Functional derivative of the kinetic energy functional for spherically symmetric systems

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Abstract

Ensemble non-interacting kinetic energy functional is constructed for spherically symmetric systems. The differential virial theorem is derived for the ensemble. A first-order differential equation for the functional derivative of the ensemble non-interacting kinetic energy functional and the ensemble Pauli potential is presented. This equation can be solved and a special case of the solution provides the original non-interacting kinetic energy of the density functional theory.

I. INTRODUCTION

In orbital-free density functional theory [1] one has to solve only the Euler equation, which is a huge simplification in comparison with solving the Kohn-Sham equations [2]. However, the lack of accurate approximation of the kinetic energy functional highly limits the applicability of orbital-free calculations.

In this article an exact expression is presented for spherically symmetric systems. Instead of treating the original orbital-free problem, we suggest to solve an enlarged task. We construct ensembles using the original non-interacting Kohn-Sham system. Then the differential virial theorem is derived for the ensemble, which is applied to obtain a first-order

differential equation for the functional derivative of the ensemble non-interacting kinetic energy functional. This equation can be solved and a special case of the solution provides the solution of the original orbital-free problem.

In the following section ensembles are constructed in the Kohn-Sham system. In Sec. III. the differential virial theorem is derived for the ensemble. Sec. IV presents the derivation of the differential equation for the functional derivative of the ensemble non-interacting kinetic energy functional. The last section is devoted to discussion. In the appendix the functional derivative of the ensemble non-interacting kinetic energy is derived in another way.

II. CONSTRUCTION OF ENSEMBLES IN THE KOHN-SHAM SYSTEM

Consider the original Kohn-Sham equations

$$[-\frac{1}{2}\nabla^2 + v_{KS}(\mathbf{r})]u_i(\mathbf{r}) = \varepsilon_i u_i(\mathbf{r}), \tag{1}$$

where the electron density has the form

$$n_0(\mathbf{r}) = \sum_i^N n_i(\mathbf{r}). \tag{2}$$

$$n_i(\mathbf{r}) = |u_i(\mathbf{r})|^2 \tag{3}$$

is the one-electron density. N, u_i, and v_{KS} are the number of electrons, the Kohn-Sham orbitals and the Kohn-Sham potential, respectively. $\varepsilon_1 \leq \varepsilon_2 \leq ... \leq \varepsilon_N$ are the one-electron energies. The Kohn-Sham orbitals satisfy orthonormality

$$\int u_i^*(\mathbf{r})u_j(\mathbf{r})d\mathbf{r} = \delta_{ij}. \tag{4}$$

To derive the exact expression for the functional derivative of the kinetic energy functional we first define auxiliary quantities in the non-ineracting Kohn-Sham system. The most important one is the density defined as

$$n(\mathbf{r}) = \sum_{i=1}^N w_i n_i(\mathbf{r}), \tag{5}$$

where the weighting factors satisfy the inequalities:

$$w_1 \geq w_2 \geq ... \geq w_N \geq 0. \tag{6}$$

This density can be considered as an ensemble density as it is similar to the ensemble density defined in the real, interacting system. However, it is different in several aspects. For example, the 'ensemble' density defined here (Eq. (5) is generally not normalized to the number of electrons. This is just artificially constructed auxiliary quantity that is used only to derive the functional derivative of the non-interacting kinetic energy. In the following it will be referred as ensemble density. Note that if all $w_i = 1$ the ensemble density equals the electron density: $n = n_0$. In Section 3 the weighting factors are defined by Eq. (34) and $0 < w_i \leq 1$.

The second auxiliary quantity is the ensemble non-interacting kinetic energy density defined as:

$$t(\mathbf{r}) = \sum_{i=1}^{N} w_i t_i(\mathbf{r}), \tag{7}$$

where t_i are the one-electron kinetic energy density. In this article we use the form

$$t_i(\mathbf{r}) = -\frac{1}{2} u_i^*(\mathbf{r}) \nabla^2 u_i(\mathbf{r}). \tag{8}$$

Note that if all $w_i = 1$ the ensemble non-interacting kinetic energy density is equal to the non-interacting kinetic energy density t_0 of the original Kohn-Sham system.

