Symmetry and the Entangled Ro-vibrational Quantum States of a Fluxional Molecule

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Introduction: rotations and vibrations

Quantum states of isolated molecules:
separation of rotation and vibration essential

Quantum states of CH$_4$
- vibrational states
- rotational and ro-vibrational states

(rotational quantum number $M=0$ only)
Symmetry and the Entangled Ro-vibrational Quantum States of a Fluxional Molecule

Separation of rotation and vibrations

Molecular symmetry groups

Floppy molecules

The breakdown of separability: $A_n$ and $AB_n$ with $n>4$

A prominent example: $CH_5^+$
Separation of rotation and vibrations

Vibrational motion is described by coordinates $Q$ in a body fixed frame.

Rotational motion of the body fixed frame is described by the Euler angles $\alpha, \beta, \gamma$.

Rotational invariance of the Hamiltonian:

$$\Psi_{J,M}(\alpha, \beta, \gamma, Q) = \sum_{K=-J}^{J} \sqrt{\frac{2J+1}{8\pi^2}} D^J_{MK}(\alpha, \beta, \gamma) \cdot \psi_{J,K}(Q)$$

$D^J_{MK}(\alpha, \beta, \gamma)$ : Wigner rotation matrices

Separability of rotational and vibrational motion:

$$\Psi_{J,M}(\alpha, \beta, \gamma, Q) = \left( \sum_{K=-J}^{J} \sqrt{\frac{2J+1}{8\pi^2}} D^J_{MK}(\alpha, \beta, \gamma) \cdot c_{J,K} \right) \cdot \psi(Q)$$

$\psi(Q)$ : vibrational wavefunction
Molecular symmetry groups

Hamiltonian invariant with respect to inversion and permutation of identical atoms

Rigid or semirigid molecules: permutation-inversion symmetry mapped on point groups, vibrational wavefunctions transform according to the irreducible representations of the point group

Identical atoms used in the definition of the body fixed frame → permutations affect rotational wavefunctions

Permutations are mapped on equivalent rotations

\[
\text{CH}_4
\]
Floppy molecules

Molecules showing long range motion:
identical nuclei can dynamically exchange their positions
→ feasible permutations (and inversion)

Separation of rotational and vibrational motion:

$$\Psi(\alpha,\beta,\gamma,Q) \approx \psi_{\text{rot}}(\alpha,\beta,\gamma) \cdot \psi_{\text{vib}}(Q)$$

Vibrational wavefunction transforms according to the group of feasible permutations (and inversion).

Rotational wavefunction transforms according to the rotation group SO(3).
It must also transform according to the group of feasible permutations which affect the definition of the body fixed frame (→ equivalent rotations).
The breakdown of separability: $A_n$ and $AB_n$ with $n>4$

All permutation dynamically feasible
and relevant for the definition of the body fixed frame:

$A_3, AB_3 : S_3$ isomorphic to $C_{3v}$ (→subgroup of $SO_3$), triangle

$A_4, AB_4 : S_4$ isomorphic to $T_d$ (→subgroup of $SO_3$), tetrahedron

$A_5, AB_5 : S_5$ not isomorphic to any subgroup of $SO_3$

... (analogous for all $n > 4$)

→ rotational wavefunction of correct symmetry can not exist

→ breakdown of separability of rotational and vibrational motion
A prominent example: $\text{CH}_5^+$

PES with 120 symmetry-equivalent minima separated by tiny barriers → delocalized quantum states

PES by Brown et al.

MCTDH calculations:
iterative diagonalization approach adapted to multi-well systems, explizit symmetrization (incompletely converged)
Ro-vibrational states of $CH_5^+$

**Numerical Result:**
contributions from a small number of vibrational states dominate in the wavefunctions

**Symmetry?**
Pauli-allowed ro-vibrational states of CH$_5^+$
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