Group Theory in Quantum Mechanics

Based on AMOP Lectures 19-20

Lecture 28 (5.04.17)

Rotational energy and eigenstate surfaces for Coriolis dynamics

(Int.J.Mol.Sci, 14, 714(2013) p.755-774 , QTCA Unit 7 Ch. 21-25,)
(PSDS - Ch. 5-8, Rev. Mod. Phys. 50,1,37-83(1978) , Computer Phys. Reports 8, 319-394 (1988))

Some ways to picture Atomic Molecular and Optical (AMO) eigenstates
- J-power-law energy eigenvalue spectra and tensor operators
  - Introducing U(2), U(3),… tensor 2^k-multipole expansions and Wigner Eckart forms

Born-Oppenheimer Approximations
- (BOA) for PES
- (BOA) for RES and LAB-BOD "hook-up" frame transformation

Semiclassical Rotor-"Gyro"-Spin coupling *
- Semiclassical Rotor-"Gyro" RES

Semiclassical Rotor analogy of Anharmonic Vibrator

Analogies between energy surfaces of potential (PES) and rotation (RES)
- Jahn-Teller-Renner analogies

Rotational energy eigenvalue surfaces (REES)
- Introducing "Sherman the Shark" ZIPPed* and unZIPPed*

REES for high-J Coriolis spectra in υ_3 CF_4 (with Review: SF_6 Coriolis PQR structure)

REES for high-J and high-υ ro-vibrational polyads
- CF_4 -$\upsilon_4/2\upsilon_3$ dyad

*ZIPP (Zero-Interaction-Potential-`Proximation

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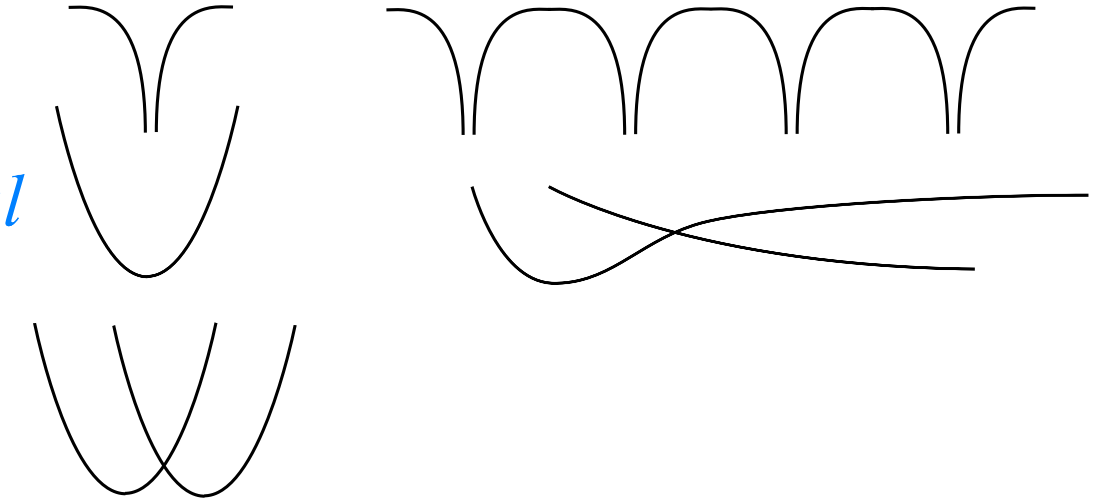
Some ways to picture AMO eigenstates

- *Potential Energy Surfaces (PES)*

  electronic

  vibrational

  vibronic



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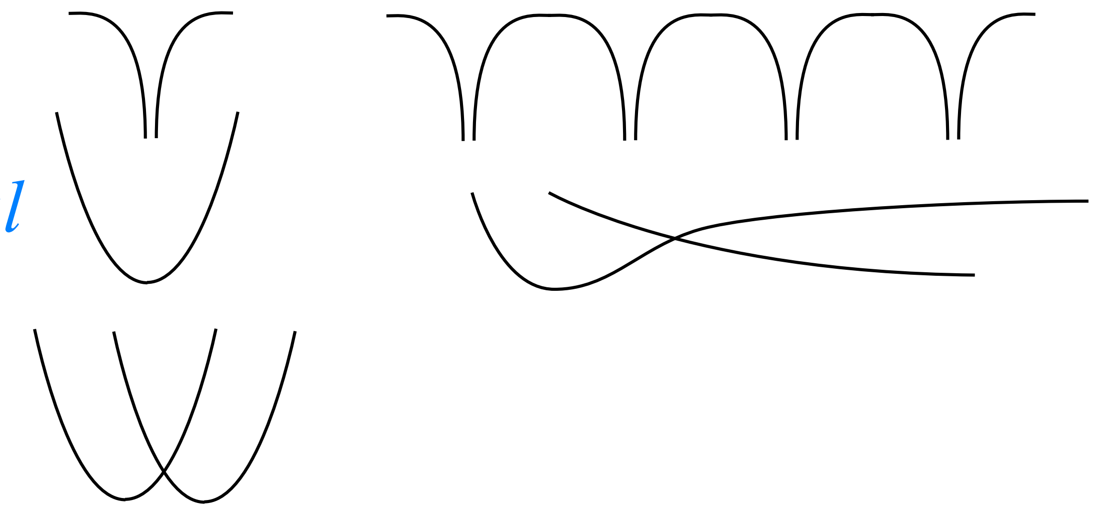
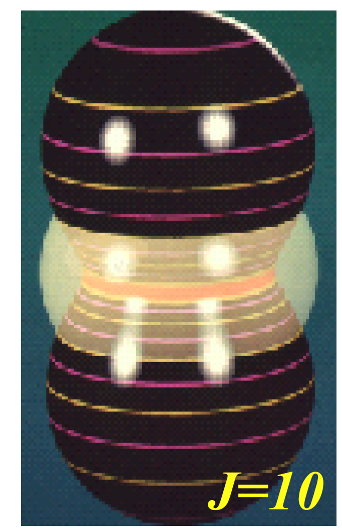


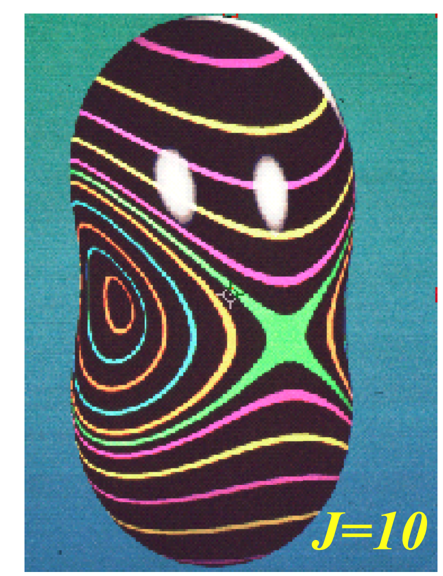
•*Rotational Energy Surfaces (RES)*

pure rotational (centrifugal) effects

rovibrational (centrifugal and Coriolis) effects

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





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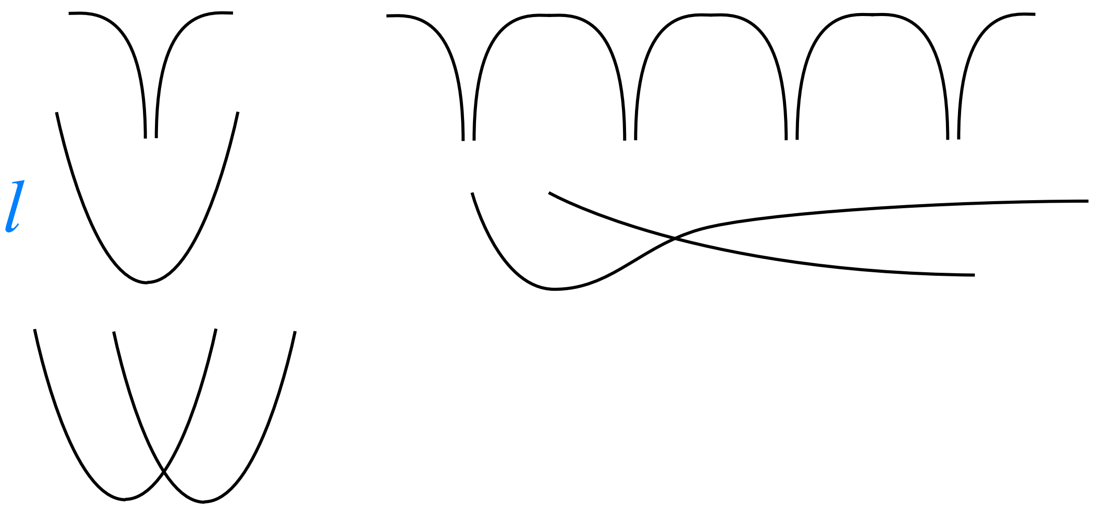

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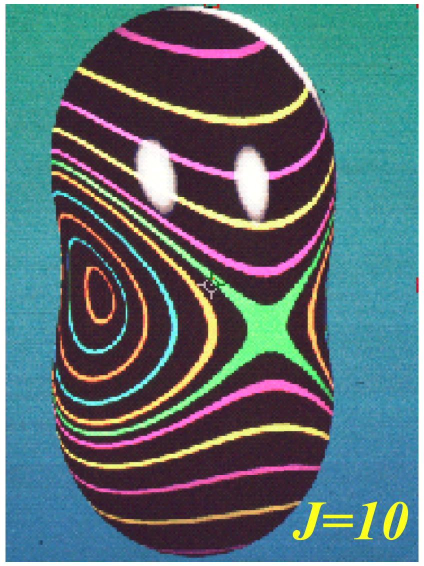

- *Generalized phase spaces*

  vibrational polyad sphere

  high energy pulse state space

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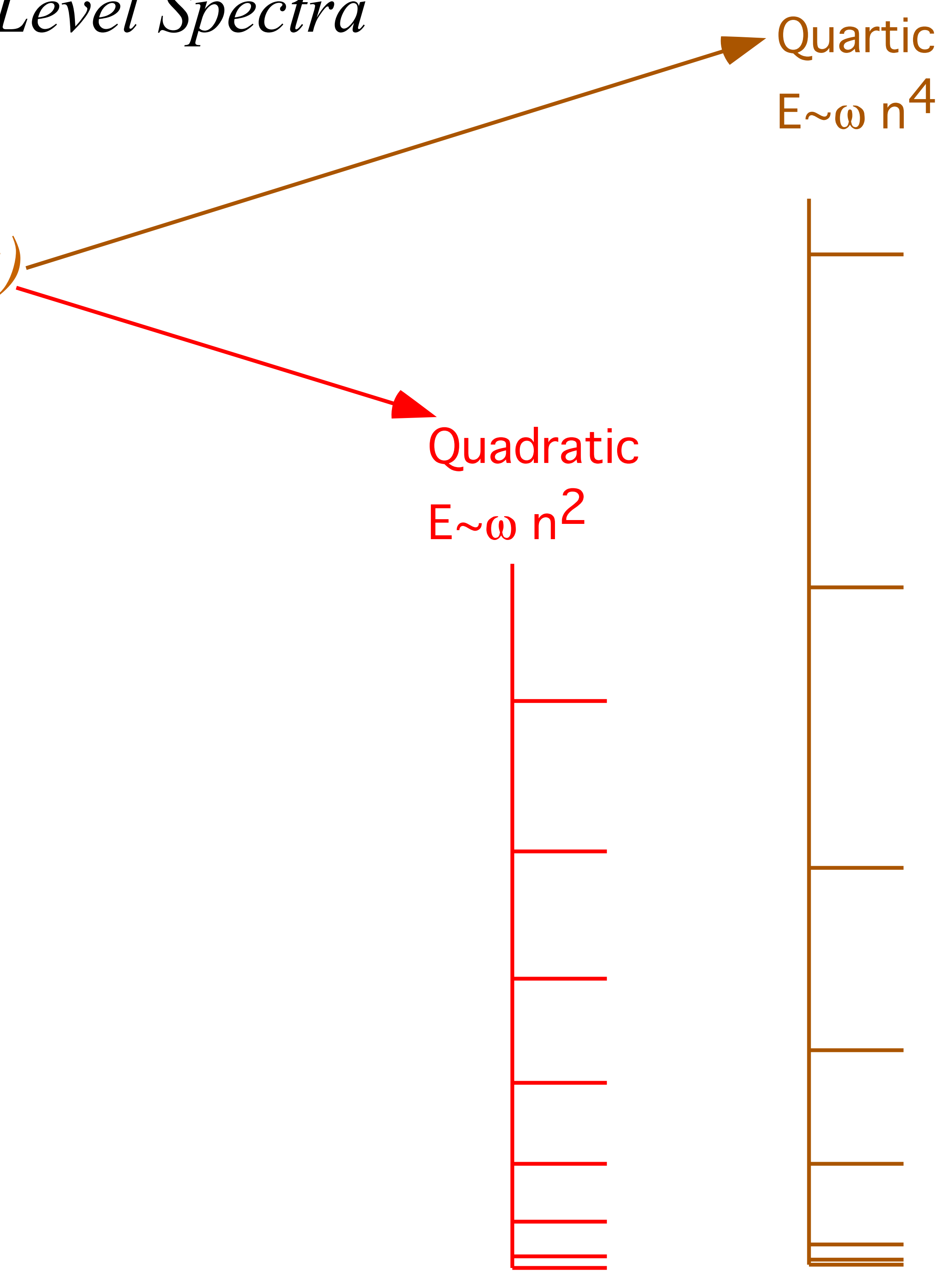
CF_4 -υ_4/2υ_3 dyad

Examples of Simple Power Law Energy Level Spectra

Single-rotor $B\,\boldsymbol{J}^2 + C\boldsymbol{J}^4 + \ldots$(even powers)

Like very anharmonic oscillator



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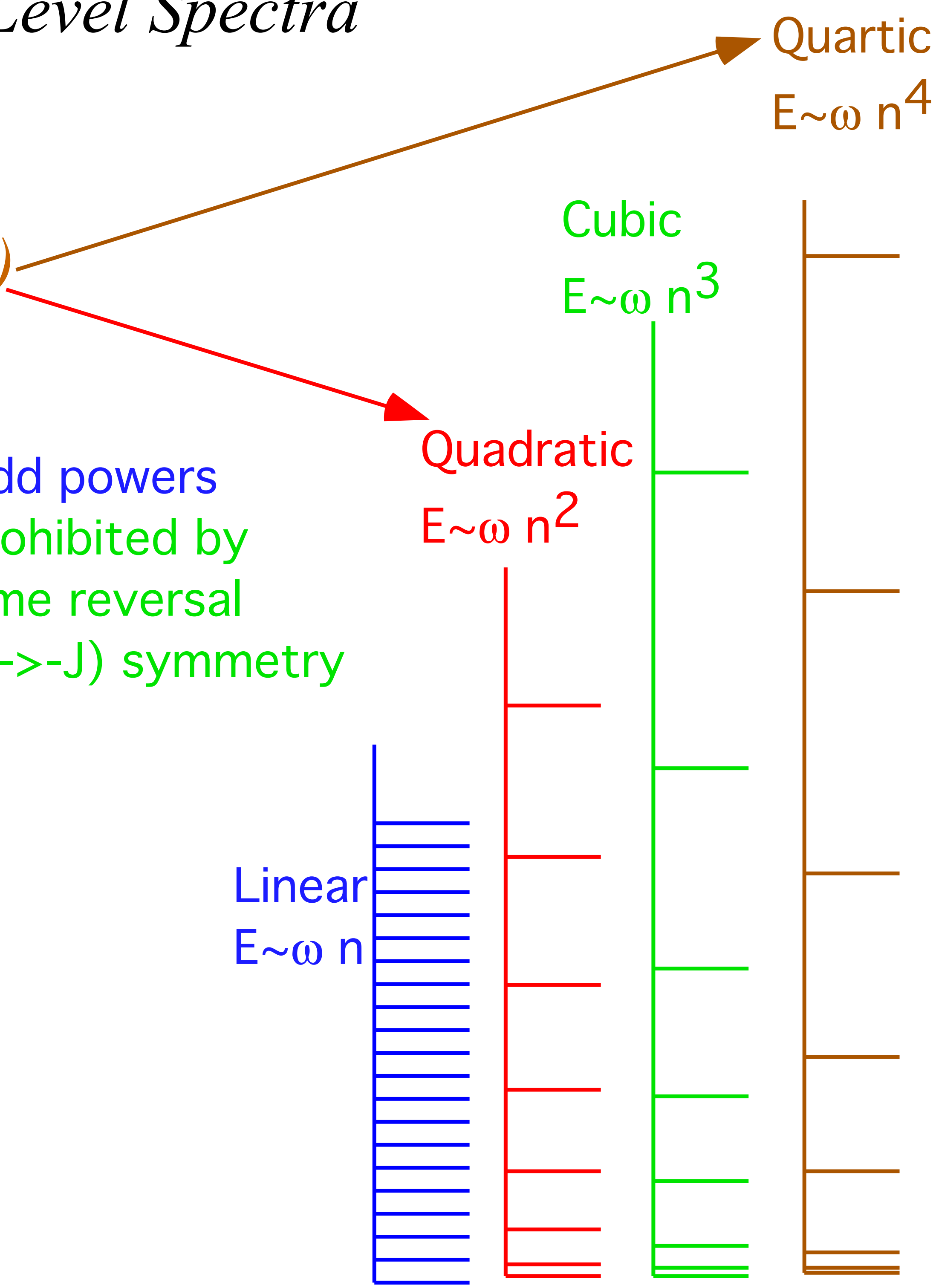
Odd powers prohibited by time reversal (J->-J) symmetry



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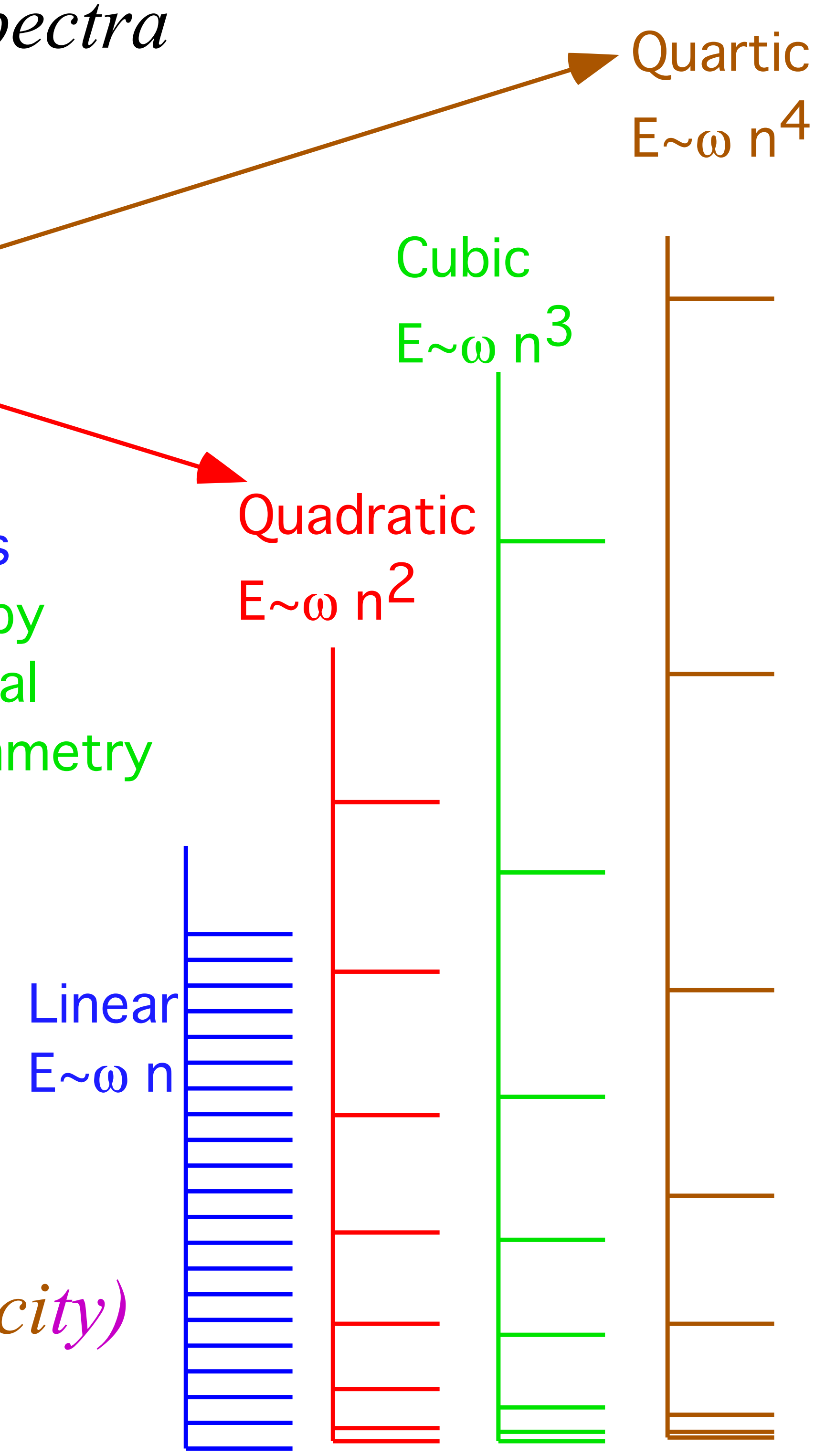

Compound-rotor $B\zeta\boldsymbol{J} + \ldots$ *(any power* $\boldsymbol{J}^2, \boldsymbol{J}^3, \boldsymbol{J}^4,$*)*

Like 2D-<u>harmonic</u> oscillator $\omega_\mu \boldsymbol{a}_\mu^\dagger \boldsymbol{a}_\mu + \ldots$ *(anharmonicity)*

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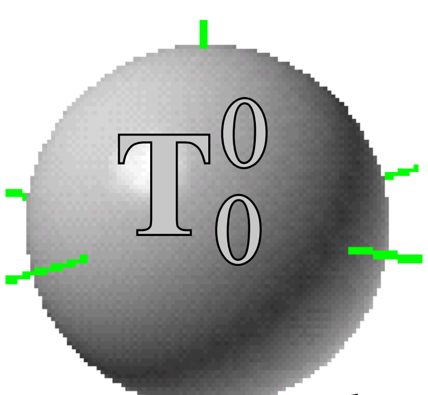
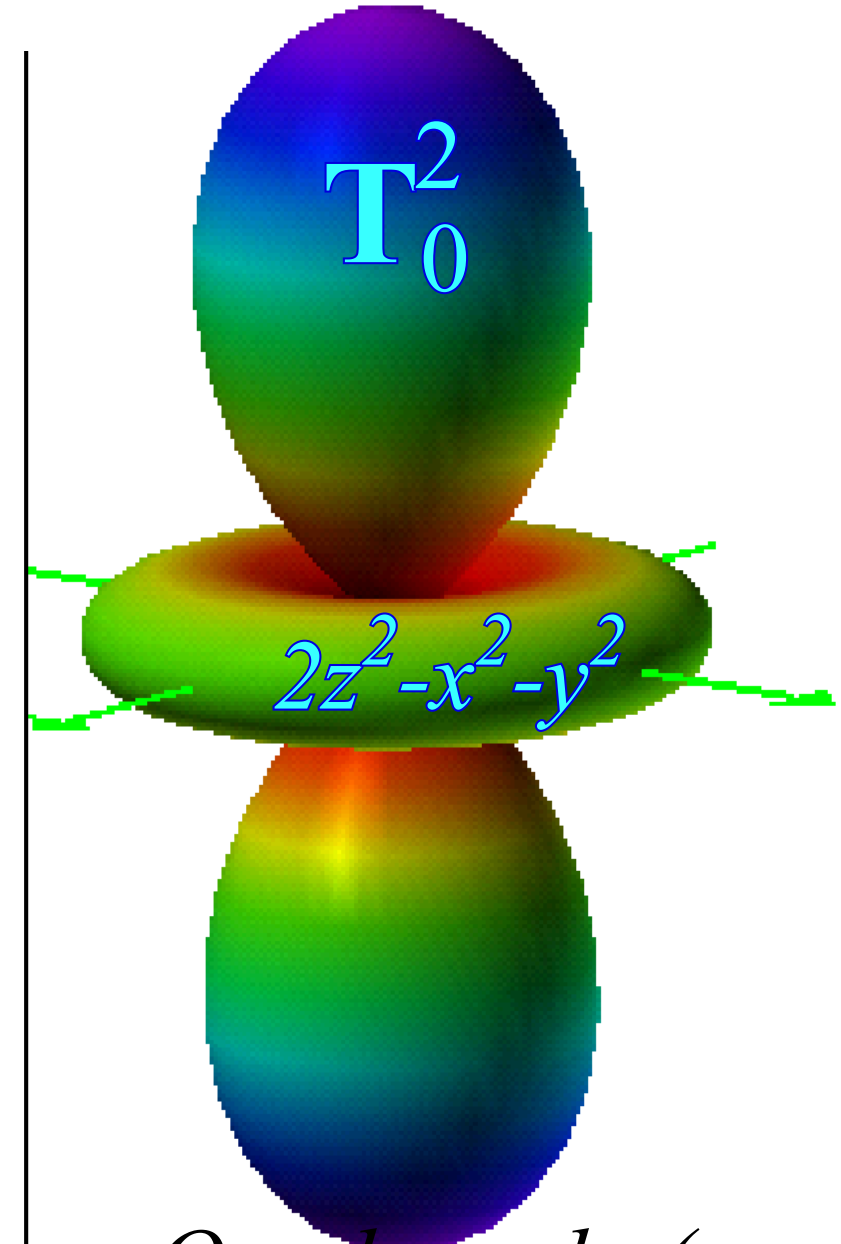
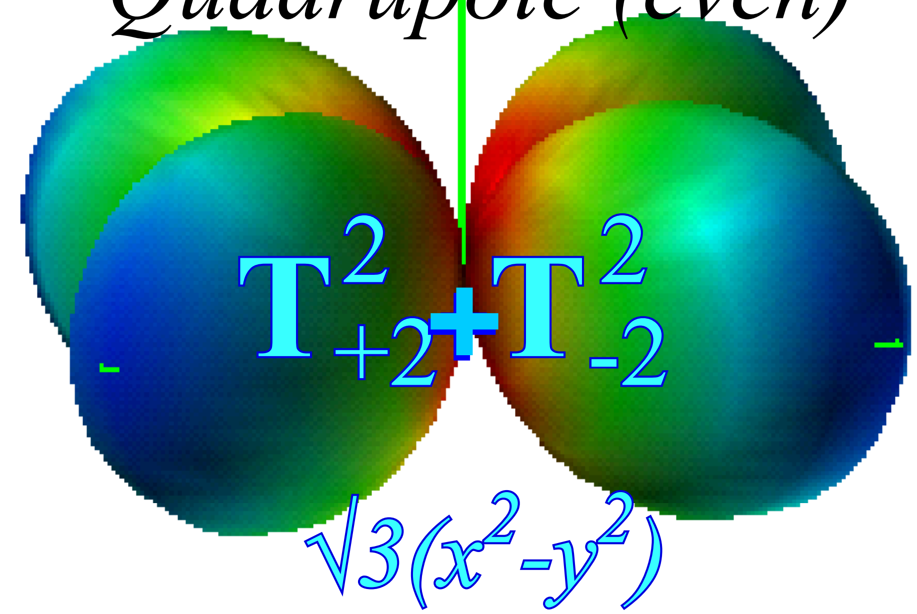
Lowest Order
RE-Surface
Components
k=0, 1, 2...

