The partitioning of Thomas–Fermi, von Weizsäcker and Dirac density functionals

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Abstract
The partitioning of several classical density functionals, including the Thomas–
Fermi (TF), Weizsäcker kinetic energies and the Dirac exchange energy, are
studied for the partitioned systems that satisfy the orthogonality condition.
The partitioning of the TF kinetic energy shows a raising of the energy of the
valence electrons which is not found for the partitioning of the Weizsäcker
kinetic energy. The partitioning of the Weizsäcker kinetic energy is not unique
and contains a correlation part. The partitioning of the Dirac exchange energy
shows that the exchange energy of a subsystem can be largely influenced by
the other subsystems when this subsystem does not correspond to the lowest
energy subspace. The self-interaction calculated from the partitioned exchange
energies is different from previous results.

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1. Introduction

The partitioning of a many-particle system is essential when one wants to describe the
properties of the system by only the part that responds mainly to external changes. Variations
range from the real-space partitioning, like the atom-in-molecule method [1, 2], to the state-
space partitioning like the effective core Hamiltonian method [3, 4] as well as the
pseudopotential method [5, 6]. Often, partitioning has been used implicitly by both theoretical
physicists and chemists. It is trivial to partition the system into parts when the single-particle
picture is used. In fact, the single-particle picture can be viewed as an extreme case of
partitioning, i.e. the system is partitioned into subsystems that contain one particle.

The density-functional theory (DFT) associates all the properties of a system with its
ground-state density [7–9]. Several explicit density functionals, such as Thomas–Fermi,
Dirac and Weizsäcker functionals [10–13], for the kinetic and exchange energy have been
introduced from which the ground-state density can be obtained variationally. Although most
DFT calculations on the real physical systems are based on the Kohn–Sham scheme (KS)

[14] by mapping the many-particle system to a system containing free particles moving in an effective potential, those classical functionals remain interesting [15]. Further modifications of these models have produced very good geometry and electronic properties for some real systems [16]. On the other hand, the partitioning of the density functionals is not very well known for either the classical functionals or the commonly used exchange-correlation functionals in the KS scheme. The studies of the partitioning of the classical functionals can be helpful for understanding the partitioning of the more sophisticated functionals.

The partitioning problem can sometimes be important to the principles of DFT. One good example is the self-interaction correction (SIC) [17, 18] of the Coulomb and exchange-correlation functional in which one needs to partition and then subtract the single particle part of the functional from its whole. In most cases, the single-particle functionals are assumed to have the same form as the functional of the total ground-state density. Of course, this is only exact in the single-particle limit. Taking the Dirac exchange functional as an example, we will examine the above SIC assumption by a detailed study on the partitioning of the exchange functional of a free-electron gas.

In this paper, we will discuss the partitioning of the classical density functionals of kinetic and exchange energy. The partitioning of the Thomas–Fermi (TF) and the von Weizsäcker kinetic functionals will be discussed in sections 2.1 and 2.2, respectively. In section 3, we will partition the Dirac or the Kohn–Sham exchange functional into two and three parts and then discuss the SIC as an application. The mathematical derivation of the partitioning of the Dirac exchange functional is presented in appendix A.

2. Partitioning of the kinetic functional

2.1. Thomas–Fermi model

The TF model [10, 11] is the first proposed density functional except for the trivial Coulomb functional. It connects the density summation of the free-electron orbitals

$$n(r) = \sum_{k=0}^{k_F} |\psi_k|^2 = \frac{k_F^3}{3\pi^2} \tag{1}$$

and the kinetic-energy summation

$$t(r) = \frac{1}{4\pi^2} \frac{1}{2} \int_0^{k_F} k^2 \, dk^3 = \frac{1}{10} k_F^5 \tag{2}$$

through the Fermi level k_F and has the form

$$t(r) = C_F n(r)^{5/3} \tag{3}$$

with $C_F = \frac{3}{10}(3\pi^2)^{2/3}$.

