ROTATIONAL REDUCTION OF THE EFFECTIVE HAMILTONIANS IN THE FRAMEWORK OF NUMERICAL-ANALYTIC VIBRATION-ROTATION OPERATOR PERTURBATION THEORY

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The customary approach for deciphering of high-resolution molecular vibra-tion-rotation spectra is based on fitting parameters of chosen effective Hamiltonians. Particular forms of such effective Hamiltonians are usually selected by trial-and-error procedures, comparing and analyzing their various possible forms. As it is well-known from Watson's works,[1] [2] the number of physically meaningful constants can be determined theoretically taking into account symmetry considerations and using a series of unitary rotational transformations (reductions) for cancellation of dependent parameters. The so-called A- and S-reductions up to octic terms can be derived analytically and are most commonly used for fitting molecular spectra of symmetric and asymmetric tops.[3] As was noted by Watson, the lower symmetry groups (C_s, C_i, etc.) can be reduced to the standard orthorhombic case (C_{2v}, D_{2h}) by an additional rotational transformation, but its form is usually not considered explicitly.

The *ab initio* solution of the direct vibration-rotation problem with Watson Hamiltonian can be accomplished by means of the numerical-analytic canonical perturbation theory in operator form.[4] This approach can be efficiently implemented using normal ordering of ladder operators of angular momentum (J_z, J_+, J_-) as it solves the central problem of evaluation of rotational commutators. After a series of even number of vibrational unitary transformations the obtained effective Hamiltonian can be further reduced to the final form by additional rotational unitary transformations, which can also be accomplished through normal ordering. Numerical examples demonstrating an efficiency of this approach are provided.

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[1] doi:10.1063/1.1840957, J.K.G. Watson, *J. Chem. Phys.*, **46**, 1935–1949 (1967).

[2] doi:10.1063/1.1668020, J.K.G. Watson, *J. Chem. Phys.*, **48**, 4517–4524 (1968).

[3] doi:10.1016/j.molstruc.2006.02.038, J.K.G. Watson, *J. Mol. Struct.*, **795**, 263–270 (2006).

[4] doi:10.1006/jmsp.1993.1245, J.-M. Flaud, W. J. Lafferty, *J. Mol. Spectrosc.*, **161**, 396–402 (1993).