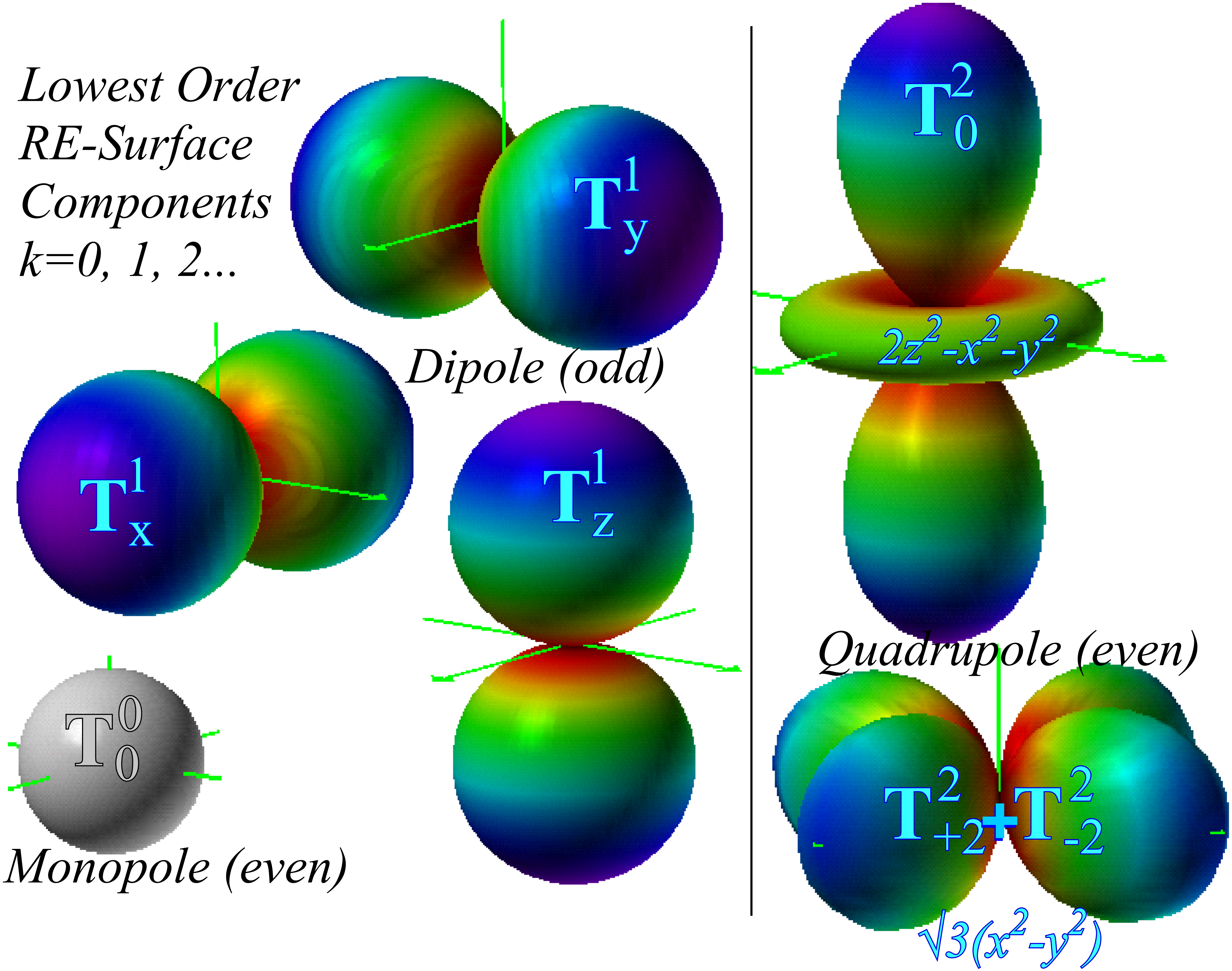


Monopole (even)



Quadrupole (even)

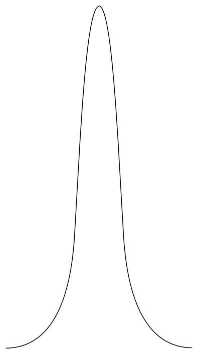


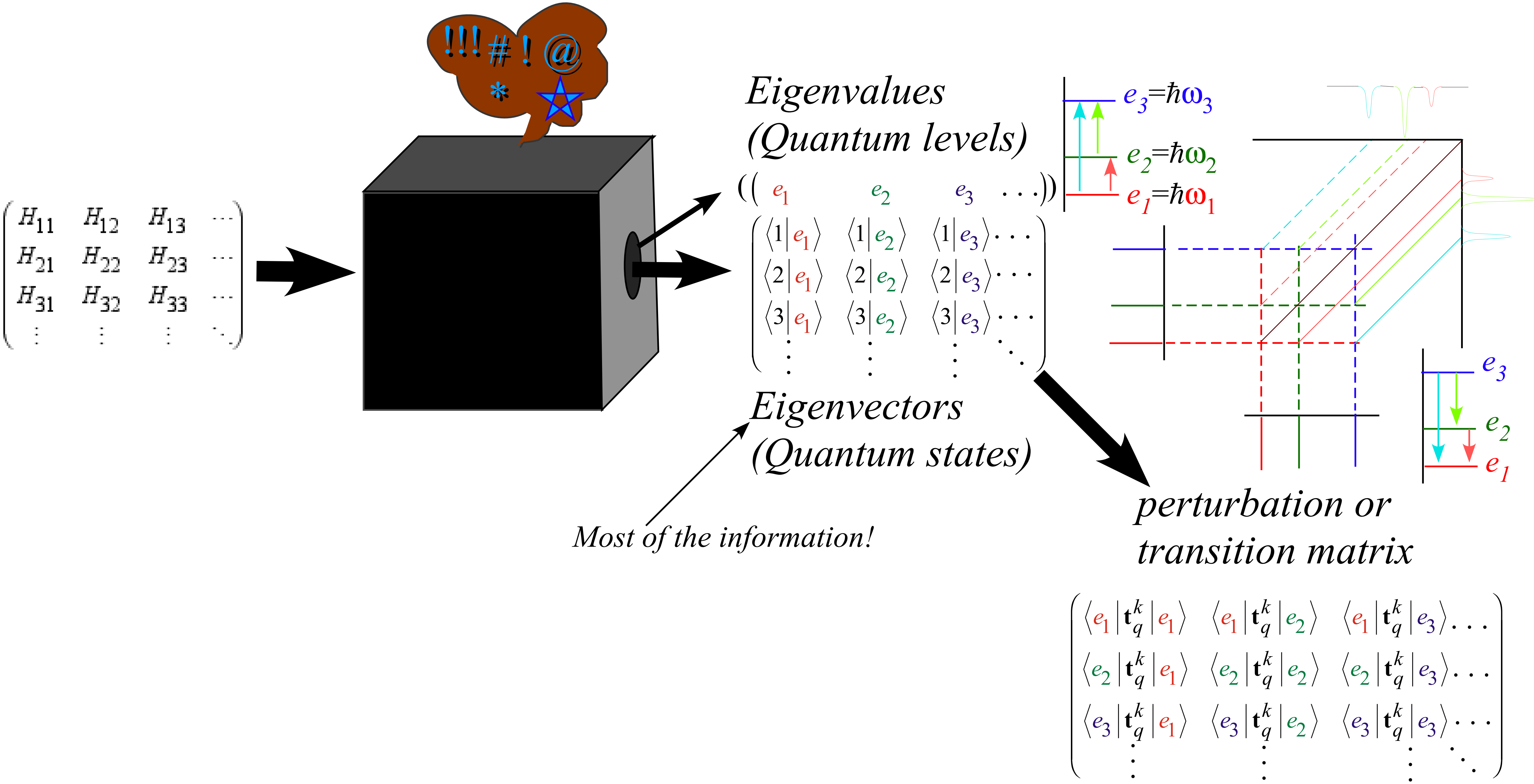


Lowest Order
RE-Surface
Components
k=0, 1, 2...
T^1_y
Dipole (odd)
T^1_x
T^1_z
T^0_0
Monopole (even)
T^2_0
$2z^2-x^2-y^2$
Quadrupole (even)
$T^2_{+2}+T^2_{-2}$
$\sqrt{3}(x^2-y^2)$

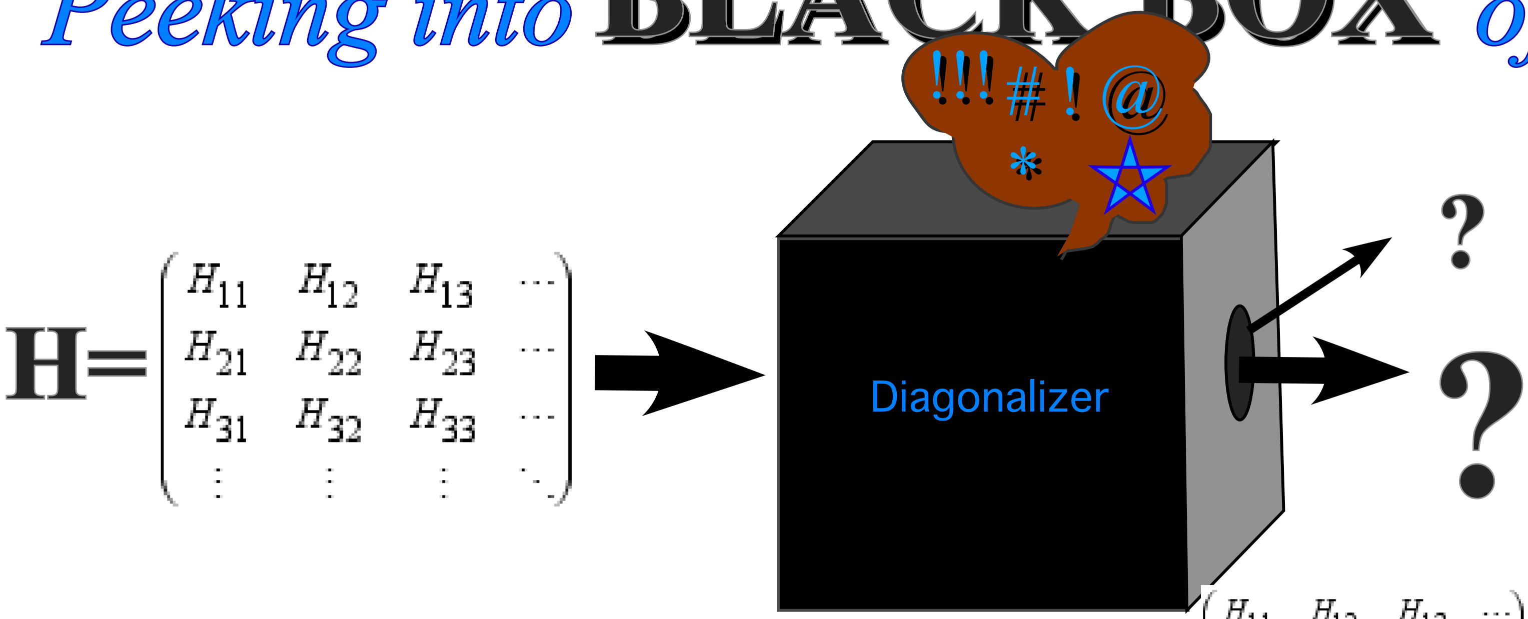
Matrix Diagonalization

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





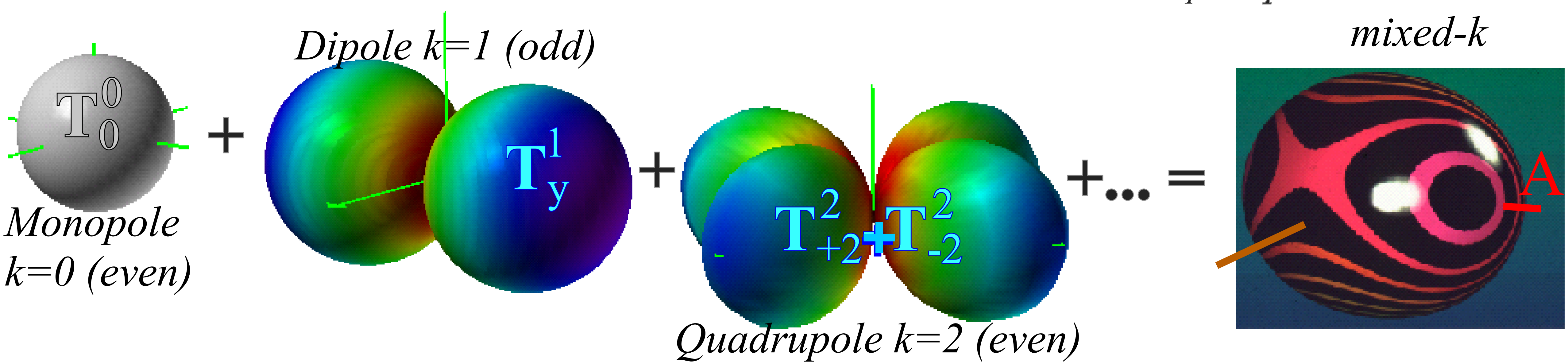
Peeking into **BLACK BOX** *of matrix diagonalization:*



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:

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

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

$$= \frac{A+D}{2}\,\mathbf{T}_0 + (B-iC)\,\mathbf{T}_1 + (B+iC)\,\mathbf{T}_{-1} + \frac{A-D}{2}\,\mathbf{T}_0$$

$$\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \qquad \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

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)

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rank-2 (tensor)

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Mutually commuting diagonal operators

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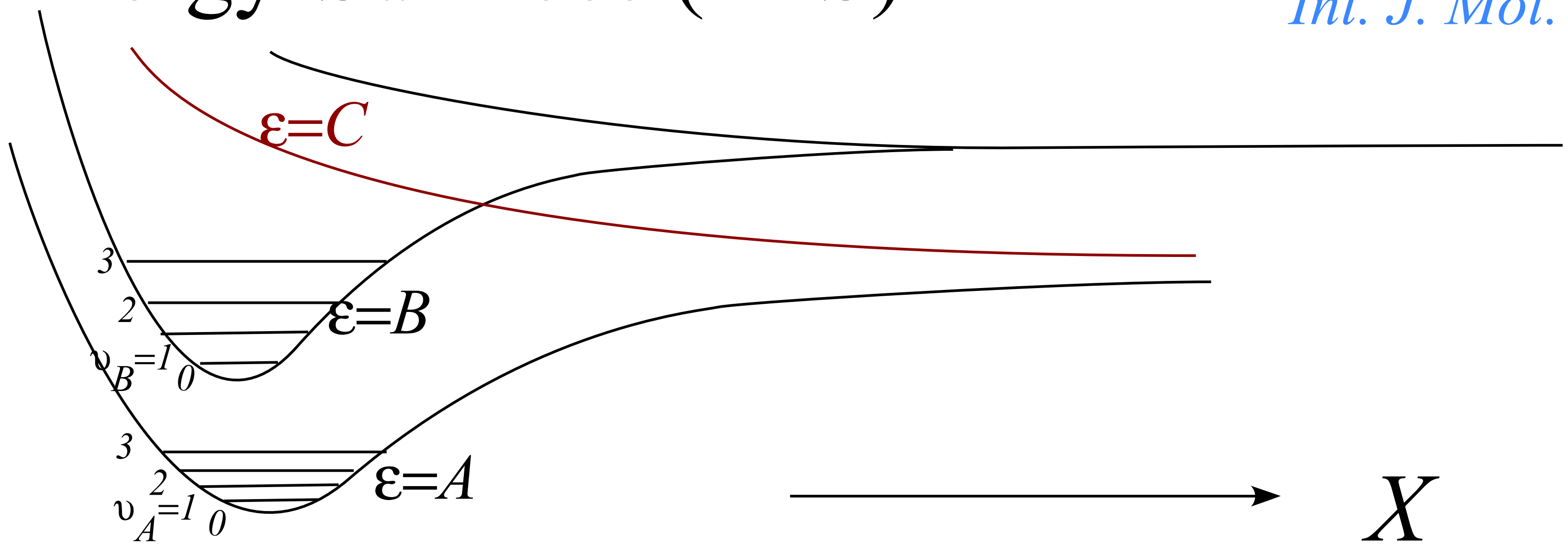
Mutually commuting diagonal operators

Wigner-Clebsch-Gordan expressions for Tensor $\left\langle \mathbf{T}^k_q \right\rangle$

$$\left\langle {J' \atop M'} \middle| \mathbf{T}^k_q \middle| {J \atop M} \right\rangle = \begin{pmatrix} J' & k & J \\ M' & q & -M \end{pmatrix} (J' \| k \| J) = C^{kJ\,J'}_{q\,M\,M'} \langle J' \| k \| J \rangle$$

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

BOA issues discussed in:
Rev. Mod. Phys. 50,1,37-83(1978)
Int. J. Mol. Sci. 14,714-806(2013)



BOA-"Entangled" or correlated products:

"FAST" stuff "SLOW"stuff

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

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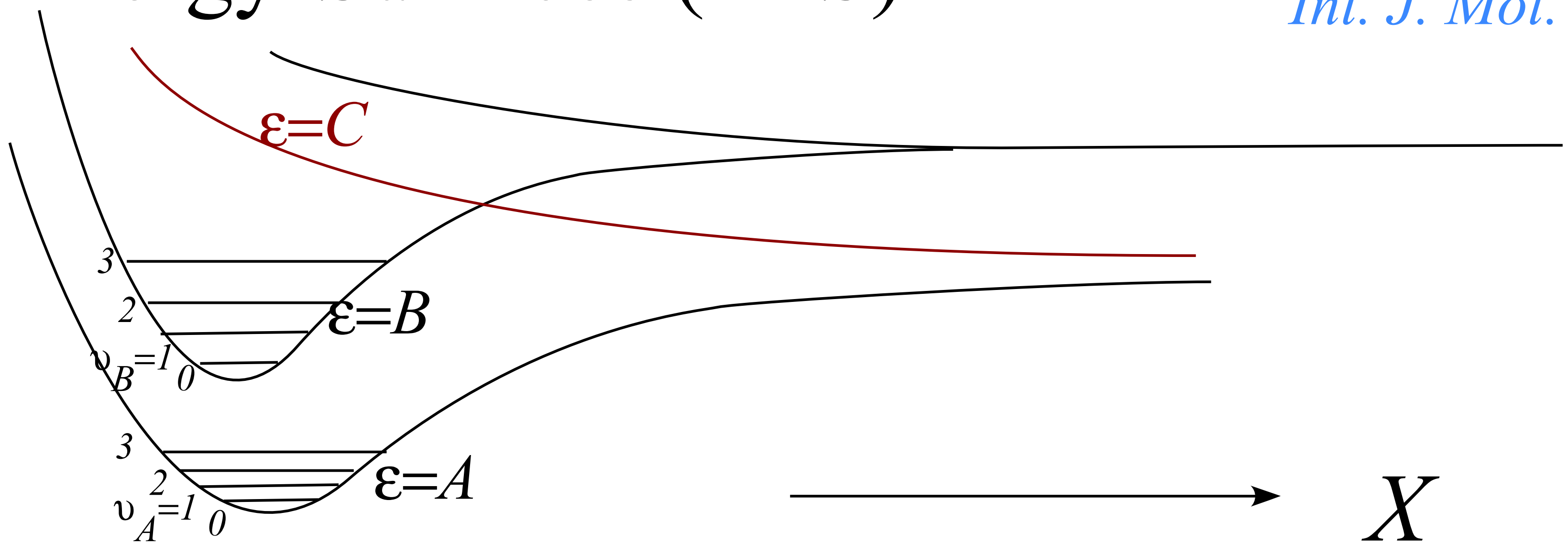

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$$\Psi_{\upsilon(\varepsilon)}(x^{electron}\ldots X^{nuclei}\ldots) = \psi_{\varepsilon}(x(X\ldots)\ldots) \cdot \eta_{\upsilon(\varepsilon)}(X\ldots)$$

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

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

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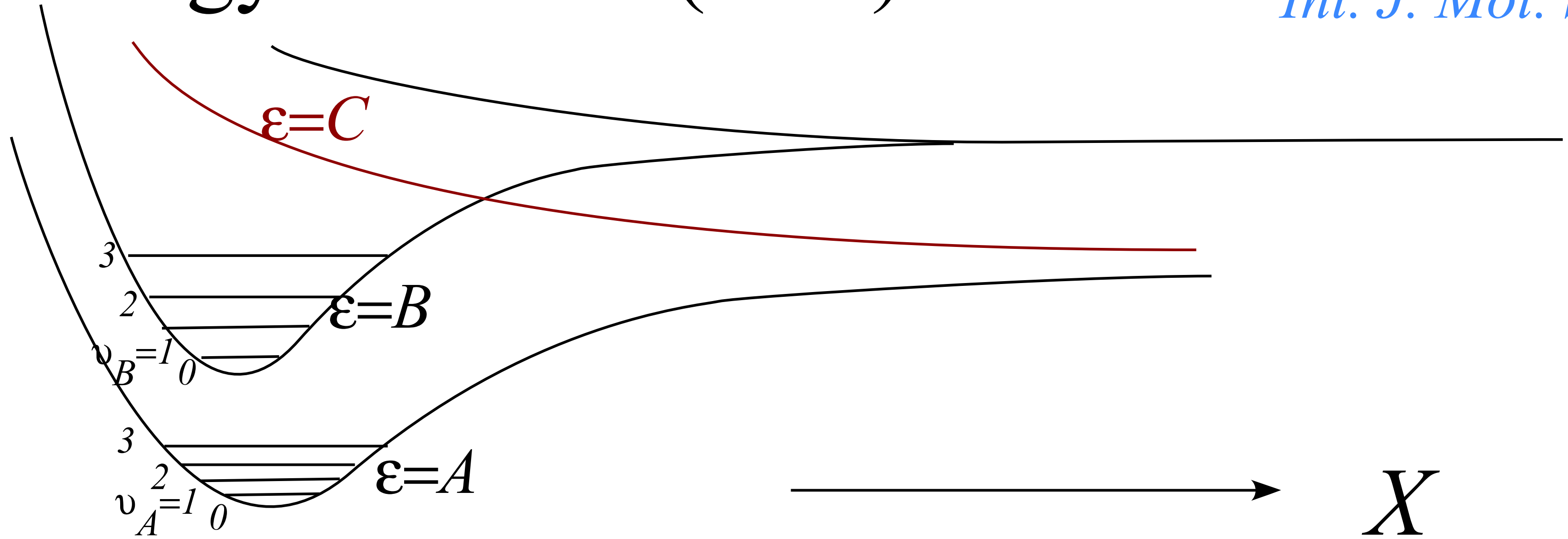

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Compare BOA to <u>un</u>entangled state: $|\varepsilon\rangle|\eta\rangle=|\varepsilon,\eta\rangle$.