Assuming that the system can be partitioned into two subsystems X and Y with densities $n_X(r)$ and $n_Y(r)$. Furthermore, let us assume that the two subsystems are orthogonal such that the densities are additive

$$n(r) = n_X(r) + n_Y(r). \tag{4}$$

We will only consider the state-space partitioning and assume system X always occupies the states with lower energy. Defining

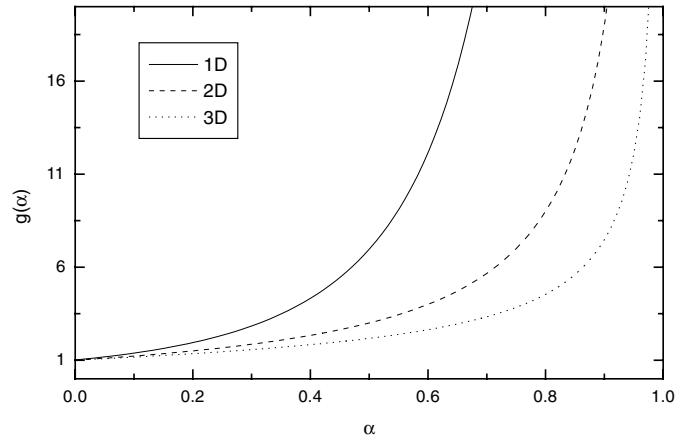$$\alpha = \frac{n_X(r)}{n(r)} \tag{5}$$

Figure 1. g function for one (solid line), two (dashed line) and three (dotted line) dimensions.

and

$$k_X = \alpha^{1/3} k_{\mathrm{F}} \tag{6}$$

it is easy to see that the TF relation holds true for the X subsystem

$$t_X(r) = \frac{1}{10} k_X^5 = C_{\mathrm{F}} n_X(r)^{5/3} = C_{\mathrm{F}} \alpha^{5/3} n(r)^{5/3}. \tag{7}$$

For the Y subsystem, the kinetic energy density is more complex

$$\begin{aligned}
t_Y(r) &= \frac{1}{10} k^5 |_{k_X}^{k_{\mathrm{F}}} = \frac{1}{10}(1 - \alpha^{5/3}) k_{\mathrm{F}}^5 \\
&= C_{\mathrm{F}}(1 - \alpha^{5/3}) n(r)^{5/3} = C_{\mathrm{F}} \frac{(1 - \alpha^{5/3})}{(1 - \alpha)^{5/3}} n_Y(r)^{5/3} \\
&= C_{\mathrm{F}} g(\alpha) n_Y(r)^{5/3}.
\end{aligned} \tag{8}$$

It reveals that the kinetic energy density of the higher occupied subsystem has a similar form as TF functional but needs to be corrected by a coefficient function g that is a local function of both the partitioned and the total densities. The g function is plotted in figure 1 (dotted line). α changes from 1 for $n_X = n$ to 0 for $n_Y = n$. It is easy to see that g is 1 while α is 0 and goes to infinity while α becomes 0, which indicates a lift-up of the kinetic energy of the upper occupied states. In the latter case, $t_Y(r)$ still goes to 0 because $n_Y(r)$ becomes 0 at the $n_X = n$ limit faster than g.

Since the exponent of the TF functional depends on dimension d, so should the g function. In general, the exponent of the TF functional is $\frac{2+d}{d}$ and the corresponding g function is

$$\frac{1 - \alpha^{\frac{2+d}{d}}}{(1 - \alpha)^{\frac{2+d}{d}}}. \tag{9}$$

The g functions for two and three dimensions are also plotted in figure 1. Interestingly, g is identical to 1 in the high dimension limit, which indicates that the TF functional is completely partitionable.

2.2. Weizsäcker kinetic energy

The Weizsäcker [12] kinetic energy density $t_W(r)$ can be subtracted from the orbital kinetic energy summation by assuming the orbitals

$$\psi_i^*(r) = n(r)^{1/2} K_i^*(r) \qquad \psi_i(r) = n(r)^{1/2} K_i(r). \tag{10}$$

Inserting the above orbitals into the KS kinetic energy, one obtains

$$t(r) = \sum_i \nabla \psi_i^*(r) \nabla \psi_i(r) = n(r) \sum_i \nabla K_i^* \nabla K + \frac{(\nabla n)^2}{n}$$

$$= t_W(r) + n(r) \sum_i \nabla K_i^* \nabla K. \tag{11}$$

In contrast to the TF functional, there is no unique way to partition the Weizsäcker kinetic energy density. One routine to partitioning the $t_W(r)$ is rather straightforward. Assuming the density is completely partitionable (see equation (4)), $t_W(r)$ can be expressed by the densities of the subsystems X and Y

$$t_W(r) = \frac{|\nabla(n_X + n_Y)|^2}{n_X + n_Y} = \frac{|\nabla n_X|^2}{n_X} \frac{n_X}{n} + \frac{|\nabla n_Y|^2}{n_Y} \frac{n_Y}{n} + \frac{2\nabla n_X \nabla n_Y}{n}$$

$$= t_W^X(r) + t_W^Y(r) + t_W^C(r) \tag{12}$$

in which $t_W^C(r)$ is a correlation term.

