ROVIBRONIC PHASE PLOTS

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

HARTER-Soft
Elegant Educational Tools Since 2001
Matrix Diagonalization:
The BLACK BOX of quantum physics, chemistry, and spectroscopy

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

Diagonalizer

Eigenvalues (Quantum levels)
$$\begin{pmatrix} \lambda_1 & \ldots & \lambda_3 & \ldots \end{pmatrix}$$
$$\begin{pmatrix} \langle 1 | \lambda_1 \rangle & \langle 1 | \lambda_2 \rangle & \langle 1 | \lambda_3 \rangle & \ldots \\ \langle 2 | \lambda_1 \rangle & \langle 2 | \lambda_2 \rangle & \langle 2 | \lambda_3 \rangle & \ldots \\ \langle 3 | \lambda_1 \rangle & \langle 3 | \lambda_2 \rangle & \langle 3 | \lambda_3 \rangle & \ldots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

Eigenvectors (Quantum states)
$$\lambda_3 = \hbar \omega_3$$
$$\lambda_2 = \hbar \omega_2$$
$$\lambda_1 = \hbar \omega_1$$

Most of the information!
Matrix Diagonalization

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

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

Eigenvalues (Quantum levels)

$$\begin{pmatrix} (e_1, e_2, e_3, \ldots) \\ (1|e_1), (1|e_2), (1|e_3), \ldots \\ (2|e_1), (2|e_2), (2|e_3), \ldots \\ (3|e_1), (3|e_2), (3|e_3), \ldots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

Most of the information!

EigenVectors (Quantum states)

$$\begin{pmatrix} \langle e_1 | t^k_q | e_1 \rangle, \langle e_1 | t^k_q | e_2 \rangle, \langle e_1 | t^k_q | e_3 \rangle, \ldots \\ \langle e_2 | t^k_q | e_1 \rangle, \langle e_2 | t^k_q | e_2 \rangle, \langle e_2 | t^k_q | e_3 \rangle, \ldots \\ \langle e_3 | t^k_q | e_1 \rangle, \langle e_3 | t^k_q | e_2 \rangle, \langle e_3 | t^k_q | e_3 \rangle, \ldots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

perturbation or transition matrix
Peeking into **BLACK BOX** of matrix diagonalization:

\[ H = \begin{pmatrix} H_{11} & H_{12} & H_{13} & \cdots \\ H_{21} & H_{22} & H_{23} & \cdots \\ H_{31} & H_{32} & H_{33} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \rightarrow \text{Diagonalizer} \]

Plotting \( 2^k \)-pole expansion of \( H \) into Fano-Racah tensors:

\[
H = aT^0_0 + bT^1_0 + cT^1_1 + \ldots + dT^2_0 + eT^2_1 + \ldots = \sum c^k_q T^k_q
\]

**Monopole** \( k=0 \) (even)

**Dipole** \( k=1 \) (odd)

**Quadrupole** \( k=2 \) (even)

**Mixed-\( k \)**
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:

\[ \Psi_{\nu}(\epsilon)(x_{electron} \ldots X_{nuclei} \ldots) = \psi_{\epsilon}(x(X\ldots)\ldots) \cdot \eta_{\nu(\epsilon)}(X\ldots) \]

“FAST” stuff

“SLOW” stuff

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

nuclear \(\nu_{\epsilon}\)-quanta have
adiabatic dependence on
electron \(\epsilon\)-quanta
Born-Oppenheimer-Approximate (BOA)
Potential-Energy-Surfaces (PES)

BOA—“Entangled” or correlated products

\[ \Psi_{\nu}(\varepsilon)(x_{\text{electron}} \ldots x_{\text{nuclei}} \ldots) = \psi_{\varepsilon}(x(X \ldots \ldots)) \cdot \eta_{\nu(\varepsilon)}(X \ldots) \]

Compare BOA to unentangled state: \[ |\varepsilon\rangle|\eta\rangle = |\varepsilon,\eta\rangle \].

