Grid–based Hartree–Fock and second-order Møller–Plesset perturbation methods for atoms and polyatomic molecules

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ABSTRACT

Exact numerical solutions of the Hartree–Fock (HF) equation of polyatomic molecules have been obtained by an extension of the numerical density-functional method of Becke and Dickson [J. Chem. Phys. **89**, 2993 (1988); **92**, 3610 (1990)]. A finite-difference method has been used to solve the Poisson equation for the Coulomb and exchange potentials and to evaluate the action of the kinetic and Poisson operators on numerical orbitals expanded on an interlocking multicentered quadrature grid. Basis-set-limit HF results for an atom and diatomic and triatomic molecules are presented with the total energies and the highest occupied orbital energies converged to within 10^{-5} E_{H} without any extrapolation.

The basis-set-limit electron-correlation energies have been obtained with the grid-based second-order Møller–Plesset perturbation (MP2) method using the aforementioned numerical HF solutions. The Sinanoğlu equation, which corresponds to the first-quantized equation of the MP2 theory, has been solved for pair-correlation functions and electron-correlation energies in the same multicentered quadrature grid for polyatomic molecules. The benchmark basis-set-limit correlation energies will be presented for some representative systems.

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