APPLICATION OF FOURTH-ORDER VIBRATIONAL PERTURBATION THEORY TO SMALL MOLECULES

JUSTIN Z. GONG, DEVIN A. MATTHEWS, and JOHN F. STANTON, *Department of Chemistry and Biochemistry, Institute for Theoretical Chemistry, The University of Texas at Austin, Austin, Texas 78712*.

Fourth-order Rayleigh-Schrödinger vibrational perturbation theory (VPT4) is applied to a variety of small molecular systems, including all terms from the Watson vibrational Hamiltonian except for the pseudopotential. The results are discussed primarily in comparison to VPT2, and the impact of Fermi and Darling-Dennison type resonances is examined. The sensitivity of the VPT4 correction to the quality of the force field is also analyzed, especially with regards to the quintic and sextic force constants.