In another way, we define the Weizsäcker kinetic energy for each subsystem and define the difference between the t_W of the total system and the summation of the t_W of each subsystem as the correlation. For doing it, we assume

$$\psi_i^{X*}(r) = n^X(r)^{1/2} K_i^{X*}(r) \qquad \psi_i^X(r) = n^X(r)^{1/2} K_i^X(r)$$

$$\psi_i^{Y*}(r) = n^Y(r)^{1/2} K_i^{Y*}(r) \qquad \psi_i^Y(r) = n^Y(r)^{1/2} K_i^Y(r) \tag{13}$$

and calculate the corresponding Weizsäcker kinetic energy densities

$$t_W^X(r) = \frac{|\nabla n_X|^2}{n_X} \qquad t_W^Y(r) = \frac{|\nabla n_Y|^2}{n_Y} \tag{14}$$

by the same procedure as that used to obtain equation (11). The correlation term is then

$$t_W^C(r) = t_W(r) - t_W^X(r) - t_W^Y(r). \tag{15}$$

For most of the partitioned systems, in practice, the subsystem densities are distributed mainly in different regions. As an example, the densities of $1s$ and $2s$ orbitals of Be are plotted in figure 2(a). Similar patterns can be found for all the partitionings of the atoms in the periodic table. The corresponding first- and second-kind partitioned Weizsäcker kinetic energy densities are shown in figures 2(b) and (c). It can be easily seen that in the core region, the correlation part of the first kind of t_W is much larger than that of the second kind. Comparing with the total kinetic energy density, the correlation parts of both kinds are small. It needs to be noted that in the region of valence electrons, the correlation is comparable with the total and the partitioned kinetic energy densities. For comparison, we also plot the total and the partitioned TF kinetic energy densities for Be in figure 2(d).

For clarity, the integrated kinetic energies are calculated and listed in table 1. It can be seen that for all the selected atoms, the correlation parts of both the first and second kinds of the partitioned Weizsäcker kinetic energies are small but comparable with the Weizsäcker kinetic energies of the valence electrons. Generally, the Weizsäcker kinetic energies are smaller than the KS as well as the TF kinetic energies, especially for large atoms in which the densities are more smooth. The second way of partitioning the Weizsäcker kinetic energy gives a valence kinetic energy more similar to the TF partitioning and a negative and smaller correlation term.

Table 1. The partitioned Thomas–Fermi and Weizsäcker kinetic energy for several selected atoms.

	T_S	T_{TF}	T_{TF}^X	T_{TF}^Y	T_W	T_W^X	T_W^Y	T_W^{XY}	T_W^X	T_W^Y	T_W^{XY}
Be	14.31	17.12	15.89	1.23	13.36	12.52	0.33	0.51	13.17	1.13	−0.44
C	37.19	22.09	19.04	3.05	31.41	28.29	1.50	1.62	31.42	2.60	−2.61
Ne	127.74	155.70	111.22	44.49	89.45	75.26	9.16	5.03	91.44	11.09	−13.08
Kr	2747.82	3448.46	3408.56	39.89	1271.72	1264.61	2.88	4.23	1273.84	15.65	−17.77

3. Partitioning of the exchange functional

3.1. Two-subsystem partitioning

The detailed derivation of the partitioning of exchange functional is lengthy and so is presented in appendix A. Here we will focus on the physical meaning of the result. For the same partitioned system X and Y as sections 2.1. and 2.2., the exchange functional K_D can be partitioned into the summation of the exchange functional of the subsystems plus an exchange functional between the two subsystems, i.e.

