Rotational energy and eigenstate surfaces for Coriolis dynamics


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 \(\nu_3\) \(\text{CF}_4\) (with Review: \(\text{SF}_6\) Coriolis PQR structure)
REES for high-J and high-\(\nu\) ro-vibrational polyads
  \(\text{CF}_4\) -\(\nu_4/2\nu_3\) dyad

*ZIPP (Zero-Interaction-Potential-`Proximation
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Some ways to picture AMO eigenstates

- Potential Energy Surfaces (PES)
  - electronic
  - vibrational
  - vibronic
Some ways to picture AMO eigenstates

- **Potential Energy Surfaces (PES)**
  - electronic
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- **Rotational Energy Surfaces (RES)**
  - pure rotational (centrifugal) effects
  - rovibrational (centrifugal and Coriolis) effects
  - rovibronic (centrifugal, Coriolis, and Jahn-Teller) effects
Some ways to picture AMO eigenstates

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  - electronic
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  - 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
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Examples of Simple Power Law Energy Level Spectra

Single-rotor $B J^2 + CJ^4 + \ldots$ (even powers)

Like very anharmonic oscillator

Quartic $E \sim \omega n^4$

Quadratic $E \sim \omega n^2$
Examples of Simple Power Law Energy Level Spectra

Single-rotor \( B J^2 + CJ^4 + \ldots \) (even powers)

Like very anharmonic oscillator

Quartic \( E \sim \omega n^4 \)

Cubic \( E \sim \omega n^3 \)

Quadratic \( E \sim \omega n^2 \)

Linear \( E \sim \omega n \)

Odd powers prohibited by time reversal (J->-J) symmetry
Examples of Simple Power Law Energy Level Spectra

Single-rotor: \( B \mathbf{J}^2 + C \mathbf{J}^4 + \ldots \) (even powers)

Like very **anharmonic oscillator**

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

Like 2D-**harmonic oscillator** \( \omega_\mu a_\mu \dagger a_\mu + \ldots \) (anharmonicity)
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CF$_4$ -$v_4/2v_3$ dyad
Lowest Order
RE-Surface
Components
$k=0, 1, 2...$
Lower Order RE-Surface Components
$k=0, 1, 2...$

Dipole (odd)

Monopole (even)

Quadrupole (even)
Matrix Diagonalization

The BLACK BOX of quantum physics, chemistry, and spectroscopy

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

$$\begin{pmatrix} e_1 & e_2 & e_3 \end{pmatrix}$$

Eigenvalues
(Quantum levels)

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

Eigenvectors
(Quantum states)

$$\begin{pmatrix} e_1 = \hbar \omega_1 \\ e_2 = \hbar \omega_2 \\ e_3 = \hbar \omega_3 \end{pmatrix}$$

Most of the information!

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

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

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

\[\xrightarrow{\text{Diagonalizer}}\]

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-\(k\)
$U(2)$ and $U(3)$ tensor expansions

**$2^k$-pole expansion of an $N$-by-$N$ matrix $H$**

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

$= \frac{A+D}{2} \begin{pmatrix} 1 \\ 0 \end{pmatrix} + B \sigma_z + C \sigma_y + \frac{A-D}{2} \sigma_z$

$= \frac{A+D}{2} T_0 + (B-iC) T_1 + (B+iC) T_{-1} + \frac{A-D}{2} T_0$

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

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

**$U(2)$ generators (spin $J=1/2$)**

$u^1_{+1} = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$, $u^1_0 = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$, $u^1_{-1} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}$ (vector)

$u^0_0 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$ (scalar)
$U(2)$ and $U(3)$ tensor expansions

**$2^k$-pole expansion of an $N$-by-$N$ matrix $H$**

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**U(2) generators** (spin $J=1/2$)

- $U(2)$ generators
- $u_{+1}^1 = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$ rank-1 (vector)
- $u_0^1 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}^{1/2}$ rank-0 (scalar)

