Towards higher rotational excitation:



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Dramatis personæ



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Doers (do...)





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Ponderers (answer phone, pontificate...)



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$\begin{array}{c} J_{J,0} \\ J_{J,1} \\ J_{J-1,1} \\ J_{J-1,2} \end{array} \end{array} \equiv \equiv$

$\Gamma_{\text{Cluster}} = A_1 \oplus A_2 \oplus B_1 \oplus B_2$ in $C_{2v}(M)$

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Rotational Energy Level Clusters

CH₄ 8-fold and 6-fold clusters 1972 Dorney and Watson H_2O 4-fold clusters (E_{rb}) 1978 Zhilinskii and Pavlichenkov 1978 Harter and Patterson Rotational energy surfaces and clusters 1991 Lehmann Local mode theory and clusters 1992 Kozin et al H₂Se 4-fold clusters observed H_2Se 4-fold cluster theory (E_{rbs}) 1993 Kozin and Jensen H₂X 4-fold cluster symmetry 1994 Jensen and Bunker 1996 Kozin et al H₂Te 4-fold clusters (exp and theory) 1997 Jensen et al Review paper on 4-fold clusters 2000 Jensen Review paper on LMT and clusters 2012 Another review paper of LMT and clusters Jensen [WIREs Comput. Mol. Sci. 2, 494–512 (2012). DOI: <u>10.1002/wcms.1089</u>]

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Are there similar effects for XH₃ molecules – say PH₃?

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Programs: XY3 and TROVE

(Theoretical Rotation-Vibration Energies)

XY3: Rotation-vibration energies for pyramidal, ammonia-type molecule in isolated electronic state, calculated variationally.

[1] H. Lin *et al., J. Chem. Phys.* **117**, 11265 (2002)
[2] S.N. Yurchenko *et al., Mol. Phys.* **103**, 359 (2005) and references given there.

TROVE.

[3] S.N. Yurchenko, W. Thiel, and P. Jensen, J. Mol. Spectrosc. 245, 126 (2007)

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Variational rotation-vibration calculations for PH₃

 $J \le 80$

Vibrational basis set:

$$2(v_1 + v_2 + v_3) + v_{inv} + V_{bend} \le 6$$

Potential energy surface:

cc-pwCVTZ [1] refined by fitting to experimental vibrational term values [2]

[1] D. Wang, Q. Shi, and Q.-S. Zhu, J. Chem. Phys., **112**, 9624 (2000)
[2] S.N. Yurchenko et al., Chem. Phys. **290**, 59 (2003)

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Yes, there are six-fold clusters!



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Rotational coordinates



- (θ, φ, χ) define orientation of molecule (*xyz*) relative to laboratory (*XYZ*).
- (θ, χ) define orientation of Z axis relative to molecule (xyz).

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For a rovibronic eigenstate Φ_i

$$F_{J,m}(\theta,\chi) = \int (\Phi_i)^* \Phi_i \sin\theta \, dV$$



is the probability distribution for the orientation of the *Z* axis relative to the molecule.

$$|\mathbf{J}| = J\,\hbar\,\sqrt{1+\frac{1}{J}}$$

 $(\mathbf{0})$

For states with m = J (and J large), $F_{J,m}(\theta, \chi)$ is the probability distribution for the orientation of the angular momentum relative to the molecule

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 $J\hbar$



 $F_{J,m}(\theta,\chi)$



"Top cluster states" for J = m = 40, vibrational ground state of PH₃

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Primitive cluster states | *j* PCS >

First symmetrize, e.g.

$$\Psi_{1}^{A_{1}} = \frac{1}{\sqrt{6}} \left(|1 \text{ PCS}\rangle + |2 \text{ PCS}\rangle + |3 \text{ PCS}\rangle + |4 \text{ PCS}\rangle + |5 \text{ PCS}\rangle + |6 \text{ PCS}\rangle \right)$$

$$P_6^{-2} = \sqrt{6} \left(|1PCS\rangle + |2PCS\rangle + |3PCS\rangle - |4PCS\rangle - |3PCS\rangle -$$

with similar expressions for the *E* functions....

