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Quantum chemical computation and
characterization of
rotational-vibrational states of semirigid
and flexible polyatomic molecules

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1 Introduction

The Born–Oppenheimer (BO) approximation, being central to the definition of many concepts of chemistry, separates adiabatically the motion of electrons and nuclei and thus defines two important fields for computational quantum chemistry: electronic structure theory and nuclear motion theory. During my doctoral work I focused on the effective variational solution of the time-independent nuclear-motion Schrödinger equation and I have developed and implemented general algorithms for the accurate and efficient variational computation and interpretation of rotational-vibrational energy levels and wave functions of N -atomic molecules.

The first approach, called DEWE, employs the exact and general N -atomic Eckart–Watson nuclear kinetic energy operator expressed in rectilinear internal coordinates. Though DEWE does apply to N -atomic molecules, it is limited to semirigid molecules exhibiting a well-defined single minimum on their PES. The second and most general approach, called GENIUSH, allows nuclear motion computations employing arbitrarily chosen internal coordinates and body-fixed frame embeddings for N -atomic molecules.

Besides the computation of the rovibrational states I developed methods allowing the interpretation of the rovibrational results by assigning zeroth-order quantum numbers and symmetry labels to them.

2 Methods

The primary aim of my doctoral research was to develop and implement general algorithms suitable for the accurate computation and interpretation of rotational-vibrational energy levels and wave functions of N -atomic molecules. For this purpose I used the Fortran 90, C++ and Python programming languages, and the BLAS, LAPACK and MKL libraries.

3 Results and discussion

Method development

1. I added the capability of computing rotational-vibrational energy levels and wave functions to the original vibrational-only DEWE (Discrete variable representation of the Eckart–Watson Hamiltonian with a numerically Exact inclusion of arbitrary

potential energy surfaces) program developed principally by Dr. Edit Mátyus in our group. DEWE employs the universal and exact Eckart–Watson (EW) Hamiltonian and the iterative Lanczos eigensolver for computing the eigenvalues and eigenvectors of the Hamiltonian matrix. Though DEWE can be applied for N -atomic systems, it is limited to the case of semirigid molecules with a single well-defined minimum structure. The variational solution of the rotational-vibrational problem within the framework of DEWE is described in Ref. [1].

2. I formulated and added the rotational functionality to the original vibrational-only GENIUSH (General rovibrational code with Numerical, Internal coordinate, User-Specified Hamiltonians) program developed principally by Dr. Edit Mátyus in our group. The GENIUSH approach successfully circumvents the main drawbacks of DEWE and thus can be applied to N -atomic molecules exhibiting multiple accessible PES minima and large amplitude motions. The main idea behind GENIUSH is the numerical representation of the rovibrational kinetic energy operator which allows us to employ arbitrary sets of internal coordinates and body-fixed frame embeddings during the rovibrational computations. Another important characteristics of GENIUSH is the possibility to introduce reduced-dimensional vibrational models in a straightforward manner. The variational solution of the rovibrational problem and the formulation of the general N -atomic rovibrational Hamiltonian is outlined in Ref. [2].
3. I addressed the problem of assigning symmetry labels to the computed rovibrational energy levels and wave functions. As DEWE and GENIUSH employs the iterative Lanczos eigensolver, it seemed to be a good choice to adopt the symmetry-adapted Lanczos method (SAL). During the SAL process Lanczos vectors are projected onto the different irreducible representations of the molecular symmetry (MS) group. This procedure results in rovibrational states belonging to the i th irreducible representation of the MS group if the Lanczos vectors are projected onto the i th irreducible representation. My own SAL implementation currently works for DEWE employing normal coordinates and Hermite-DVR vibrational basis functions, and applies to Abelian MS groups having ± 1 characters (for the $D_{2h}(M)$ MS group and its subgroups).
4. I discussed how the rotational Eckart condition, giving an optimal separation between

the vibrational and rotational motions, can be maintained in variational rovibrational computations. As DEWE employs the Eckart–Watson Hamiltonian, the rotational Eckart condition holds automatically in this case. However, when GENIUSH is used, an additional procedure is needed to compute rovibrational energy levels and wave functions with Eckart-embedded kinetic energy operators. I implemented the Eckart embedding within the GENIUSH algorithm for arbitrary N -atomic molecules.

5. Labelling the computed rovibrational energy levels and wave functions with zeroth-order harmonic oscillator and rigid rotor quantum numbers is of great importance as these labels are widely used in the field of experimental spectroscopy. For this purpose I implemented and used extensively the rigid-rotor decomposition (RRD) procedure described in Ref. [3].
6. I developed an algorithm for the efficient and accurate computation of highly-excited rovibrational states. The so-called vibrational subspace (VS) procedure employs the vibrational wave functions as vibrational basis functions during the rotational-vibrational computations. After formulating the theory I implemented VS within the DEWE and GENIUSH programs. Assignment of zeroth-order quantum numbers and symmetry labels to the rovibrational states computed by VS has been also solved.

