

AUTOMATIC GENERATION OF ANALYTIC EQUATIONS FOR VIBRATIONAL AND ROVIBRATIONAL CONSTANTS FROM FOURTH-ORDER VIBRATIONAL PERTURBATION THEORY

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The derivation of analytic expressions for vibrational and rovibrational constants, for example the anharmonicity constants χ_{ij} and the vibration-rotation interaction constants α_r^B , from second-order vibrational perturbation theory (VPT2) can be accomplished with pen and paper and some practice. However, the corresponding quantities from fourth-order perturbation theory (VPT4) are considerably more complex, with the only known derivations by hand extensively using many layers of complicated intermediates and for rotational quantities requiring specialization to orthorhombic cases or the form of Watson's reduced Hamiltonian. We present an automatic computer program for generating these expressions with full generality based on the adaptation of an existing numerical program based on the sum-over-states representation of the energy to a computer algebra context. The measures taken to produce well-simplified and factored expressions in an efficient manner are discussed, as well as the framework for automatically checking the correctness of the generated equations.