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

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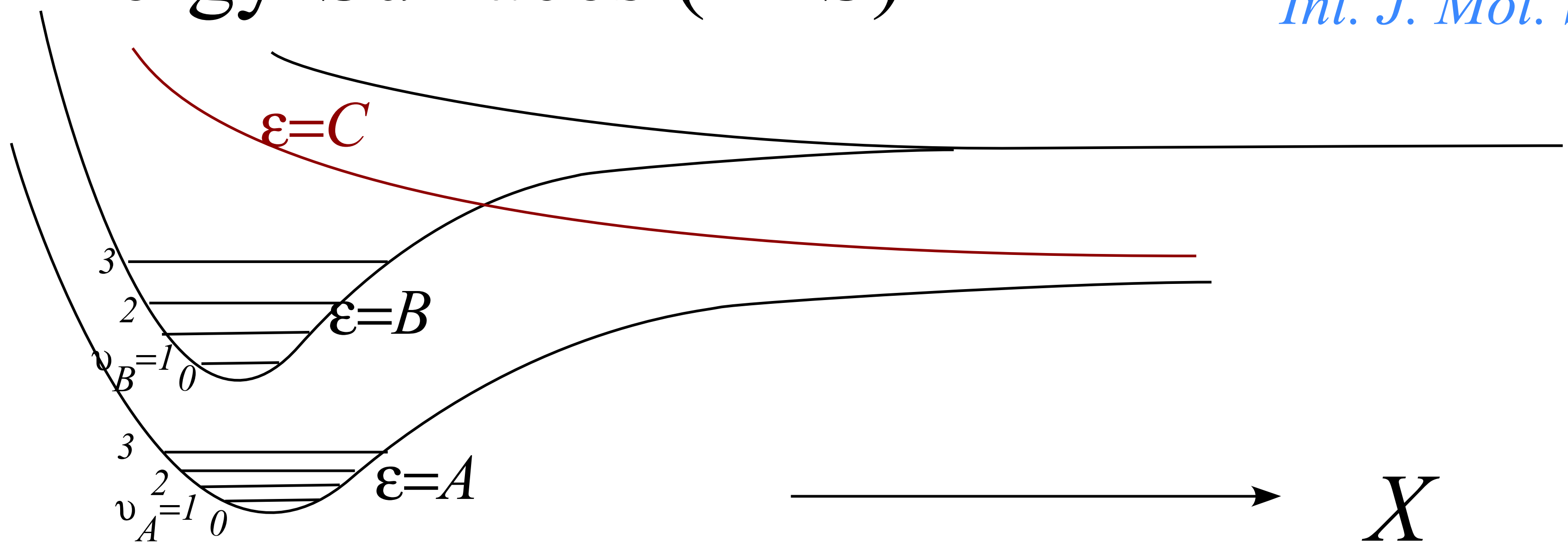

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$$\psi_\varepsilon(x)\cdot\eta_\upsilon(X) = \langle x|\varepsilon\rangle\langle X|\eta\rangle = \langle x,X|\varepsilon,\eta\rangle$$

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

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

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Introducing "Sherman the Shark" ZIPPed and unZIPPed**

REES for high-J Coriolis spectra in υ_3 CF_4 (with Review: *SF_6 Coriolis PQR structure)*

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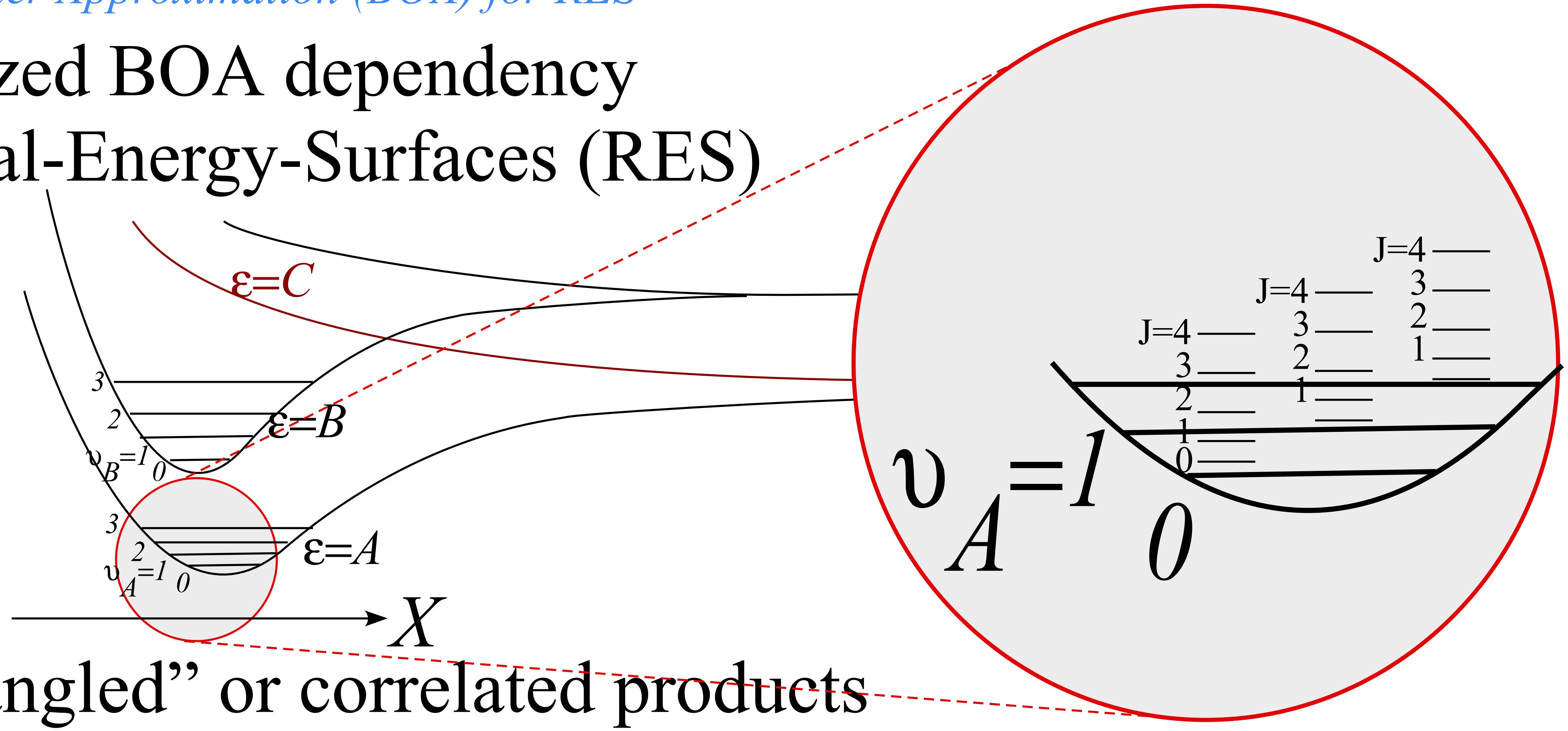
CF_4 -υ_4/2υ_3 dyad

Generalized BOA dependency
Rotational-Energy-Surfaces (RES)



BOA-"Entangled" or correlated products

"FAST" "SLOW" "SLOWER"

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

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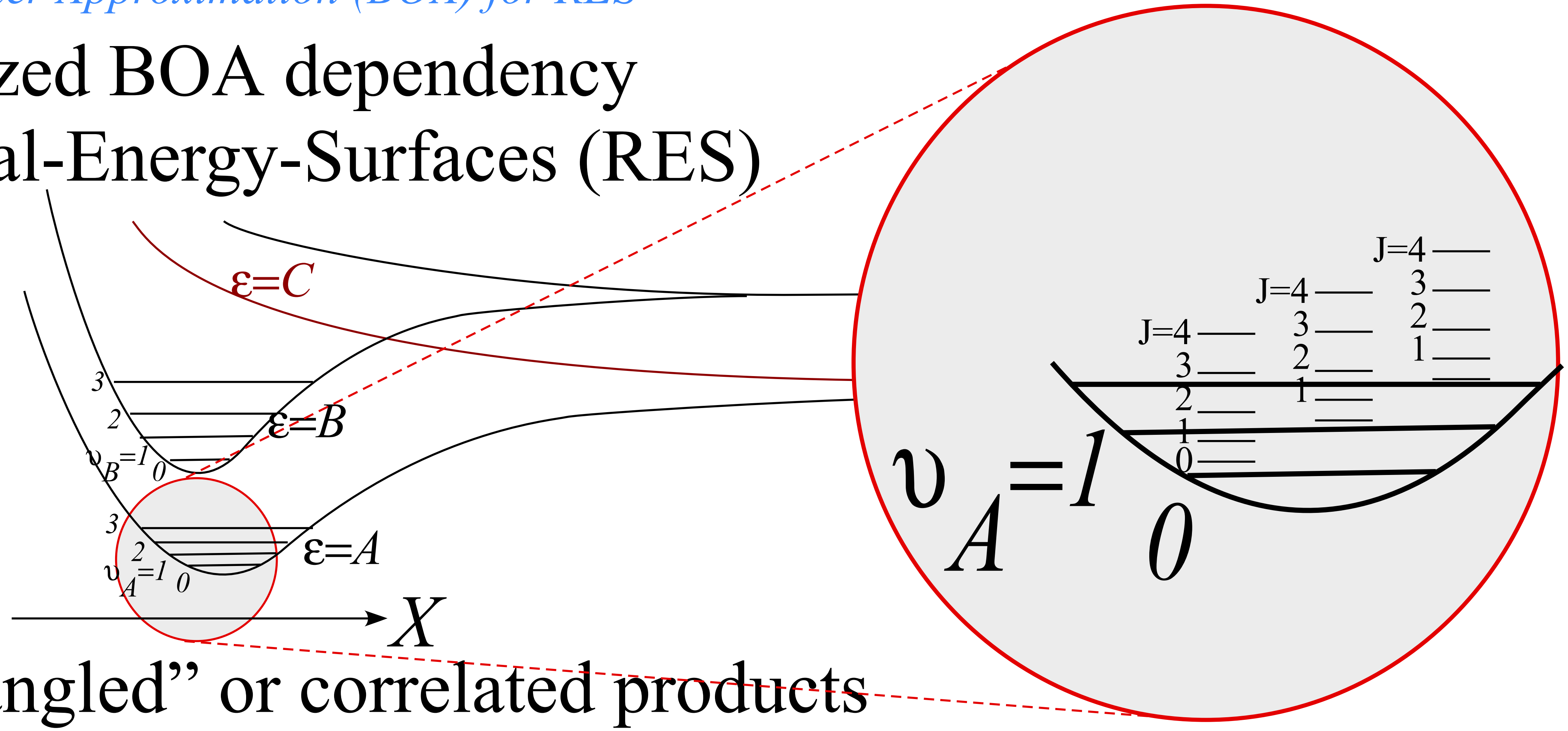

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vibe $\upsilon(\varepsilon)$-quanta depend on electron ε-quanta

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

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

BOA issues discussed in:
Rev. Mod. Phys. 50,1,37-83(1978)
Int. J. Mol. Sci. 14,714-806(2013)

Generalized BOA dependency
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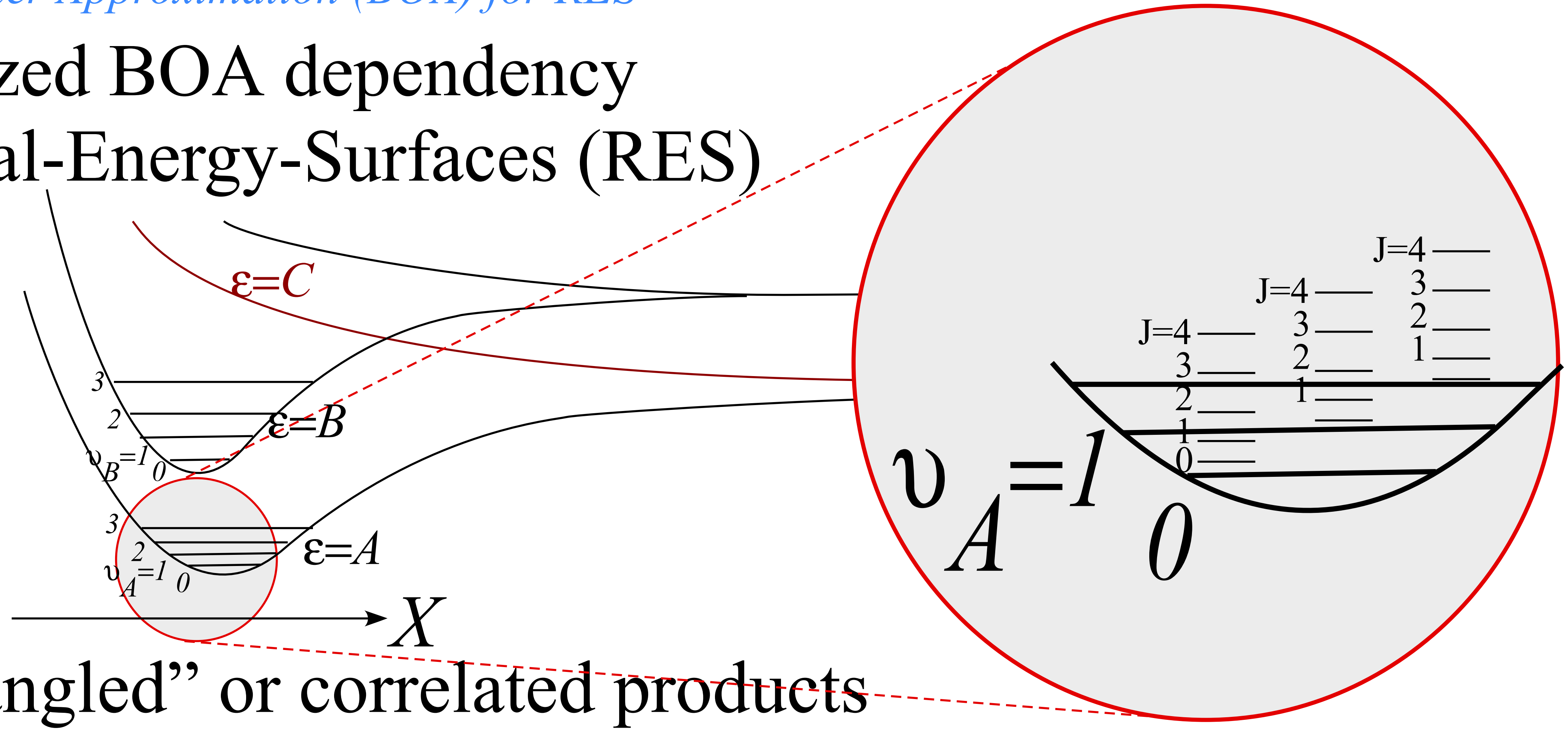

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electron $x_{(Q(\Theta))}$-coords depend on vibration Q-coords and rotation Θ coords

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

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Born-Oppenheimer Approximation (BOA) for RES

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

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

Detailed model of BOA rotor entanglement

Using rotational symmetry analysis

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

bod-based vibronic factor

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bod-based vibronic factor

body-wave from lab-wave		*lab-wave from body-wave*
$\psi^{\ell}_{\bar{\mu}}(\bar{x}) = \psi^{\ell}_{\mu}(x) D^{\ell}_{\bar{\mu},\mu}(\alpha,\beta,\gamma)$	frame rotation	$\psi^{\ell}_{\mu}(x) = \psi^{\ell}_{\bar{\mu}}(\bar{x}) D^{\ell *}_{\mu,\bar{\mu}}(\alpha,\beta,\gamma)$
sum $\mu = -J \ldots +J$		sum $\bar{\mu} = -J \ldots +J$

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lab-wave from body-wave

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

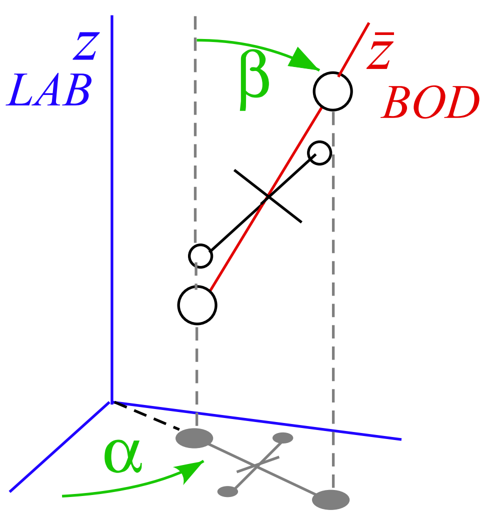
sum $\bar{\mu} = -J \ldots +J$

"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* $m = M - \mu$



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Compare wave Products:

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

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

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

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

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

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

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

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

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 $\bar{\mu}=-J...+J$

This has form:

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

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

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

...that follows from well known coupling identity.

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

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

Compare wave Products:

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

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

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

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

BOTH HAVE...

sharp n	sharp n

An elementary "rovibronic species"

"...gyro in a briefcase"

Some ways to picture Atomic Molecular and Optical (AMO) eigenstates

J-power-law energy eigenvalue spectra and tensor operators

Introducing U(2), U(3),… tensor 2^k-multipole expansions and Wigner Eckart forms

Born-Oppenheimer Approximations

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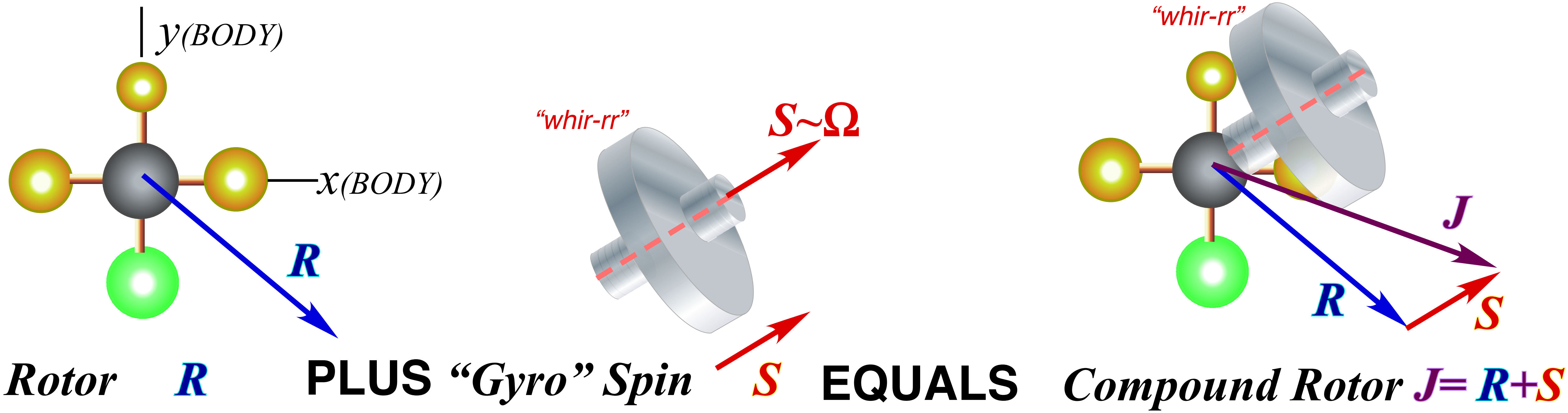
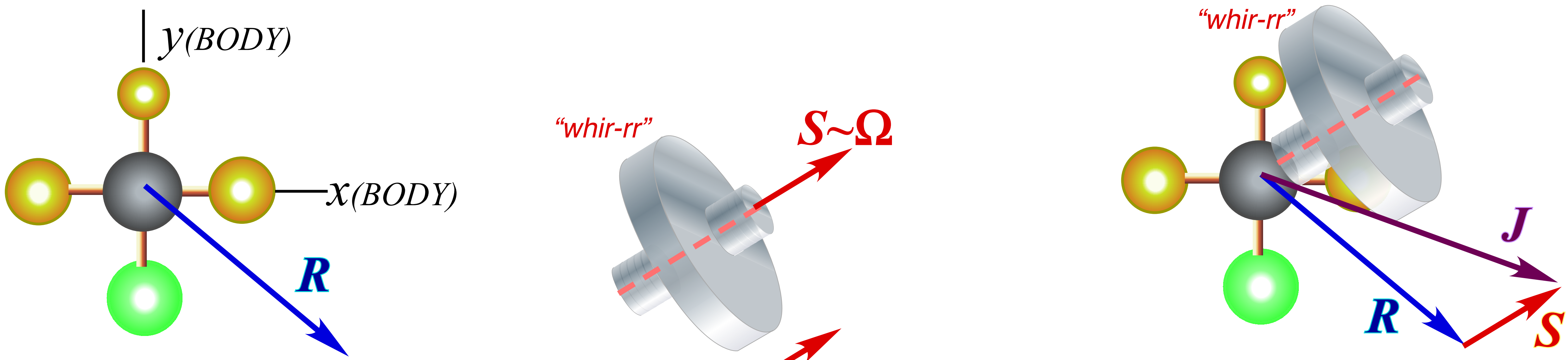


Compound Rotor Hamiltonian: *Rigid rotor with body-fixed "gyro"...*

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

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

Rotor-Gyro RES issues discussed in:
Computer Phys. Reports 8, 319-394 (1987)
Spring Handbook of AMOP Ch. 32 (2006)



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

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...but suppose it's zero!

Constraints do no work.

