

ROVIBRATIONAL CONSTANTS FROM FOURTH-ORDER PERTURBATION THEORY AND THE RELATIONSHIP TO THE CONTACT TRANSFORMATION APPROACH

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The nuclear Schrödinger equation forms the basis for vibrational perturbation theory. However, the canonical “ $\hat{H}\Psi = E\Psi$ ” form is shown to be insufficient for computing elements of the rotational effective Hamiltonian and ultimately the various rovibrational and vibrationally-averaged rotational molecular properties. The necessary modifications are shown to be a natural result of derivation of the Schrödinger equation in a non-commutative algebra. The resulting equation is also compared to the contact transformation approach (CVVPT) and the two are shown to be equivalent (as is well known in the pure vibrational case). Lastly, equations for various rovibrational constants using this corrected approach and fourth-order perturbation theory (VPT4) are presented and compared to the available literature results.