A SEMI-CLASSICAL APPROACH TO THE CALCULATION OF HIGHLY EXCITED ROTATIONAL ENERGIES FOR ASYMMETRIC-TOP MOLECULES

HANNO SCHMIEDT, STEPHAN SCHLEMMER, University of Cologne, Germany SERGEI N. YURCHENKO, University College London, United Kingdom ANDREY YACHMENEV, Center for Free-Electron Laser Science, DESY, Hamburg, Germany

PER JENSEN, University of Wuppertal, Germany



Theoretical (quantum mechanical) line list



Source: Website of Jonathan Tennyson, UCL, London

Ab initio: Solve Schrödinger equation for electrons

PES: Potential energy surface

DMS: Dipole moment surface

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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:

 $\widehat{H}_{\text{rot}}[\widehat{J}_{x}, \widehat{J}_{y}, \widehat{J}_{z}] \to H_{\text{rot}}(J_{x}, J_{y}, J_{z})$

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.





The rotational energy surface: Explaining ro-vibrational energy clusters



Example: BiHD₂

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

Qualitative description of high-J states



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

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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



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

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

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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 leads to energies comparable with the fully quantum-mechanical calculations.

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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?

Dramatis personæ

Hanno Schmiedt Principal doer

Doers (do...)

Andrei Yachmenev

Sergei Yurchenko

Ponderers (answer phone, pontificate...)

Stephan Schlemmer

Per Jensen

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