Perturbative treatment of kinetic coupling terms in the Eckart−Watson Hamiltonian

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In this work we report recent advances implemented in the fourth-age quantum chemical program DEWE (*Discrete variable representation, Eckart−Watson Hamiltonian, Exact inclusion of arbitrary potential energy surfaces*) developed in our lab, which is an efficient, DVR-based implementation of the Eckart−Watson Hamiltonian for rotational-vibrational computations. The main focus of the poster is the perturbative treatment of the Coriolis and rotational-vibrational coupling terms present in the Eckart−Watson kinetic energy operator. To the best of our knowledge, this is the first Eckart−Watson-based rovibrational program which (a) employs discrete variable representation (DVR); (b) does not expand the μ tensor; and (c) is capable of a first- and second-order perturbative treatment of the kinetic coupling terms.

Based on a thorough analysis of the computed vibrational and rotational-vibrational energy levels of the triatomic H_2O and hexatomic C_2H_4 molecules we make the following observations: (a) first-order perturbation theory performs well for all the energy levels computed; (b) the effect of the second-order perturbative corrections to the rovibrational levels is almost negligible; (c) the perturbative treatment can reduce the computational costs by up to an order of magnitude, while in many cases maintaining an accuracy better than that of the potential energy surface. Based on these observations the use of a first-order perturbative treatment of the Coriolis and rotational-vibrational coupling terms of the Eckart−Watson operator is recommended for larger and heavier semirigid molecules.