The ensemble non-interacting kinetic energy is defined

$$T = \int t(\mathbf{r}) d\mathbf{r} \tag{9}$$

as another auxiliary quantity. From Eqs. (1) - (8) we immediatelly obtain that

$$T + \int n(\mathbf{r}) v_{KS}(\mathbf{r}) d\mathbf{r} = \mathcal{E}, \tag{10}$$

where, the ensemble non-interacting energy

$$\mathcal{E} = \sum_{i=1}^{N} w_i \varepsilon_i \tag{11}$$

is introduced as another auxiliary quantity. Again, if all $w_i = 1$ the ensemble non-interacting energy is equal to the total non-interacting energy :

$$\mathcal{E}_0 = \sum_{i=1}^{N} \varepsilon_i. \tag{12}$$

Now, we refer to the generalized Rayleigh-Ritz variational principle [3,4]. Gross et al. applied this principle for ensembles of ground and excited states to generalize density functional theory to excited states. The principle is valid for non-interacting systems, too. We apply it to the ensemble non-interacting energy $\mathcal{E}$. The only condition for the variational principle be valid is that the inequality (6) is satisfied. Any normalization of the ensemble density is possible. In this paper we use the following normalization.

$$\int n(\mathbf{r}) d\mathbf{r} = \sum_{i=1}^{N} w_i = const \tag{13}$$

is a fixed constant, but it is equal to the number of electrons N only for the case when all $w_i = 1$, that is, for the originl Kohn-Sham case. From the generalized variational principle follows the ensemble Euler equation. Making use of Eq. (10), the ensemble Euler equation takes the form

$$\frac{\delta T}{\delta n} + v_{KS} = \mu. \tag{14}$$

Compare it with the Euler equation of the non-interacting system:

$$\frac{\delta T_0}{\delta n_0} + v_{KS} = \mu_0. \tag{15}$$

Note that both Eqs. (14) and (15) have the same Kohn-Sham potential. It is because we are considering a non-interacting system.

Following Liu and Ayers [5] we prove in the Appendix that the functional derivative of the ensemble non-interacting kinetic energy $\frac{\delta T}{\delta n(\mathbf{r})}$ does exist and up to an arbitrary additive constant is unique.

III. ENSEMBLE DIFFERENTIAL VIRIAL THEOREM FOR SPHERICALLY SYMMETRIC SYSTEMS

The ground-state differential virial theorem for spherically symmetric Kohn–Sham potential was derived by Nagy and March [6]. Now, we generalize the theorem for ensembles. The Kohn–Sham-like equations for spherically symmetric systems take the form

$$-\frac{1}{2}\frac{d^2 P_i}{dr^2} + \frac{l_i(l_i+1)}{2r^2}P_i + v_{KS}P_i = \epsilon_i P_i \;, \tag{16}$$

where $P_i = rR_i(r)$ are the radial wave functions and l_i are the azimuthal quantum numbers. They can be rewritten as

$$\frac{d^2 P_i(r')}{(dr')^2}P_i(r) - P_i(r)\frac{d^2 P_i(r)}{dr^2} = 2\left[v_{KS}(r') - v_{KS}(r) + \frac{l_i(l_i+1)}{2}\left(\frac{1}{(r')^2} - \frac{1}{r^2}\right)\right]$$
$$\cdot P_i(r')P_i(r) \;. \tag{17}$$

Introducing another auxiliary quantity

$$\varrho(r', r) = \sum_i \lambda_i w_i \varrho_i(r', r) \;, \tag{18}$$

where

$$\varrho_i(r', r) = P_i(r')P_i(r), \tag{19}$$

Eq. (17) leads to

$$\frac{\partial^2 \varrho_i(r, r')}{\partial(r')^2} - \frac{\partial^2 \varrho_i(r, r')}{\partial r^2} = 2[v_{KS}(r') - v_{KS}(r)]\varrho_i + l_i(l_i+1)\left(\frac{1}{(r')^2} - \frac{1}{r^2}\right)\varrho_i \;. \tag{20}$$