*Zero-Interaction Potential 'Proximation (ZIPP)**

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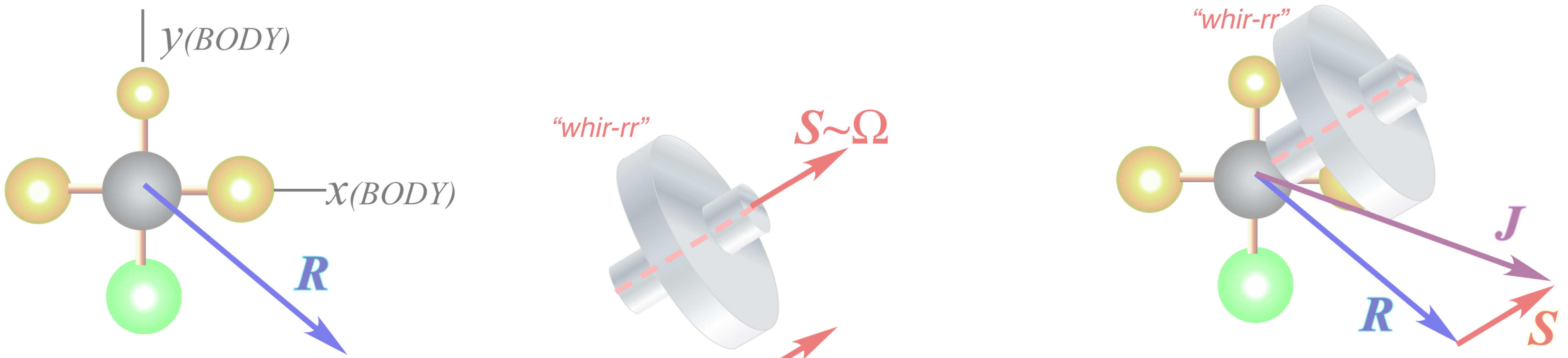
**ZIPP (Zero-Interaction-Potential-`Proximation*

Semiclassical Rotor-"Gyro"-Spin coupling



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

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

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

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

...but suppose it's zero!

Constraints do <u>no</u> <u>work</u>.

*Zero-Interaction Potential 'Proximation (ZIPP)**

(ZIPPed)

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

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

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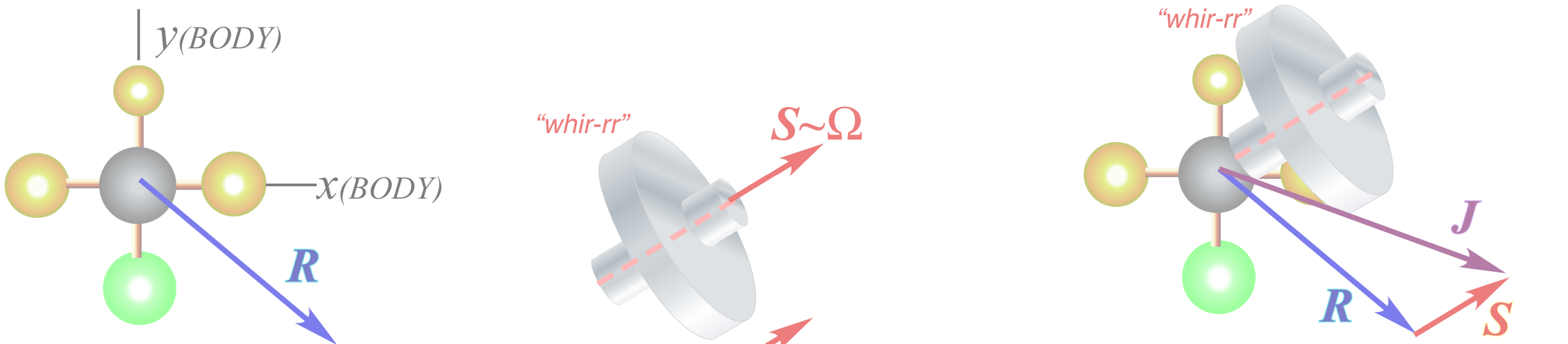

Rotor $\boldsymbol{R}$ **PLUS "Gyro" Spin** $\boldsymbol{S}$ **EQUALS** **Compound Rotor** $\boldsymbol{J}=\boldsymbol{R}+\boldsymbol{S}$

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

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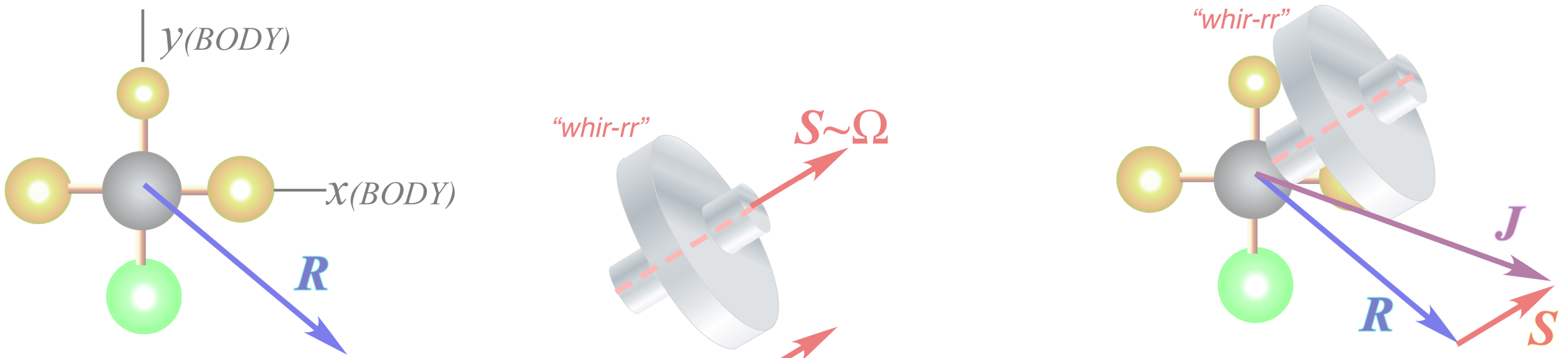

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“Coriolis effect“ subtracts linear or 1st-order $\mathbf{J}_m$ *or* $\mathbf{T}^1{}_m$ *terms for gyro-rotor H*

$B\boldsymbol{R}^2$ *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* $e\boldsymbol{p}\bullet\boldsymbol{A}$

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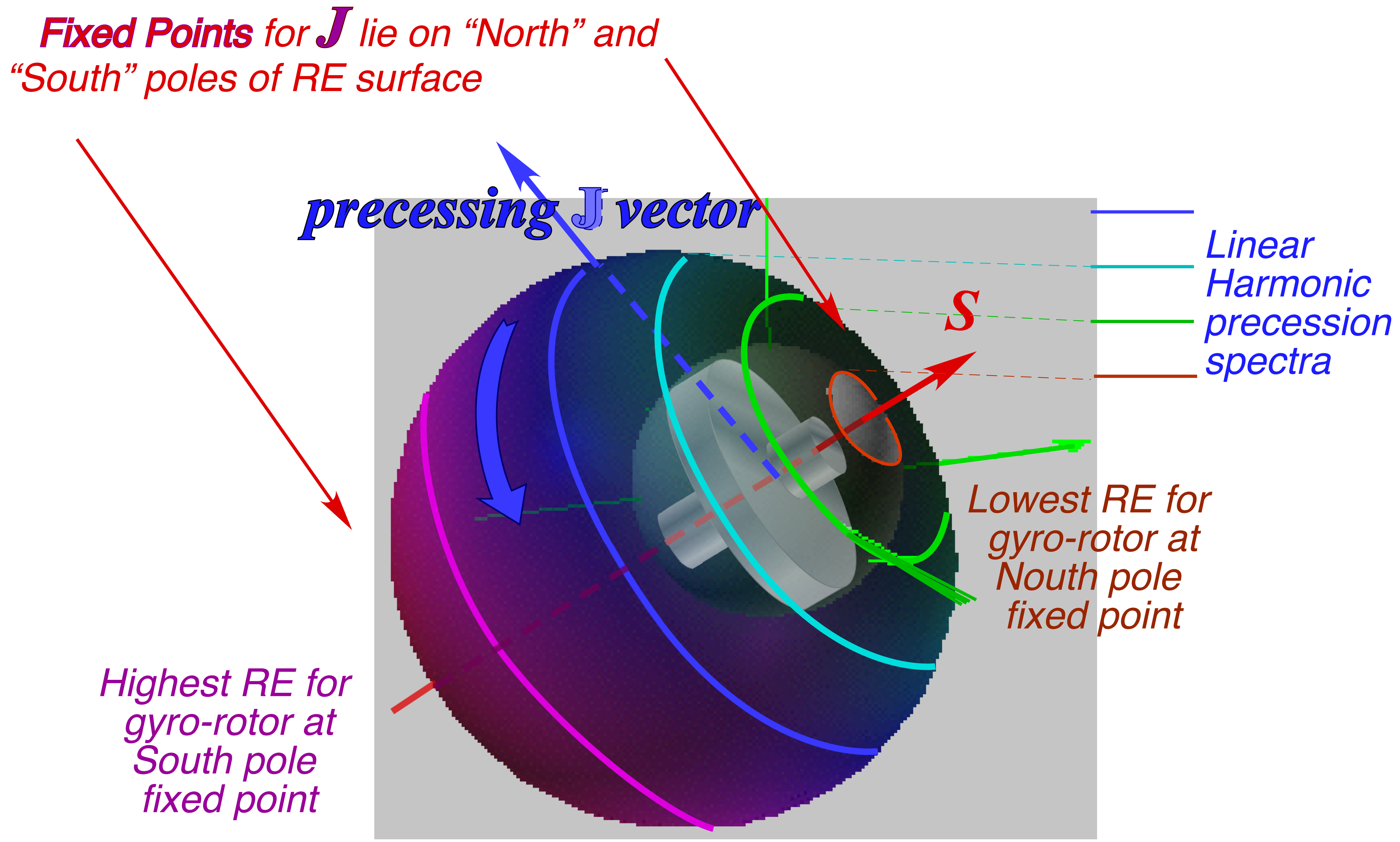
RE Surface for1st-order $\mathbf{J}_m$ *or* $\mathbf{T}^1{}_m$ *term is a cardioid displaced in J-direction*
Energy sphere intersections are concentric circular precession paths
All paths precess with the same sense around gyro S-vector



Rotor-Gyro RES issues discussed in:
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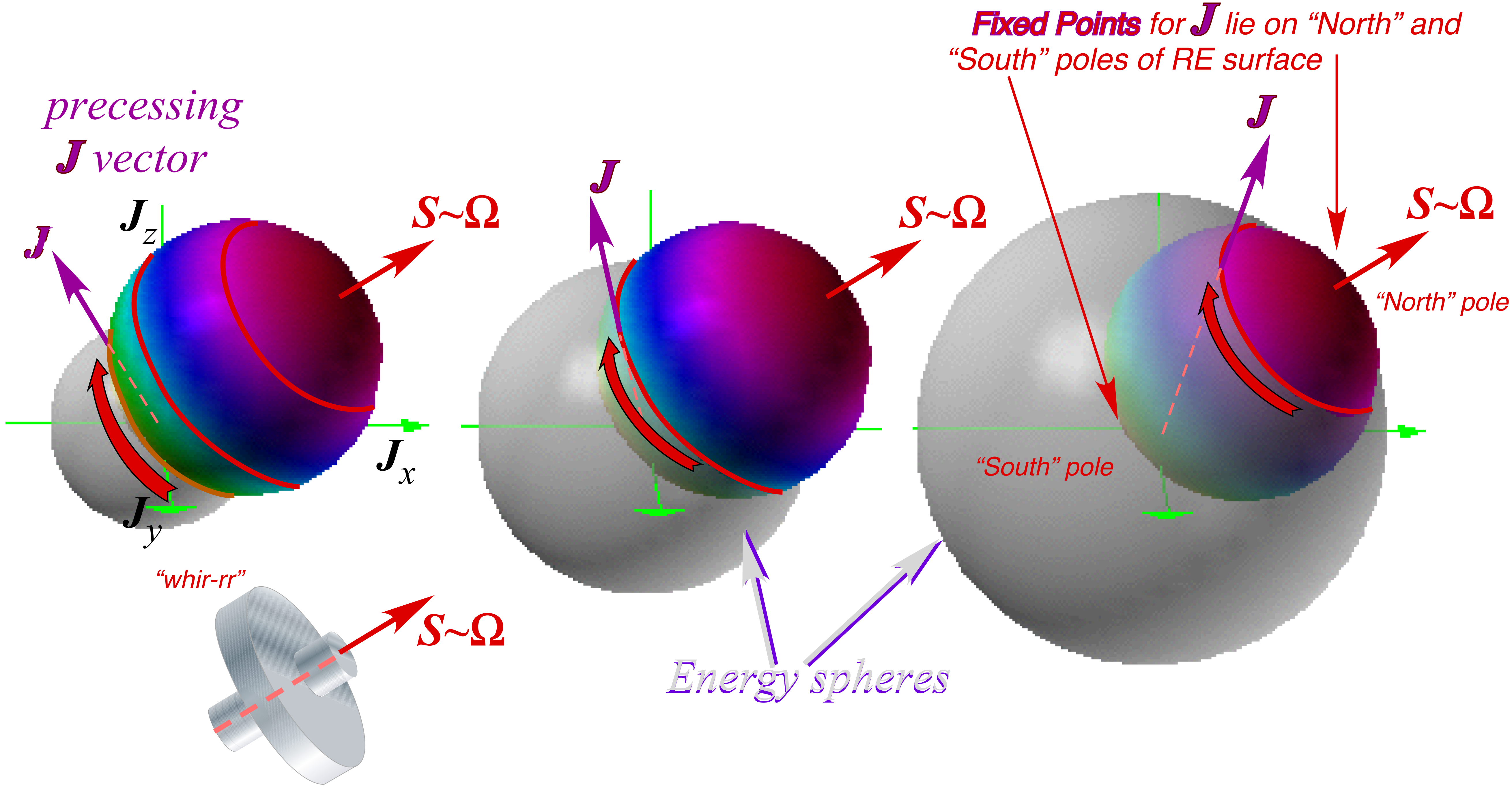
RE Surface for1st-order $\mathbf{J}_m$ *or* $\mathbf{T}^1{}_m$ *term is a quasi-sphere displaced in* **S**-*direction*

Energy sphere intersections are concentric circular precession paths

All paths precess with the same sense around gyro S-vector *(Using left-hand rule here)*



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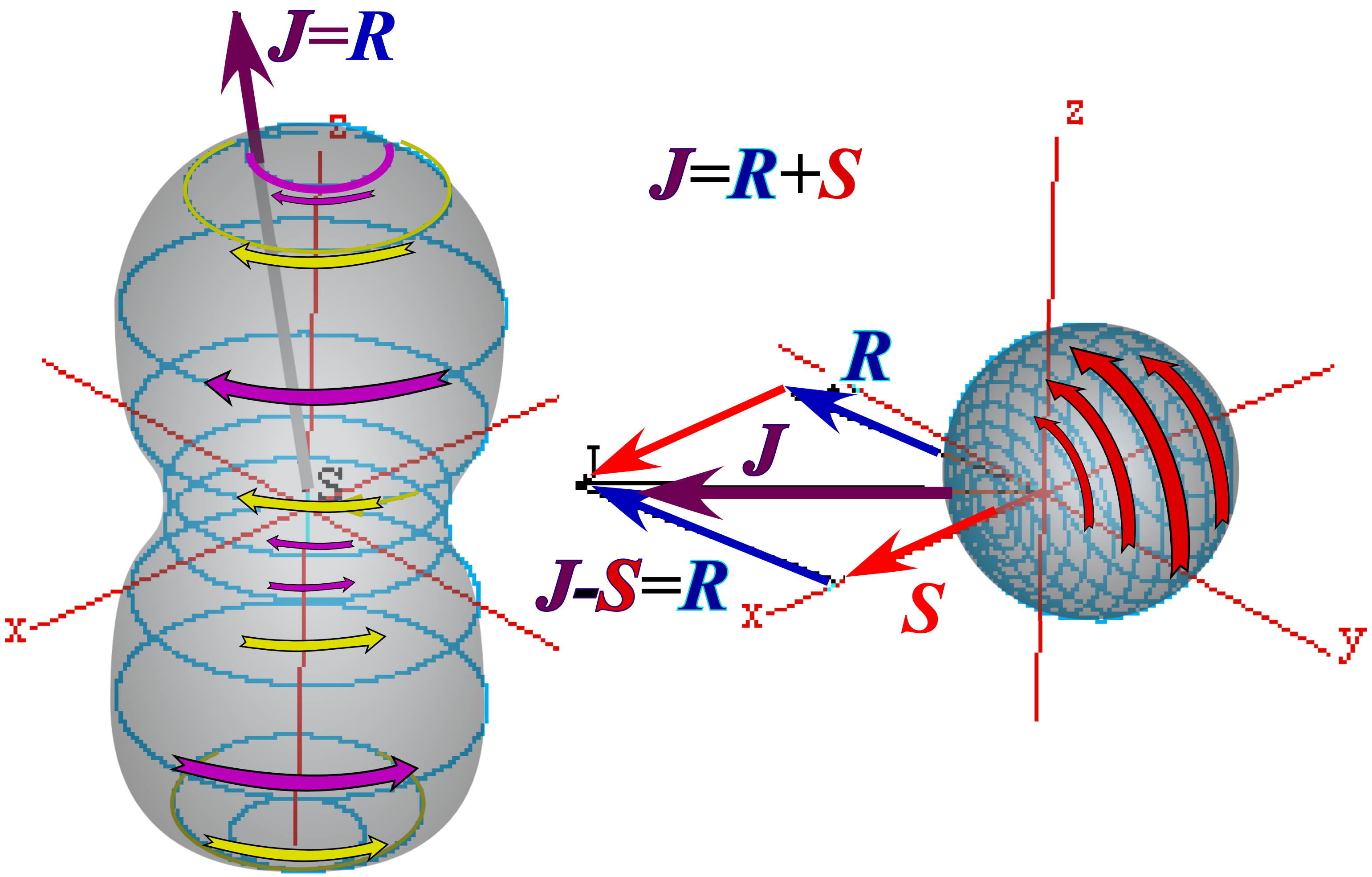
Prolate Rotor ***R*** **MINUS** *"Gyro" x-Spin* S_x



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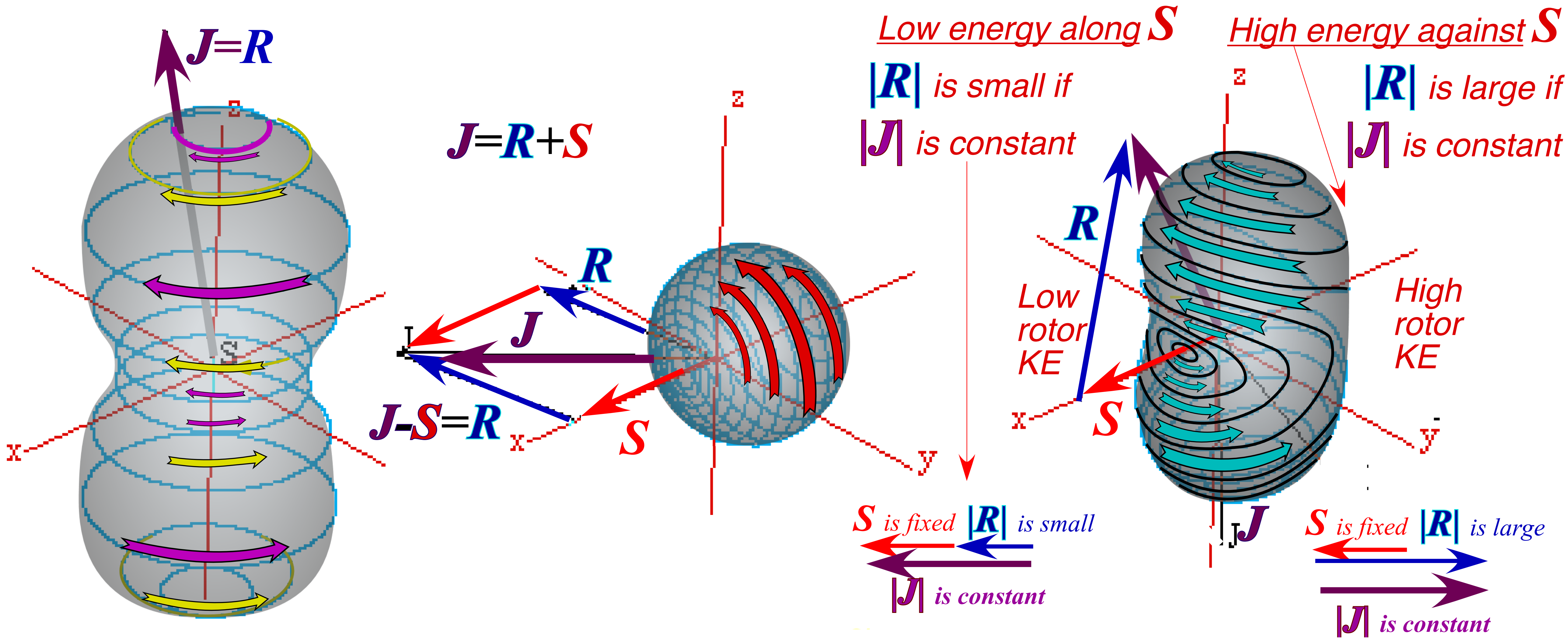

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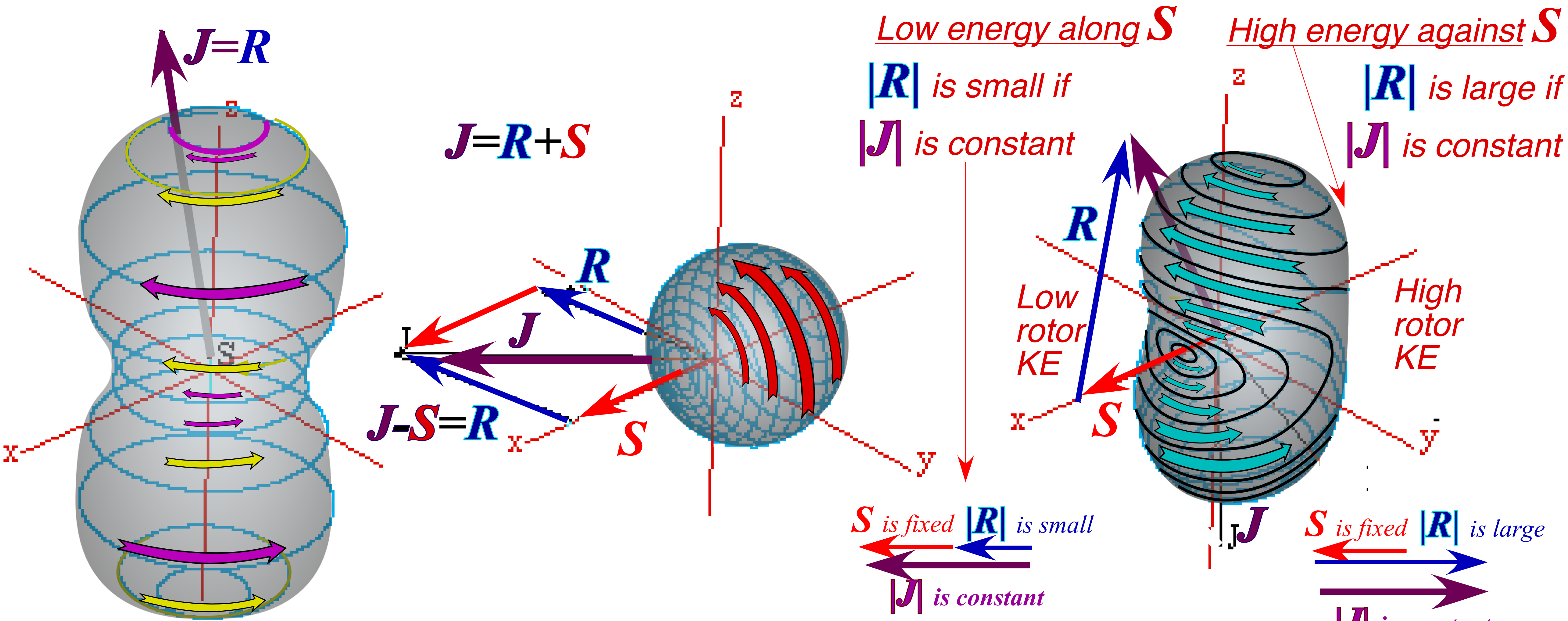
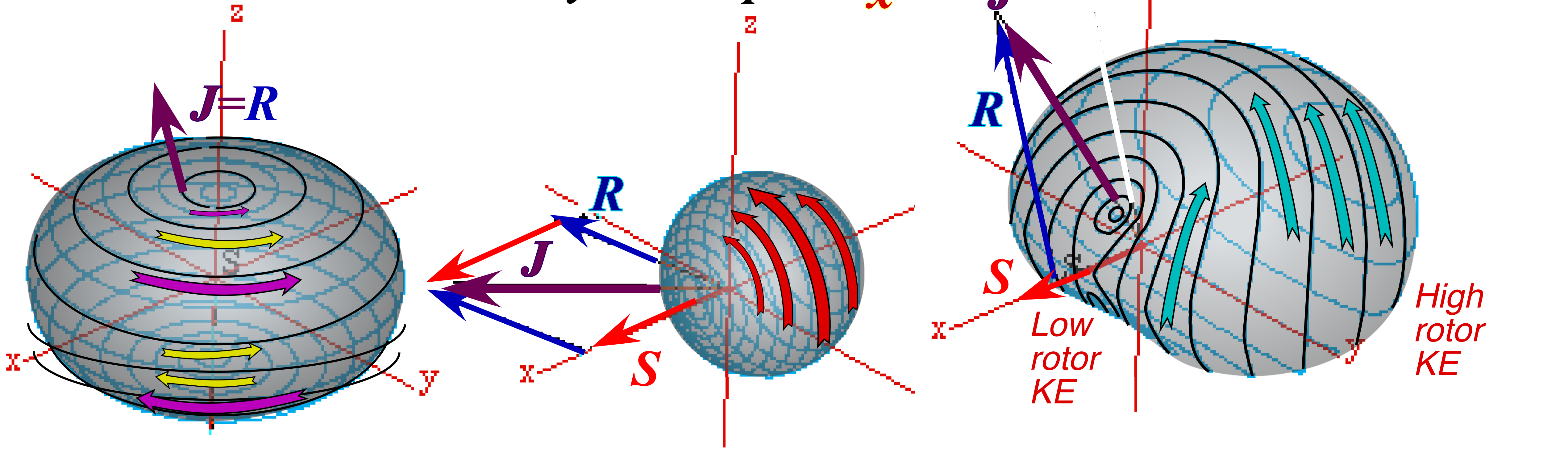
Prolate Rotor R MINUS "Gyro" x-Spin S_x



