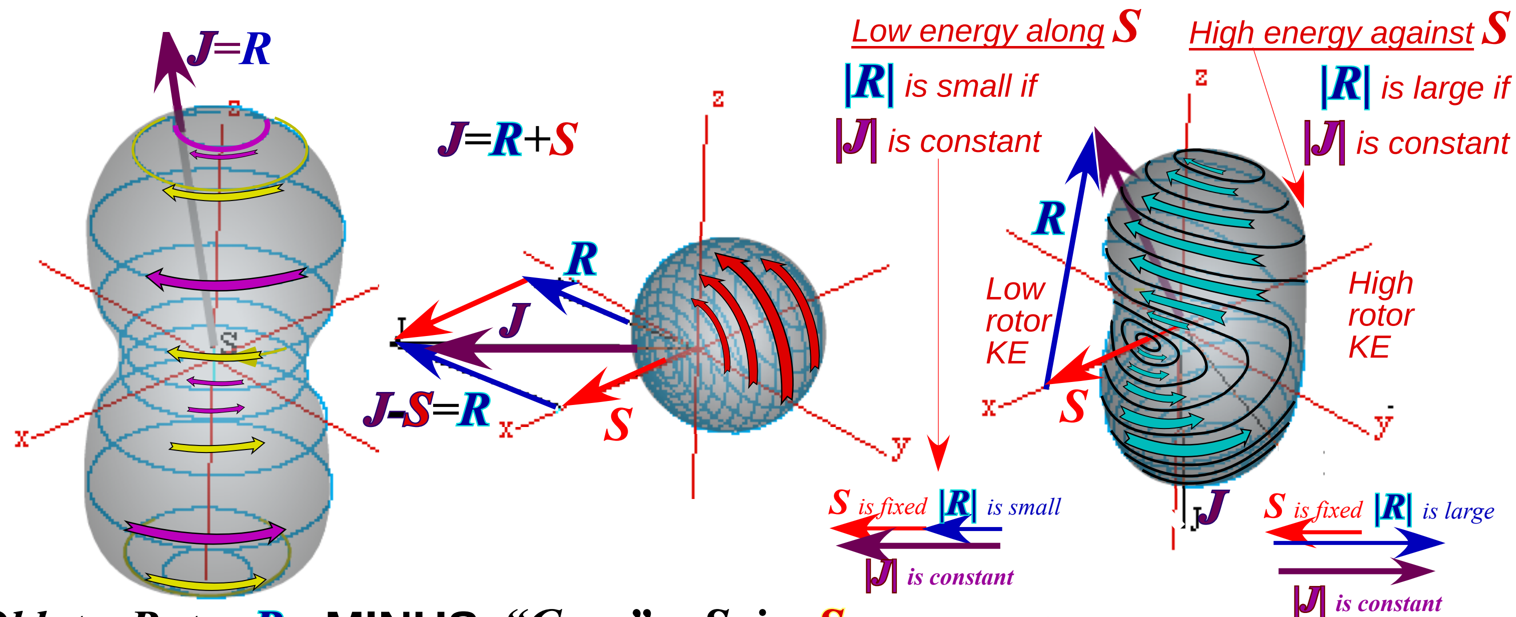
RE Surface for1st-order $\mathbf{J}_m$ *or* $\mathbf{T}^{1}{}_m$ *term is a cardioid displaced in J-direction*

Energy sphere intersections are concentric circular precession paths

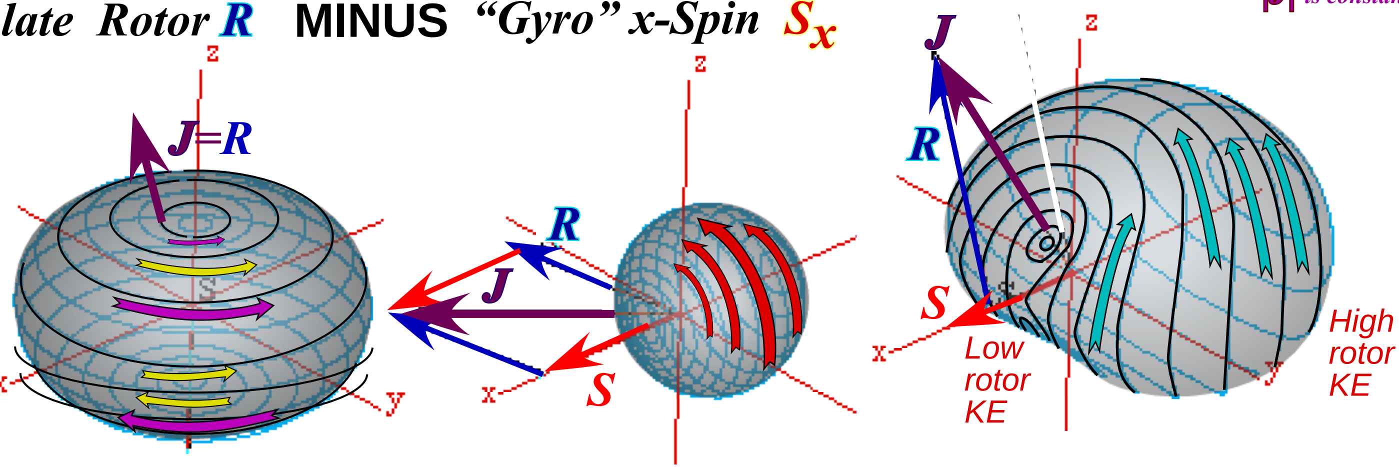
All paths precess with the same sense around gyro S-vector

