RECENT ADVANCES IN THE DENSITY MATRIX FUNCTIONAL THEORY

Jerzy Cioslowski and Katarzyna Pernal

Department of Chemistry and School of Computational Science and Information Technology, Florida State University, Tallahassee, Florida 32306-4309, USA

Recent advances in the density matrix functional theory (DMFT), in which the total energy of a Coulombic system is given by a fuctional of one-electron reduced density matrix (1-matrix), are presented. In this formalism, the only energy term for which the corresponding functional is not known explicitly is that arising from the electron-electron repulsion. Consequently, unlike the density functional theory, DMFT does not have to rely in its practical implementations upon the concept of a fictitious non-interacting system. This property of DMFT as well as the fact that it is capable of yielding natural spinorbitals makes it a promising new approach to the electron correlation problem.

Properties of several approximate density matrix functionals for the electron-electron repulsion energy are reviewed. It is shown that the Goedecker-Umrigar functional and its generalizations are incapable of properly describing a dense (i.e. weakly correlated) homogenous electron gas. A theory of the first- and second-order DMFT response properties, which gives rise to quadratically convergent DMFT procedure as well as to stability conditions, is derived. Such a formalism allows rigorous calculations of chemical potential and hardness of electrons in any Coulombic system.

The new theoretical developments are illustrated with several numerical examples.