Oblate Rotor R MINUS "Gyro" x-Spin S_x



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CF_4 -υ_4/2υ_3 dyad

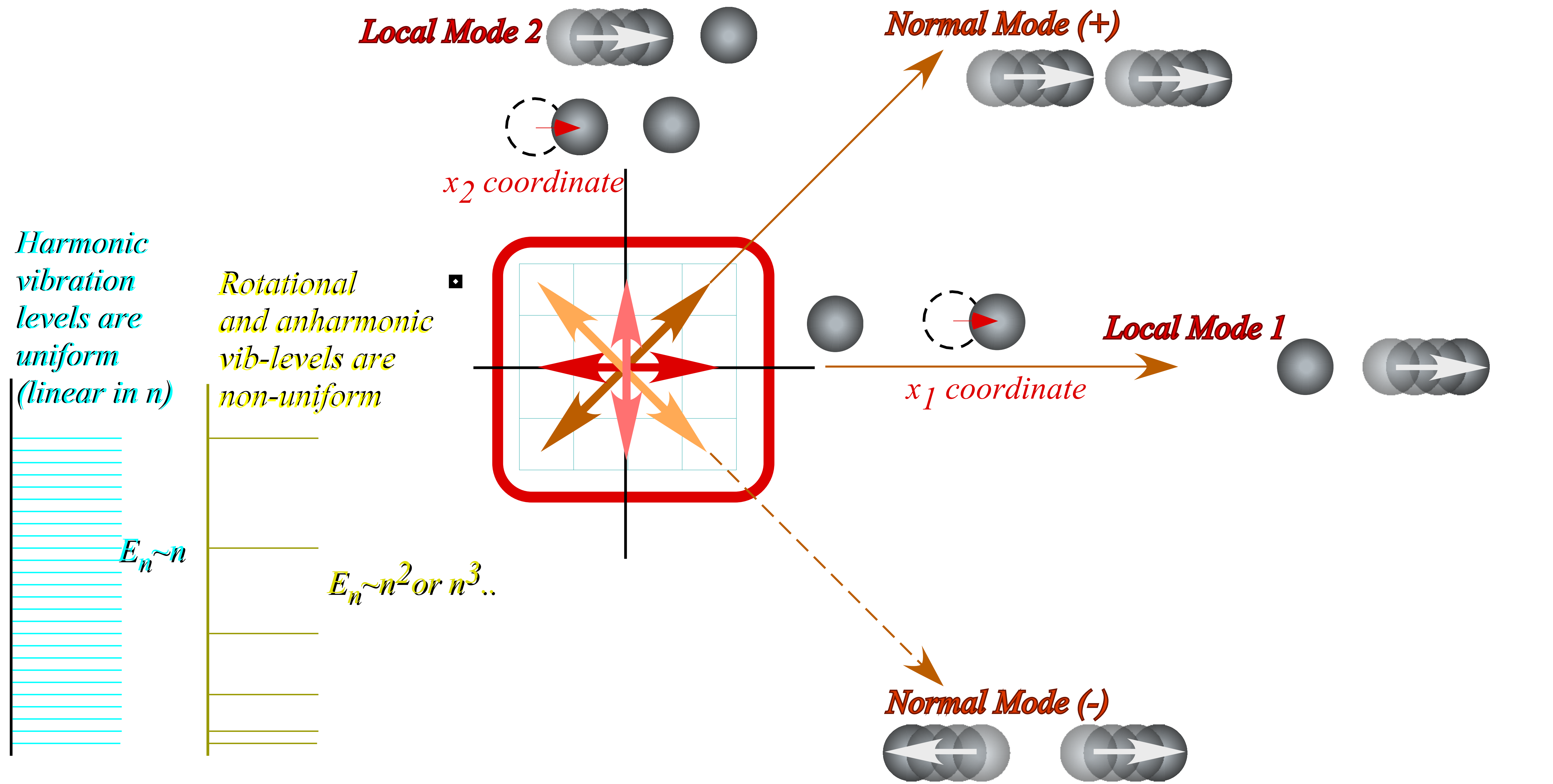
Recall Hamiltonian for 2D vibration has a (quasi-)spin theory, too

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

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

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

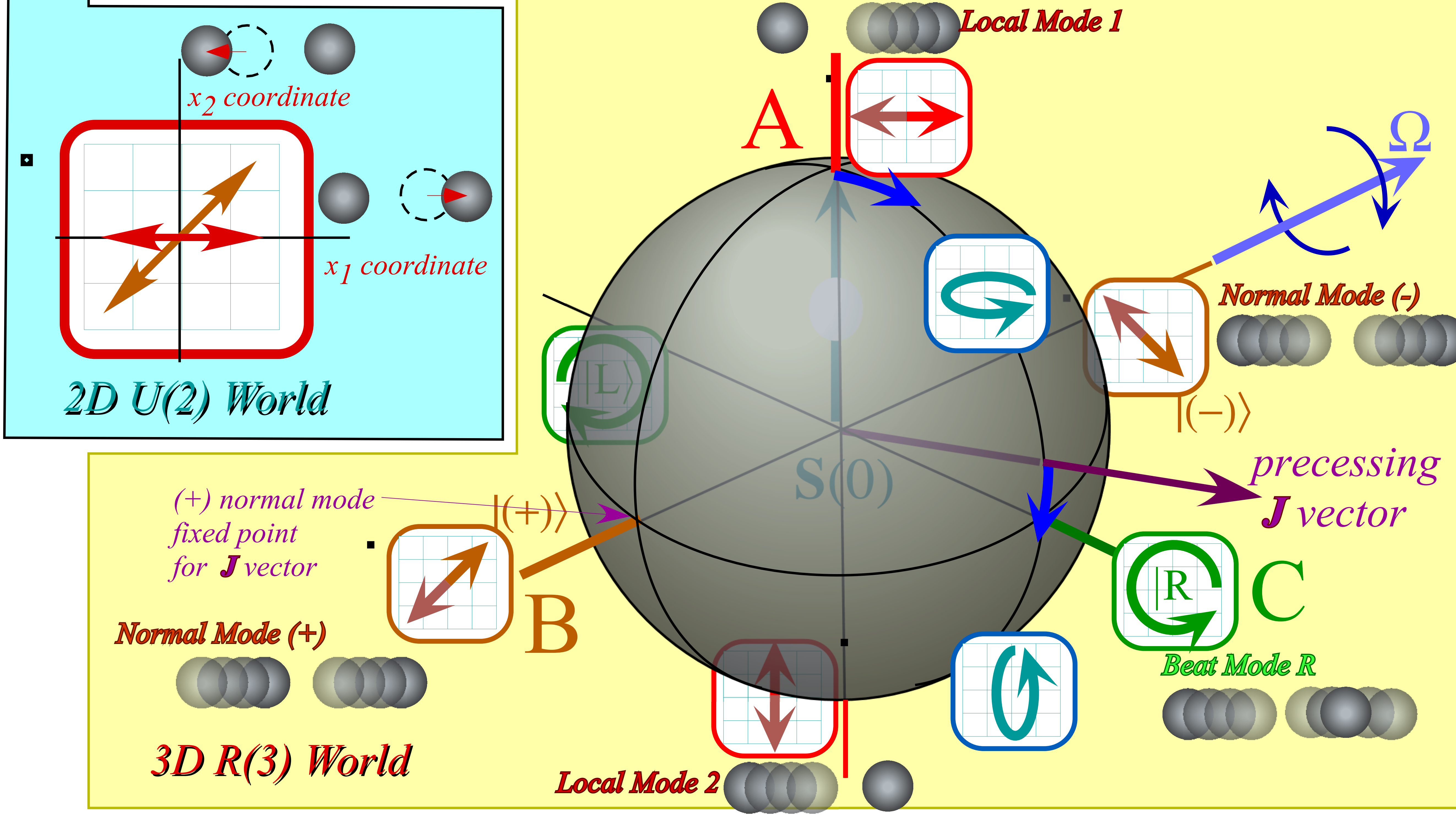
Higher-order $\mathbf{J}_m$ *or* $\mathbf{T}^1_m$ *terms are anharmonic parts of* $\mathbf{H}$



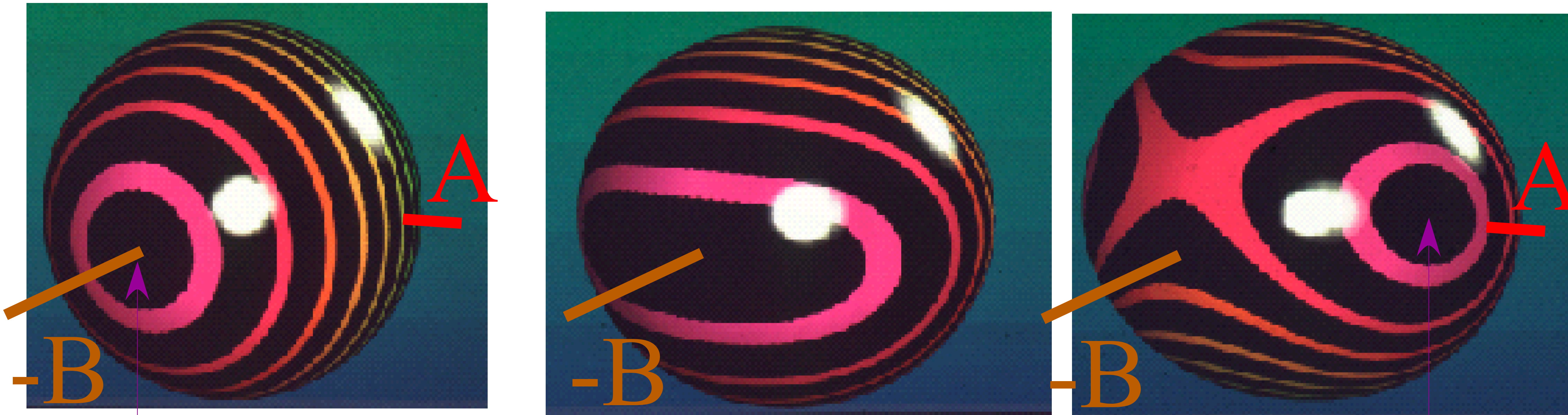
*(contd) 2D vibration are related to 3D rotation of "quasi-spin" **J***

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

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

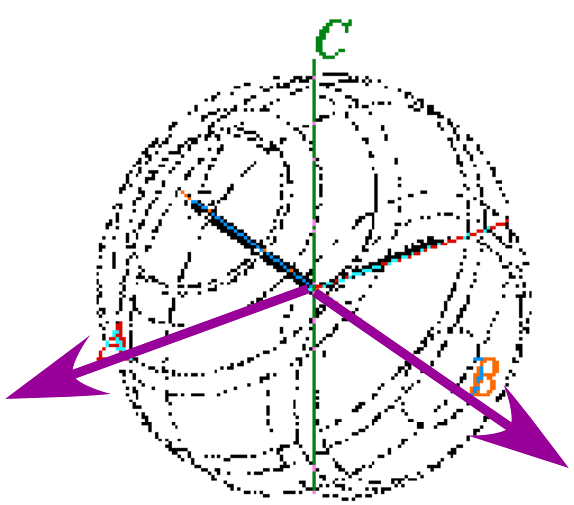


For higher J values, anharmonic terms grow to make stable local modes



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

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

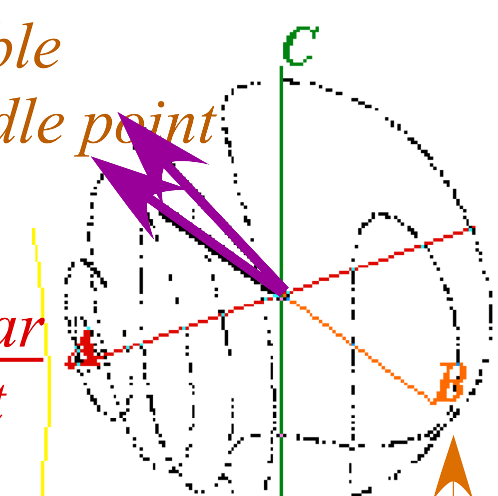


±B-*axes are* ***J***-*fixed points*

A-*axis is* <u>*NOT*</u> ***J***-*fixed point*

(Using *ColorU(2)* or the newer *BoxIt)*

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



A-*axis is* <u>*near*</u> ***J***-*fixed point*

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

Semiclassical Rotor analogy of Anharmonic Vibrator

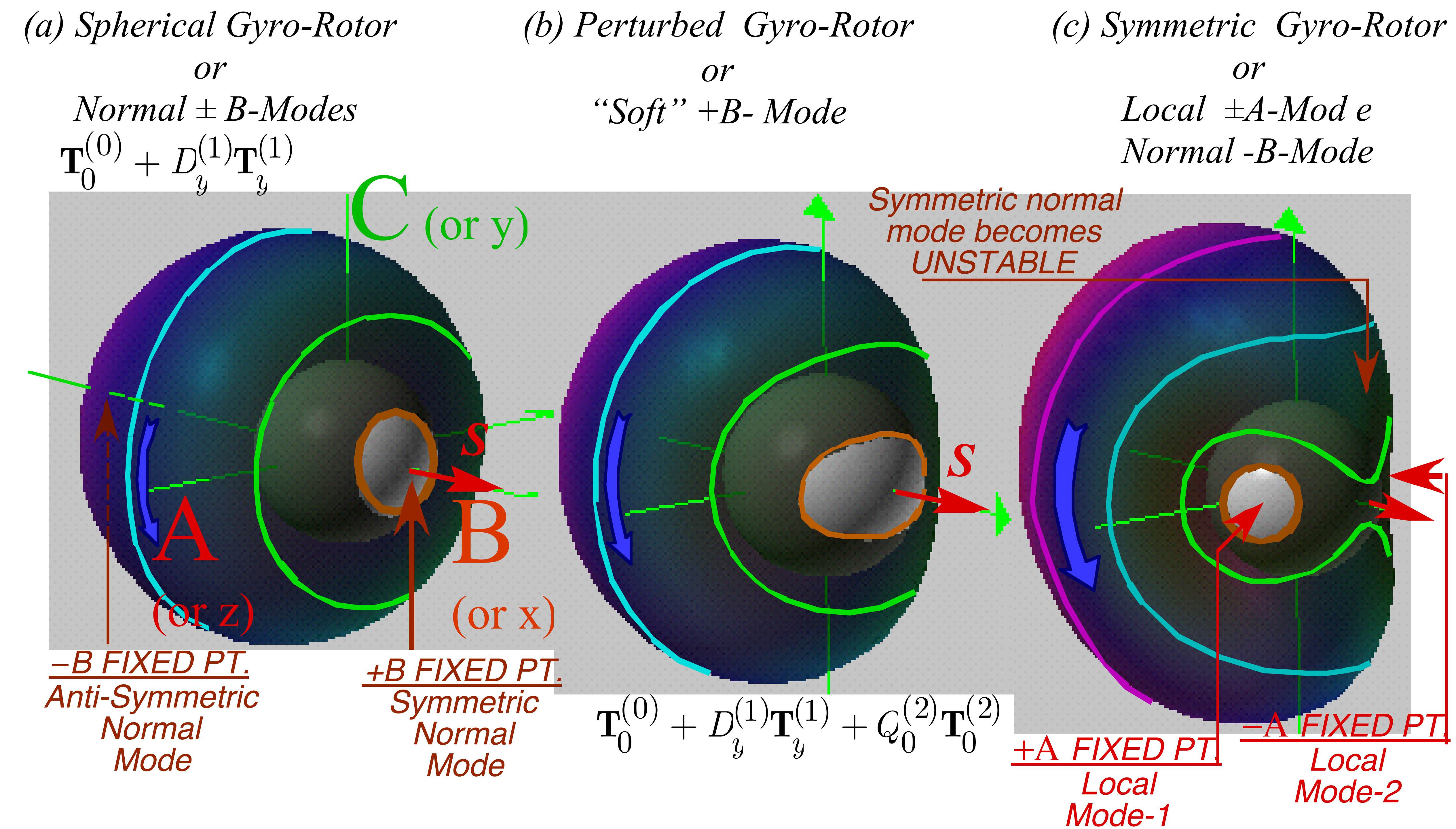


Fig. 25.5.3 A spherical gyro-rotor becomes asymmetric gyro-rotor by adding tensor $\mathbf{T}_0^2$ *to vector* $\mathbf{T}_y^1$.

From Ch. 25 of QTCA Unit 8.

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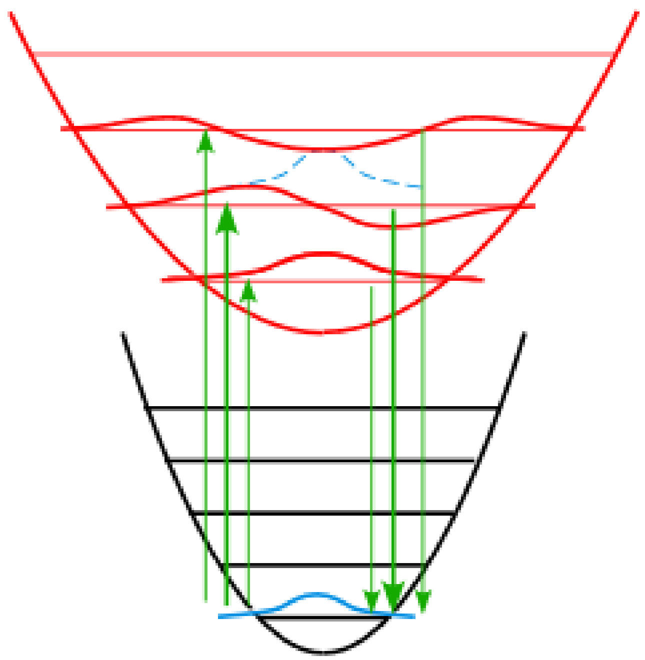
Analogies between energy surfaces of potential (PES) and rotation (RES)

Potenial Energy Surface (PES) Dynamics

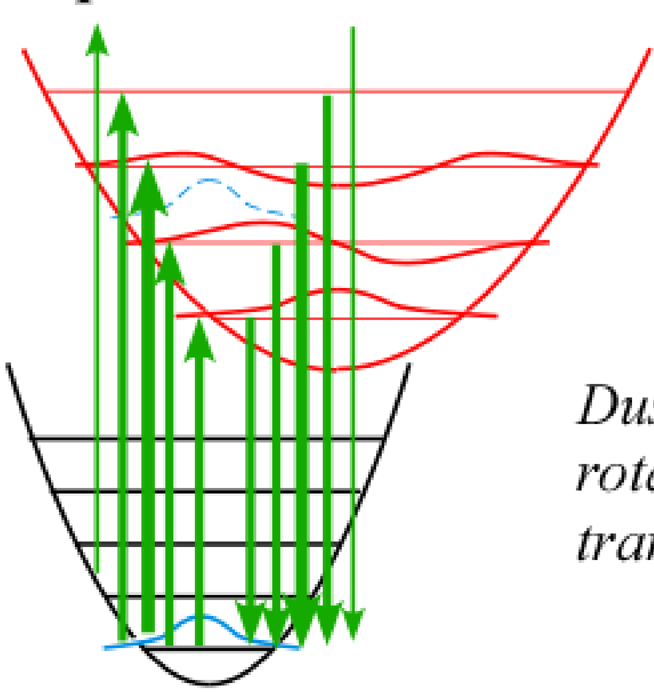
Inter-PES electronic transitions

Vibrational Franck-Condon effects

•Frequency mismatch of PES



•Shape or position mismatch of PES



Duschinsky rotation or translation

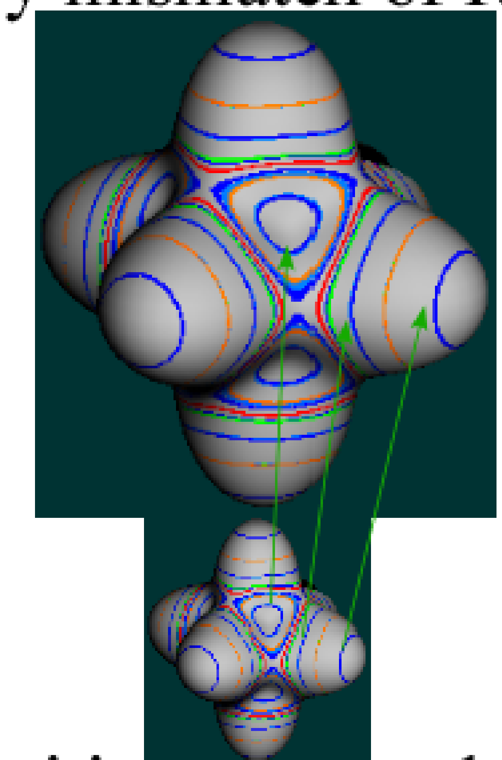
Analogy between Vibronic and Rovibronic

Rotation Energy Surface (RES) Dynamics

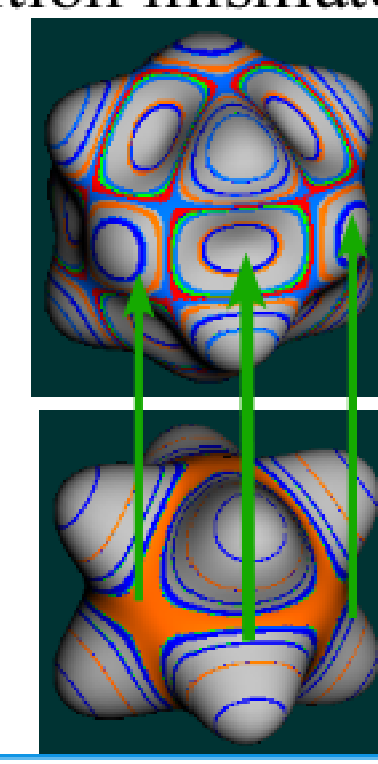
Inter-PES electronic transitions

Rotational "Franck-Condon" effects

•Frequency mismatch of RES



•Shape or position mismatch of RES



Analogies between energy surfaces of potential (PES) and rotation (RES)