\[ \psi_{\varepsilon}(x) \cdot \eta_{\nu}(X) = \langle x|\varepsilon\rangle \langle X|\eta\rangle = \langle x,X|\varepsilon,\eta\rangle \]

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

\[ \psi_{\varepsilon}(x) \cdot \eta_{\nu}(X) + \psi_{\varepsilon'}(x) \cdot \eta_{\nu'}(X) = (\langle x|\varepsilon\rangle \langle X|\eta\rangle + \langle x|\varepsilon'\rangle \langle X|\eta'\rangle)/\sqrt{2} \]
Generalized BOA dependency
Rotational-Energy-Surfaces (RES)

BOA-“Entangled” or correlated products

$$\Phi_{J[\nu(\varepsilon)]}(x_{elect.}, ..., Q_{vib.}, ..., \Theta_{rotate}) = \psi_\varepsilon(x_{(Q(\Theta),...)}), \eta_\nu(\varepsilon)((Q_{(\Theta)}),...), \rho_{J[\nu(\varepsilon)]}(\Theta)$$

- **"FAST"**
  - Electron $x_{(Q(\Theta))}$-coords depend on vibration $Q$-coords and rotation $\Theta$-coords
  - Vibe $\nu(\varepsilon)$-quanta depend on electron $\varepsilon$-quanta

- **"SLOW"**
  - Vibe $Q(\Theta)$-coords depend on rotation $\Theta$-coords

- **"SLOWER"**
  - Rotation $J[\nu(\varepsilon)]$-quanta depend on vibe $\nu$-quanta and electron $\varepsilon$-quanta
\[ \Phi^{BOA}_{J[\nu(\epsilon)]} (x^{vibronic}, \Theta^{rotate}) = \psi_{\epsilon}(x_{(\Theta)}) \cdot \rho_{J[\epsilon]}(\Theta) \]

Using rotational symmetry analysis:
\[ = \psi_{\epsilon}(x_{\text{(body)})} \cdot \rho_{J,M,K}(\alpha, \beta, \gamma) \]

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

**Detailed model of BOA rotor entanglement**

**body-wave from lab-wave**
\[ \psi_{\mu}(x) = \psi_{\mu}^{\ell}(x) D_{\mu,\mu}^{\ell}(\alpha, \beta, \gamma) \quad \text{sum} \quad \mu = -J \ldots + J \]

**lab-wave from body-wave**
\[ \psi_{\mu}^{\ell}(x) = \psi_{\mu}^{\ell}(x) D_{\mu,\mu}^{\ell*}(\alpha, \beta, \gamma) \quad \text{sum} \quad \mu = -J \ldots + J \]

“Hook-up” unentangled lab-based products:
\[ \psi_{\mu}^{\ell}(x) \cdot D_{m,n}^{R*}(\alpha, \beta, \gamma) \sqrt{[R]} \]

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

\[ \Phi_{J(\ell R)}^{LAB_{\text{hook-up}}} = C_{\mu}^{\ell R J} m M \psi_{\mu}^{\ell}(x) \cdot D_{m,n}^{R*}(\alpha, \beta, \gamma) \sqrt{[R]} \]

\[ \text{with} \quad \mu = -J \ldots + J \quad \text{sum} \quad m = M - \mu \]
Compare wave Products:
Lab “hook-up” versus “BOA-constricted bod”
\[ \Phi_{J(\ell \mu)}^{BOA} = \psi_{\mu}(\vec{x}) \cdot D_{MK(\alpha, \beta, \gamma)}^{J} \sqrt{[J]} \]

\[ \Phi_{J(\ell R)}^{LAB_{hook-up}} = C_{\mu m M}^{\ell R J} \sum_{\mu=-J...+J} \psi_{\mu m M}(x) D_{m, n}^{R \ast (\alpha \beta \gamma)} \sqrt{[R]} \]

\[ \Phi_{J(\ell R)}^{LAB_{hook-up}} = C_{\mu m M}^{\ell R J} \sum_{\mu=-J...+J} \psi_{\mu m M}(x) D_{m, n}^{R \ast (\alpha \beta \gamma)} \sqrt{[R]} = C_{\mu n K}^{\ell R J} \sum_{\mu=-J...+J} \psi_{\mu m M}(x) D_{MK(\alpha \beta \gamma)}^{J} \sqrt{[J]} \]

with: \( K = \bar{\mu} + n \)