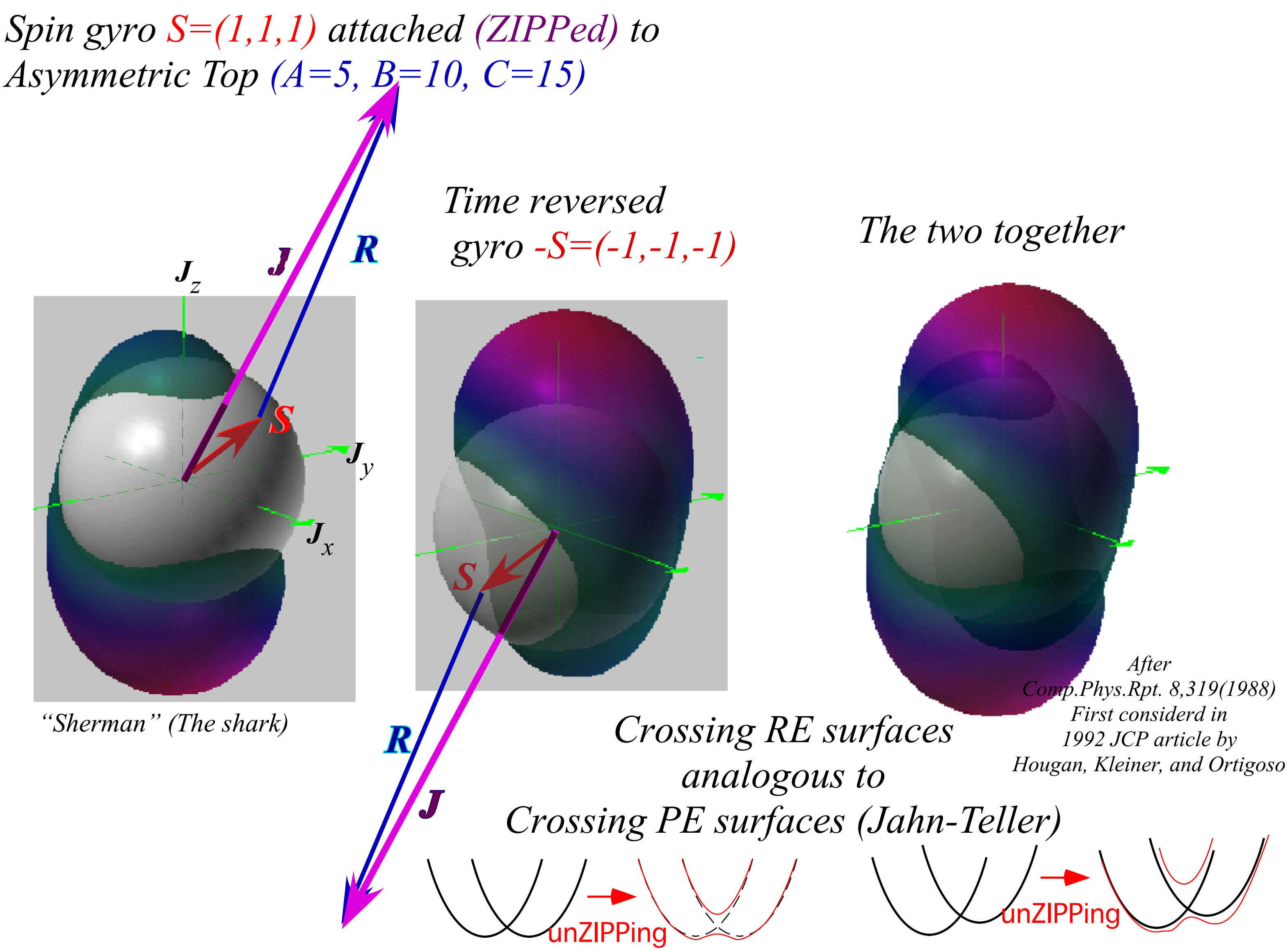


*Prolate Rotor **R*** MINUS *“Gyro” x-Spin* S_x



*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)
Time reversed
gyro -S=(-1,-1,-1)
The two together
J
R
S
J_z
J_y
J_x
"Sherman" (The shark)
After
Comp.Phys.Rpt. 8,319(1988)
First considerd in
1992 JCP article by
Hougan, Kleiner, and Ortigoso
Crossing RE surfaces
analogous to
