CONNECTIONS BETWEEN THE RAYLEIGH-SCHRÖDINGER AND VAN VLECK PERTURBATION THEORIES AND THEIR APPLICATION TO RESONANCES IN MOLECULAR VIBRATIONS

D. A. MATTHEWS, J. VÁZQUEZ, AND J. F. STANTON, *Institute for Theoretical Chemistry, The University of Texas at Austin, Austin, Texas 78712*.

The similarities of Rayleigh-Schrödinger (RSPT) and Van Vleck (VVPT) perturbation theories are discussed. It is shown that a straightforward application of RSPT produces the VVPT Hamiltonian at the highest order of the contact transformations applied, which is always a diagonal matrix. VVPT Hamiltonians at an order higher than this are non-diagonal, but it is shown that a careful application of RSPT can produce the same matrices. The usefulness of these higher-order "dressed" Hamiltonians in treating resonance is discussed, as well as specific discussions of first-order Fermi, second-order Darlington-Dennison, and higher-order resonances. Lastly, VVPT is discussed in a wavefunction-based context and RSPT in a Hamiltonian-based context, and the approaches are contrasted.