

Density and Pair Density Scaling in Density and Pair Density Functional Theories

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Abstract

A link between density and pair density functional theories is presented. Density and pair density scaling are used to derive the Euler equation in both theories. Density scaling provides a constructive way of obtaining approximations for the Pauli potential. The Pauli potential (energy) of the density functional theory is expressed as the difference of the scaled and original exchange-correlation potentials (energies).

I. INTRODUCTION

Nowadays, studies on electronic and spectroscopic properties of atoms, molecules and clusters are generally based on density functional theory. Besides the Kohn-Sham approach there is a growing role of the orbital-free theory. The fact that only the Euler equation has to be solved instead of the Kohn-Sham equations, might lead to an enormous simplification provided that a good approximation for the unknown kinetic energy functional is found.

Therefore the Euler equation is a fundamental equation of the density functional theory [1]. There exist several derivations of the Euler equation [2–4]. The Euler equation of the non-interacting system has the form

$$\frac{\delta T_s}{\delta \varrho} + v_{KS} = \mu, \quad (1)$$

where T_s is the non-interacting kinetic energy, v_{KS} is the Kohn-Sham potential and μ is the chemical potential.

Here we present a novel derivation using density scaling. Density scaling was proposed by Chan and Handy [5]. In density scaling the density $\varrho(\mathbf{r})$ is changed to $\zeta\varrho(\mathbf{r})$. Earlier we used density scaling to treat electron correlation [6,7] and generalized to multiplets [8] and excited states [9]. Now, we extend density scaling to pair density and derive the two-particle equation that can be considered the 'Euler equation' of the pair density functional theory. The method provides a link between the two theories. Moreover, it is found that the Pauli potential (energy) of the density functional theory is expressed as the difference of the scaled and original exchange-correlation potentials (energies). This relation gives a novel, constructive way of obtaining approximations for the Pauli potential.

II. DERIVATION OF EULER EQUATION OF DENSITY FUNCTIONAL THEORY VIA DENSITY SCALING

Consider the ground-state of the Hamiltonian

$$\hat{H} = \hat{T} + \hat{V} + \hat{V}_{ee} , \quad (2)$$

where

$$\hat{T} = \sum_{j=1}^N \left(-\frac{1}{2} \nabla_j^2 \right) , \quad (3)$$

$$\hat{V}_{ee} = \sum_{k=1}^{N-1} \sum_{j=k+1}^N \frac{1}{|\mathbf{r}_k - \mathbf{r}_j|} \quad (4)$$

and

$$\hat{V} = \sum_{k=1}^N \sum_{J=1}^{N_n} \frac{-Z_J}{|\mathbf{r}_k - \mathbf{R}_J|} \quad (5)$$

are the kinetic energy, the electron-electron energy and the electron-nuclear energy operators, respectively. N and N_n are the number of electrons and nuclei. The density ϱ has the

properties that $\varrho \geq 0$, $\int \varrho(\mathbf{r})d\mathbf{r} = N$ and $\int (\nabla \varrho^{1/2})^2 d\mathbf{r}$ is finite [10,11]. The non-interacting system is usually defined via adiabatic connection [12,13] considering a Hamiltonian

$$\hat{H}_{KS} = \hat{T} + \hat{V}_{KS} , \quad (6)$$

where

$$\hat{H}_{KS} = \sum_{j=1}^N v_{KS}(\mathbf{r}_j) . \quad (7)$$

The effective potential v_{KS} is constructed by keeping the ground-state density $\varrho(\mathbf{r})$ fixed.

In density scaling we construct another non-interacting system with a scaled density $\varrho_\zeta(\mathbf{r}) = \varrho(\mathbf{r})/\zeta$, where $\zeta = N/N_\zeta$ is a positive number. If $\zeta = 1$ we get back the original non-interacting (Kohn-Sham) system. If the original real system has N -electrons the Kohn-Sham system with the scaled density ϱ_ζ has N_ζ -electrons:

$$\int \varrho_\zeta(\mathbf{r})d\mathbf{r} = N_\zeta . \quad (8)$$

In this section we take $N_\zeta = 2$ and denote this value of ζ as $\zeta_d = N/2$. It means that we have a non-interacting system with two electrons. Then we apply the constrained search [14,10]: minimize the scaled kinetic energy

$$-2\frac{1}{2} \int \phi^*(\mathbf{r})\nabla^2\phi(\mathbf{r})d\mathbf{r} \quad (9)$$

with a fixed scaled density

$$\varrho_{\zeta_d} = 2|\phi|^2 : \quad (10)$$

$$Min \left(- \int \phi^*(\mathbf{r})\nabla^2\phi(\mathbf{r})d\mathbf{r} + \int \varrho_{\zeta_d}(\mathbf{r})v_{\zeta_d}(\mathbf{r})d\mathbf{r} + \mu \int \varrho_{\zeta_d}(\mathbf{r})d\mathbf{r} \right) . \quad (11)$$