This has form:
\[ C_{\mu m M}^{\ell R J} D_{\mu m M}^{\ell \ast R J} D_{\mu m M}^{\ast R J} (\alpha \beta \gamma) = C_{\mu n K}^{\ell R J} D_{MK(\alpha \beta \gamma)}^{J} \]

...that follows from well known coupling identity.
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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The Simplest Cases:
Rigid top with one body fixed “Gyro” (one spin-1/2, one CH₃, ...)


Rotational energy surfaces of molecules exhibiting internal rotation

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Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899
(Received 14 March 1994; accepted 28 April 1994)

See also:
Hougen, Kleiner, and Ortigoso
JCP 96, 455 (1992)

One of the first Applications of

Problem: Mathematica graphic engines were not terrific!
(....and Los Alamos graphics was too $$expensive$$)
**Compound Rotor Hamiltonian:** Rigid rotor with body-fixed “gyro”...

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

*Zero-Interaction Potential ‘Proximation (ZIPP)*

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

...but suppose it’s zero! Constraints do no work.
**Compound Rotor Hamiltonian**: Rigid rotor with body-fixed “gyro”...

\[ H = A R_x^2 + B R_y^2 + C R_z^2 + \ldots + (\text{coupling or constraint}) + \ldots + B_S S \cdot S \]

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

Let: \( R = J - S \) and consider non-constant terms

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

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(ZIPPed)
Rotor $R$ PLUS "Gyro" Spin $S$ EQUALS Compound Rotor $J = R + S$

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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 $J_m$ or $T^1_m$ terms for gyro-rotor $H$
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$$(ZIPPed)$$

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$H = AJ_x^2 + BJ_y^2 + CJ_z^2 + ... - 2AJS_x - 2BJyS_y - 2CJS_z + ... + \text{(more constant terms)}$

"Coriolis effect" subtracts linear or 1st-order $J_m$ or $T^1_m$ terms for gyro-rotor $H$

$BR^2$ to $B(J-S)^2$ is analogous to $p^2/2M$ to $(p - eA)^2/2M$ gauge-transformation

...$J \cdot S$ is analogous to $e p \cdot A$
RE Surface for 1st-order $J_m$ or $T^1_m$ 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.

**Fixed Points** for $J$ lie on “North” and “South” poles of RE surface.
**Prolate Rotor** $R$ MINUS “Gyro” $x$-Spin $S_x$

$J = R$

$J = R + S$

$J - S = R$

$J = R$ is small if $|R|$ is small

$|J|$ is constant

$S$ is fixed

$R$ is small

Low energy along $S$

$|R|$ is large if $|J|$ is large

High energy against $S$

$|J|$ is constant

$R$ is fixed

$|J|$ is constant

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

$J = R$

$J = R + S$

$J - S = R$

$S$ is fixed

$R$ is small

Low energy along $S$

$|J|$ is constant

$R$ is fixed

$|J|$ is constant

High energy against $S$

$|J|$ is constant

$R$ is fixed

$|J|$ is constant
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

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

“Sherman” (The shark)
Two or more RE’s beg to be unZIPPed. Base RE surfaces are eigenvalues of matrix.

