



Solving the self-interaction problem in Kohn–Sham density functional theory: Application to atoms



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ARTICLE INFO

Article history:

Received 16 June 2014

Received in revised form

8 September 2014

Accepted 14 September 2014

Available online 14 October 2014

Keywords:

C. Ab initio calculations

D. Electronic structure

ABSTRACT

In previous work, we proposed a computational methodology that addresses the elimination of the self-interaction error from the Kohn–Sham formulation of the density functional theory. We demonstrated how the exchange potential can be obtained, and presented results of calculations for atomic systems up to Kr carried out within a Cartesian coordinate system. In this paper, we provide complete details of this self-interaction free method formulated in spherical coordinates based on the explicit equidensity basis ansatz. We prove analytically that derivatives obtained using this method satisfy the Virial theorem for spherical orbitals, where the problem can be reduced to one dimension. We present the results of calculations of ground-state energies of atomic systems throughout the periodic table carried out within the exchange-only mode.

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1. Introduction

The self-interaction (SI) error has been present in quantum mechanical calculations of electronic states of matter since the inception of quantum mechanics. It arises through the use of the Hartree term to approximate the electrostatic energy of a cloud of electronic charges by a density. The product of densities, as used in the Hartree term, allows the interaction of two electrons in the same single particle state (or of an electron simultaneously in two different states), that is in clear violation of the Pauli exclusion principal. The SI error was first pointed out by Fock [1] in the 1030s, when even Fermi weighed in with a suggestion for a solution [2]. The problem remained more-or-less dormant until the introduction of the density functional theory (DFT) [3] in 1964 and its Kohn–Sham formulation [4] the following year, from which point the realization of its damaging effects has mushroomed, and so have the efforts at its alleviation [5].

At the same time, the computational simplicity of the Kohn–Sham method and the overall good agreement with experiment has resulted in an explosion of implementations. It was conjectured that the agreement resulted because of the cancellation of errors between the Hartree term and the so-called exchange correlation term (see below). Unfortunately, however, it was soon realized that the method failed in describing systems in which the

effects of correlation (Coulomb interaction) are judged to be strong, such as semiconductors and wide-gap insulators. The method was also found to fail in describing physical effects such as binding energies, activation barriers and rates in catalytic materials, and many others. For a recent review of these problems and the generally unsatisfactory nature of various formal schemes introduced for their alleviation, of which the list included in [5] provides but a small sample, the reader is directed to the literature [6].

A method proposed recently [7,8] addresses the SI problem for the non-interacting system in the Kohn–Sham density functional theory in computationally unexpected simple fashion, using the explicit equidensity basis (EEB) ansatz. We define its solution as the term is used in our work: to solve the self-interaction problem one must show that the Coulomb energy is calculated in terms of the pair density, and that the Coulomb potential is obtained by functional differentiation of the Coulomb energy with respect to the density. The formalism is founded on the expansion of the Slater determinant obtained in the Kohn–Sham formalism in terms of an orthonormal and complete basis, the equidensity basis, that exhibits explicitly the density, $n(\mathbf{r})$. The advantages provided by this feature are set forth in the papers just referred to. In these papers, the equidensity basis was expressed in a Cartesian coordinate system and a corresponding grid used to store the orbitals and their spatial derivatives along with those of the density. In order to complete the algebraic aspects of the formalism we repeat key parts of the derivation in terms of a spherical coordinate system. This formulation can be used advantageously

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in electronic structure codes based on atom-centered coordinate systems, e.g., in linear muffin-tin orbital (LMTO) or Korringa–Kohn–Rostoker (KKR) methods. For systems where all orbitals are spherical (s-orbitals), we prove analytically that the obtained potential using the explicit equidensity ansatz satisfies the Virial theorem.

2. Theory

2.1. Conventional Kohn–Sham theory

The solution, $\Psi(\mathbf{r}_{(N)})$, of the many-body Schrödinger equation for a quantum system of N interacting electrons under an external potential, $v(\mathbf{r})$, depends on all coordinates and is therefore hard to solve. The Kohn–Sham system [4] got introduced in conjunction with density functional theory [3] as a fictitious system of non-interacting particles which yields the same density as the original problem for the ground state. In the traditional Kohn–Sham theory the energy as a functional of the density, $n(\mathbf{r})$, is given by the expression

$$E[n] = \int v(\mathbf{r})n(\mathbf{r}) d\mathbf{r} + T_s[n] + U_H[n] + E_{xc}[n]. \quad (1)$$

$E_{xc}[n]$ denotes the exchange–correlation functional. The kinetic energy of a system of non-interacting particles is given by (the subscript s marks the non-interacting system)

$$T_s[n] = \langle \Phi | \hat{T}^N | \Phi \rangle, \quad (2)$$

where $\Phi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \Phi(\mathbf{r}_{(N)})$ is a single Slater determinant constructed out of the N lowest in energy solutions, $f_j(\mathbf{r})$, of the Kohn–Sham equations

$$\left[-\frac{1}{2}\nabla_{\mathbf{r}}^2 + v_{KS}(\mathbf{r}) \right] f_j(\mathbf{r}) = \epsilon_j f_j(\mathbf{r}), \quad (3)$$

and

$$U_H = \frac{1}{2} \iint \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2, \quad (4)$$

is the Hartree energy, a classical expression for the Coulomb energy. The density given by the expression

$$n(\mathbf{r}_1) = \int |\Phi(\mathbf{r}_{(N)})|^2 d\mathbf{r}_2 \dots d\mathbf{r}_N = \sum_{j=1}^N |f_j(\mathbf{r}_1)|^2. \quad (5)$$