The ensemble radial density is

$$\varrho(r) = \sum_i \lambda_i w_i \varrho_i(r), \tag{21}$$

where

$$\varrho_i(r) = \varrho_i(r, r). \tag{22}$$

λ_i are the occupation numbers, that is, λ_i is the number of electrons with a given l_i. For example, for the Be atom with the electron configuration $1s^2 2s^2$ the occupation numbers are $\lambda_1 = \lambda_2 = 2$.

The ensemble non-interacting radial kinetic energy density

$$\tau(r) = 4r^2 \pi t(r) \tag{23}$$

can also be expressed as

$$\tau(r) = -\frac{1}{2} \left. \frac{\partial^2 \varrho(r', r)}{\partial r^2} \right|_{r'=r} + \frac{1}{2} \sum_i w_i \lambda_i l_i (l_i + 1) \frac{\varrho_i(r)}{r^2}. \tag{24}$$

Following the derivation in [6] the transformation

$$\xi = \frac{1}{2}(r + r'), \qquad \eta = \frac{1}{2}(r' - r) \tag{25}$$

is applied. $\varrho_i(r, r')$ and $\varrho(r, r')$ are expanded around $\eta = 0$:

$$\varrho_i(\xi, \eta) = \varrho(\xi) + \sum_{j=1}^{\infty} \eta^{2j} b_{2j}^i(\xi), \tag{26}$$

$$\varrho(\xi, \eta) = \varrho(\xi) + \sum_{j=1}^{\infty} \eta^{2j} a_{2j}(\xi), \tag{27}$$

where

$$\varrho_i(\xi) = \varrho_i(\xi, 0) \tag{28}$$

and

$$\varrho(\xi) = \varrho(\xi, 0). \tag{29}$$

From Eqs. (20) - (29) we obtain

$$\frac{da_2}{d\xi} = 2v'_{KS}\varrho(\xi) - 2\sum_i w_i \lambda_i \frac{l_i(l_i + 1)}{\xi^3} \varrho_i. \tag{30}$$

The ensemble non-interacting radial kinetic energy density can also be written as

$$\tau(r) = -\frac{1}{4} \left[\frac{1}{2}\varrho'' + a_2 - 2\sum_i w_i \frac{\lambda_i l_i(l_i + 1)}{r^2} \varrho_i \right]. \tag{31}$$

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After some algebra the differential virial theorem can be obtained

$$\tau' = -\frac{1}{8}\varrho''' - \frac{1}{2}\varrho v'_{KS} + \frac{\tilde{q}'}{r^2} - \frac{\tilde{q}}{r^3} , \tag{32}$$

where

$$\tilde{q} = \frac{1}{2}\sum_i w_i \lambda_i l_i(l_i + 1)\varrho_i . \tag{33}$$

Note that if all $w_i = 1$ the ensemble differential virial theorem reduces to the differential virial theorem of Nagy and March [6].

Now, we select the following weighting factors:

$$w_i = e^{\beta \varepsilon_i - \gamma l_i(l_i+1)} \tag{34}$$

with $\beta \geq 0$, $\gamma \geq 0$ and $\varepsilon_i < 0$. Then we obtain that

$$\tilde{q} = -\frac{1}{2}\frac{\partial \varrho}{\partial \gamma} . \tag{35}$$

Consequently the ensemble differential virial theorem (32) has the form:

$$\tau' = -\frac{1}{8}\varrho''' - \frac{1}{2}\varrho v'_{KS} - \frac{1}{2r^2}\frac{\partial}{\partial r}\left(\frac{\partial \varrho}{\partial \gamma}\right) + \frac{1}{2r^3}\frac{\partial \varrho}{\partial \gamma} . \tag{36}$$