Classical RE

\[ H = AJ_x^2 + BJ_y^2 + CJ_z^2 + \ldots - 2AJ_x S_x - 2BJ_y S_y - 2CJ_z S_z + \ldots + (\text{more constant terms}) \]

Semi-Classical Spin-1/2 RE

\[ \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, 1 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \]

makes matrix

\[ H = (AJ_x^2 + BJ_y^2 + CJ_z^2) 1 - AJ_x S_x \sigma_x - BJ_y S_y \sigma_y - CJ_z S_z \sigma_z + \ldots + 1 \]

(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 \( A=0.2, B=0.8, C=1.4 \)

\( s_x=0.0, s_y=0.1, s_z=0.2 \)
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.
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That takes some thought and work. Let us know how you do.
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Bad news 😞
Don’t count on it.
What’s up, Doc?

Durer’s “Melancholia”
1514
1st semi-classical approximation of \( \langle \mathbf{v}_k^J \rangle_m^J = \langle \mathbf{J}_m^k \mathbf{v}_0^J \rangle \)  

Example: \( \langle \mathbf{v}_0^4 \rangle_{m=5}^{J=6} = \langle \mathbf{6}_5^4 \mathbf{v}_0^6 \rangle \)

\( \Theta_5^6 = 39.5^\circ \)

\( \langle \mathbf{6}_5^4 \mathbf{v}_0^6 \rangle = \text{radius of intersection of } \Theta_5^6 \text{cone with } \mathbf{v}_0^4 \text{surface} \)

\( \langle \mathbf{6}_5^4 \mathbf{v}_0^6 \rangle \) \text{ energy level } \sim -0.3 \text{units}

\( \mathbf{v}_0^4 \) \text{ zero-energy level}
<table>
<thead>
<tr>
<th></th>
<th>( A_1 )</th>
<th>( B_1 )</th>
<th>( A_2 )</th>
<th>( B_2 )</th>
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</thead>
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<tr>
<td>( 26 \text{ kHz} )</td>
<td>1</td>
<td>•</td>
<td>1</td>
<td>•</td>
</tr>
<tr>
<td>( 84 \text{ MHz} )</td>
<td>1</td>
<td>•</td>
<td>1</td>
<td>•</td>
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<tr>
<td>( 230 \text{ kHz} )</td>
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<td>•</td>
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<td>•</td>
</tr>
<tr>
<td>( 2 \text{ GHz} )</td>
<td>1</td>
<td>•</td>
<td>1</td>
<td>•</td>
</tr>
<tr>
<td>( 150 \text{ GHz} )</td>
<td>1</td>
<td>•</td>
<td>1</td>
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</tbody>
</table>

### Diagrams
- **\( C_2(x) \)**: Node 1 and 2 with labels 0 and 1.
- **\( C_2(y) \)**: Node 1 and 2 with labels 0 and 1.
- **\( C_2(z) \)**: Node 1 and 2 with labels 0 and 1.

### Labels
- \( A_1 \) with labels 0, 1, 2,
- \( B_1 \) with labels 0, 1, 2,
- \( A_2 \) with labels 0, 1, 2,
- \( B_2 \) with labels 0, 1, 2,
OhorTd Spherical Top: (Hecht Ro-vib Hamiltonian 1960)

\[ H = B \left( J_x^2 + J_y^2 + J_z^2 \right) + t_{440} \left( \frac{5}{2} J_x^4 + \frac{5}{14} \left( T_4^4 + T_{-4}^4 \right) \right) + \cdots \]

\[ J = 30 \]

precessing \( J \) vector

\( J = 88 \)

\( K_4 = 30 \)

\( = 29 \)

\( = 28 \)

etc.
SF₆ ν₄ rovib FT spectra ~615 cm⁻¹
McDowell et al. LosAlamos

Saddle Point

Herzberg rules still apply near separatrices or saddle points

precessing J vector
What reasoning can lead to!

*Durer’s “Melancholia”*

1514

(Why it is mostly in disfavor)

It’s not always the most comfortable occupation!
Example: \( J=6 \)
Example: $J=4$

Classical J-polynomials

$$|J|^k P_k(J_x, J_y, J_z)$$
Example: \((J=6)\)-eigenvalues of \(\mathbf{v}_0^6\)