A PRACTICAL PROCEDURE FOR AB INITIO DETERMINATION OF VIBRATIONAL SPECTROSCOPIC CONSTANTS, RESONANCES, AND POLYADS

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Although recent advances in computing power permit the high-accuracy computation of molecular potential energy surfaces (PES's), a challenge remains in relating the PES to spectroscopic observations. The relative importance of PES anharmonic terms, i.e., whether to treat them perturbatively or explicitly, will be discussed. Modifications will be made to the well-known second-order perturbation theory formulas for determining vibrational spectroscopic constants x_{ij} to account for resonances, and generalized formulas for determining Fermi and generalized Darling-Dennison resonance constants will be reviewed. The new program POLYAD uses these quantities to automatically generate polyad matrices, allowing for the ab initio prediction of excited vibrational energy levels in small polyatomic molecules.