$$K_D = K_D^X + K_D^Y + K_D^{XY}$$
$$= C_x \int G^X[\alpha(r)] \, n(r)^{4/3} \, dr + C_x \int G^Y[\alpha(r)] \, n(r)^{4/3} \, dr$$
$$+ C_x \int G^{XY}[\alpha(r)] \, n(r)^{4/3} \, dr \tag{16}$$

in which $C_X = \frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3}$ and

$$G^X[\alpha(r)] = \alpha^{4/3}(r)$$
$$G^{XY}[\alpha(r)] = [2\alpha(r) - 2\alpha^{4/3}(r)] \tag{17}$$
$$G^Y[\alpha(r)] = [1 - 2\alpha(r) + \alpha^{4/3}(r)]$$

or in another form

$$K_D = K_D^X + K_D^Y + K_D^{XY}$$
$$= C_x \int g^X[\alpha(r)] \, n^X(r)^{4/3} \, dr + C_x \int g^Y[\alpha(r)] \, n^Y(r)^{4/3} \, dr$$
$$+ C_x \int g^{XY}[\alpha(r)] \, n^X(r)^{2/3} n^Y(r)^{2/3} \, dr \tag{18}$$

with

$$g^X[\alpha(r)] = 1$$
$$g^Y[\alpha(r)] = [1 - 2\alpha(r) + \alpha^{4/3}(r)](1 - \alpha(r))^{-4/3} \tag{19}$$
$$g^{XY}[\alpha(r)] = [2\alpha(r) - 2\alpha^{4/3}(r)] \alpha(r)^{-2/3} (1 - \alpha(r))^{-2/3}.$$

The coefficients G and g are plotted as functions of α in figures 3(a) and (b), respectively.

It is interesting to know how the exchange energy of the subsystem Y will be changed by the existence of the subsystem X which occupies the lower orbitals. Omitting the effects of the X subsystem, the coefficient function g is 1 and the corresponding

$$G_0[\alpha] = (1 - \alpha(r))^{4/3}. \tag{20}$$

As shown in figure 3(a), in both limits of $\alpha \to 0$ and $\alpha \to 1$, $G^Y[\alpha]$ is identical to $G_0[\alpha]$. And more interestingly, while $\alpha = 1/2$, i.e. in an equal-partitioning case, $n^X(r) = n^Y(r)$ and $G^Y[\alpha] = G_0[\alpha]$. It can be easily imagined that the difference between $G^Y[\alpha]$ and $G_0[\alpha]$
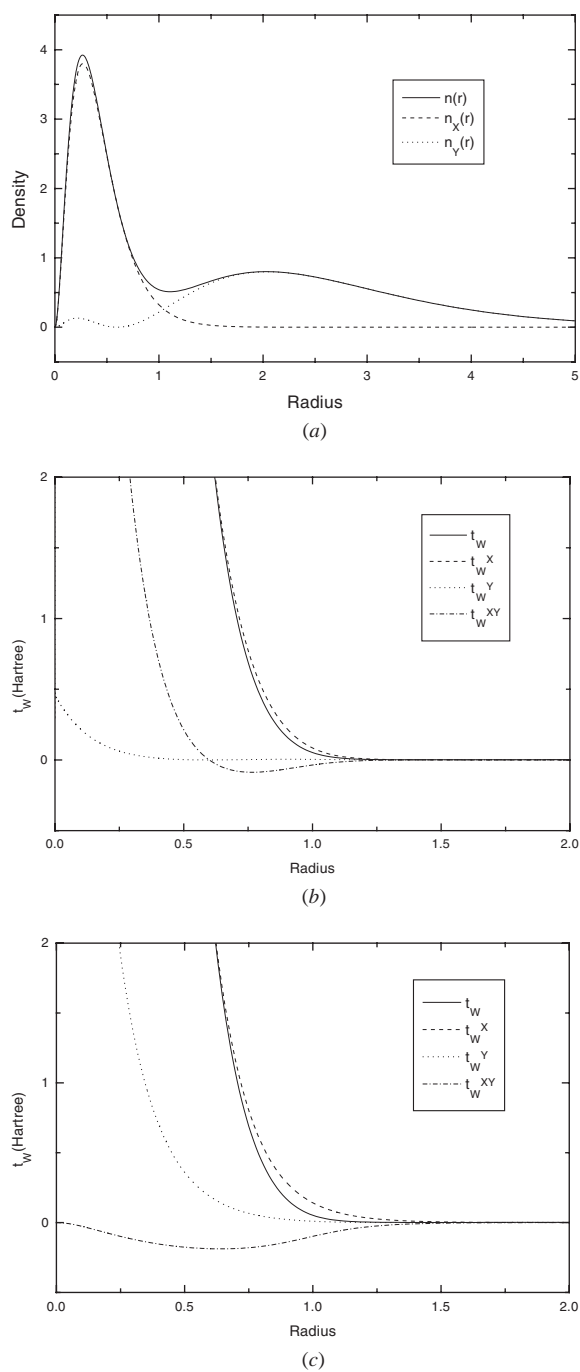
Figure 2. The total and partitioned Weizsäcker and TF kinetic energy density for beryllium. (*a*) The total-, core- and the valence-electron density. (*b*) The total and the partitioned Weizsäcker kinetic energy density for the first kind. (*c*) The total and the partitioned Weizsäcker kinetic energy density for the second kind. (*d*) The total and the partitioned TF kinetic energy density.
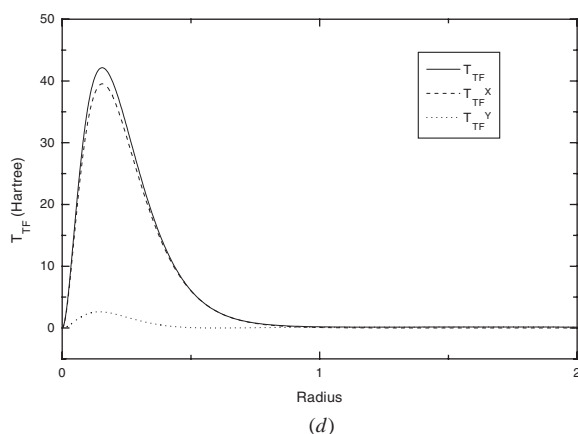
(d)