The constraints of the minimization include fixing the density ϱ_{ζ_d} and its norm (Eq. (8)) with the Lagrange multipliers $v_{\zeta_d}(\mathbf{r})$ and μ , respectively. The minimization leads to the equation

$$-\frac{1}{2}\nabla^2\phi + v_{\zeta_d}\phi = \mu\phi . \quad (12)$$

This equation can also be written as

$$\left(-\frac{1}{2}\nabla^2 + v_{\zeta_d}\right) \varrho_{\zeta_d}^{1/2} = \mu \varrho_{\zeta_d}^{1/2} \quad (13)$$

or

$$\left(-\frac{1}{2}\nabla^2 + v_{\zeta_d}\right) \varrho^{1/2} = \mu \varrho^{1/2}. \quad (14)$$

Eqs. (13) and (14) can be transcribed as

$$-\frac{1}{2\varrho^{1/2}}\nabla^2 \varrho^{1/2} + v_{\zeta_d} = \mu. \quad (15)$$

From Eqs. (13),(14) and (15) we can see that v_{ζ_d} exists and unique up to a constant (μ):

$$v_{\zeta_d} = \mu + \frac{1}{2\varrho^{1/2}}\nabla^2 \varrho^{1/2}. \quad (16)$$

Taking into account that the first term in Eq. (15) is the functional derivative of the Weizsäcker kinetic energy [15]

$$T_w = \frac{1}{8} \int \frac{|\nabla \varrho|^2}{\varrho} d\mathbf{r} \quad (17)$$

$$\frac{\delta T_w}{\delta \varrho} = -\frac{1}{2\varrho^{1/2}}\nabla^2 \varrho^{1/2} \quad (18)$$

Eq. (15) has the form

$$\frac{\delta T_w}{\delta \varrho} + v_{\zeta_d} = \mu. \quad (19)$$

Define the potential v_p as

$$v_p = v_{\zeta_d} - v_{KS}. \quad (20)$$

From the existence of v_{ζ_d} (Eq. (16)) and v_{KS} (Eq. (7)) follows the existence of the potential v_p . Eqs. (19) and (20) lead to

$$v_p = \mu - \frac{\delta T_w}{\delta \varrho} - v_{KS}. \quad (21)$$

It is customary to partition the original non-interacting kinetic energy as

$$T_s = T_w + T_p , \quad (22)$$

where T_p is the Pauli energy. Writing Eq. (21) in the form

$$\frac{\delta T_w}{\delta \varrho} + v_p + v_{KS} = \mu \quad (23)$$

we immediately see that this equation is the Euler equation (1) and v_p is the Pauli potential [16,2,17], that is, the functional derivative of the Pauli energy

$$v_p = \frac{\delta T_p}{\delta \varrho}. \quad (24)$$

From the existence of v_p (Eq. (20)) follows that the functional derivative of the Pauli energy (Eq. (24)) exists.

III. DERIVATION OF PAIR DENSITY FUNCTIONAL THEORY VIA PAIR DENSITY SCALING

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

$$n(\mathbf{r}_1, \mathbf{r}_2) = \frac{N(N-1)}{2} \int |\Phi(\mathbf{r}_1, d\sigma_1, \mathbf{r}_2, d\sigma_2, \mathbf{r}_3, d\sigma_3, \dots, \mathbf{r}_N, d\sigma_N)|^2 d\sigma_1 d\sigma_2 d\mathbf{r}_3 d\sigma_3 \dots d\mathbf{r}_N d\sigma_N, \quad (25)$$

where \mathbf{r}_i, σ_i stand for the spatial and the spin coordinates and the integral symbol when referred to spin denotes summation. There is a simple relation between the density and the pair density

$$\varrho(\mathbf{r}_1) = \frac{2}{N-1} \int n(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 \quad (26)$$

It has been shown [18–20] that in the ground state the pair density can be determined by solving a single auxiliary equation of a two-particle problem.

$$\left[-\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 + v_p^{pdf}(\mathbf{r}_1, \mathbf{r}_2) + v_{eff}(\mathbf{r}_1, \mathbf{r}_2) \right] n^{1/2}(\mathbf{r}_1, \mathbf{r}_2) = \mu_p n^{1/2}(\mathbf{r}_1, \mathbf{r}_2), \quad (27)$$

$$v_{eff}(\mathbf{r}_1, \mathbf{r}_2) = v(\mathbf{r}_1) + v(\mathbf{r}_2) + \frac{N-1}{r}. \quad (28)$$

v is the external potential and the notation $r = |\mathbf{r}_1 - \mathbf{r}_2|$ is used. μ_p is the energy needed to remove two electrons from the N -electron system. The meaning of the potential v_p^{pdf} will be detailed below.