**3-by-3 case: $H = \begin{pmatrix} H_{11} & H_{12} & H_{13} \\ H_{21} & H_{22} & H_{23} \\ H_{31} & H_{32} & H_{33} \end{pmatrix}$**

**U(3) generators** (spin $J=1$)

- $U(3)$ generators
- $u_{+2}^2 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$ rank-2 (tensor)
- $u_{+1}^1 = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}^{1/2}$ rank-1 (vector)
- $u_0^0 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}^{1/3}$ rank-0 (scalar)

Mutually commuting diagonal operators
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**U(2) and U(3) tensor expansions**

### 2\(^k\)-pole expansion of an N-by-N matrix \( \mathbf{H} \)

#### 2-by-2 case: \( \mathbf{H} = \begin{pmatrix} A & B - iC \\ B + iC & D \end{pmatrix} = \frac{A+D}{2} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + B \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + C \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} + \frac{A-D}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \frac{A+D}{2} I + B \mathbf{\sigma}_x + C \mathbf{\sigma}_y + \frac{A-D}{2} \mathbf{\sigma}_z \)

\( \mathbf{U(2)} \) generators (spin \( J=1/2 \))

- \( \mathbf{u}^1_{+1} = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \)
- \( \mathbf{u}^1_{-1} = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \)
- \( \mathbf{u}^0_0 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \)

\( \mathbf{u}^0_0 \) rank-0 (scalar) \n\( \mathbf{u}^1_0 \) rank-1 (vector)

#### 3-by-3 case: \( \mathbf{H} = \begin{pmatrix} H_{11} & H_{12} & H_{13} \\ H_{21} & H_{22} & H_{23} \\ H_{31} & H_{32} & H_{33} \end{pmatrix} \)

\( \mathbf{U(3)} \) generators (spin \( J=1 \))

- \( \mathbf{u}^2_{+2} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \)
- \( \mathbf{u}^2_{+1} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \)
- \( \mathbf{u}^2_0 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \)
- \( \mathbf{u}^2_{-1} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \)
- \( \mathbf{u}^2_{-2} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \)

\( \mathbf{u}^0_0 \) rank-0 (scalar) \n\( \mathbf{u}^1_0 \) rank-1 (vector)

Mutually commuting diagonal operators

**Wigner-Clebsch-Gordan expressions for Tensor** \( \langle T_q^k \rangle \)

\[ \langle J' M' | T_q^k | J M \rangle = \left( \begin{pmatrix} J' & k \\ M' & q - M \end{pmatrix} \right) (J' | k | J) = C_{q M M'}^{J' J} \langle J' | k | J \rangle \]
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Born-Oppenheimer-Approximate (BOA) for PES

BOA issues discussed in:
Rev. Mod. Phys. 50,1,37-83(1978)

BOA-“Entangled” or correlated products:

\[ \Psi_\nu(\varepsilon)(x_{\text{electron}} \ldots x_{\text{nuclei}} \ldots) = \psi_\varepsilon(x(X\ldots)) \cdot \eta_{\nu(\varepsilon)}(X\ldots) \]
Born-Oppenheimer-Approximate (BOA)
Potential-Energy-Surfaces (PES)

Born-Oppenheimer Approximation (BOA) for PES

BOA issues discussed in:
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BOA-“Entangled” or correlated products:

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

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

- **"SLOW"** stuff
  - nuclear \(\nu_\varepsilon\)-quanta
  - have adiabatic dependence on electron \(\varepsilon\)-quanta
Born-Oppenheimer-Approximate (BOA) Potential-Energy-Surfaces (PES)

BOA—“Entangled” or correlated products

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

Compare BOA to _unentangled_ state: \(|\epsilon\rangle|\eta\rangle = |\epsilon,\eta\rangle . 

\[
\psi_\epsilon(x) \cdot \eta_\nu(X) = \langle x|\epsilon\rangle \langle X|\eta\rangle = \langle x,X|\epsilon,\eta\rangle
\]
Born-Oppenheimer Approximation (BOA) for PES