IV. FUNCTIONAL DERIVATIVE OF THE KINETIC ENERGY FUNCTIONAL

Combining Eqs. (1), (3), (14) and (23) we arrive at the relation:

$$\tau = \varrho\frac{\delta T}{\delta n} - \mu\varrho + \tilde{g}, \tag{37}$$

where

$$\tilde{g} = \sum_i w_i \lambda_i \epsilon_i \varrho_i. \tag{38}$$

Differentiating Eq. (37) with respect to r and substituting it into the ensemble differential virial theorem (36) we obtain

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$$\frac{1}{2}\varrho\left(\frac{\delta T}{\delta n}\right)' + \varrho'\frac{\delta T}{\delta n} = \tilde{f}, \tag{39}$$

where

$$\tilde{f} = -\frac{1}{8}\varrho''' - \tilde{g}' + \mu\varrho' - \frac{1}{2r^2}\frac{\partial}{\partial r}\left(\frac{\partial\varrho}{\partial\gamma}\right) + \frac{1}{2r^3}\frac{\partial\varrho}{\partial\gamma}. \tag{40}$$

From Eq. (38) follows that

$$\tilde{g} = \frac{\partial\varrho}{\partial\beta}\,. \tag{41}$$

Therefore Eq. (42) takes the form

$$\tilde{f} = -\frac{1}{8}\varrho''' - \frac{\partial}{\partial r}\left(\frac{\partial\varrho}{\partial\beta}\right) + \mu\varrho' - \frac{1}{2r^2}\frac{\partial}{\partial r}\left(\frac{\partial\varrho}{\partial\gamma}\right) + \frac{1}{2r^3}\frac{\partial\varrho}{\partial\gamma}. \tag{42}$$

The solution of the first-order differential equation (39) provides the functional derivative of the ensemble non-interacting kinetic energy

$$\frac{\delta T}{\delta n} = \frac{2}{\varrho^2}\int_\infty^r \varrho(r_1)\tilde{f}(r_1)dr_1. \tag{43}$$

The total ensemble non-interacting kinetic energy can be partitioned as

$$T = T_w + T_p\,, \tag{44}$$

where T_w is the ensemble Weizsäcker kinetic energy

$$T_w = \frac{1}{8}\int\frac{|\nabla n|^2}{n} \tag{45}$$

and we call the term T_p ensemble Pauli energy. Note that if all $w_i = 1$ the ensemble Weizsäcker kinetic energy and the ensemble Pauli energy reduce to the Weizsäcker kinetic energy [7] and the Pauli energy [8–10], respectively. We mention in passing that the Weizsäcker kinetic energy functional is also the Fisher information (up to a multiplying factor), which has been of recent research interest as well in the literature [13].

The functional derivatives are

$$\frac{\delta T_w}{\delta n} = \frac{1}{8}\left|\frac{\nabla n}{n}\right|^2 - \frac{1}{4}\frac{\nabla^2 n}{n} = n^{-1/2}\left(-\frac{1}{2}\nabla^2\right)n^{1/2} \tag{46}$$

and

$$v_p = \frac{\delta T_p}{\delta n} \ . \tag{47}$$

Substituting Eqs. (44)-(47) into Eq. (14) the Euler equation can be rewritten

$$[-\frac{1}{2}\nabla^2 + v_p + v_{KS}]n^{1/2} = \mu n^{1/2}. \tag{48}$$

Substituting Eqs. (44)-(47) into Eq. (39) we arrive at a first-order differential equation for the functional derivative of the ensemble Pauli energy, that is, for the ensemble Pauli potential v_p:

$$\frac{1}{2}\varrho v'_p + \varrho' v_p = f, \tag{49}$$

where

$$f = -\frac{\partial}{\partial r}\left(\frac{\partial \varrho}{\partial \beta}\right) + \mu \varrho' - \frac{1}{2r^2}\frac{\partial}{\partial r}\left(\frac{\partial \varrho}{\partial \gamma}\right) + \frac{1}{2r^3}\frac{\partial \varrho}{\partial \gamma}. \tag{50}$$

The differential equation (49) can be solved and the Pauli potential can be written as

$$v_p = \frac{2}{\varrho^2}\int_\infty^r \varrho(r_1)f(r_1)dr_1. \tag{51}$$

Eqs. (39) and (49) and the solutions (43) and (51) are the main results of this article. If all $w_i = 1$ Eq. (49) reduce to the differential equation for the Pauli potential of [11].

