An Efficient Real Space Method for Orbital-Free Density-Functional Theory

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Abstract. We consider the Thomas-Fermi-von Weizsacker energy functional, with the Wang-Teter correction, and present an efficient real space method for Orbital-Free Density Functional Theory. It is proved that the energy minimizer satisfies a second order quasilinear elliptic equation, even at the points where the electron density vanishes. This information is used to construct an efficient energy minimization method for the resulting constrained problem, based on the truncated Newton method for unconstrained optimization. The Wang-Teter kernel is analyzed, and its behavior in real space at short and far distances is determined. A second order accurate discretization of the energy is obtained using finite differences. The efficiency and accuracy of the method is illustrated with numerical simulations in an Aluminium FCC lattice.

AMS subject classfications: 65M05, 74G65, 78M50

Key words: Density functional theory, truncated Newton method, constrained optimization.

1   Introduction

All material properties in a solid derive from the interactions between its constituent atoms. A full description of such interactions requires the solution of Schrödinger's equation in an ambient space of dimension $3N$, where N is the number of particles. In the Born-Oppenheimer approximation the positions of the nuclei of the atoms are fixed, so N represents the total number of electrons.

It was first realized by Thomas [1] and Fermi [2] that the electronic structure of solids in their ground state could be fully understood in terms of the electron density alone, ρ. This fact, which gave origin to Density-Functional Theory (DFT), was later formalized

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by Hohenberg and Kohn [3, 4]. In [3] it was proved that there exists a functional of the density $F[\rho]$, such that the ground state energy associated to an external potential v can be obtained by minimizing the energy

$$E[\rho] = F[\rho] + \int_\Omega v(\mathbf{x})\rho(\mathbf{x})\,d\mathbf{x}, \tag{1.1}$$

where Ω may be a bounded domain, a periodic cell, or the whole space. The exact form of $F[\rho]$, however, is not known. Kohn and Sham [5] presented an approximation scheme for $F[\rho]$, and wrote the energy as

$$E[\rho] = F_s[\rho] + F_H[\rho] + F_{XC}[\rho] + \int_\Omega v(\mathbf{x})\rho(\mathbf{x})\,d\mathbf{x}, \tag{1.2}$$

where $F_s[\rho]$ is the exact kinetic energy of a system of non-interacting electrons with density ρ. The other contributions to the energy in (1.2) are Hartree, exchange and correlation, and external potential energies, respectively.

The Hartree energy describes the Coulombic interactions between electrons:

$$F_H[\rho] = \frac{1}{2}\int_\Omega\int_\Omega \frac{\rho(\mathbf{x})\rho(\mathbf{y})}{|\mathbf{x}-\mathbf{y}|}\,d\mathbf{x}d\mathbf{y} = \frac{1}{2}\int_\Omega \rho K_H * \rho, \tag{1.3}$$

where we have defined $K_H(\mathbf{x}) = |\mathbf{x}|^{-1}$.

The exchange and correlation energy, $F_{XC}[\rho]$, introduces corrections to the energy that derive from using the non-interacting electron approximation for the kinetic and Hartree energies. Although the expression for the total energy in (1.2) is exact, $F_{XC}[\rho]$ is unknown. Here we approximate $F_{XC}[\rho]$ using the local density approximation (LDA) [4, 5]:

$$F_{XC}[\rho] = \int_\Omega f(\rho), \tag{1.4}$$

where $f(\rho)$ is given in (2.1) below.

The last term in energy (1.2) represents the effect of an external potential. In what follows we consider ρ to be the density of the valence electrons only. The core electrons and the nuclei are treated as a unit which interacts with the valence electrons through the pseudopotential $v(\mathbf{x})$.

The exact computation of the Kohn-Sham kinetic energy functional requires the computation of the N non-interacting electron orbitals, which is equivalent to solving a system of N coupled Schrödinger equations in $\mathbb{R}^3$. In the spirit of the Thomas-Fermi approach, it is desirable to approximate the kinetic energy by a functional of the density alone, free of orbitals. Several such approximations have been proposed in what is called Orbital-Free Density-Functional Theory (OFDFT) [1, 2, 6–10]. We consider the Thomas-Fermi-von Weizsacker kinetic energy functional, with the additional correction of Wang and Teter [7]:

$$F_s[\rho] = \frac{1}{8}\int_\Omega \frac{|\nabla\rho|^2}{\rho} + C_{TF}\int_\Omega \rho^{5/3} + F_{WT}[\rho]. \tag{1.5}$$