The ground state of the system is determined through minimizing of the total energy functional (1). As shown by Hohenberg and Kohn [3], the basic variable of the density functional theory is the density, and the condition for the ground state is that the energy be stationary with respect to changes in the density, $\delta E[n]/\delta n = 0$. From that condition and $\delta T_s/\delta n = -v_{KS}$, the Kohn–Sham potential appearing in Eq. (3) must satisfy

$$v_{KS}(\mathbf{r}) = v(\mathbf{r}) + \frac{\delta U_H[n]}{\delta n(\mathbf{r})} + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}. \quad (6)$$

As already pointed out in the original paper of Hohenberg and Kohn [3], the classical expression, $U_H[n]$, for the Coulomb energy was used out of convenience, allowing a simple and efficient way of performing the functional derivative of the Coulomb energy with respect to the density. The simplicity, however, comes with a steep price: as shown above, the use of this term introduces self-interaction effects, the unphysical interaction of an electron with itself.

When the density in (5) is used in the Hartree term, it produces in the numerator inside the integral terms of the kind, $f_j(\mathbf{r}_1)f_j(\mathbf{r}_2)$,

describing the interaction of two particles in the same state. The use of the Hartree term with respect to a single-electron system clearly shows the SI problem, namely a particle in a given state interacting with itself in that state, that is in practice not compensated by the exchange correlation functional, which was defined to cancel the SI error exactly. However, this functional is unknown and in practice replaced by some approximate expression. Numerous implementations with respect to various approximate schemes for $E_{xc}[n]$ have helped to reveal the true state of affairs: approximate expressions can be designed to yield acceptable approximations to known results in a case-by-case basis, even in broad classes of systems and properties, but none can be shown *a priori* to satisfy the fundamental requirement of the second Hohenberg–Kohn theorem, namely that any approximate handling of the energy functional should yield an upper bound to the exact value of the ground state energy within the full solution of the corresponding Schrödinger equation. For example, the use of a given exchange–correlation functional within Kohn–Sham DFT could lead to a lower energy compared to the ground state energy of the many body solution of the equivalent Hamiltonian of the theory, where the Kohn–Sham formalism is not used.

2.2. Reformulation of the Kohn–Sham equations

The quantum mechanically correct expression of the Coulomb energy is expressed in terms of the pair density, $n(\mathbf{r}_1, \mathbf{r}_2)$, rather than the product of densities

$$U^{QM} = \iint \frac{n(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2, \quad (7)$$

where the pair density can be obtained by integrating the anti-symmetric, N -particle wave function, $\Psi(\mathbf{r}_{(N)})$, over all coordinates but two

$$n(\mathbf{r}_1, \mathbf{r}_2) = \frac{N(N-1)}{2} \int |\Psi(\mathbf{r}_{(N)})|^2 d\mathbf{r}_3 \dots d\mathbf{r}_N. \quad (8)$$

Clearly, the corresponding Coulomb energy is self-interaction free. For the Kohn–Sham system, described by a single Slater determinant, the non-interacting pair density (denoted by the subscript s) is given by the expression

$$n_s(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{4} \sum_{ij} \delta_{\sigma_i, \sigma_j} \left[f_i^{\sigma_i}(\mathbf{r}_1) f_j^{\sigma_j}(\mathbf{r}_2) - f_j^{\sigma_j}(\mathbf{r}_1) f_i^{\sigma_i}(\mathbf{r}_2) \right]^2, \quad (9)$$

where the $f_i^{\sigma_i}(\mathbf{r})$ are the occupied states or orbitals that are the N lowest in energy solutions of the Kohn–Sham equations, and σ_i is the spin index of that particular orbital. The non-interacting pair density can be split into two parts, the contribution to the classical Hartree term and the exchange part, J_s

$$n_s(\mathbf{r}_1, \mathbf{r}_2) = \frac{n(\mathbf{r}_1)n(\mathbf{r}_2) + J_s(\mathbf{r}_1, \mathbf{r}_2)}{2}, \quad (10)$$

with

$$J_s(\mathbf{r}_1, \mathbf{r}_2) = - \sum_{ij} \left[f_i^{\sigma_i^*}(\mathbf{r}_1) f_j^{\sigma_j^*}(\mathbf{r}_2) f_j^{\sigma_j}(\mathbf{r}_1) f_i^{\sigma_i}(\mathbf{r}_2) \delta_{\sigma_i, \sigma_j} \right]. \quad (11)$$

The expression for the non-interacting Coulomb energy reads as

$$U_s^{QM}[n] = \frac{1}{2} \iint \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 + \frac{1}{2} \iint \frac{J_s(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2. \quad (12)$$

The non-interacting Coulomb energy within the Kohn–Sham system, by construction self-interaction free, can be obtained by replacing the classical Hartree energy (Eq. (4)) by the quantum mechanical expression (Eq. (12)). The energy functional (Eq. (1))

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