V. DISCUSSION

As an illustration consider a Be-like system in a bare Coulomb field. For this simple case the Pauli potential can be analitically given. In this 4-electon, 2-level system the ensemble density can be written as

$$\varrho = \lambda_1 w_1 \varrho_1 + \lambda_2 w_2 \varrho_2, \tag{52}$$

where

$$\varrho_1 = 4Z^3 r^2 \exp{(-2Zr)} \tag{53}$$

and

$$\varrho_2 = \frac{1}{2} Z^3 r^2 (1 - Zr/2)^2 \exp{(-Zr)} \tag{54}$$

are the 1s and 2s H-like radial orbital densities with atomic number Z. The occupation numbers are $\lambda_1 = \lambda_2 = 2$. The weighting factors have the form

$$w_1 = \exp{(\beta \varepsilon_1)} = \exp{(-\beta Z^2/2)} \tag{55}$$

and

$$w_2 = \exp{(\beta \varepsilon_2)} = \exp{(-\beta Z^2/8)}. \tag{56}$$

As the azimuthal quantum numbers $l_1 = l_2 = 0$ the parameter γ does not appear in the weighting factors and in the ensemble density. Calculating the derivatives of the ensemble density, substituting into Eqs. (50) and (51) and integrating we obtain the ensemble Pauli potential

$$v_p(r; \beta) = \frac{3Z^2}{8} e^{-\frac{\beta}{2}Z^2} \frac{8e^{-4Zr} + (1 - Zr + \frac{(Zr)^2}{3})e^{-3Zr}}{[4e^{-\frac{\beta}{2}Z^2}e^{-2Zr} + \frac{1}{2}e^{-\frac{\beta}{8}Z^2}(1 - \frac{Zr}{2})^2 e^{-Zr}]^2}. \tag{57}$$

Substituting $\beta = 0$ we arrive at the Pauli potential

$$v_p(r) = \frac{3Z^2}{8} \frac{8e^{-4Zr} + (1 - Zr + \frac{(Zr)^2}{3})e^{-3Zr}}{[4e^{-2Zr} + \frac{1}{2}(1 - \frac{Zr}{2})^2 e^{-Zr}]^2}. \tag{58}$$

The differential equations (39) and (49) and their solutions (43) and (51) provide the exact kinetic energy functional for spherically symmetric systems and open the way to perform orbital free density functional calculations.

We sketch how orbital-free calculations should be done.

(i) Guess an initial ensemble electron density ϱ and the constant μ.

(ii) Using Eq. (50) calculate the function f.

(iii) Solve Eq. (49) for the ensemble Pauli potential v_p using Eq. (50) and (51).

(iv) Solve equation (48) to obtain the ensemble electron density ϱ.

(v) Repeat steps (i)-(iv) until convergence. Calculate the total ensemble non-interacting kinetic energy from Eq. (37). Then take the case $\beta = \gamma = 0$ to obtain the electron density and the total non-interacting kinetic energy of the original density functional problem.

Instead of treating the original orbital-free problem, we suggest to solve an enlarged task, that is to handle an ensemble case. These ensembles are artificial constructions in the non-interacting scheme. The solution seems to be difficult as the density depends also the parameters β and γ. But the ensemble kinetic energy functional can be exactly obtained as it is described in this article and the case $\beta = \gamma = 0$ gives the solution of the original orbital-free problem.

The weighting factors are selected according to Eq. (34), therefore the ensemble density is not normalized to the number of electrons except the case where all w_i are equal, that is, $\beta = \gamma = 0$. On the other hand, one can immediatelly see that if a density ϱ satisfies the differential equations (39) and (49), than any density $c\varrho$ $(c > 0)$ satisfies the differential equations (39) and (49). Therefore, one can use any appropriate normalization.

