AB INITIO PREDICTION OF THE VIBRATION-ROTATION SPECTRA AND EFFECTIVE HAMILTONIANS USING HIGH-ORDER OPERATOR PERTURBATION THEORY

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Nowadays, two concurrent approaches are being used for prediction and interpretation of high-resolution vibration-rotation spectra. The direct problem can be accurately solved by matrix diagonalization with exact KEO/*ab initio* PES, followed by their small adjustments to fit the observed spectra. On the contrary, more traditional and precise techniques of fitted effective Hamiltonians are being used for solving the inverse problem. The need of building the bridge between these direct and inverse problems is evident, while only a few attempts in this direction were made.[1]

The operator version of the vibration-rotation canonical Van Vleck perturbation theory (CVPT(n)) is a suitable tool for solving the direct problem.[2] The CVPT(n) is based on a series of vibrational operator unitary transformations of the full Watson Hamiltonian followed by rotational transformations (reduction) that allow to derive numerical values of observable quartic (Δ, δ), sextic (H, h) and even octic (L, l) spectroscopic constants (in 6th order), as well as obtain constants of effective resonance operators. Also, the derived vibrationally transformed effective Hamiltonian can be composed in the matrix form for a chosen value of J_{max} with accounting of Fermi, Darling-Dennison and Coriolis resonances. Its diagonalization produces vibration-rotation energy levels as well as wave functions that can be used for evaluation of intensities, provided that the dipole moment operator is also unitary transformed.

The traditional analytic form of CVPT is rather simple in the second order, while going to higher orders requires evaluation of complex rotational commutators that can reliably be done with the aid of analytic computations software. However, even for triatomic molecules such computations become rather heavy in orders higher than second. For a suitable solution of this problem and extension of applicability of CVPT(n) to larger molecules it is necessary to employ high-performance programming languages and solve certain theoretical problems for efficient evaluation of rotational commutators with possible participation of Wigner $D_{0,\varepsilon}^1$ functions.

We created a suite of high-performance routines written in Fortran90 that systematically performs CVPT(n),$n = 2, 4, 6$ calculations on a desk-top computer with a minimum manual control. This approach is largely based on evaluation of vibrational

[1] doi:10.1080/00268976.2022.2096140, V. Tyuterev, S. Tashkun, M. Rey, A. Nikitin, *Mol. Phys.*, **120**, e2096140 (2022).

[2] D. Papoušek, M. R. Aliev, *Molecular Vibrational-rotational Spectra: Theory and Applications of High Resolution Infrared, Microwave and Raman Spectroscopy of Polyatomic Molecules*, Elsevier, 323 pp (1982).

and rotational commutators using the normal ordering of ladder operators of angular momentum (J_z, $J_\pm = J_x \mp iJ_y$):[3]

$$: J_z^a J_+^b J_-^c J_z^d J_+^e J_-^f := \sum_{k=0}^{d} \binom{d}{k}(c-b)^k \sum_{m=0}^{min(c,e)} \binom{e}{m} \frac{c!}{(c-m)!} \sum_{l=0}^{m} s(m,l) \times$$
$$\times \sum_{j=0}^{l} (-2)^j \binom{l}{j} (2b-c+e)^{l-j} J_z^{a+d-k+j} J_+^{b+e-m} J_-^{c+f-m}. \tag{1}$$

The reduction can also be accomplished with the aid of such normal ordering. Similarly, unitary transformations of the dipole moment operator can be made using the normal ordering with the Wigner $D_{0,\varepsilon}^1$-functions ($\varepsilon = -1, 0, +1$):

$$: J_z^a J_+^b J_-^c D_{0,\varepsilon}^1 := \sum_\tau D_{0,\tau}^1 \sum_j c_{\tau j} J_z^{k_{\tau j}} J_+^{l_{\tau j}} J_-^{m_{\tau j}}. \tag{2}$$

The obtained effective Hamiltonian and dipole moment operators can be further used for calculation of simulated IR spectra for a chosen spectral range and vibrational transitions. The spectroscopic constants $\Delta, \delta, H, h, L, l$ can also be calculated after the a series of rotational unitary transformations. The effectiveness of this procedure for the $^{32}S^{16}O_2$ molecule is illustrated below, where the *ab initio* values are compared with empirical fittings: [4] [5]

Table 1: Comparison of the effective sextic spectroscopic constants, cm^{-1}

Constant		CVPT(4)	CVPT(6)	Observed[4]	Observed[5]
H_J	$\times 10^{12}$	0.3803	0.3859	0.3821	0.3746
H_{JK}	$\times 10^{12}$	-0.1247	1.3860	1.3250	1.1603
H_{KJ}	$\times 10^{12}$	-598.3840	-647.5335	-649.4890	-649.6069
H_K	$\times 10^{12}$	10773.5277	11986.1209	12412.9000	12360.4280
h_J	$\times 10^{12}$	0.1850	0.1875	0.1831	0.1830
h_{JK}	$\times 10^{12}$	-0.4181	-0.2406	-0.3787	-0.2430
h_K	$\times 10^{12}$	480.5198	556.6921	557.9130	567.9872

[3]doi:10.1063/5.0142809, X. Chang, D. V. Millionshchikov, I. M. Efremov, S. V. Krasnoshchekov, *J. Chem. Phys.*, **158**, 104802(1–12) (2023).

[4]doi:10.1006/jmsp.1993.1174, J.M. Flaud, A. Perrin, L.M. Salah, W.J. Lafferty, G. Guelachvili, *J. Mol. Spectrosc.*, **160**, 272–278 (1993).

[5]doi:10.1016/j.jqsrt.2013.04.011, O.N. Ulenikov, G.A. Onopenko, O.V. Gromova, E.S. Bekhtereva, V.-M. Horneman, *J. Quant. Spectrosc. Radiat. Transfer*, **130**, 220–232 (2013).