Prediction of many-electron wavefunctions using atomic potentials

Jerry L. Whitten

Department of Chemistry, North Carolina State University, Raleigh, NC 27695 USA

A one-electron Schrödinger equation based on special one-electron potentials for atoms is shown to exist that produces orbitals for an arbitrary molecule that are often sufficiently accurate to be used without modification to construct single- and multi-determinant wavefunctions. The exact Hamiltonian is used to calculate the energy variationally and to generate configuration interaction expansions. Atomic potentials are reported for H, C, N, O, F and several other nuclei. These potentials remain invariant in molecular calculations, e.g., the potential for C is the same in methane and chlorophyll, and similarly for other atoms thus far investigated. For a test set of twenty molecules representing different bonding environments in equilibrium geometries, a single set of invariant atomic potentials gives wavefunctions with energies that deviate from configuration interaction energies based on SCF orbitals by less than 0.04 eV per bond or valence electron pair. On a single diagonalization of the Fock matrix, the corresponding errors are reduced to 0.01 eV. Atomization energies are also in good agreement with CI values based on canonical SCF orbitals. Configuration interaction applications to single bond dissociations of water and glycine, and multiple bond dissociations of ethylene and oxygen produce dissociation energy curves in close agreement with CI calculations based on canonical SCF orbitals for the entire range of internuclear distances. New computational strategies are discussed.