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

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**Theoretical (quantum mechanical) line list**

- **Ab initio**: Solve Schrödinger equation for electrons
- **PES**: Potential energy surface
- **DMS**: Dipole moment surface

**Diagram:**
- **Ab initio calculations**
  - **DMS**
  - **PES**
    - **Variational calculations**
      - **Rovibrational wavefunctions**
      - **Rovibrational energies**
        - **Intensities (Einstein $A_{rr}$)**
        - **Line list**

**Source:** Website of Jonathan Tennyson, UCL, London
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:

$$\hat{H}_{\text{rot}}[\hat{J}_x, \hat{J}_y, \hat{J}_z] \rightarrow H_{\text{rot}}(J_x, J_y, J_z)$$

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

**Step 3:** Plot $H_{\text{rot}}$ 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

- Increasing $J$ potentially leads to changing topology
- Formation of energy clusters
- Qualitative description of high-$J$ states

Example: BiHD$_2$

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

Hamiltonian

\[ G(q_f, q_i, E) = \langle q_f \left| (E - H)^{-1} \right| q_i \rangle \approx \sum_{\text{paths}} \exp(-i \int_{q_i}^{q_f} S[q_{cl}] \, dq) \det \left( \frac{i}{2\pi} \frac{\partial^2 S[q_{cl}]}{\partial q_f \partial q_i} \right) \]

Classical action

Final state

Initial state

The poles of the Green’s functions are the energies of the system!

Goal: Find and parametrize paths on rotational energy surface to find the energies

Reminder: Classical paths are solutions of classical equations of motion
Paths on the rotational energy surface of \( \text{SO}_2 \)

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, \( p = J_x, q = \angle(J_x, J_y) \). The analogy to well-known potential energy surface is evident.
Quantization conditions

- Principal idea: The integral along certain path must be a multiple of $2\pi$
- 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 $2\pi$)

$$\det\left[e^{-i\mathcal{S}}D_m^\dagger(\omega) - r \, 1_m - t \, D_m(\tau)\right] = 0$$

Classical path rotation
Tunneling path rotation
Reflection/Transmission amplitude at turning point
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 $\text{SO}_2$

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.
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 $(2J + 1)^3$
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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Dramatis personæ

Doers (do...)
- Andrei Yachmenev
- Sergei Yurchenko

Ponderers (answer phone, pontificate...)
- Stephan Schlemmer
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Thanks to the doers and the other ponderer...

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