Then invert the unitary transformation to obtain

0 rus/

$$|j| \text{PCS} \rangle = \sum_{i,\Gamma} C_{i,\Gamma}^{(j)} \psi_i^{\Gamma}, \quad j = 1, 2, \dots, 6$$

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Motivation – Ultrafast rotations

- Large angular momentum *J* poses considerable challenge to computational quantum methods.
- At large *J*, classical mechanics can be used to describe the motion
- Classical approach: Define rotational energy surface (RES)



Step 1: Change angular momentum operators to classical analogues, i.e. functions of angular coordinates:

 $\widehat{H}_{\rm rot}[\widehat{J}_x, \widehat{J}_y, \widehat{J}_z] \to H_{\rm rot}(J_x, J_y, J_z)$

Step 2: Fix length of J – vector $|J| = \sqrt{J_x^2 + J_y^2 + J_z^2} = J(J+1) h/2\pi$

Step 3: Plot $H_{\rm rot}$ radially as a function of angular coordinates with fixed |J|

On the RES, J is constant, energy varies.

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The rotational energy surface: Explaining ro-vibrational energy clusters



Example: BiHD₂

Yurchenko et al. J. Mol. Spec 256, 119 (2009).

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- Increasing J potentially leads to changing topology
 - ➡ Formation of energy clusters

Qualitative description of high-J states





Our aim: A quantitative description to lower the computational costs

• *Main idea:* Define quantized paths on RES to get semi-classical energies for rotational states

Calculating these paths is *much* faster than full quantum calculations

- Second idea: Use TROVE to calculate the RES by treating the vibrations quantum mechanically
- *Application:* Hot environments, i.e. large angular momentum states, where quantum calculations are of limited accuracy but very costly in terms of time and memory

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The rotational energy surface produced by TROVE

- Use *ab-initio* (or spectroscopic) potential energy surface
- Replace $\hat{J}_x, \hat{J}_y, \hat{J}_z$ in the kinetic energy operator by classical components of \vec{J}
- Solve the vibrational $|\vec{J}| = \text{const.}$ Schrödinger equation on a grid to obtain RES also for vibrationally excited states



The semi-classical approximation

Starting point: Green's function and its semi-classical approximation



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Paths on the rotational energy surface of SO₂



- 3d-plot of RES with constant energy sphere indicating the possible paths on the surface.
- They are parameterized by the rotations of the molecule, i.e. the respective symmetry elements

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Projected RES, $p = J_x$, $q = \measuredangle(J_x, J_y)$. The analogy to well-known potential energy surface is evident



Quantization conditions

- Principal idea: The integral along certain path must be a multiple of 2π
- Paths are parametrized by the symmetry elements of the molecular symmetry elements
- The semi-classical approximation of Green's function has poles at certain values, distinguished by symmetry (even or odd multiples of 2π)



A numerical routine to find the quantized paths

- TROVE calculations produce a grid of H(p,q) for real and imaginary p
- Numerical calculations are done in *Mathematica* (simple to use and lots of integrated functions)





Results for the test-case molecule SO₂



Comparison of:

- Full quantum calculations
- TROVE generated RES & path quantization
- Effective Watson-type RES & path quantization

Result:

The semi-classical procedure lead to energies comparable to the fully quantum calculations.



More details on the results: Relative deviation for different *J* quantum numbers



- Definition of rel. deviation: $(E_{sc} - E_{qm})/E_{qm}$
- Increasing J decreases relative "error" of semi-classical calculations
- For large "k" values, the error is minimal
 - Computing time scales only with energy range in which states are calculated
 - Quantum calculations scale with $(2J + 1)^3$

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Conclusion and next steps

Conclusion and achievement

- Attachment of semi-classical procedure to TROVE variational approach for vibrations
- Quantized energies are in good agreement with full quantum values
- Computing time is reduced for large angular momentum

Open problems and future aims

- More complicated molecules, e.g. include rotational clustering
- Can we define dipole transitions on the RES?
- Definition of Rotation-Torsion energy surface?





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