Non-Born-Oppenheimer Surfaces

Strong vibration-electronic mixing

Jahn-Teller-Renner effects

•Multiple and variable conformer minima

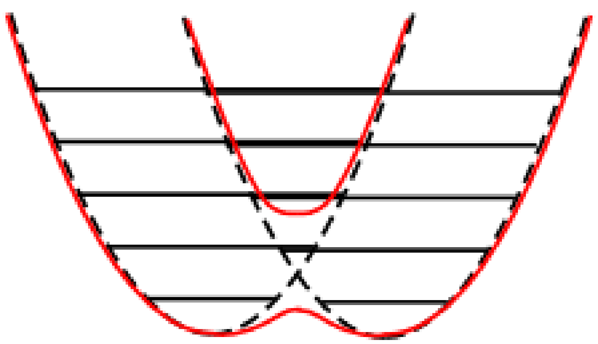
Rotation Energy Eigen-Surfaces (REES)

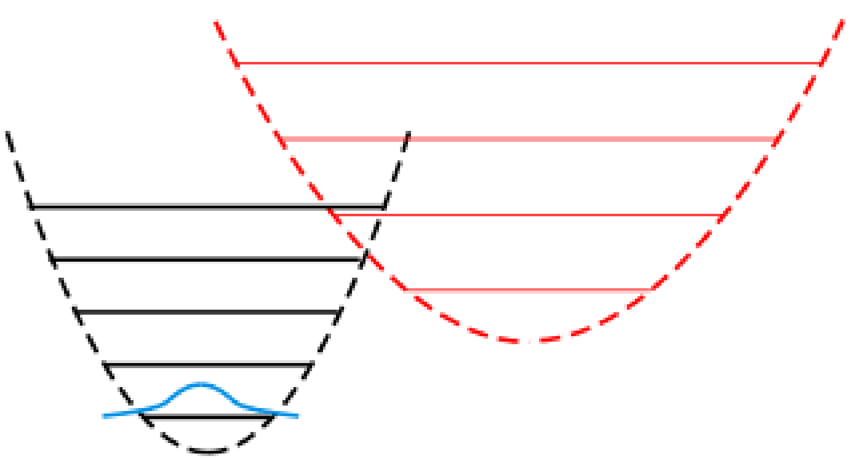
Inter-PES electronic transitions

Rotational JTR effects

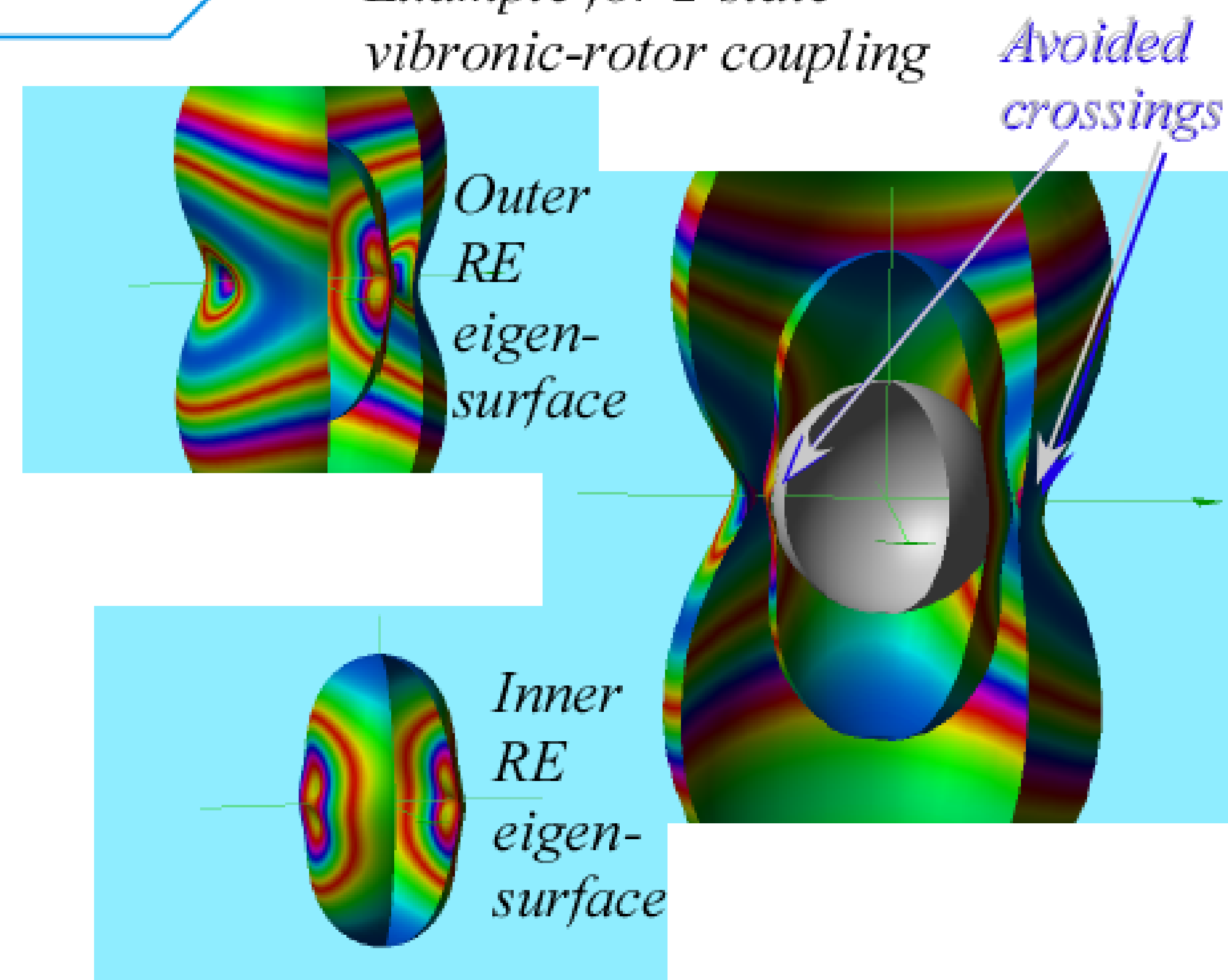
•Multiple and variable J-axes

Analogy between Vibronic and Rovibronic





Example for 2-state vibronic-rotor coupling



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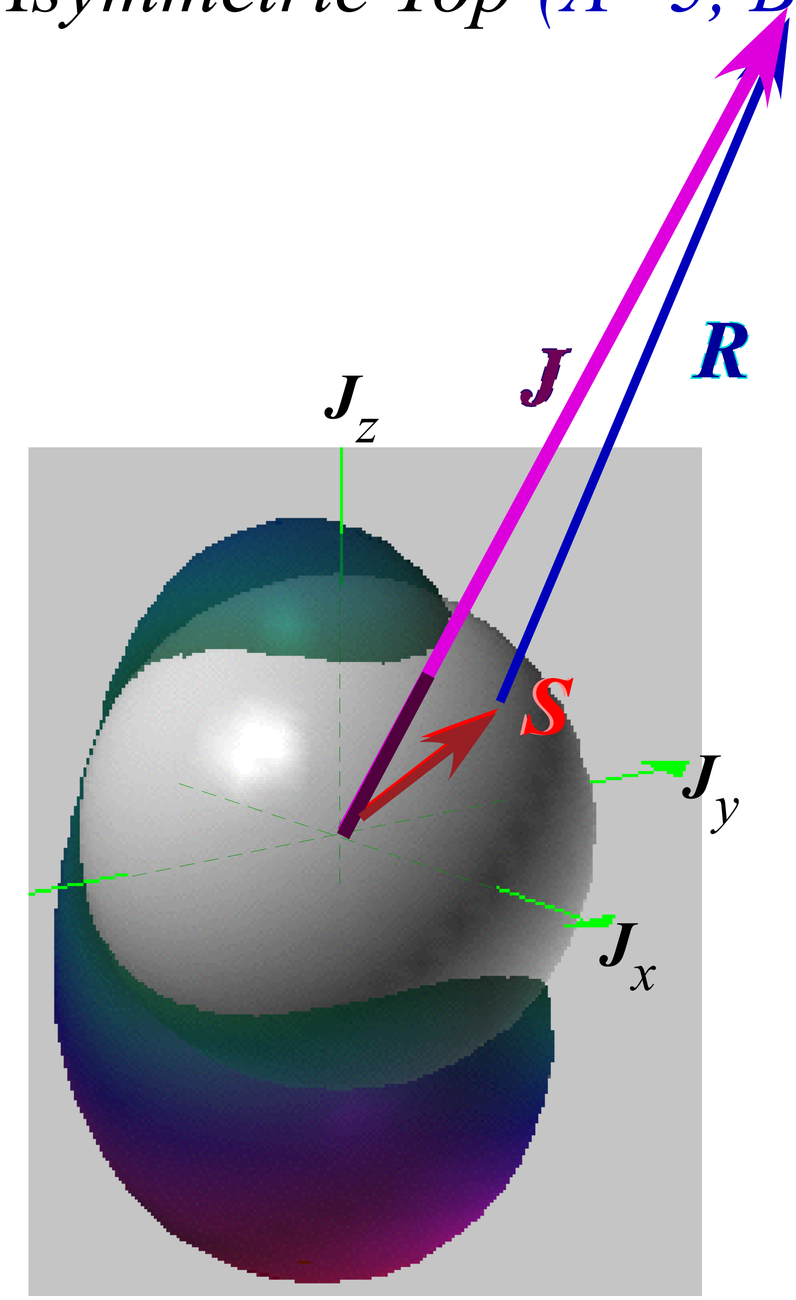
**ZIPP (Zero-Interaction-Potential-`Proximation*

Rotational energy eigenvalue surfaces (REES) Introducing "Sherman the Shark" ZIPPed*

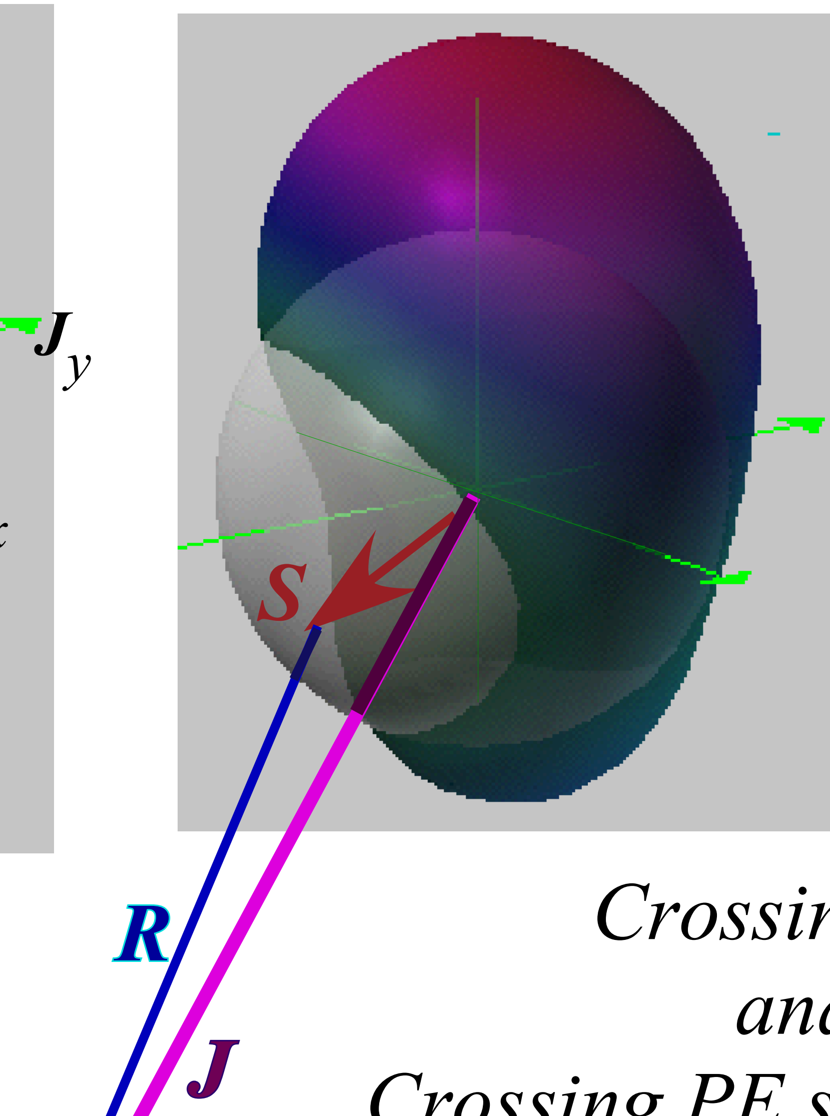
Spin gyro $S=(1,1,1)$ attached (ZIPPed) to
Asymmetric Top $(A=5, B=10, C=15)$

*ZIPP (Zero-Interaction-Potential-`Proximation

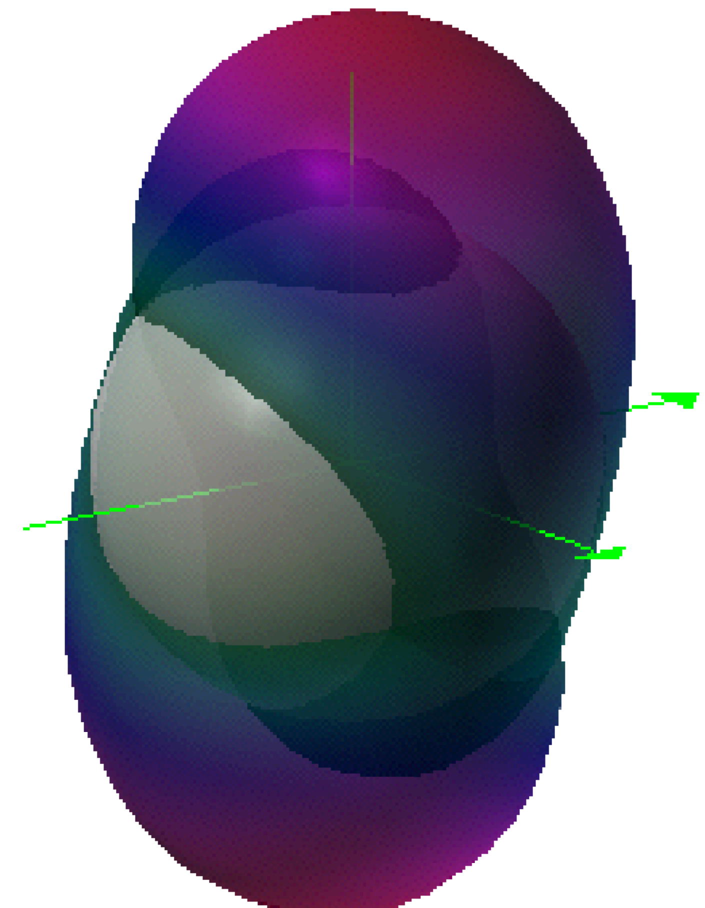


"Sherman" (The shark)

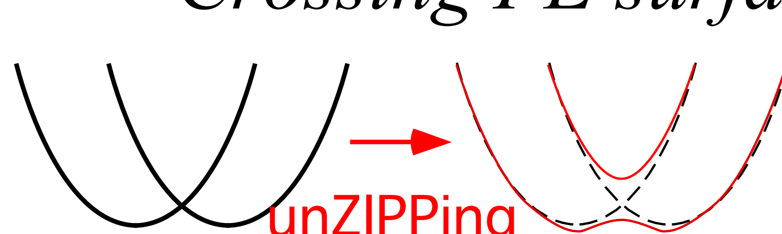
Time reversed
gyro $-S=(-1,-1,-1)$

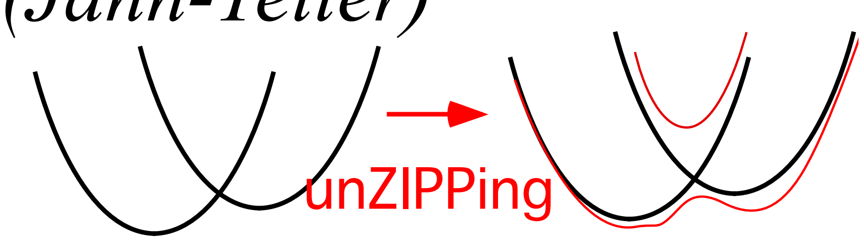


The two together (ZIPPed*)



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





Rotational energy eigenvalue surfaces (REES) Introducing "Sherman the Shark" unZIPPed

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

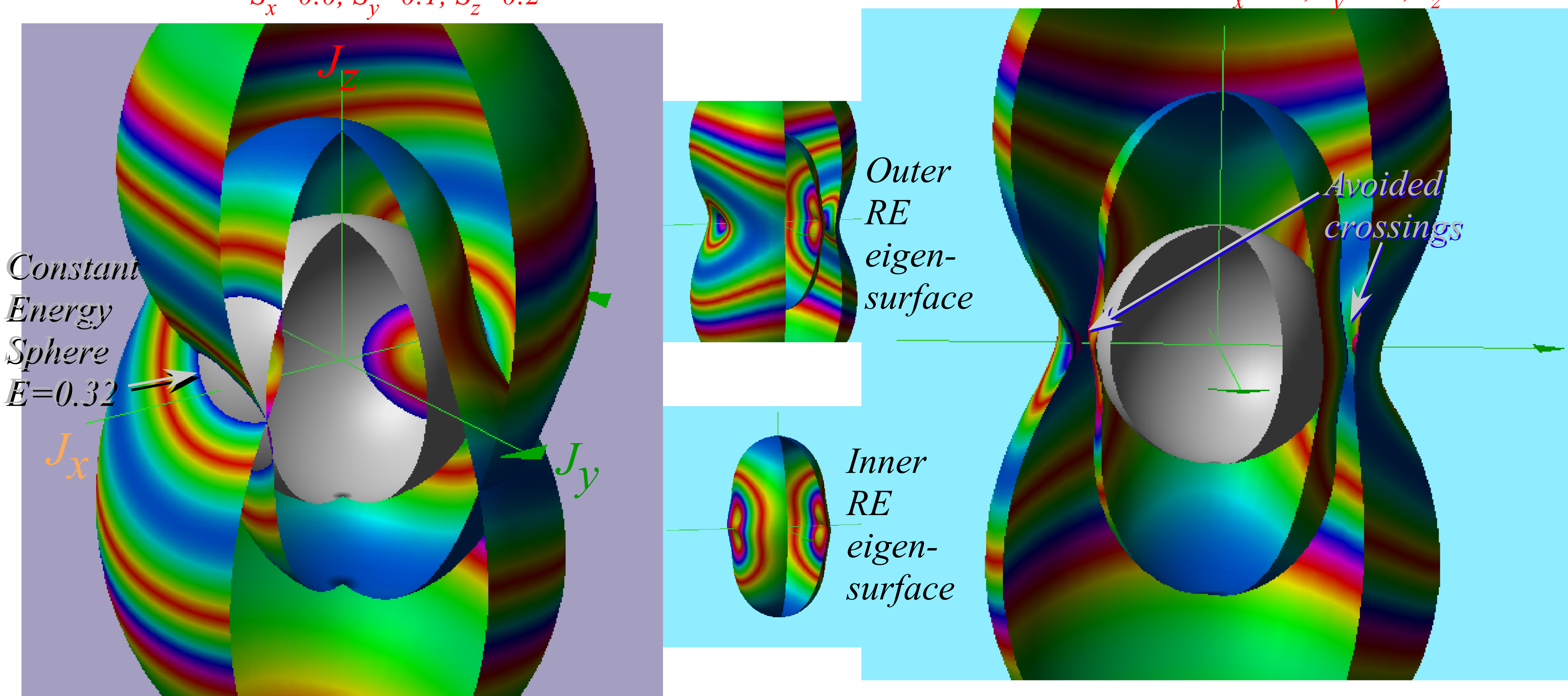
$$H = AJ_x^{\,2} + BJ_y^{\,2} + CJ_z^{\,2} + \ldots - 2AJ_xS_x - 2BJ_yS_y - 2CJ_zS_z + \ldots + (\text{more constant terms})$$

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*

$$\mathbf{H} = (AJ_x^{\,2} + BJ_y^{\,2} + CJ_z^{\,2})\mathbf{1} \ldots - AJ_x s_x \sigma_x \; - BJ_y s_y \sigma_y \; - CJ_z s_z \sigma_z + \ldots + \mathbf{1}(\text{more constant terms})$$

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 $A=0.2,\ B=0.8,\ C=1.4$
$s_x=0.0,\ s_y=0.1,\ s_z=0.2$



Rotational energy eigenvalue surfaces (REES) Other views of "Sherman the Shark" unZIPPed

$$H_{R,S(quantized)} = A\mathbf{J}_x^2 + B\mathbf{J}_y^2 + C\mathbf{J}_z^2 - A\mathbf{J}_x\boldsymbol{\sigma}_x - B\mathbf{J}_y\boldsymbol{\sigma}_y - C\mathbf{J}_z\boldsymbol{\sigma}_z + const.$$

$$= \begin{pmatrix} \mathrm{RE}_{\mathrm{rotor}} - JC\cos\beta & -AJ\cos\gamma\sin\beta - iBJ\sin\gamma\sin\beta \\ -AJ\cos\gamma\sin\beta + iBJ\sin\gamma\sin\beta & \mathrm{RE}_{\mathrm{rotor}} + JC\cos\beta \end{pmatrix}$$

where: $\mathrm{RE}_{\mathrm{rotor}} = J^2(A\cos^2\gamma\sin^2\beta + B\sin^2\gamma\sin^2\beta + C\cos^2\beta)$

(ZIPPed)*

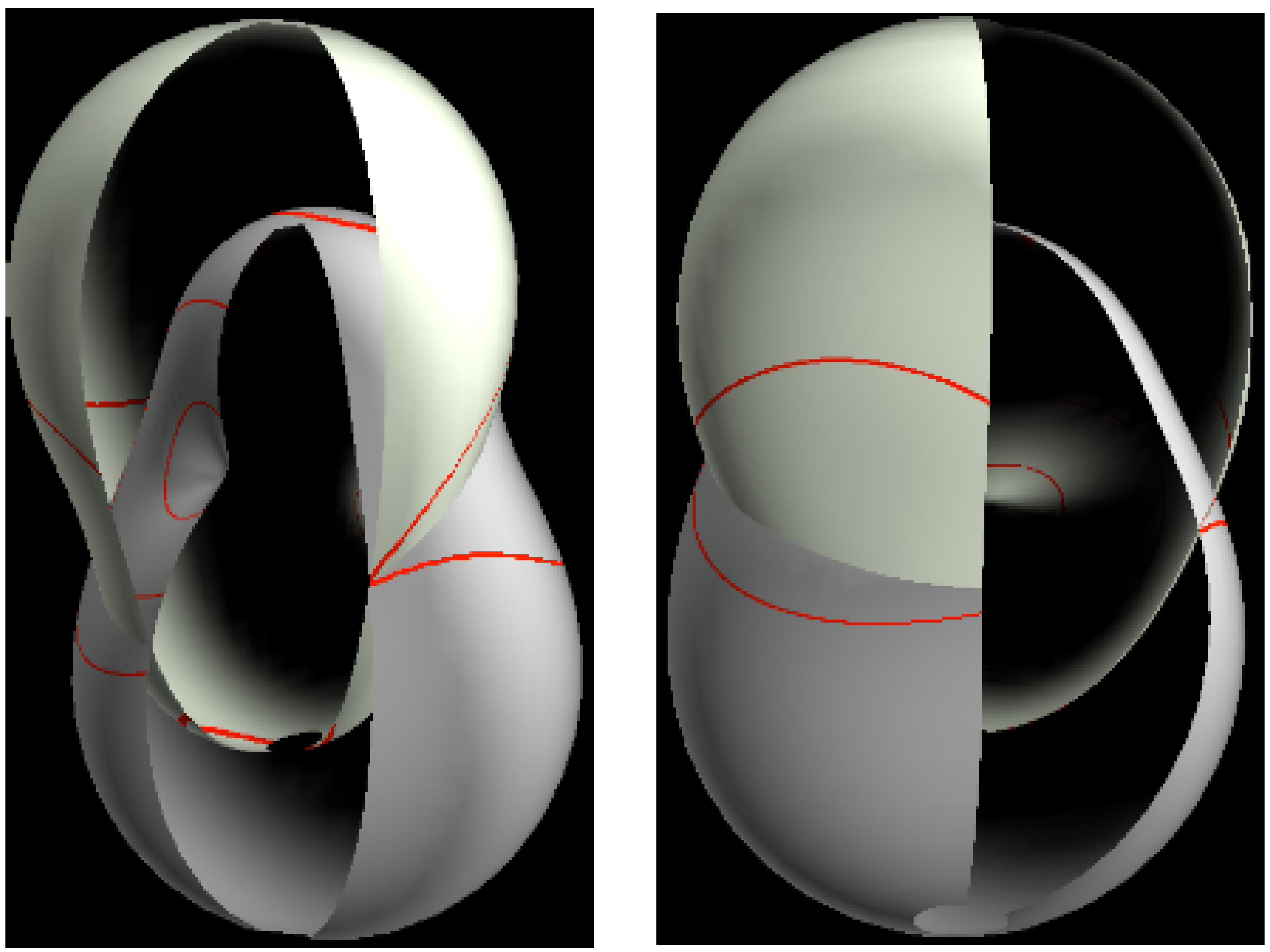


Fig. 25.5.5 (a) Views of classical gyro-rotor c-RES in Fig. 25.5.4 (a) based on (25.5.2).