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

BOA-“Entangled” or correlated products

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

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)

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

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Generalized BOA dependency
Rotational-Energy-Surfaces (RES)

BOA-“Entangled” or correlated products

Φ_{J[\nu(\varepsilon)]}(x_{\text{elect}}, \ldots, Q_{\text{vib}}, \ldots \Theta_{\text{rotate}}) = \psi_{\varepsilon}(x_{(Q_0(\Theta_0), \ldots)}) \cdot \eta_{\nu(\varepsilon)}(Q_{(\Theta)}, \ldots) \cdot \rho_{J[\nu(\varepsilon)]}(\Theta)
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Generalized BOA dependency
Rotational-Energy-Surfaces (RES)

BOA-“Entangled” or correlated products

Φ_J[υ(ε)](x_{\text{elect.}}..., Q_{\text{vib.}}..., Θ_{\text{rotate}}) = \psi_ε(x_{(Q(Θ))}..., \eta_υ(ε)(Q(Θ)...)) \cdot \rho_J[υ(ε)](Θ)

“FAST”
- electron x_{(Q(Θ))}-coords depend on vibration Q-coords and rotation Θ-coords
- vibe υ(ε)-quanta depend on electron ε-quanta

“SLOW”
- vibe Q(Θ)-coords depend on rotation Θ-coords

“SLOWER”
- rotation J[υ(ε)]-quanta depend on vibe υ-quanta and electron ε-quanta

BOA issues discussed in:
Rev. Mod. Phys. 50,1,37-83(1978)
Born-Oppenheimer Approximation (BOA) for RES

\[ \Phi_{J[\nu(\epsilon)]}^{BOA}(x_{\text{vibronic}}, \Theta_{\text{rotate}}) = \psi_{\epsilon}(x_{(\Theta)}) \cdot \rho_{J[\epsilon]}(\Theta) \]

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

Using rotational symmetry analysis

\[ = \psi_{\mu}(\bar{x}) \cdot D_{M,K=n+\mu(\alpha,\beta,\gamma)}^{J*} \]

\[ \text{bod-based vibronic factor} \]

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Born-Oppenheimer Approximation (BOA) for RES

\[ \Phi_{J[\nu(\epsilon)]}^{BOA}(x_{\text{vibronic}}, \Theta_{\text{rotate}}) = \psi_{\epsilon}(x_{\Theta}) \cdot \rho_{J[\epsilon]}(\Theta) \]

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

Using rotational symmetry analysis

\[ = \psi_{\mu}(\vec{x}) \cdot D_{M,K=\mu+n}(\alpha,\beta,\gamma) \sqrt{[J]} \]

Detailed model of BOA rotor entanglement

\[ \text{body-wave from lab-wave} \]

\[ \psi_{\mu}(\vec{x}) = \psi_{\mu}(x) D_{\mu,\mu}(\alpha,\beta,\gamma) \]

\[ \sum_{\mu=-J...+J} \]

\[ \text{lab-wave from body-wave} \]

\[ \psi_{\mu}(x) = \psi_{\mu}(\vec{x}) D_{\mu,\mu}(\alpha,\beta,\gamma) \]

\[ \sum_{\mu=-J...+J} \]

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\[ = \psi_{\epsilon}(x_{(\text{body})}) \cdot \rho_{J,M,K}^{\alpha,\beta,\gamma} \]

Using rotational symmetry analysis

\[ = \psi_{\mu}(\bar{x}) \cdot D_{M,K=n+\mu}^{\alpha,\beta,\gamma}[J] \]

**bod-based vibronic factor**

\[ \text{body-wave from lab-wave} \]

\[ \psi_{\mu}^{\ell}(\bar{x}) = \psi_{\mu}^{\ell}(x) D_{\mu,\mu}^{\ell}(\alpha,\beta,\gamma) \]

\[ \uparrow \text{sum} \]

\[ \mu = -J \ldots +J \]

\[ \text{lab-wave from body-wave} \]

\[ \psi_{\mu}^{\ell}(x) = \psi_{\mu}^{\ell}(\bar{x}) D_{\mu,\mu}^{\ell*}(\alpha,\beta,\gamma) \]

\[ \uparrow \text{sum} \]

\[ \mu = -J \ldots +J \]