Crossing PE surfaces (Jahn-Teller)
unZIPPing
unZIPPing

Two or more RE's beg to be unZIPPed. *Base RE surfaces are eigenvalues of matrix.*

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

Classical RE

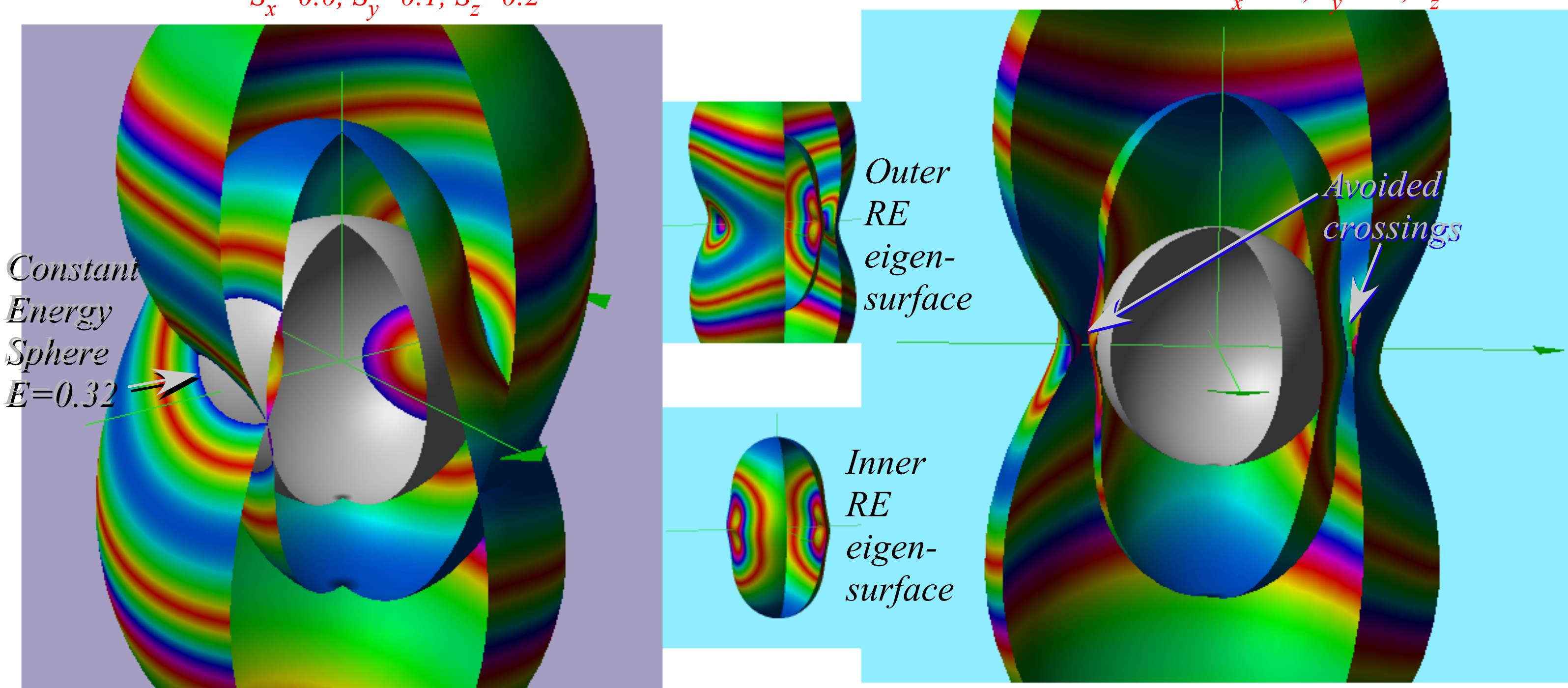
$$H = AJ_x^2 + BJ_y^2 + CJ_z^2 + \ldots - 2AJ_xS_x - 2BJ_yS_y - 2CJ_zS_z + \ldots + \textit{(more constant terms)}$$

