COMPARISON OF SELF-CONSISTENT FIELD TREATMENTS OF KINETIC COUPLINGS IN CALCULATIONS ON POLYATOMIC MOLECULES

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The accuracy of the vibrational self-consistent field (VSCF) and time-dependent self-consistent field (TDSCF) approximations for studies of vibrational dynamics of polyatomic systems is investigated for systems in which the most important off-diagonal coupling terms in the Hamiltonian are in the kinetic energy operator. These terms become rigorously zero in the VSCF treatment, leading to large differences between the energies calculated using this approximation, compared to those obtained from a variational calculation. In contrast, when the energy levels are obtained from a wave function calculated within the TDSCF approximation, the calculated energy levels are in good agreement with variational results. These questions are investigated using a collinear model of HCN in an internal coordinate representation.