Consider an auxiliary system with a scaled pair density $n_\zeta(\mathbf{r}) = n(\mathbf{r})/\zeta$, where ζ is a positive number. (It is similar to the non-interacting system of the density functional theory.) In this section we take $\zeta = \zeta_p = N(N-1)/2$. It means that we have an auxiliary system with two electrons and $n_\zeta(\mathbf{r})$ is normalized to 1

$$\int n_{\zeta_p}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 = 1. \quad (29)$$

Then we apply the constrained search: minimize the scaled kinetic energy

$$-\frac{1}{2} \int \chi_{\zeta_p}^*(\mathbf{r}_1, \mathbf{r}_2) (\nabla_1^2 + \nabla_2^2) \chi_{\zeta_p}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (30)$$

with a fixed scaled pair density

$$n_{\zeta_p} = |\chi_{\zeta_p}|^2 : \quad (31)$$

$$\begin{aligned} \text{Min} \left[-\frac{1}{2} \int \chi_{\zeta_p}^*(\mathbf{r}_1, \mathbf{r}_2) (\nabla_1^2 + \nabla_2^2) \chi_{\zeta_p}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 + \right. \\ \left. \int n_{\zeta_p}(\mathbf{r}_1, \mathbf{r}_2) v_{\zeta_p, eff}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 + \mu_p \int n_{\zeta_p}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \right]. \end{aligned} \quad (32)$$

Note that the function χ_{ζ_p} is defined up to a phase factor. The minimization leads to the equation

$$\left[-\frac{1}{2} (\nabla_1^2 + \nabla_2^2) + v_{\zeta_p, eff} \right] \chi_{\zeta_p} = \mu_p \chi_{\zeta_p}. \quad (33)$$

This equation can also be written as

$$\left[-\frac{1}{2} (\nabla_1^2 + \nabla_2^2) + v_{\zeta_p, eff} \right] n_{\zeta_p}^{1/2} = \mu_p n_{\zeta_p}^{1/2} \quad (34)$$

or

$$[-\frac{1}{2}(\nabla_1^2 + \nabla_2^2) + v_{\zeta_p, eff}]n^{1/2} = \mu_p n^{1/2}. \quad (35)$$

Eqs. (34) and (35) can be transcribed as

$$-\frac{1}{2n^{1/2}}(\nabla_1^2 + \nabla_2^2)n^{1/2} + v_{\zeta_p, eff} = \mu_p. \quad (36)$$

Note that the potential $v_{\zeta_p, eff}$ exists and unique up to a constant(μ_p) as it can be expressed from Eq. (36)

$$v_{\zeta_p, eff} = \mu_p + \frac{1}{2n^{1/2}}(\nabla_1^2 + \nabla_2^2)n^{1/2}. \quad (37)$$

Earlier we defined [18,21] (see also [22,23]) the Weizsäcker kinetic energy with the pair density

$$T_w^{pdf} = \int n^{1/2}(\mathbf{r}_1, \mathbf{r}_2) \left(-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 \right) n^{1/2}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2. \quad (38)$$

(Note that for convenience there is a different (from [18,21]) factor here in the definition of the Weizsäcker kinetic energy.) The functional derivative with respect to the pair density has the form

$$\frac{\delta T_w^{pdf}}{\delta n} = -\frac{1}{2n^{1/2}}(\nabla_1^2 + \nabla_2^2)n^{1/2}. \quad (39)$$

