Relationship between the effective potentials determining the density and the pair density

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ABSTRACT

A link between density and pair density functional theories is presented. The method of Levy, Perdew and Sahni is used to derive a relationship between the effective potentials of the Euler equation of the density functional theory and the Pauli potential of the pair density functional theory and between the effective potential for the spherically and system-averaged pair density and the Pauli potential of the pair density functional theory. These expressions can be considered constraints that the Pauli potential and the effective potentials should fulfil. They might be very useful in constructing approximations.

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1. Introduction

Electronic and spectroscopic properties of atoms, molecules and clusters are frequently calculated with the Kohn–Sham equations of the density functional theory. Recently, there is a growing interest in the orbital-free theory, because of an enormous simplification due to the fact that only the Euler equation has to be solved instead of the Kohn–Sham equations.

The Euler equation is the fundamental equation of the orbital-free density functional theory [1]. There exist several derivations of the Euler equation [2–4]. Levy et al. [2] derived a differential equation for the square root of the density and derived the local effective potential of this equation. Their method will be applied here to establish a relationship between the density functional and the pair density functional theories.

There is a renewed interest in the density matrix theory. Here we study the pair density functional theory. It was shown [5–8] that the problem of an arbitrary system can be reduced to a two-particle problem. It means an enormous simplification as we always have to solve a two-particle equation independently of the number of electrons. This remarkable result has the drawback that there is an unknown term in the effective potential. It was shown that this term is completely of kinetic nature and called Pauli potential.

It turned out that exact relations and theorems are important in the density functional theory as they proved to be useful in improving the accuracy of approximate energy functionals. It is be-

lieved that exact relations are also very useful in the pair density functional theory. Here an exact relation is derived that might be useful in inventing accurate approximations for the Pauli potential.

Some years ago Savin [9] proposed a theory that provides simple radial equations for a quantity $f(r)$ called spherically and system-averaged pair density. Savin [9] conjectured that $f(r)$ can be given by a weighted sum of the square of 'effective geminals'. Later, the present author [10] derived a radial equation for the square root of $f(r)$ via a double adiabatic connection. It was shown that it is possible to give a theory in which a single 'effective geminal' gives the function $f(r)$ contrary to the theory of Savin. The effective potential of this radial equation has also an unknown part. Using the method of Levy et al. [2] a relationship is established here between the effective potential for f and the Pauli potential of the pair density functional theory.

In Section 2. a relation between the effective potential of the Euler equation and the Pauli potential of the pair density functional theory is derived. Section 3 presents a link between the effective potential for f and the Pauli potential of the pair density functional theory. Section 4 is devoted to discussion.

2. Derivation of a relation between the effective potential of the Euler equation and the Pauli potential of the pair density functional theory

The Euler equation of the orbital-free density functional theory [1] can be written

$$\frac{\delta T_s}{\delta \varrho} + v_{KS} = \mu. \tag{1}$$

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There exist several forms of the Euler equation [2–4]. The form above is written in the non-interacting system. T_s, ϱ, v_{KS} and μ are the non-interacting kinetic energy, the electron density, the Kohn–Sham potential and the chemical potential, respectively. Levy et al. [2] derived a differential equation for the density

$$\left(-\frac{1}{2}\nabla^2 + v + v_{eff}\right)\varrho^{1/2} = \mu\varrho^{1/2}, \tag{2}$$

where v is the external potential and v_{eff} is a local effective potential. Another often applied form of the Euler equation is

$$\left(-\frac{1}{2}\nabla^2 + v_p + v_{KS}\right)\varrho^{1/2} = \mu\varrho^{1/2}, \tag{3}$$

where $v_p = v + v_{eff} - v_{KS}$ is the Pauli potential.

Turning to the pair density functional theory [6,7] first a short summary follows, then a relationship between v_{eff} above and the effective potential of the pair density functional theory is derived.

The pair density n can be calculated from the wave function by integrating $|\Psi|^2$ for all coordinates except $\mathbf{r}_1$ and $\mathbf{r}_2$:

$$n(\mathbf{r}_1, \mathbf{r}_2) = \frac{N(N-1)}{2}\int |\Psi(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2, \mathbf{r}_3, \sigma_3, \ldots, \mathbf{r}_N, \sigma_N)|^2$$
$$\times d\sigma_1 d\sigma_2 d\mathbf{r}_3 d\sigma_3, \ldots, d\mathbf{r}_N d\sigma_N, \tag{4}$$

where $\mathbf{r}_i, \sigma_i$ stand for the spatial and the spin coordinates and the integral symbol when referred to spin denotes summation. N is the number of electrons. The electron density, on the hand, can be given as

$$\varrho(\mathbf{r}) = N\int |\Psi(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2, \ldots, \mathbf{r}_N, \sigma_N)|^2 d\sigma_1 d\mathbf{r}_2 d\sigma_2, \ldots, d\mathbf{r}_N d\sigma_N. \tag{5}$$

The relation between the density and the pair density is

$$\varrho(\mathbf{r}_1) = \frac{2}{N-1}\int n(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2. \tag{6}$$

It has been proved [6–8] that the ground-state pair density can be determined by solving a single auxiliary equation of a two-particle problem

$$\left[-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 + v_p^{pdft}(\mathbf{r}_1, \mathbf{r}_2) + v_{eff}^{pdft}(\mathbf{r}_1, \mathbf{r}_2)\right]n^{1/2}(\mathbf{r}_1, \mathbf{r}_2)$$
$$= \mu_p n^{1/2}(\mathbf{r}_1, \mathbf{r}_2), \tag{7}$$

where

$$v_{eff}^{pdft}(\mathbf{r}_1, \mathbf{r}_2) = v(\mathbf{r}_1) + v(\mathbf{r}_2) + \frac{N-1}{r}. \tag{8}$$

μ_p is the energy needed to remove two electrons from the N-electron system. v_p^{pdft} is the Pauli potential of the pair density functional theory [6,7].