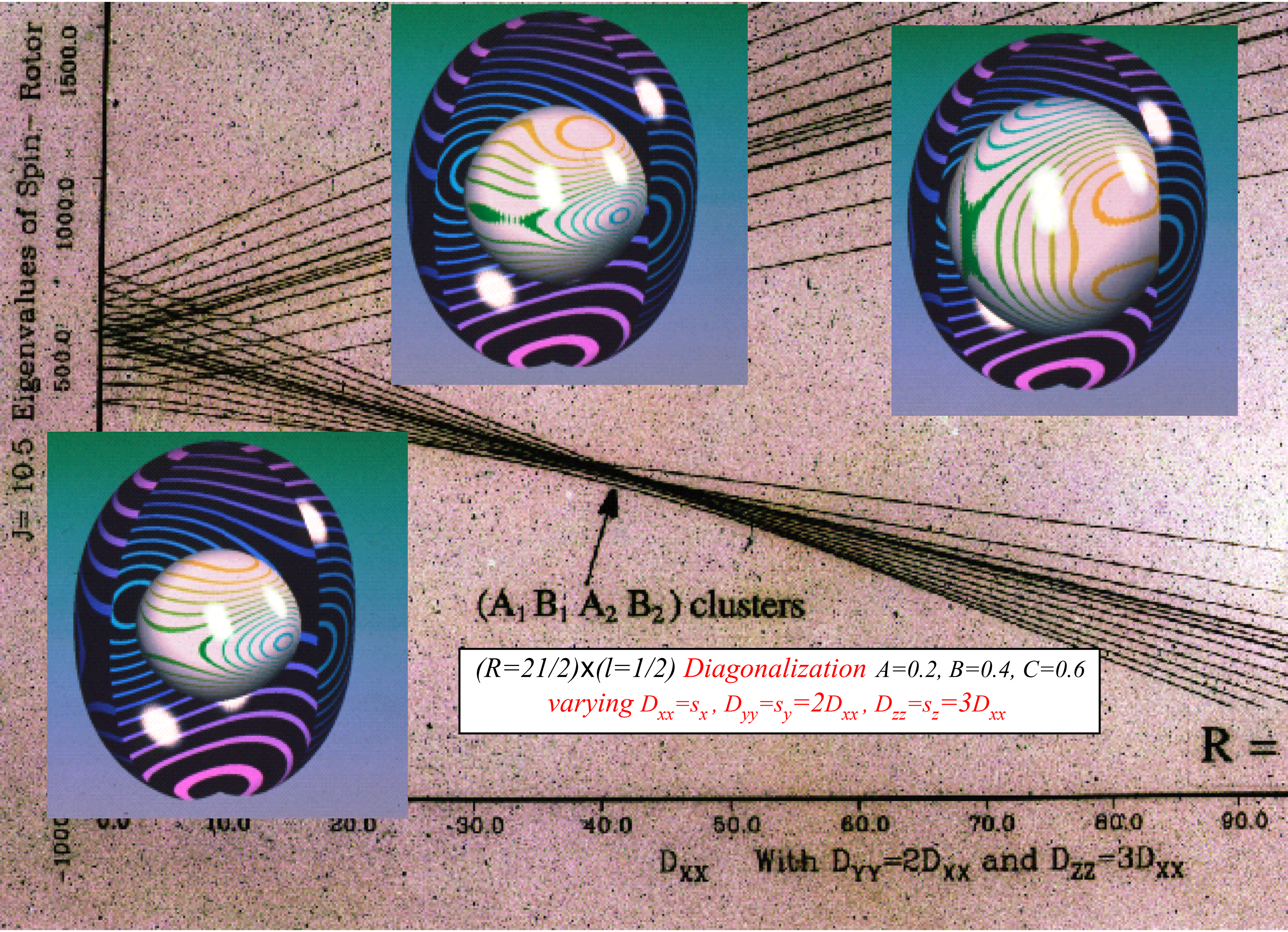
Semi-Classical Spin-1/2 RE $\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \mathbf{1} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$ *makes matrix*

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

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
(A1 B1 A2 B2) clusters
R =
DXX With DYY=2DXX and DZZ=3DXX
(R=21/2)x(l=1/2) Diagonalization A=0.2, B=0.4, C=0.6
varying Dxx=sx, Dyy=sy=2Dxx, Dzz=sz=3Dxx

Rotational Energy (RE) surfaces: Future?

Two or more RE's beg for full interaction unZIPPed for higher spin quanta

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

Base RE surfaces are eigensolutions of such matrices.
Combination RES depends on eigenvector chosen.

Interesting mechanics and dynamics. (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 and opportunity for sensitive control schemes.)

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.