(unZIPPed)*

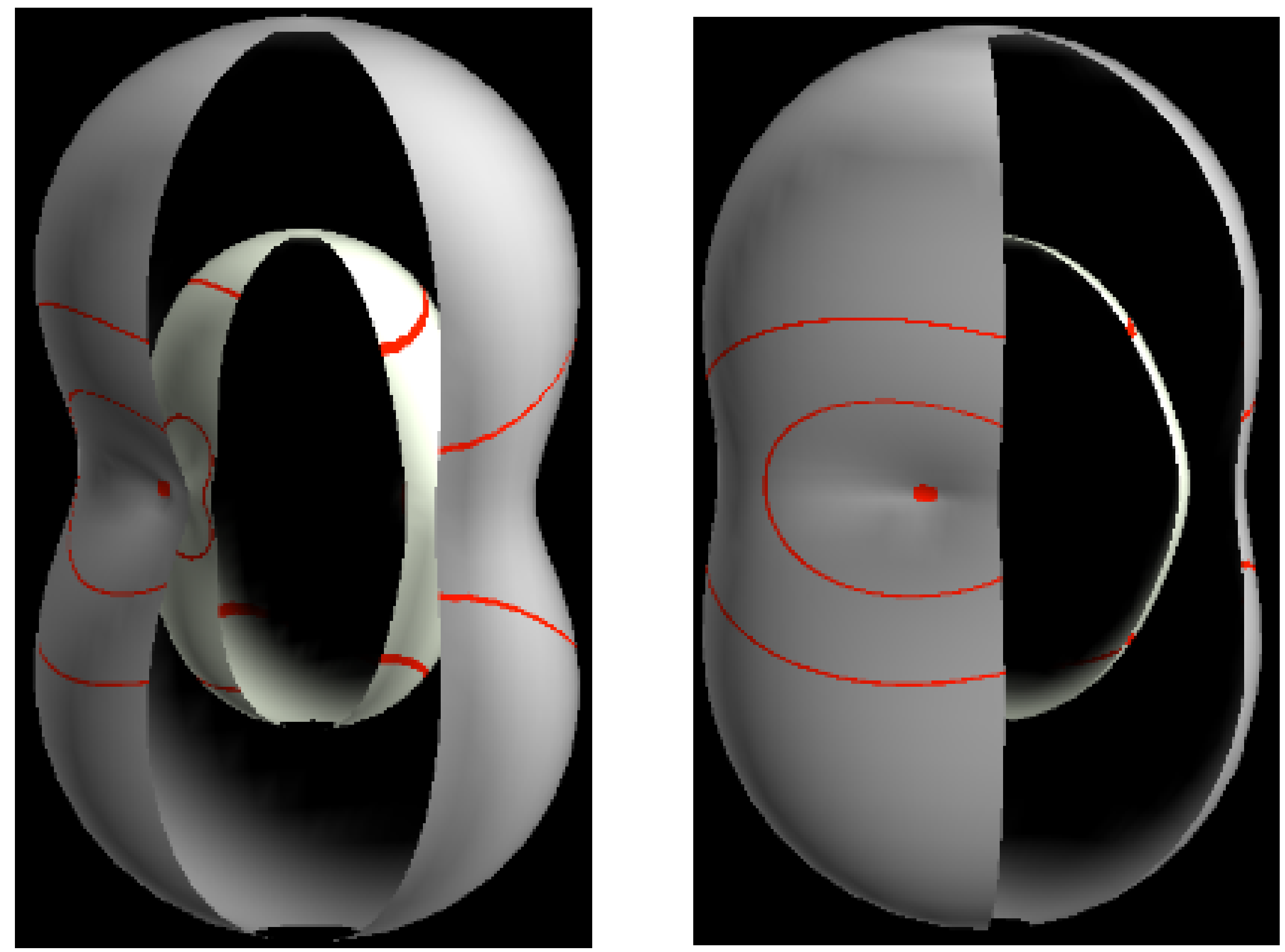


Fig. 25.5.5(b) Views of semi-classical gyro-rotor sc-RES plot of eigenvalues of (25.5.12) with **S**=σ/2.

**ZIPP (Zero-Interaction-Potential-`Proximation*

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CF_4 -υ_4/2υ_3 dyad

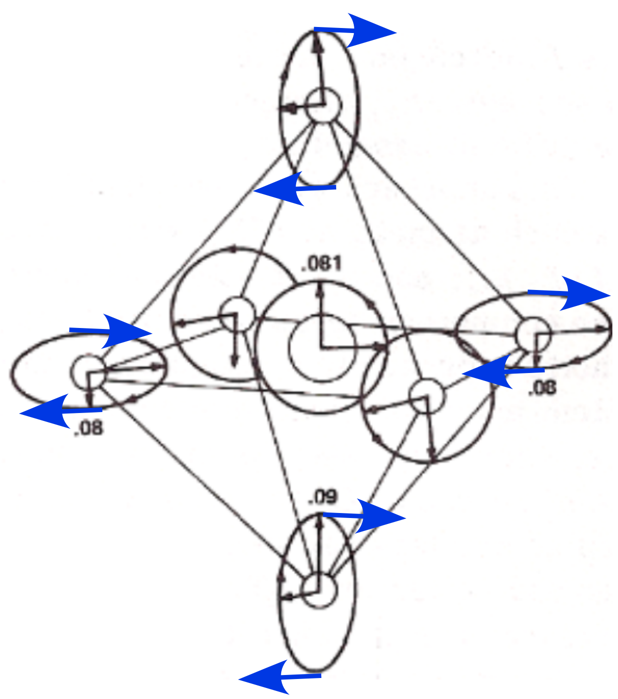
$$\langle H\rangle \sim \nu_{vib} + BJ(J+1) + \langle H^{Scalar\ Coriolis}\rangle + \langle H^{Tensor\ Centrifugal}\rangle + \langle H^{Tensor\ Coriolis}\rangle + \langle H^{Nuclear\ Spin}\rangle + \ldots$$

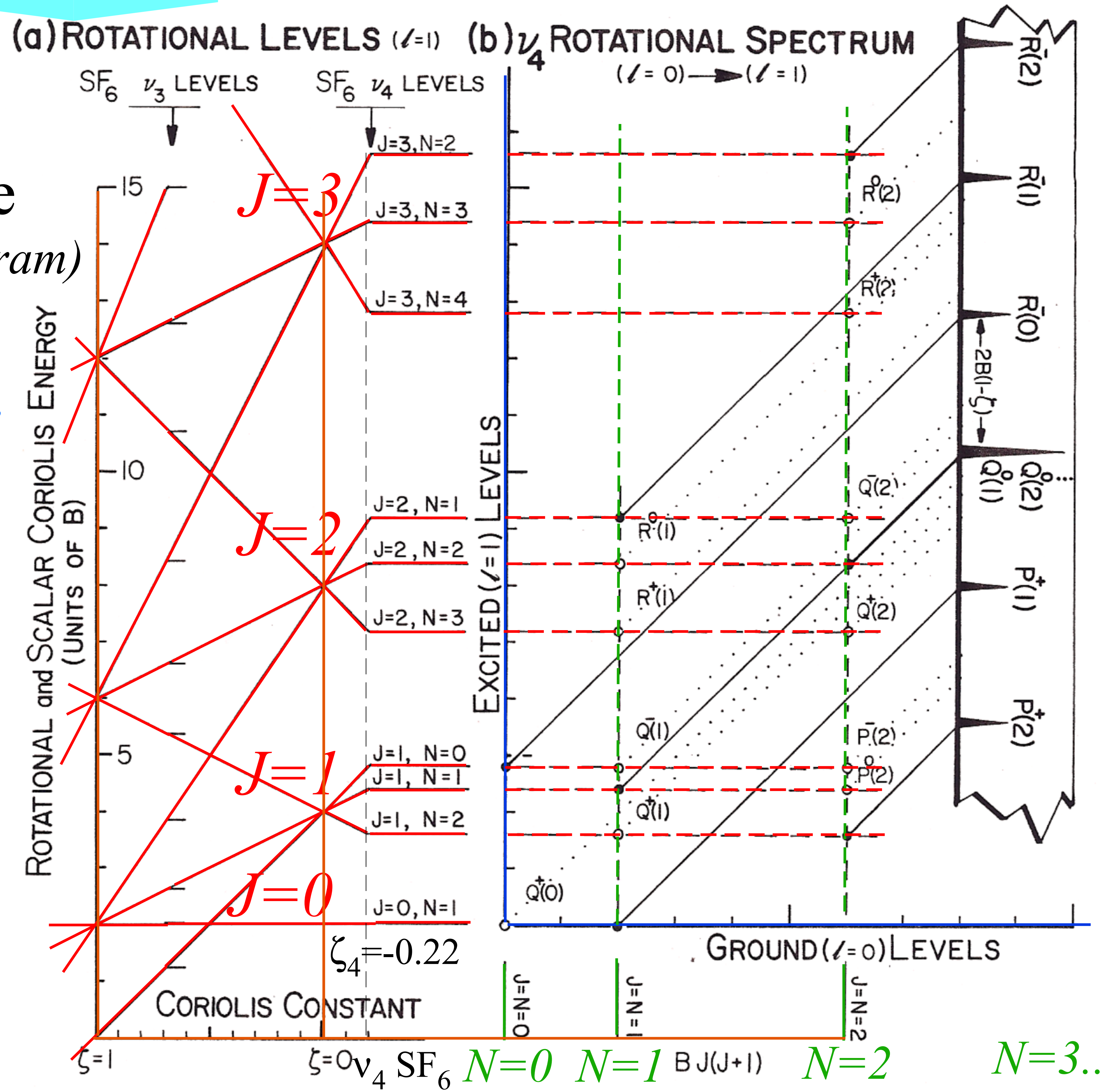
Summary of low-J (PQR) ro-vibe structure

(Using rovib. nomogram)

Review:

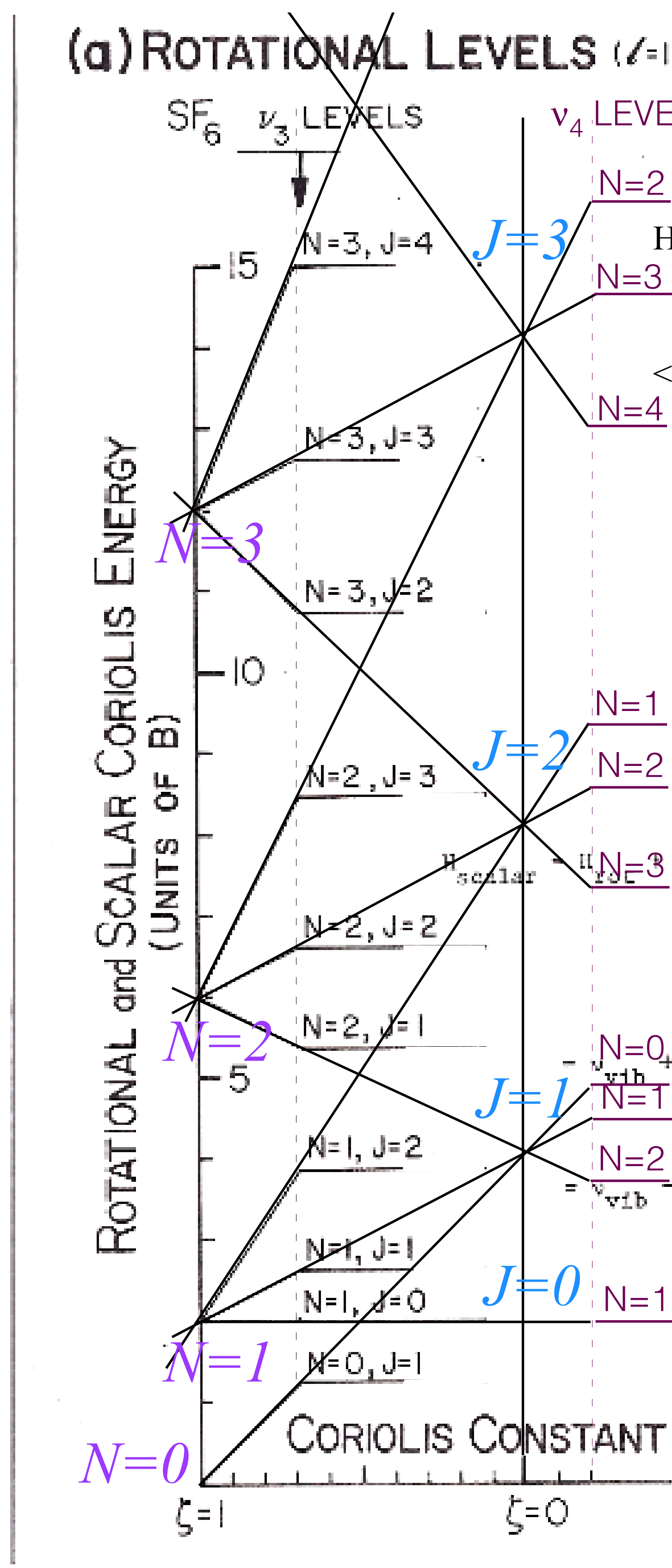
SF_6 Coriolis PQR structure





Review:

SF₆ Coriolis PQR structure



$$H^{Scalar\ Coriolis} = -B\zeta\, 2\mathbf{J}^{Total}\bullet\ell^{vibe}$$
$$= -B\zeta\,[\,\mathbf{J}^2-(\mathbf{J}^2-\ell)^2+\ell^2]$$
$$= -B\zeta\,[\,\mathbf{J}^2-\ \mathbf{N}^2\ +\ell^2]$$
$$\langle H^{Scalar\ Coriolis}\rangle = -B\zeta\,[\,J(J+1)-N(N+1)+\ell(\ell+1)]$$

$$J^{Total} = N^{Rotation} + \ell^{Vibration}$$

$$H_{scalar} = H_{rot} + \nu_{vib} - 2B\zeta\ \ J\cdot\ell$$

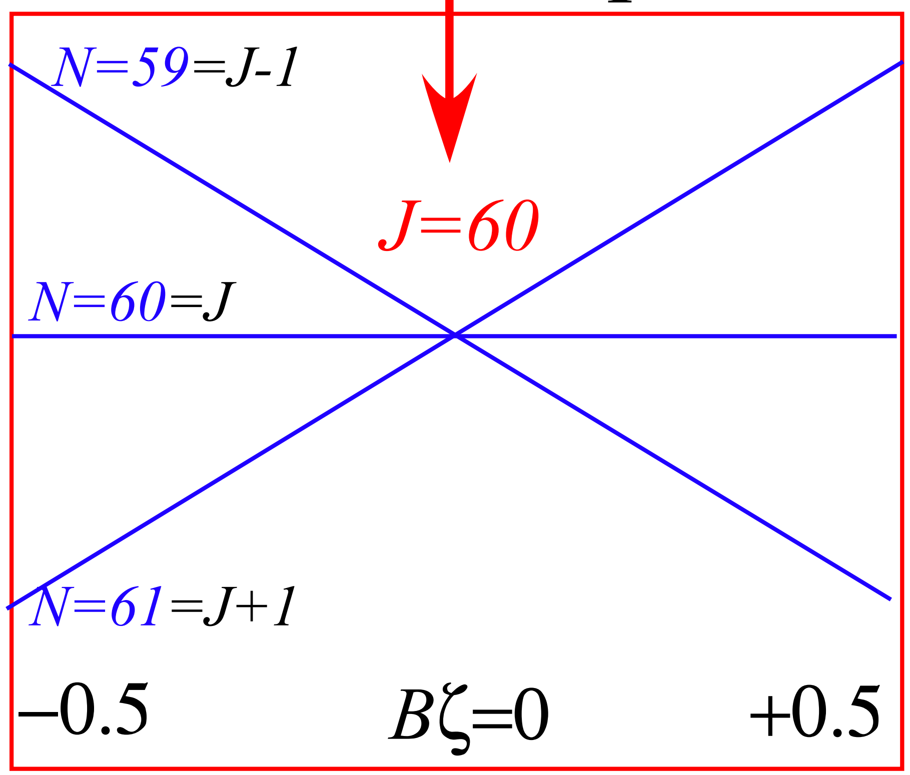
$$2J\cdot\ell = J^2-(J-\ell)^2+\ell^2 = J^2-N^2+\ell^2$$

$$= \nu_{vib} + BJ(J+1) - B\zeta[J(J+1) - N(N+1)+\ell(\ell+1)]$$

$$= \nu_{vib} - 2B\zeta + BN(N+1) + \begin{cases} 2B(1-\zeta)(N+1) & \text{for: } J=N+1 \\ 0 & \text{for: } J=N \\ -2B(1-\zeta)N & \text{for: } J=N-1 \end{cases}$$

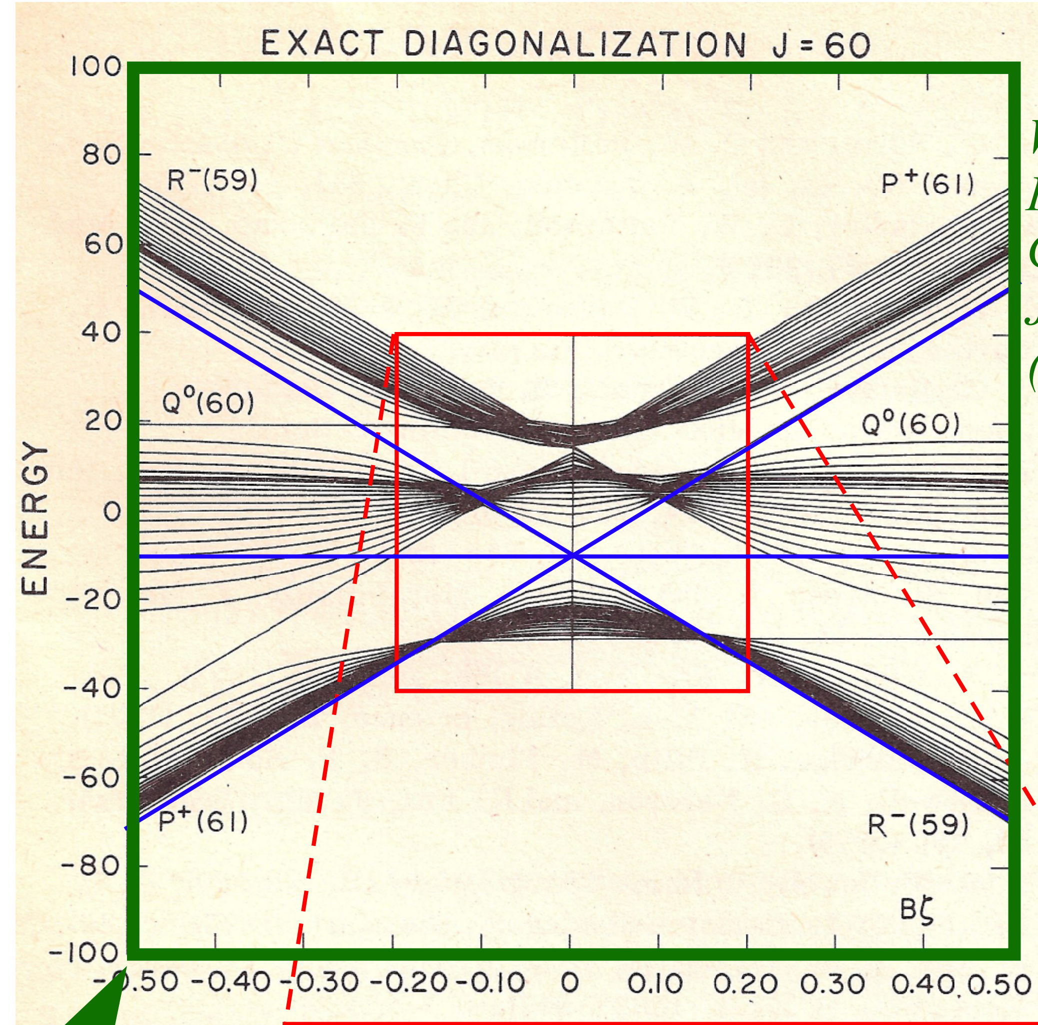
Recall scalar Coriolis *PQR* plots vs. $B\zeta$

Here is a *J=60* piece of it:

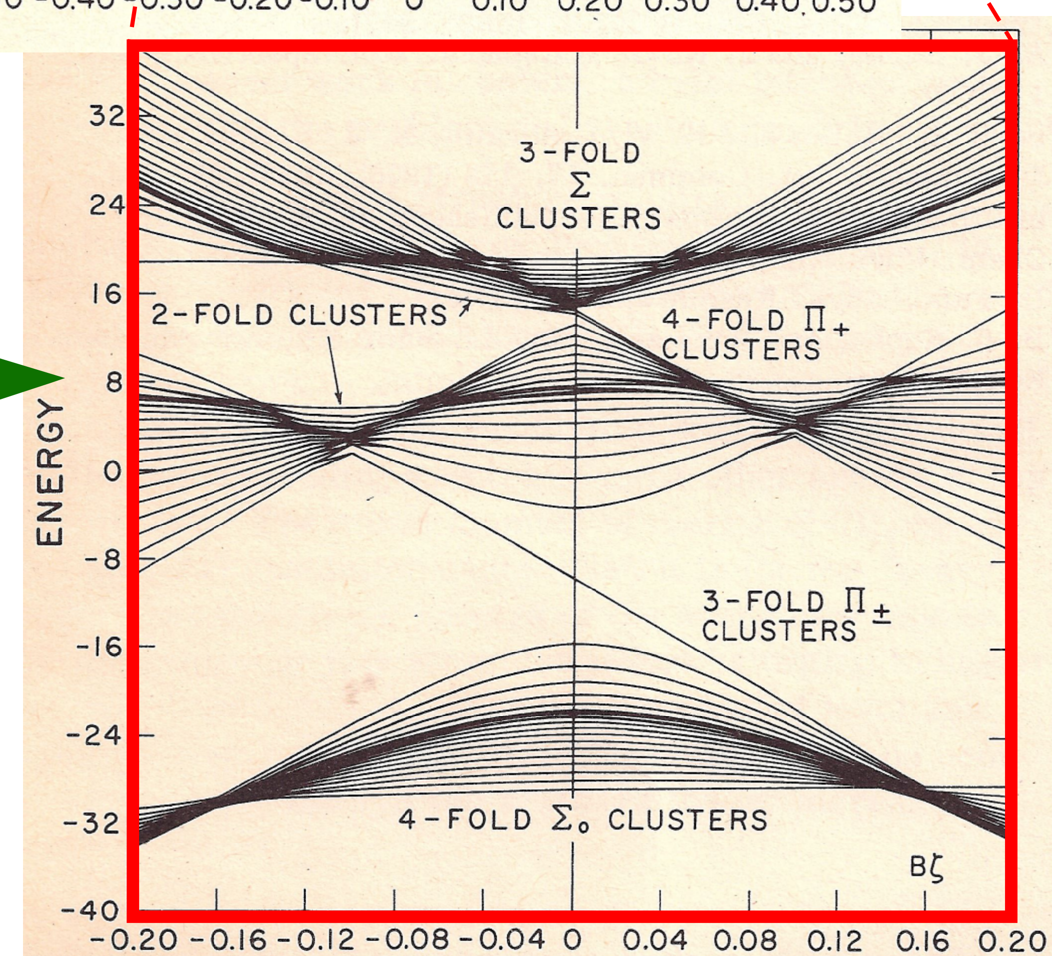


Now consider this plot with *tensor* Coriolis, too

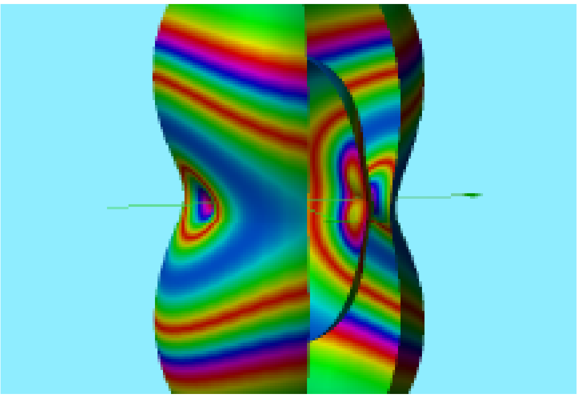
(Just 4th-rank $[2x2]^4$ tensor here.)