To derive a relation between the effective potential of the Euler equation and the Pauli potential of the pair density functional theory first Eq. (7) is rewritten with the density amplitude χ as

$$\left[-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 + v_p^{pdft}(\mathbf{r}_1, \mathbf{r}_2) + v_{eff}^{pdft}(\mathbf{r}_1, \mathbf{r}_2)\right]\chi(\mathbf{r}_1, \mathbf{r}_2)$$
$$= \mu_p \chi(\mathbf{r}_1, \mathbf{r}_2), \tag{9}$$

where

$$n(\mathbf{r}_1, \mathbf{r}_2) = \frac{N(N-1)}{2}|\chi(\mathbf{r}_1, \mathbf{r}_2)|^2. \tag{10}$$

Now, the method of Levy et al. [2] is applied to the two-electron Eq. (9) (instead of the N-electron Schrödinger equation of their original paper). The density amplitude is written as

$$\chi(\mathbf{r}_1, \mathbf{r}_2) = N^{-1/2}\varrho^{1/2}(\mathbf{r}_1)\phi(\mathbf{r}_1, \mathbf{r}_2). \tag{11}$$

Substituting Eq. (11) into Eq. (10) and taking into account the relation between the density and the pair density (6) we are led to

$$\int |\phi(\mathbf{r}_1, \mathbf{r}_2)|^2 d\mathbf{r}_2 = 1 \tag{12}$$

for any point $\mathbf{r}_1$. Substituting Eq. (11) into the two-electron Eq. (9), multiplying it with $\phi^*(\mathbf{r}_1, \mathbf{r}_2)$ and integrating for $\mathbf{r}_2$ we arrive at the relation

$$\int \phi^*(\mathbf{r}_1, \mathbf{r}_2)\left[-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 + v_p^{pdft}(\mathbf{r}_1, \mathbf{r}_2) + v_{eff}^{pdft}(\mathbf{r}_1, \mathbf{r}_2)\right]$$
$$\times \varrho^{1/2}(\mathbf{r}_1)\phi(\mathbf{r}_1, \mathbf{r}_2)d\mathbf{r}_2$$
$$= \int |\phi(\mathbf{r}_1, \mathbf{r}_2)|^2 \varrho^{1/2}(\mathbf{r}_1)d\mathbf{r}_2 = \mu_p\varrho^{1/2}(\mathbf{r}_1), \tag{13}$$

Combining Eqs. (2) and (13) the effective potential of the Euler equation has the form

$$v_{eff} = \frac{1}{2}\int |\nabla_1\phi(\mathbf{r}_1, \mathbf{r}_2)|^2 d\mathbf{r}_2 + \mu - \mu_p$$
$$+ \int \phi^*(\mathbf{r}_1, \mathbf{r}_2)\left[-\frac{1}{2}\nabla_2^2 + v(\mathbf{r}_2) + \frac{N-1}{r} + v_p^{pdft}(\mathbf{r}_1, \mathbf{r}_2)\right]\phi(\mathbf{r}_1, \mathbf{r}_2)d\mathbf{r}_2. \tag{14}$$

To obtain this expression the relation $\nabla_1\int |\phi(\mathbf{r}_1, \mathbf{r}_2)|^2 d\mathbf{r}_2 = 0$ (following from Eq. (12)) was used.

Eq. (14) establishes a relationship between the effective potential of the Euler equation and the Pauli potential of the pair density functional theory [6,7]. Note that because of relation (11), Eq. (14) contains only the density ϱ and the pair density n.

3. Derivation of a relation between the effective potential for f and the Pauli potential of the pair density functional theory

The spherically and system-averaged pair density is defined as

$$f(r) = \int n(\mathbf{r}, \mathbf{R})\frac{d\Omega_r}{4\pi} d\mathbf{R}, \tag{15}$$

where

$$\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2. \tag{16}$$

and

$$\mathbf{R} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2). \tag{17}$$

Savin [9] put forward a theory in which $f(r)$ can be given by a weighted sum of the square of 'effective geminals' ψ_i

$$\sum_i \theta_i|\psi_i(r)|^2 = f(r), \tag{18}$$

with weighting factors of 'occupancy' θ_i. These 'effective geminals' ψ_i satisfy simple radial equations

$$\left[-\nabla_r^2 + \tilde{w}_{eff}(r)\right]\psi_i(r) = \epsilon_i\psi_i(r). \tag{19}$$

Later, a double adiabatic connection was applied [10] to derive a radial equation for the square root of $f(r)$

$$\left[-\nabla_r^2 + w_{eff}(r)\right]f^{1/2}(r) = \varepsilon f^{1/2}(r). \tag{20}$$

It turned out that a theory in which a single 'effective geminal' gives the function $f(r)$ is also possible.

The starting point of the derivation is the two-particle Eq. (9). Using relative and center of mass coordinates (Eqs. (16) and (17)) the two-particle equation has the form

$$\left[-\frac{1}{4}\nabla_{\mathbf{R}}^2 - \nabla_{\mathbf{r}}^2 + v_p^{pdft}(\mathbf{R}, \mathbf{r}) + v_{eff}^{pdft}(\mathbf{R}, \mathbf{r})\right]\chi(\mathbf{R}, \mathbf{r}) = \mu_p\chi(\mathbf{R}, \mathbf{r}). \tag{21}$$