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

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

\[ \Phi_{J(\ell R)} = \sum_{\mu = -J \ldots +J}^{\ell} \psi_{\mu}^{\ell}(x) \cdot D_{m,\mu}^{R*}[(\alpha,\beta,\gamma)] \]

\[ \text{LAB hook-up} \]

BOA issues discussed in:

*Rev. Mod. Phys. 50,1,37-83(1978)*

**Born-Oppenheimer Approximation (BOA) for RES**

Compare wave Products:
Lab “hook-up” *versus* “BOA-constricted bod”

\[
\Phi^{BOA}_{J(\mu)} = \psi_{\mu}(\bar{x}) \cdot D_{MK}^{J^*}(\alpha, \beta, \gamma) \sqrt{[R]}
\]

\[
\Phi^{LAB}_{J(\ell R)} = C_{\mu} \ell R J, \underbrace{\sum_{\mu=-J+J}}_{m=M-\mu} \psi_{\mu}(\bar{x}) \cdot D_{m,n}^{R*}(\alpha \beta \gamma) \sqrt{[R]}
\]
Born-Oppenheimer Approximation (BOA) for RES

Compare wave Products:
Lab “hook-up” versus “BOA-constricted bod”

\[ \Phi_{J(\ell)}^{BOA} = \psi_{\mu}(\bar{x}) \cdot D_{MK(\alpha,\beta,\gamma)}^{J} \]

\[ \Phi_{J(\ell)}^{hook-up} = C_{J} \sum_{m=-J+1}^{J} \psi_{\mu}(x) \cdot D^{R}_{m,n(\alpha\beta\gamma)\sqrt{[R]}} \]

\[ \Phi_{J(\ell)}^{hook-up} = C_{J} \sum_{m=-J+1}^{J} \psi_{\bar{\mu}}(\bar{x}) \cdot D^{\ell*}_{\mu,\mu}(\alpha,\beta,\gamma) \cdot D^{R}_{m,n(\alpha\beta\gamma)\sqrt{[R]}} \]
Born-Oppenheimer Approximation (BOA) for RES

Compare wave Products:

Lab “hook-up” versus “BOA-constricted bod”

\[ \Phi_{J(\ell R)}^{BOA} = \psi_{\bar{\mu}}(\bar{x}) \cdot D_{MK}(\alpha, \beta, \gamma)^{J*}[R] \]

**LAB**

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

with:

- \( \mu = \bar{\mu} + n \)
- \( \bar{\mu} = -J...+J \)
- \( m = M - \mu \)

**LAB**

\[ \Phi_{J(\ell R)}^{LAB} = C_{\mu m M}^{\ell R J} \sum_{\mu=-J...+J} \psi_{\bar{\mu}}(\bar{x}) \cdot D_{m,n}^{R*}(\alpha \beta \gamma) \sqrt{[R]} \]

with:

- \( \mu = -J...+J \)
- \( m = M - \mu \)
Compare wave Products:
Lab “hook-up” versus “BOA-constricted bod”

\[ \Phi^{BOA}_{J(\mu)} = \psi_{\mu}(\bar{x}) \cdot D_{MK}(\alpha, \beta, \gamma)^{J*} \]

\[ \Phi^{LAB}_{hook-up} = C^{\mu} m M \left\{ \begin{array}{c}
\sum_{\mu=-J_0...+J} \psi_{\mu}(x) \cdot D_{\mu,m,n}(\alpha, \beta, \gamma)^{J*} \\
\end{array} \right. \]

This has form:

...that follows from well known coupling identity.
Born-Oppenheimer Approximation (BOA) for RES

Compare wave Products:
Lab “hook-up” versus “BOA-constricted bod”

\[ \Phi_{BOA}^{J(\mu)} = \psi_{\mu}(\chi) \cdot D_{MK(\alpha,\beta,\gamma)}^{J*} n[J] \]

This has form:

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

...that follows from well-known coupling identity.
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
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Semiclassical Rotor-“Gyro”-Spin coupling

Rotor \( R \) PLUS “Gyro” Spin \( S \) EQUALS Compound Rotor \( J = R + S \)

Compound Rotor Hamiltonian: Rigid rotor with body-fixed “gyro”...