Numerical results

1. I executed variational rovibrational computations with GENIUSH for the four-atomic NH_3 molecule, exhibiting one large-amplitude motion usually called “umbrella motion”. Besides the full-dimensional results, reduced-dimensional rovibrational models, with dimensions ranging from 1D to 4D, have also been examined and their quality is determined by comparison with results obtained from the full-dimensional treatment.
2. I executed variational rovibrational computations for the semirigid five-atomic ketene ($\text{C}_2\text{H}_2\text{O}$) molecule with DEWE. Zeroth-order vibrational and rotational quantum numbers and symmetry labels were evaluated for the computed rovibrational states by the normal mode decomposition (NMD), RRD and SAL procedures. Rovibrational energy levels and wave functions with high J rotational quantum numbers were computed by the DEWE-VS program. After the MARVEL analysis based on the measured rovibrational transitions of $\text{C}_2\text{H}_2\text{O}$, resulting in “experimental” energy

levels of ketene, new experimental transitions have been assigned based on the variational and MARVEL results.

3. I validated the MARVEL energy levels of the H_2^{16}O isotopologue by comparing their approximate labels to those of the energy levels computed by the GENIUSH-VS algorithm. Rovibrational energy levels and wave functions up to $J = 25$ were computed by the GENIUSH-VS procedure. During the computations the Eckart frame, which has proven to be beneficial for the accuracy of the GENIUSH-VS results, was used. The resulting rovibrational energy levels and wave functions were analyzed by the RRD procedure by evaluating J , K_a , K_c rigid rotor quantum numbers and $C_{2v}(\text{M})$ symmetry labels.

4 Publications

Scientific papers

- 1 [C. Fábri](#), E. Mátyus, T. Furtenbacher, B. Mihály, T. Zoltáni, L. Nemes, A. G. Császár, *J. Chem. Phys.* **135**, 094307 (2011).
- 2 [C. Fábri](#), E. Mátyus, A. G. Császár, *J. Chem. Phys.* **134**, 074105 (2011).
- 3 E. Mátyus, [C. Fábri](#), T. Szidarovszky, G. Czakó, W. D. Allen, A. G. Császár, *J. Chem. Phys.* **133**, 034113 (2010).
- 4 A. G. Császár, [C. Fábri](#), T. Szidarovszky, E. Mátyus, T. Furtenbacher, G. Czakó, The fourth age of quantum chemistry: molecules in motion, *Phys. Chem. Chem. Phys.* **14**, 1085 (2012).

Posters

- P1 [C. Fábri](#), A. G. Császár, Efficient rovibrational computations: the vibrational subspace method and the Eckart embedding using internal coordinates, Anharmonicity in medium-sized molecules and clusters, Marne la Vallée, France, 2012
- P2 [C. Fábri](#), A. G. Császár, Toward the line list of methane, WATOC, Santiago de Compostela, Spain, 2011

- P3 C. Fábri, T. Szidarovszky, G. Magyarfalvi, G. Tarczay: Transferable scaling factors for the analysis of gas-phase and matrix isolation vibrational spectra, 20th International Conference on High Resolution Molecular Spectroscopy, Prague, Czech Republic, 2008
- P4 G. Czakó, C. Fábri, A. G. Császár, V. Szalay, B. T. Sutcliffe, G. Tasi, Adiabatic Jacobi Corrections in H²⁺-Like Systems, Molecular Quantum Mechanics: Analytic Gradients and Beyond, A Conference in Honor of Peter Pulay, Budapest, Hungary, 2007

Lectures

- L1 Fábri Csaba, Mátyus Edit, Császár Attila: Sokatomos molekulák rezgési-forgási állapotai, XVI. Nemzetközi Vegyészkonferencia, Kolozsvár, Romania, 2010.
- L2 Csaba Fábri: Variational rotational-vibrational computations for medium-sized molecules, Center for Computational Chemistry, University of Georgia, Athens, GA, USA, 2010
- L3 A. Császár, E. Mátyus, G. Czakó, C. Fábri, T. Furtenbacher, T. Szidarovszky: Quantum Spectroscopy, 23rd Austin Symposium on Molecular Structure and Dynamics, Austin, TX, USA, 2010
- L4 Fábri Csaba, Czakó Gábor, Császár Attila: Túl a Born-Oppenheimer közelíté sen: A H₂⁺ izotopológjainak rezgései, XII. Anyagszerkezet-kutatási Konferencia, Mátrafüred, Hungary, 2009
- L5 Császár Attila, Furtenbacher Tibor, Mátyus Edit, Czakó Gábor, Fábri Csaba, Szidarovszky Tamás: Spectropedia, Molecular Modeling in Chemistry and Biochemistry, Kolozsvár, Romania, 2009