

# On the development of theoretical methods for describing highly excited ro-vibrational states in polyatomic molecules

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Although the quantum mechanical problems that can be solved exactly are rather sparse they received considerable interests over the past decades. Nowadays, the exactly solvable potentials are still widely used in many branches of physics, in particular to describe anharmonic molecular vibrations. This class of potentials has the nice property of being analytically integrable and possesses underlying compact and/or non-compact dynamical symmetries. They indeed proved to be useful for describing bound-state, scattering and coherent-state problems. In this context they gave rise to the development of many approximation methods, such as variational methods, where the primitive functions can be chosen as eigenfunctions of related zeroth-order problems. In this talk we are concerned with the calculation of very excited ro-vibrational energy levels in di- and polyatomic systems using techniques generally not encountered in spectroscopy. The first part is focused on the variational methods using eigensolutions of one-dimensional exactly solvable potentials for describing bending and stretching motions. To perform efficient calculations, the knowledge of matrix elements for various quantities is needed. Algebraic methods and supersymmetric quantum mechanics generally do not give access in a direct way to matrix elements of arbitrary powers of  $x$  or of more complicated functions found for example in the complete-kinetic+potential-nuclear Hamiltonian in curvilinear coordinates. In that purpose I will present a way to obtain closed analytical expressions for various matrix elements.

The second part is concerned with the construction of the complete nuclear Hamiltonian in normal coordinates expressed in terms of irreducible tensor operators. This allows the most complete account of molecular symmetry properties. Examples of ro-vibrational calculations will be given for  $XY_3$ ,  $XY_3Z$  and  $XY_4$  -type molecules from our recent *ab initio* potential energy surfaces (PES). To conclude, an extensive perturbative method based on contact transformations will be briefly presented. This allows to build non-empirical effective Hamiltonians directly from PES which will be block-diagonal with respect to molecular vibrational polyad patterns. As an illustrative example, the methane molecule will be considered.