

REVIEW ARTICLE

Orbital-Free Density Functional Theory for Molecular Structure Calculations

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Abstract. We give here an overview of the orbital-free density functional theory that is used for modeling atoms and molecules. We review typical approximations to the kinetic energy, exchange-correlation corrections to the kinetic and Hartree energies, and constructions of the pseudopotentials. We discuss numerical discretizations for the orbital-free methods and include several numerical results for illustrations.

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1. Introduction

In modeling either atomic or molecular systems, the most common strategy relies on approximate solutions of Schrödinger equations; and the so-called density functional theory (DFT) has been established as one of the most widely used first-principles methods in many fields. DFT may be dated back to 1927 [68, 74, 98, 113]. It was first realized by Thomas [91] and Fermi [25] that the electronic structure of solids in their ground states could be fully understood in terms of the electron density ρ alone. This fact, which gave the origin to the DFT, was later formalized by Hohenberg and Kohn [44] in 1964. It was proved in [44] that there exists a functional, $E(\rho)$, of the electron density ρ of the system, such that for any external potential V_{ext} , the exact ground state energy of the system is the global minimum value of $E(\rho)$, and the density ρ that minimizes $E(\rho)$ is the exact ground state density ρ_0 , namely

$$E(\rho_0) = \min \left\{ E(\rho) : \rho \geq 0, \int_{\mathbb{R}^3} \rho = N \right\}, \quad (1.1)$$

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where N is the number of the electrons and

$$E(\rho) = T(\rho) + E_{ee}(\rho) + \int_{\mathbb{R}^3} V_{ext} \rho \quad (1.2)$$

with $T(\rho)$ the kinetic energy and $E_{ee}(\rho)$ the electron-electron interaction energy. The problem remains how to evaluate the kinetic energy $T(\rho)$ and the electron-electron interaction energy $E_{ee}(\rho)$, which is of surpassing difficulty. In 1965, Kohn and Sham [56] invented an indirect approach to the kinetic energy, the so-called Kohn-Sham (KS) method. They proposed introducing a set of N wavefunctions $\{\psi_i\}_{i=1}^N$ and expressing the total energy of the system as [56]

$$E(\rho) = T_s(\{\psi_i\}) + E_H(\rho) + E_{xc}(\rho) + \int_{\mathbb{R}^3} V_{ext} \rho, \quad (1.3)$$

where $T_s(\{\psi_i\})$ is the exact kinetic energy of the system of non-interacting electrons with density ρ :

$$T_s(\{\psi_i\}) = \frac{1}{2} \sum_{i=1}^N \int_{\mathbb{R}^3} |\nabla \psi_i|^2, \quad \rho = \sum_{i=1}^N |\psi_i|^2. \quad (1.4)$$

Other terms in the right hand of (1.3) are the Hartree energy, the exchange-correlation energy and the external potential energy, respectively. The Hartree energy describes the repulsion Coulomb interactions between electrons

$$E_H(\rho) = \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\rho(x)\rho(y)}{|x-y|}. \quad (1.5)$$

The exchange-correlation energy $E_{xc}(\rho)$ introduces corrections to the energy that derive from using the non-interacting electron approximation for the Hartree and kinetic energies. Although the expression for the total energy in (1.3) is exact, $E_{xc}(\rho)$ is unknown. For a system with slow varying density, we can make the local density approximation (LDA) [55]:

$$E_{xc}(\rho) = \int_{\mathbb{R}^3} \varepsilon_{xc}(\rho) \rho, \quad (1.6)$$

where $\varepsilon_{xc}(\rho)$ is the exchange-correlation energy per particle of a uniform electron gas of density ρ . The last term in (1.3), i.e., the integral term, represents the effect of an external potential. For a simple many-particle system without any electric and magnetic potentials, the external potential can be expressed by

$$V_{ext}(r) = - \sum_{\alpha=1}^M \frac{Z_{\alpha}}{|r - R_{\alpha}|}, \quad (1.7)$$