WGH, Patterson, Galbraith JCP 69, 4906 (1978)



How to display such monstrous avoided cluster crossings:
REES: *Rotational Energy Eigenvalue Surfaces*



Vibration (or vibronic) momentum ℓ retains its quantum representaion(s).

For $\ell=1$ that is the usual *3-by-3* matrices.

Rotational momentum *J* is treated semi-classically. $|J|=\sqrt{J(J+1)}$

Usually **J** is written in Euler coordinates: $J_x=|J|\cos\gamma\sin\beta$, etc.

Plot resulting H-matrix eigenvalues *vs.* classical variables.

($\ell=1$) *3-by-3* H-matrix e-values are polar plotted *vs.* azimuth γ and polar β.

REES for high-J Coriolis spectra in SF_6

Body-ΣΠ±-Basis

$|\Pi+\rangle \quad |\Sigma+\rangle \quad |\Pi-\rangle$

$$\langle H\rangle = (\nu_3 + B|J|^2)\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix} + 2B\zeta|J|\begin{pmatrix}\cos\beta & \frac{1}{\sqrt{2}}e^{-i\gamma}\sin\beta & 0\\ \frac{1}{\sqrt{2}}e^{i\gamma}\sin\beta & 0 & \frac{1}{\sqrt{2}}e^{-i\gamma}\sin\beta \\ 0 & \frac{1}{\sqrt{2}}e^{i\gamma}\sin\beta & -\cos\beta\end{pmatrix}$$

$$+2t_{224}|J|^2\begin{pmatrix}3\cos^2\beta-1 & -\sqrt{8}e^{-i\gamma}\sin\beta\cos\beta & \sin^2\beta\,(6\cos2\gamma+i4\sin2\gamma)\\ -\sqrt{8}e^{i\gamma}\sin\beta\cos\beta\ \ 0 & -6\cos^2\beta+2 & \sqrt{8}e^{-i\gamma}\sin\beta\cos\beta\\ \sin^2\beta\,(6\cos2\gamma-i4\sin2\gamma) & \sqrt{8}e^{i\gamma}\sin\beta\cos\beta & 3\cos^2\beta-1\end{pmatrix}$$

Lab-PQR-Basis

$|P\rangle|Q\rangle|R\rangle$

$$\langle H\rangle = (\nu_3 + B|J|^2)\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix} + 2B\zeta|J|\begin{pmatrix}+1&0&0\\0&0&0\\0&0&-1\end{pmatrix}$$

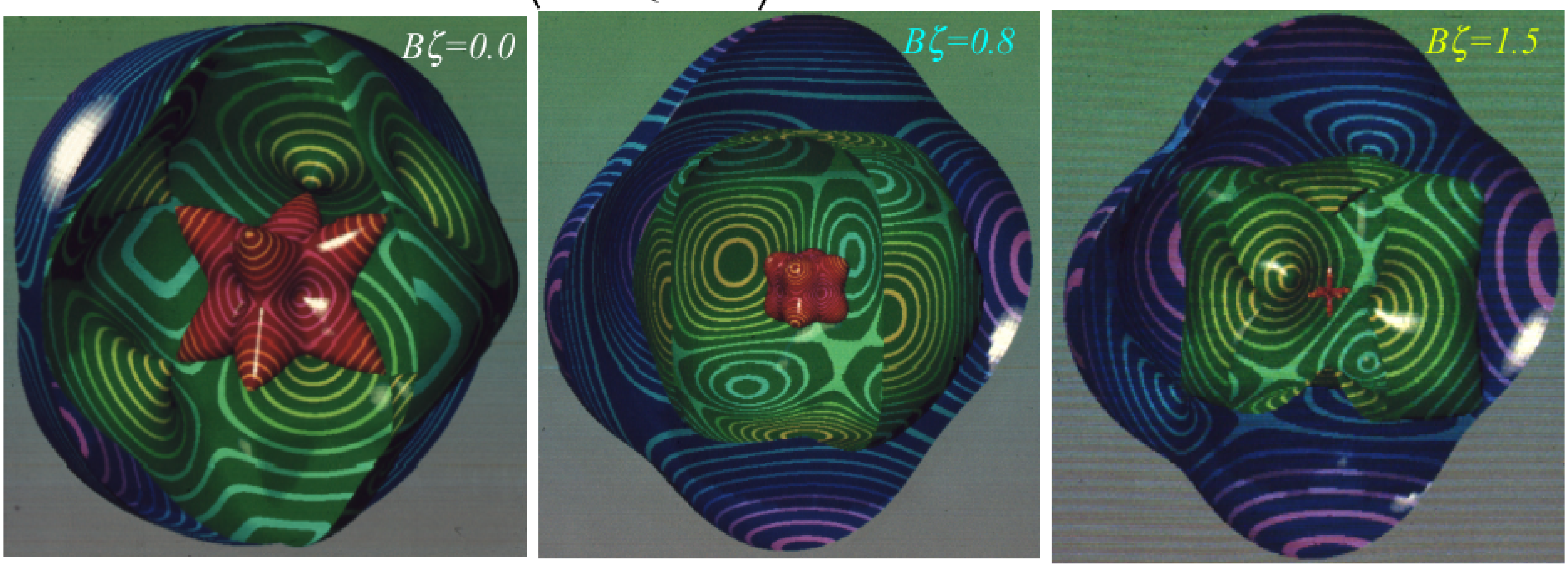
(Either basis should give same REES)

$$+2t_{224}|J|^2\begin{pmatrix}H_{PP} & H_{PQ} & H_{PR}\\ H^*_{PQ} & H_{QQ} & H_{QR}\\ H^*_{RP} & H^*_{QR} & H_{RR}\end{pmatrix}$$

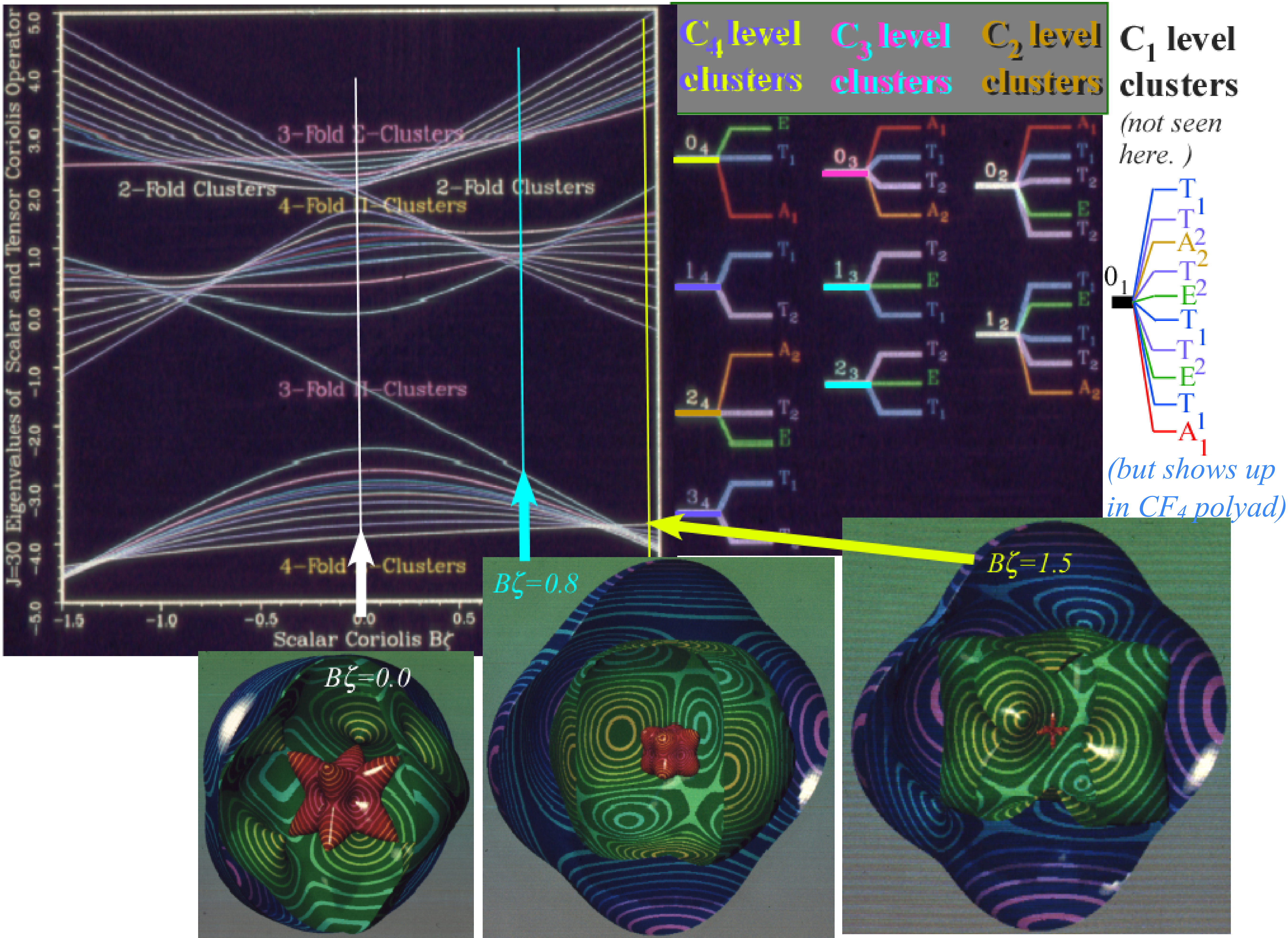
$$H_{PP}=(35\cos^4\beta-30\cos^2\beta+5\sin^2\beta\sin4\gamma+5)/4=H_{RR}$$

$$H_{PQ}=5\sin\beta(7\cos^2\beta-3\cos\beta-\sin^2\beta(\cos\beta\cos4\gamma+i\sin4\gamma))/\sqrt{8}=H_{QR}$$

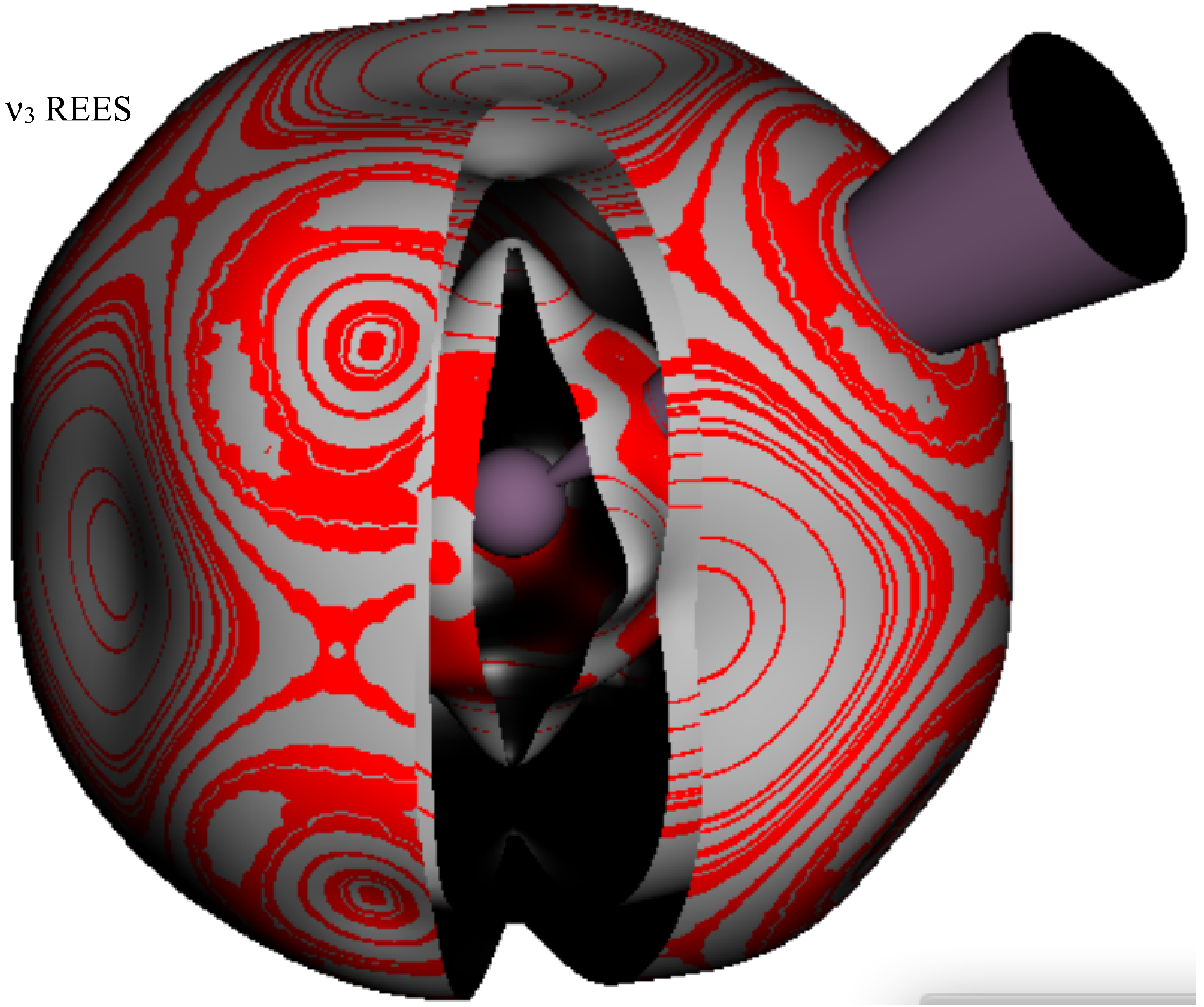
$$H_{PQ}=5(-7\cos^4\beta+8\cos^2\beta+(1-\cos^4\beta)\cos4\gamma+2i\cos\beta\sin^2\beta\sin4\gamma-1)/4$$



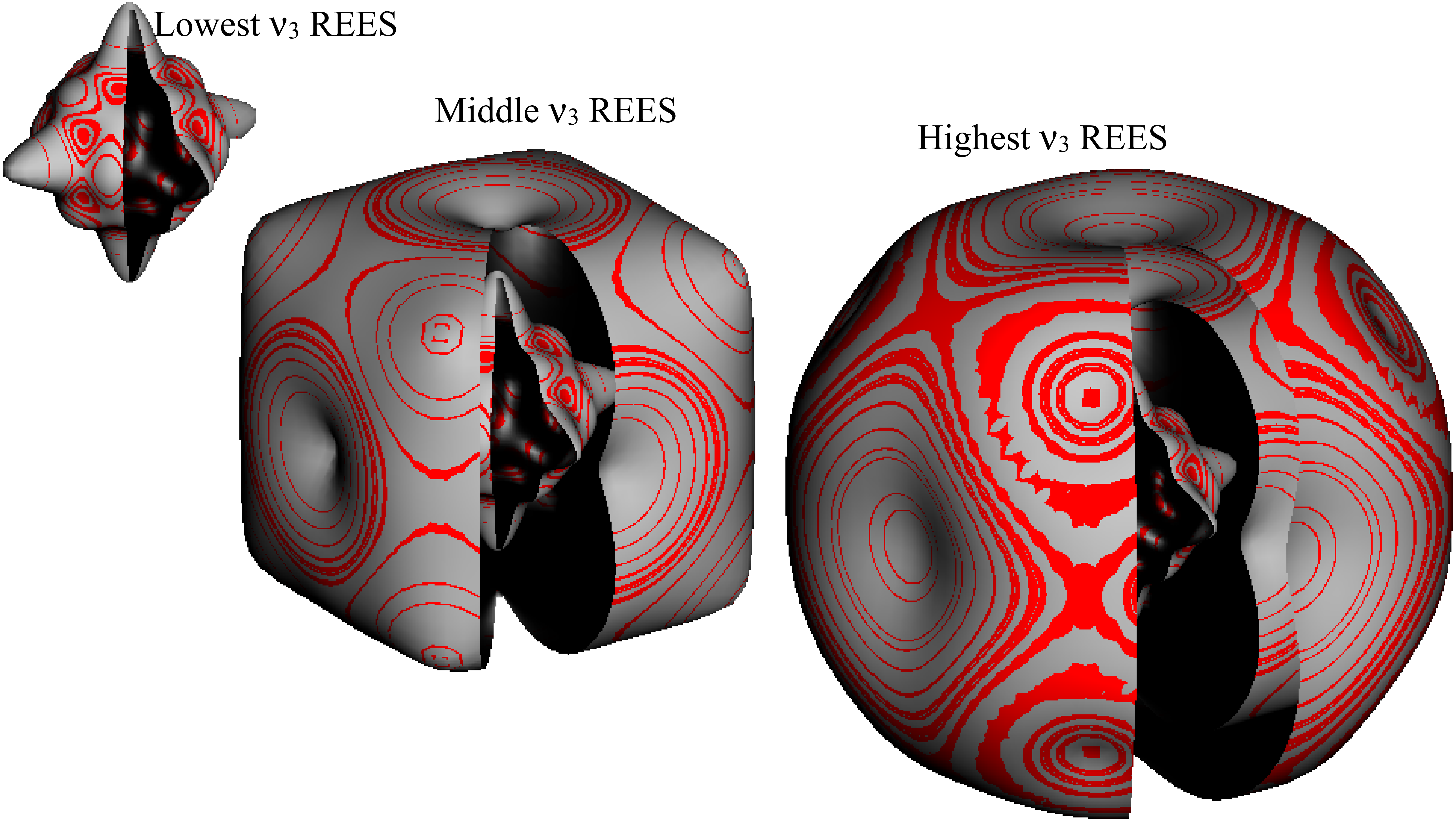
REES for high-J Coriolis spectra in SF_6



REES for high-J Coriolis spectra in υ_3 CF_4



REES for high-J Coriolis spectra



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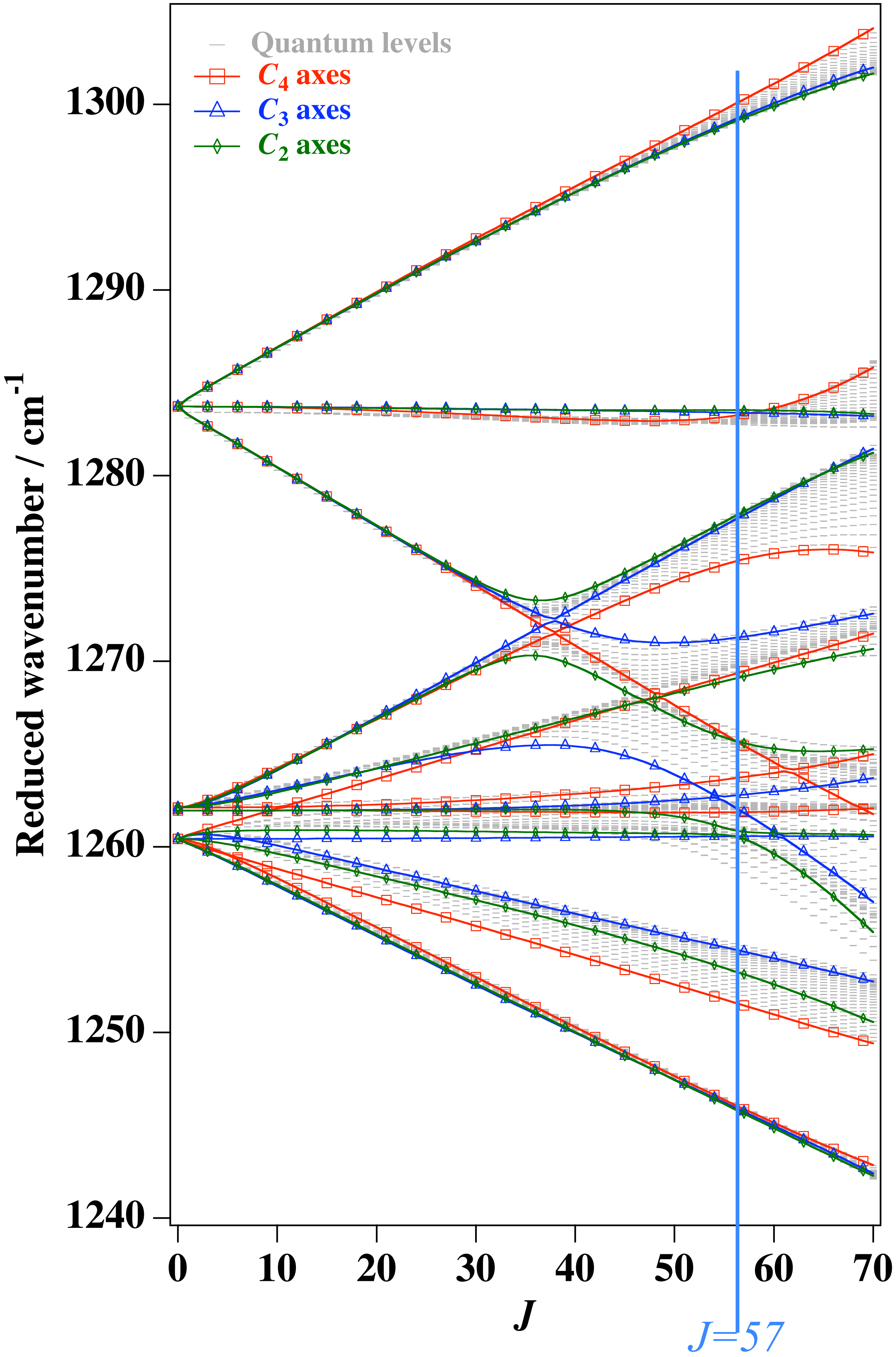
REES for high-J and high-υ ro-vibrational polyads

CF_4 -$\upsilon_4/2\upsilon_3$ dyad

REES for high-J and high-υ rovibration polyads



REES of CF_4 -$\upsilon_4/2\upsilon_3$ dyad showing rare (J=57)-$1_2(C_2)\uparrow O$ 24-level cluster on 5th REES