Efficient exploitation of molecular symmetry in variational rotational-vibrational computations and applications to fluxional molecular systems

(research report on the STSM of Csaba Fábri spent in Prof. Attila G. Császár's
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The main objective of this STSM was the development and implementation of efficient methods for exploiting molecular symmetry in variational rotational-vibrational computations. Realization of this objective would be an important step towards highly accurate theoretical investigations of the vibrational and rovibrational quantum dynamics of highly fluxional, including astructural, molecular systems. The algorithm should find applications in ongoing and prospective research projects on the rovibrational dynamics of H_5^+, CH_5^+, and their deuterated isotopologues. The following parts of the submitted research plan have been accomplished during the STSM:

Exploitation of symmetry in variational rovibrational computations employing DVR basis sets: if multidimensional DVR grid points transform into each other under symmetry operations of the molecular symmetry (MS) group of the molecule, certain matrix elements and smaller blocks of the Hamiltonian must be the same. In order to utilize this chance for the most general case we have developed a code that is able to deduce the structure of the Hamiltonian and generate smaller, symmetrized blocks corresponding to different irreducible representations of the MS group. Illustrative results and details of the underlying theory were presented at a scientific seminar.

Radau kinetic energy operator in GENIUSH: the general rovibrational kinetic energy operator (KEO) implemented in GENIUSH enables the accurate solution of the rovibrational Schrödinger equation for arbitrary molecular systems. This functionality has been extended with a Radau KEO, which is expressed in terms of orthogonal Radau vectors and assumes a relatively simple analytical form. Although the Radau KEO is not fully general, it can be readily applied to XY_n molecules and renders matrix-vector multiplications more efficient. Another advantage of the Radau KEO is that elements of the **G** matrix do not have to be evaluated at the DVR points and stored in memory. Moreover, in case of a contracted vibrational basis there is no need for transforming **G** matrix elements from DVR to the contracted basis. The current implementation does not contain all terms present in the Radau KEO, the complete form will be finished in the near future.

Exchange of knowledge: highly efficient new Lanczos eigensolver versions developed in Budapest have been incorporated into the Zürich version of the code GENIUSH. Symmetry relations were investigated for H_5^+ to support an ongoing research project of the Budapest group.