Figure 2. (*Continued*)

should not be too large for the other values of α. In fact, the extreme values of $G^Y[\alpha] - G_0[\alpha]$ can be obtained from the zero points of its first-order derivative, which is the solution of

$$\alpha^{1/3} + (1 - \alpha)^{1/3} = \tfrac{3}{2}. \tag{21}$$

Two symmetric solutions are $\alpha_1 = 0.1791$ and $\alpha_2 = 0.8209$. At both points, $G^Y[\alpha] - G_0[\alpha]$ is about 0.026, which is very small in comparison with the $G_0(\alpha)$ values, 0.7686, while $\alpha_1 = 0.1791$ and 0.1010 while $\alpha_2 = 0.8209$.

The features of the exchange energy between the two subsystems are also revealed by figure 3. As one may expect, $G^{XY}(\alpha)$ is 0 in both $\alpha \to 0$ and $\alpha \to 1$ limits. But the maximum

(a)

(b)

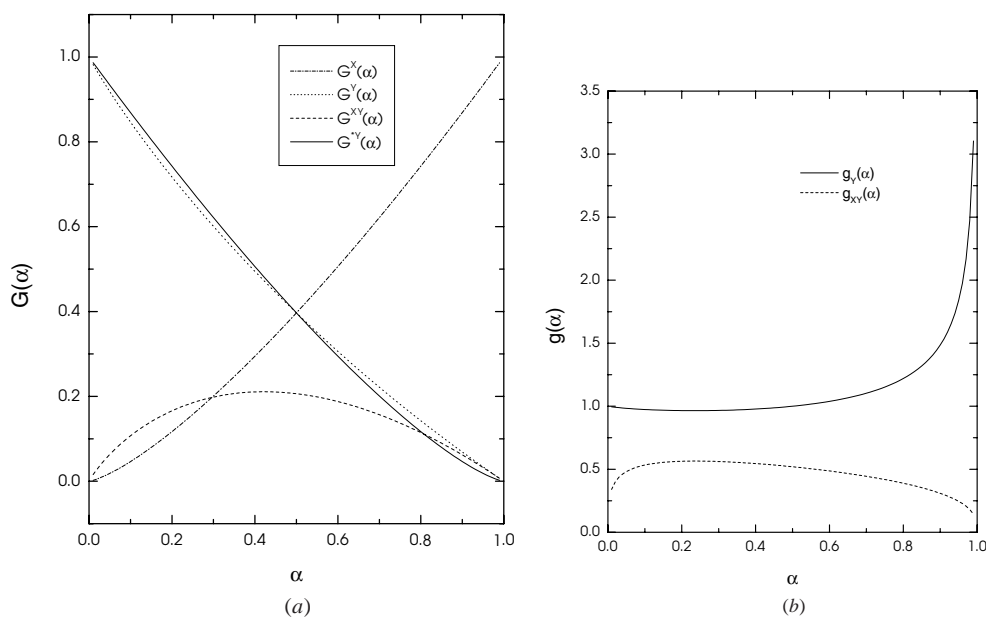**Figure 3.** The coefficient-correction functions G and g exchange energies for two-subsystem partitioning. (*a*) Function G and (*b*) function g.

of the exchange between the subsystems is not at the equal-partitioning point. The extreme point can again be calculated from the zero point of the first-order derivative of the G^{XY} function. It is calculated to be $\alpha = \left(\frac{3}{4}\right)^3 = 0.422$ and the corresponding G^{XY} function value is $2\left[\left(\frac{3}{4}\right)^3 - \left(\frac{3}{4}\right)^4\right] = 0.211$.

