

## *A new approach for calculating rotational spectra*

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A perturbation scheme to find approximate solutions of a generalized spectral problem is presented. The spectral problem is generalized in the sense that the "eigenvalues" searched for, are not real numbers but effective rotational Hamiltonians, and the associated "eigenfunctions" are wave operators used to construct effective observables [0]. The spectra of these effective rotational Hamiltonian gives the exact eigenstates of the rotation-vibration Hamiltonian.

The theory is applied to the effective Hamiltonian of methane vibrational ground state up to order 4 of perturbation and to its effective dipole moment up to order 2. The ab initio energy levels are in very good agreement with those derived from experiment up to  $J=30$ , so that the calculated transition wave numbers can be used to complement databases or at least can serve as starting guesses in refinements of experimental data sets.

Furthermore, it is shown that the effective rotational dipole moment is a more complex operator than previously anticipated. At the first order of our perturbation theory, as in the case of a single contact transformation [1-3], we do find that the laboratory-fixed effective dipole moment operator is a symmetrized scalar product of a direction cosine vector and another vector of Hermitian operators which can be interpreted as a body-fixed effective dipole moment. However, this interpretation seems no longer possible at order 2, because the operators that one could identify with body-fixed effective dipole components are not Hermitian, and in addition, there are also terms where direction cosine operators are in between angular momentum operators with no prospect of simplification by using their commutation relations [4].

A numerical test of our dipole moment formulas using ab initio data, with a careful assessment of the contributions of the different terms and of their convergence, will be presented. Given the high interest of methane effective dipole moment in high resolution spectroscopy and in space sciences [5-7], our formulas could also be used by spectroscopists to refined their experimental data with a more detailed effective dipole moment expression.

### **References**

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