Therefore Eq. (36) can be rewritten as

$$\frac{\delta T_w^{pdf}}{\delta n} + v_{\zeta_p, eff} = \mu_p. \quad (40)$$

Define the potential v_p^{pdf} as

$$v_p^{pdf} = v_{\zeta_p, eff} - v_{eff}. \quad (41)$$

From the existence of $v_{\zeta_p, eff}$ (Eq. (37)) and v_{eff} (Eq. (26)) follows the existence of the potential v_p^{pdf} . Eqs. (40) and (41) lead to

$$v_p^{pdf} = \mu_p - \frac{\delta T_w^{pdf}}{\delta n} - v_{eff}. \quad (42)$$

Partition now the kinetic energy as

$$T = T_w^{pdf} + T_p^{pdf}, \quad (43)$$

where T_p^{pdf} is the Pauli energy of the pair density functional theory. Writing Eq. (42) in the form

$$\frac{\delta T_w^{pdf}}{\delta n} + v_p^{pdf} + v_{eff} = \mu_p. \quad (44)$$

we immediately see that this equation is the two-particle equation (27) and v_p^{pdf} is the functional derivative of the Pauli energy with respect to the pair density functional

$$v_p^{pdf} = \frac{\delta T_p^{pdf}}{\delta n}. \quad (45)$$

From the existence of the Pauli potential v_p^{pdf} follows that the functional derivative of the Pauli energy with respect to the pair density functional exists.

IV. DISCUSSION

The Euler equations derived above in the density and pair density functional theories are very similar. They have a similar form. Both equations include a Pauli potential. The kinetic energy functionals (as functionals of the density or the pair density) are unknown. Separating from them the known Weizsäcker term, the unknown part is incorporated into the Pauli term in both theories.

The forms of Euler equations obtained via density scaling (Eqs. (15) and (35)) are of importance. These are very simple, exact equations of the many-body problem. However, the potentials v_{ζ_d} and $v_{\zeta_p,eff}$ include unknown terms. Density and pair density scaling might give a practical way of construction of these potentials. Finding adequate approximation for the Pauli potential is a very hard problem. Density scaling induces a hope of construction of good approximate Pauli potentials. It should be the subject of further research.

Beyond the similarity there are differences between the density and pair density functional theories. The main difference, we have to emphasize here, comes from the fact that we considered non-interacting kinetic energy in the density functional theory. In the pair density functional theory, on the other hand, the true interacting kinetic energy was treated. We

discuss now an important consequence of using T_s . As it was presented earlier [5–7] there is a relation between the original non-interacting kinetic (T_s) and exchange-correlation (E_{xc}) and the scaled non-interacting kinetic (T_ζ) and exchange-correlation ($E_{\zeta xc}$) energies:

$$T_s + E_{xc} = T_\zeta + E_{\zeta xc}. \quad (46)$$

The functional derivation leads to an expression containing the original and scaled exchange-correlation potentials:

$$\frac{\delta T_s}{\delta \rho} + v_{xc} = \frac{\delta T_\zeta}{\delta \rho} + v_{\zeta xc}. \quad (47)$$

Taking the case $\zeta = \zeta_d$ and the separation $T_s = T_w + T_p$ we arrive at

$$T_w + T_p + E_{xc} = T_w + E_{\zeta_d xc} \quad (48)$$

or

$$T_p = E_{\zeta_d xc} - E_{xc}. \quad (49)$$

Use of Eq. (24) leads to the corresponding equation for the functional derivatives:

$$v_p = v_{\zeta_d xc} - v_{xc}. \quad (50)$$

Eqs. (49) and (50) are novel expressions for the Pauli energy and potential. What is remarkable here is the fact that the completely kinetic terms E_p and v_p are expressed as the difference of the scaled and original exchange-correlation energies and potentials. It is, of course, the consequence of Eq. (46), that shows how the density scaling mixes the kinetic and exchange-correlation terms. Expressions (49) and (50) make it possible to seek alternative approximations for the Pauli energy and potential. There are several good exchange-correlation functionals that might prove to be useful to approximate E_p and v_p .

The non-interacting kinetic energy functional T_s has been in the center of interest [24–29]. The key issue is the existence and uniqueness of its functional derivative with respect to the electron density. Liu and Ayers [4] showed from three theoretical viewpoints that $\delta T_s / \delta \rho$ can

be expressed as the negative of the Kohn-Sham potential. It is unique up to an arbitrary additive constant that plays the role of chemical potential μ in the Euler equation (1). The present procedure provides an alternative derivation. Of course, all methods are restricted to v_{KS} -representable densities. Here it means that we consider densities for which the scaled density is associated with the ground-state of a non-interacting system.

Recently, there has been a growing interest in orbital-free density functional theory. The present derivation of the Euler equation might give fresh insight into the problem and the novel expression for the Pauli potential and energy might help the search for better approximations.

The pair density functional theory can be an alternative approach of the density functional theory provided that an adequate approximation for the Pauli potential of the pair density functional theory is found. The problem is much more difficult than in the density functional theory because of the N -representability problem [30–44]. It is hoped that the present derivation of the two-particle effective equation of the pair density functional theory will turn to be useful in seeking approximate approaches for the Pauli potential.

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