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

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

Rotor-Gyro RES issues discussed in:
Spring Handbook of AMOP Ch. 32 (2006)
Semiclassical Rotor-“Gyro”-Spin coupling

Rotor \( \mathbf{R} \) \( \oplus \) “Gyro” Spin \( \mathbf{S} \) \( \equiv \) Compound Rotor \( \mathbf{J} = \mathbf{R} + \mathbf{S} \)

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

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

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

...but suppose it’s zero!

Constraints do no work.

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

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

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

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

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

...but suppose it’s zero!

Constraints do no work.

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

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

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

*ZIPP (Zero-Interaction-Potential-`Proximation

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

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

\[ \ldots \text{but suppose it’s zero!} \]

Zero-Interaction Potential ‘Proximation (ZIPP)

Let: \( R = J - S \) and consider \text{non}\-constant terms \( \text{(ZIPPed)} \)

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

“Coriolis effect“ subtracts \text{linear} or 1st-order \( J_m \) or \( T^1_m \) terms for gyro-rotor \( H \)

\[ BR^2 \text{ to } B(J - S)^2 \text{ is analogous to } p^2/2M \text{ to } (p - eA)^2/2M \text{ gauge-transformation} \]

\[ \ldots J \cdot S \text{ is analogous to } e p \cdot A \]

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$CF_4 - v_4/2 v_3$ dyad
Semiclassical Rotor-“Gyro” RES

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.

RoToR-Gyro RES issues discussed in:

*Computer Phys. Reports 8, 319-394 (1987)*

*Spring Handbook of AMOP Ch. 32 (2006)*
Semiclassical Rotor-“Gyro” RES

RE Surface for 1st-order $J_m$ or $T^1_m$ 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)

Fixed Points for $J$ lie on “North” and “South” poles of RE surface.

Rotor-Gyro RES issues discussed in:
- Spring Handbook of AMOP Ch. 32 (2006)
Semiclassical Rotor-"Gyro" RES

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

Rotor-Gyro RES issues discussed in:
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Semiclassical Rotor-“Gyro” RES

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

$J = R$

$J = R + S$

$J - S = R$

Low energy along $S$

$|R|$ is small if $|J|$ is constant

High energy against $S$

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

$S$ is fixed $|R|$ is small

$|J|$ is constant

$S$ is fixed $|R|$ is large

$|J|$ is constant

Rotor-Gyro RES issues discussed in:
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Semiclassical Rotor-“Gyro” RES

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

Oblate Rotor $R$ MINUS “Gyro” $x$-Spin $S_x$
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Semiclassical Rotor analogy of Anharmonic Vibrator
Recall Hamiltonian for 2D vibration has a (quasi-)spin theory, too

\[
\begin{align*}
H &= \omega_0 1 + \Omega \left( a_+^\dagger a_+ - a_-^\dagger a_- \right) / 2 + \ldots + \text{(anharmonic } a_\mu^\dagger a_\nu a_\lambda^\dagger a_\kappa \text{ terms)} \\
&= \omega_0 1 + \Omega J_x \\
&\quad + \ldots + BJ_x^2 + CJ_y^2 + AJ_z^2 \ldots + a_{xy} J_x J_y + \ldots
\end{align*}
\]

1st-order \( J_m \) or \( T_1^1 \) term is harmonic part of \( H \)

Higher-order \( J_m \) or \( T_1^1 \) terms are anharmonic parts of \( H \)

Local Mode 2

Normal Mode (+)

