# A hybrid variation-perturbation method for calculating vibrational energy levels of a polyatomic molecule

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We present a hybrid variation-perturbation method to calculate vibrational energy levels of polyatomic molecules. Most accurately the Schrödinger equation for the motion of nuclear is solved employing variational methods based in conjunction with large enough basis sets. Experience has shown that to obtain vibrational term values ($v_1$,$v_2$,$v_3$,…) with the accuracy better than 1 $cm^{-1}$ the vibrational basis must include excitations at least up to $n_i = v_i + 6$. This can lead to extremely large variational basis sets (more than 1,000,000 functions) for molecules containing more than 10 degrees of freedom. To overcome this difficulty we propose a hybrid approach where the variational scheme is combined with the perturbation theory. In this approach the contribution from high vibrational excitations ($n_i > v_i + 6$) to the Hamiltonian matrix are accounted in a perturbative manner by means of a single Jacobi rotation. The vibrational term values are then found variationally by diagonalising a smaller, perturbatively corrected Hamiltonian matrix (with excitations of $v_i + 6$ and less).

Our variational procedure is based on the vibrational Hamiltonian represented in terms of the bond lengths and inter-bond angles as described in [1]. Our vibrational basis set is given by a product of the Morse (stretching modes) and Harmonic (bending modes) oscillators. In this case the Hamiltonian matrix has a simple analytical form [1], which ensures its fast calculation. At the same time the non-diagonal matrix elements are relatively small [1].

We applied the new approach to calculate the vibrational energies of $H_2O$, $C_2H_4$, and $HNO_3$, as part of the ExoMol project [2]. Our tests show that it is sufficient to use the excitations of $n_i \leq v_i + 4$ in the smaller, variational matrix with the perturbative contributions of $n_i = v_i + 6$ and higher. The matrix elements required for the Jacobi rotations are evaluated on the fly. The comparisons of the resulted obtained using our hybrid approach will be compared that of the pure perturbative and variational schemes.

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[1] L.A. Gribov, A.I. Pavlyuchko, Variational Methods for Solving Anharmonic Problems in the Theory of Vibrational Spectra of Molecules, Nauka, Moscow, **1998** (in Russian).
[2] J. Tennyson and S. N. Yurchenko, *Mon. Not. R. Astron. Soc.* **2012**, *425*, 21.