Abstract Submitted
for the MAR10 Meeting of
The American Physical Society

Molecular applications of analytical gradient approach for the improved virtual orbital-complete active space configuration interaction method. KARL FREED, University of Chicago, RAJAT CHAUDHURI, Indian Institute of Astrophysics — The improved virtual orbital-complete active space configuration interaction (IVO-CASCI) method is extended to determine the geometry and vibrational frequencies for ground and excited electronic states using an analytical total energy gradient scheme involving both first and second order analytical derivatives. Illustrative applications consider the ground state geometries of the benzene, biphenyl, and alanine dipeptide molecules and the first excited singlet and triplet states of benzene. Comparisons with Hartree-Fock, second order Moller-Plesset perturbation theory, complete active space self-consistent field (CASSCF), and density functional theory demonstrate that the IVO-CASCI approach generally fares comparable to or better for all systems studied, demonstrating the efficacy and potential of the method. The close similarity between CASSCF and IVO-CASCI optimized geometries and the greater computational efficiency of the IVO-CASCI method suggests the replacement of CASSCF treatments by the IVO-CASCI approach which is free of the convergence problems that often plague CASSCF treatments.

Karl Freed
University of Chicago

Date submitted: 01 Dec 2009 Electronic form version 1.4