Local Mode 1

Normal Mode (-)
Semiclassical Rotor analogy of Anharmonic Vibrator

(contd) 2D vibration are related to 3D rotation of “quasi-spin” $\mathbf{J}$

$$H = \omega_0 \mathbf{1} + \Omega \left( \mathbf{a}_0 \mathbf{a}_0^\dagger - \mathbf{a}_0 \mathbf{a}_0^\dagger \right) / 2 + \ldots + \text{(anharmonic } \mathbf{a}_\mu \mathbf{a}_\nu \mathbf{a}_\lambda \mathbf{a}_\kappa \text{ terms)}$$

$$H = \omega_0 \mathbf{1} + \Omega \mathbf{J}_x$$

$\mathbf{J}_x$ coordinate

$\mathbf{J}_y$ coordinate

$\mathbf{J}_z$ coordinate

$\mathbf{J}$ vector

Normal Mode (+)

Normal Mode (-)

Precessing $\mathbf{J}$ vector

Beat Mode $R$

Local Mode 1

Local Mode 2

$S(0)$
Semiclassical Rotor analogy of Anharmonic Vibrator

For higher J values, anharmonic terms grow to make stable local modes.
Semiclassical Rotor analogy of Anharmonic Vibrator

(a) Spherical Gyro-Rotor

Normal $\pm B$-Modes

$T_{0}^{(0)} + D_{y}^{(1)} T_{y}^{(1)}$

(b) Perturbed Gyro-Rotor

"Soft" $+B$-Mode

(c) Symmetric Gyro-Rotor

Local $\pm A$-Mode

Normal $-B$-Mode

$T_{0}^{(0)} + D_{y}^{(1)} T_{y}^{(1)} + Q_{0}^{(2)} T_{0}^{(2)}$

Symmetric normal mode becomes UNSTABLE

Fig. 25.5.3 A spherical gyro-rotor becomes asymmetric gyro-rotor by adding tensor $T_{0}^{2}$ to vector $T_{y}^{1}$.

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CF$_4$ -$\nu_4$/2$\nu_3$ dyad
Analogies between energy surfaces of potential (PES) and rotation (RES)

Potential Energy Surface (PES) Dynamics
Inter-PES electronic transitions
Vibrational Franck-Condon effects
• Frequency mismatch of PES

Rotation Energy Surface (RES) Dynamics
Inter-PES electronic transitions
Rotational "Franck-Condon" effects
• Frequency mismatch of RES

Analogy between Vibronic and Rovibronic

• Shape or position mismatch of PES

Duschinsky rotation or translation

• 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

Example for 2-state vibronic-rotor coupling
Avoided crossings

Vibronic and Rovibronic Analogy
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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)

unZIPPing

unZIPPing
Rotational energy eigenvalue surfaces (REES)  Introducing “Sherman the Shark” unZIPPed

Two or more RE’s beg to be unZIPPed. \( \langle H \rangle = \begin{pmatrix}
\text{Spin-up RE}(\beta_\gamma) & \text{Coupling}(\beta_\gamma) \\
\text{Coupling}(\beta_\gamma) & \text{Spin-down RE}(\beta_\gamma)
\end{pmatrix} \)

Base RE surfaces are eigenvalues of matrix.

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

Semi-Classical Spin-1/2 RE
\[
\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \ 1 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}
\]

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

\[ H_{R,S(quantized)} = AJ_x^2 + BJ_y^2 + CJ_z^2 - AJ_x \sigma_x - BJ_y \sigma_y - CJ_z \sigma_z + \text{const.} \]

\[
\begin{pmatrix}
\text{RE}_{\text{rotor}} - JC \cos \beta & -AJ \cos \gamma \sin \beta - iBJ \sin \gamma \sin \beta \\
-AJ \cos \gamma \sin \beta + iBJ \sin \gamma \sin \beta & \text{RE}_{\text{rotor}} + JC \cos \beta
\end{pmatrix}
\]