As we finally need only the case $\beta = \gamma = 0$, it is enough to do the calculations for small values of β and γ. Therefore we can write the ensemble density in the form:

$$\varrho(r) = \varrho_0(r) - \beta \tilde{g}(r) - \gamma \tilde{q}(r) . \tag{59}$$

The method can be applied to degenerate states as well. The present author derived a subspace theory of multiplets [12], in which the Kohn-Sham equations are similar to the conventional Kohn-Sham equations. The difference is that the subspace density is used instead of the density and the Kohn-Sham potential is different for different subspaces.

The extension of the present derivation to non-spherically symmetric systems is not straightforward. In that case, the starting point might be the generalization of the differential virial theorem of Holas and March [14] for ensembles. It will contain, however, the ensemble kinetic energy tensor, that will make very difficult to obtain differential equations similar to (39) and (49). We note that the results presented in this article might be useful not only in spherically symmetric systems. For example, it can be generalized for muffin-tin orbitals of

solid-state calculations [15].

It is interesting to note that there is some resemblance between the approach presented here and the method from [16] where an extra parameter is introduced into the k-electron distribution functions and used to construct a hierarchy of equations, so that the kinetic-energy can be approximated.

We would like to mention that the local ionization potential $\tilde{\varepsilon}(\mathbf{r}) = \sum_i \varepsilon_i n_i(\mathbf{r})/n(\mathbf{r})$ introduced by Politzer et al. [17,18] is closely related to the function g: $\tilde{\varepsilon}(\mathbf{r})n(\mathbf{r}) = g(\mathbf{r})$. The local ionization potential is a measure of chemical reactivity and is linked to the local temperature, and thus to the local kinetic energy [19]. So there is a very intimite relationship between the function g and the local kinetic energy t, as it is demonstrated in this article.

APPENDIX

Following Liu and Ayers [5] we prove that the functional derivative of the ensemble non-interacting kinetic energy exists. Writing the ensemble non-interacting kinetic energy T as

$$T = \sum_{i=1}^{N} w_i T_i, \tag{60}$$

where

$$T_i = \langle u_i | -\frac{1}{2}\nabla^2 | u_i \rangle. \tag{61}$$

Variation of this equation gives

$$\delta T_i = \langle \delta u_i | -\frac{1}{2}\nabla^2 | u_i \rangle + \langle u_i | -\frac{1}{2}\nabla^2 | \delta u_i \rangle. \tag{62}$$

Applying the Kohn-Sham equations (1) we arrive at

$$\delta T_i = \langle \delta u_i | \varepsilon_i - v_{KS}(\mathbf{r}) | u_i \rangle + \langle u_i | \varepsilon_i - v_{KS}(\mathbf{r}) | \delta u_i \rangle. \tag{63}$$

It can be rewritten as

$$\delta T_i = \varepsilon_i \delta \int |u_i|^2 d\mathbf{r} - \int v_{KS}(\mathbf{r}) \delta |u_i|^2 d\mathbf{r}. \tag{64}$$

Since $\int |u_i|^2 d\mathbf{r} = 1$, the first term on the right-hand side of Eq. (64) vanishes, yielding

$$\delta T_i = -\int v_{KS}(\mathbf{r}) \delta |u_i|^2 d\mathbf{r}. \tag{65}$$

Consequently, for the ensemble non-interacting kinetic energy we have

$$\delta T = \sum_{i=1}^{N} w_i \delta T_i = -\int v_{KS}(\mathbf{r}) \sum_{i=1}^{N} w_i \delta |u_i|^2 d\mathbf{r} = -\int v_{KS}(\mathbf{r}) \delta n(\mathbf{r}) d\mathbf{r}. \tag{66}$$

Therefore, we obtain

$$\frac{\delta T}{\delta n(\mathbf{r})} = const - v_{KS}(\mathbf{r}), \tag{67}$$

that is, the quantity $\frac{\delta T}{\delta n(\mathbf{r})}$ does exist and up to an arbitrary additive constant is unique.

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