Determination of electronic chemical potential within density functional theory[☆]

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Abstract

The Donnelly–Parr version of the density-matrix functional theory [R.A. Donnelly, R.G. Parr, J. Chem. Phys. 69 (1978) 4431] is tested with various approximate energy functionals being used. The results obtained are discussed in the context of the functional *N*-representability condition. It has been demonstrated that the Euler–Lagrange equation proposed by Donnelly and Parr has no solutions within the set of *N*-representable density matrices. It follows that the validity of Sanderson's Principle of Electronegativity Equalization is open to question. Techniques for evaluating the electronic chemical potential within density functional theory are briefly discussed. The approximation of the electronic chemical potential with the three-point finite-difference scheme seems to be the most relevant route to its evaluation at the present stage of development. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

As far as is known [1], the electronic chemical potential (ECP) of a many-electron system can be introduced in the framework of the density functional theory in two related ways.

The first definition of ECP is based on the differential expression for the ground-state electronic energy of a system (an atom, a molecule, etc.)

$$dE = \mu dN + \int \rho(\mathbf{r}) \, \delta v(\mathbf{r}) \, d\mathbf{r}$$

that comes out of the dependence of the energy E on two independent variables: the number of electrons N and the external potential $v(\mathbf{r})$ due to nuclei. In the foregoing expression, quantities μ and $\rho(\mathbf{r})$ turn out to be very important. The latter represents the electron density of a system, and the former defined as $(\partial E/\partial N)_v$ is called ECP by the analogy with the chemical potential of ordinary macroscopic thermodynamics. The first definition of ECP assumes that E may be determined as a smooth function of N by applying suitable interpolation methods [2]. So, the three-point finite-difference approximation to μ for a system with the ionization potential I and electron affinity A is $-(I + A)/2$. This allows identifying ECP with the negative of the electronegativity of a system [1].

On the contrary, Hohenberg–Kohn theorems [3] state that the ground-state energy is a functional of the ground-state density, and at fixed N and $v(\mathbf{r})$ the energy functional assumes its infimum with the ground-state density of the system. The theorems deal with a family of Hamiltonians, which vary in an

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[☆] Dedicated to Professor R. Gáspár on the occasion of his 80th year.

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