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

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

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

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**REES for high-J and high-$\nu$ ro-vibrational polyads**

CF$_4$ -$\nu_4$/$2\nu_3$ dyad
Summary of low-J (PQR) ro-vibe structure

(Using rovib. nomogram)

Review:

$SF_6$ Coriolis PQR structure

\[
\langle H \rangle \sim \nu_{\text{vib}} + BJ(J+1) + \langle H \text{Scalar Coriolis} \rangle + \langle H \text{Tensor Centrifugal} \rangle + \langle H \text{Tensor Coriolis} \rangle + \langle H \text{Nuclear Spin} \rangle + \ldots
\]
Review:

SF$_6$ Coriolis PQR structure
Recall scalar Coriolis \( PQR \) plots vs. \( B\zeta \)

Here is a \( J=60 \) piece of it:

\[ N=59 = J-1 \]
\[ N=60 = J \]
\[ N=61 = J+1 \]

\( -0.5 \quad B\zeta = 0 \quad +0.5 \)

Now consider this plot with \textit{tensor} Coriolis, too

(Just \( 4^{\text{th}} \)-rank \([2x2]^4\) tensor here.)
How to display such monstrous avoided cluster crossings: REES: *Rotational Energy Eigenvalue Surfaces*

Vibration (or vibronic) momentum $\ell$ retains its quantum representation(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 $\gamma$ and polar $\beta$. 
**Body-ΣΠ±-Basis**

\[
<H>=(v_3+B|J|^2)\begin{pmatrix}1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}+2B\zeta|J|\begin{pmatrix}1 & 0 & 0 \\
\frac{1}{\sqrt{2}}e^{-iy}\sin\beta & 0 & \frac{1}{\sqrt{2}}e^{-iy}\sin\beta \\
0 & \frac{1}{\sqrt{2}}e^{-iy}\sin\beta & -\cos\beta
\end{pmatrix}
\]

\[+2t_{22d}|J|^2\begin{pmatrix}3\cos^2\beta-1 & -\sqrt{8}e^{-iy}\sin\beta\cos\beta & \sin^2\beta(6\cos^2\gamma+i4\sin^2\gamma) \\
-\sqrt{8}e^{-iy}\sin\beta\cos\beta & 0 & -6\cos^2\beta+2 \\
\sin^2\beta(6\cos^2\gamma-i4\sin^2\gamma) & \sqrt{8}e^{-iy}\sin\beta\cos\beta & 3\cos^2\beta-1
\end{pmatrix}
\]

**Lab-PQR-Basis**

\[
<H>=(v_3+B|J|^2)\begin{pmatrix}1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}+2B\zeta|J|\begin{pmatrix}+1 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & -1
\end{pmatrix}
\]

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

\[
H_{PQ}=(7\cos^2\beta-3\cos^2\beta-\sin^2\beta'(\cos^2\beta\cos^4\gamma\sin^4\gamma+\sin^4\gamma))/\sqrt{8}=H_{QR}
\]

\[
H_{PP}=(5(-7\cos^4\beta+8\cos^2\beta+(1-\cos^4\beta)\cos^4\gamma+2i\cos^2\beta\sin^2\beta\sin^4\gamma-1))/4
\]
REES for high-J Coriolis spectra in SF₆

C₁ level clusters
(not seen here.)

C₂ level clusters
(but shows up in CF₄ polyad)

C₃ level clusters

Bζ = 0.0

Bζ = 0.8

Bζ = 1.5
REES for high-J Coriolis spectra in $\nu_3$ CF$_4$
Lowest $\nu_3$ REES

Middle $\nu_3$ REES

Highest $\nu_3$ REES

REES for high-J Coriolis spectra
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REES for high-J and high-$\nu$ rovibration polyads

REES of CF$_4$ -$\nu_4$/2$\nu_3$ dyad showing rare (J=57)-1$_2$(C$_2$)$\uparrow$O
24-level cluster on 5th REES

24-resonant $J$-orbits indicated by arrows