3.2. Three-subsystem partitioning

The three-subsystem partitioning is needed for studying the influence of the occupation in both lower and higher states on the exchange energy of the intermediate states and the influence of the occupation of the intermediate states on the exchange between the lower and higher states. Define the density ratio of the lower, intermediate and higher subsystems, X, Y and Z as α_X, α_Y and α_Z. Obviously,

$$\alpha_X + \alpha_Y + \alpha_Z = 1. \tag{22}$$

Performing the two-subsystem partitioning twice, one can obtain the G functions for three-subsystem partitioning as

$$
\begin{aligned}
G^X &= \alpha_X^{4/3} \\
G^Y &= (\alpha_X + \alpha_Y)^{1/3}(\alpha_Y - \alpha_X) + \alpha_X^{4/3} \\
G^Z &= 1 - 2(\alpha_X + \alpha_Y) + (\alpha_X + \alpha_Y)^{4/3} \\
G^{XY} &= 2\alpha_X\left[(\alpha_X + \alpha_Y)^{1/3} - \alpha_X^{1/3}\right] \\
G^{YZ} &= 2\alpha_Y - 2(\alpha_X + \alpha_Y)^{4/3} + 2\alpha_X(\alpha_X + \alpha_Y)^{1/3} \\
G^{XZ} &= 2\alpha_X - 2\alpha_X(\alpha_X + \alpha_Y)^{1/3}.
\end{aligned}
\tag{23}
$$

Let us first consider the exchange energy of the intermediate subsystem Y. From the G^Y function, it can be easily seen that while α_X goes to 0, G^Y becomes $G_0^Y = \alpha_Y^{4/3}$. Further on, if $\alpha_X = \alpha_Y$, $G^Y = G_0^Y = \alpha_Y^{4/3}$. In contrast, in the limit of $\alpha_Y \to 0$, $G^Y \to \frac{2}{3}\alpha_Y\alpha_X^{1/3}$, i.e. the intermediate state gains more exchange energy while there is a large occupation of the lower states. Figure 4(a) plots the ratio of $G^Y[\alpha_X, \alpha_Y]/G_0^Y[\alpha_Y]$ as a function of α_X for a series of values of α_Y. It is also interesting to see that while $\alpha_X < \alpha_Y$, the ratio $G^Y[\alpha_X, \alpha_Y]/G_0^Y[\alpha_Y] < 1$ which indicates a reduction of the exchange energy for the intermediate subsystem caused by the existence of the lower occupation.

Function G^{XZ} reduces to function G'^{XY} for the two-subsystem partitioning. And while α_Y becomes large, G^{XZ} decreases indicating the reduction of the exchange energy between the two subsystems separated by the intermediate system Y. It can be proved that while $\alpha_X/\alpha_Y \to 0$, $G^{XZ} \to 2\alpha_X - 2\alpha_X\alpha_Y^{1/3}$. This is in contrast to the two-subsystem partitioning $G^{XY} = 2\alpha_X - 2\alpha_X\alpha_X^{1/3}$. Figure 4(b) plots the ratio $G^{XZ}[\alpha_X, \alpha_Y]/G_0^{XY}[\alpha_X]$ as a function of α_Y at a series of values of α_X. The larger value of α_X corresponds to a larger exchange energy between the X and Z subsystems in the range $\alpha_X < 0.5$. At any value of α_X, the exchange energy is reduced by the increasing of α_Y.

3.3. Self-interaction correction

The SIC improves the LDA results considerably. A typical SIC exchange-correlation energy is obtained by subtracting the self-interaction part of the original exchange-correlation energy that has the same functional form but only the density of the single orbital [9, 18]

$$E_{xc}^{\text{SIC}}[n(r)] = E_{xc}[n(r)] - \sum_{i=1}^{N} E_{xc}[n_i(r)]. \tag{24}$$
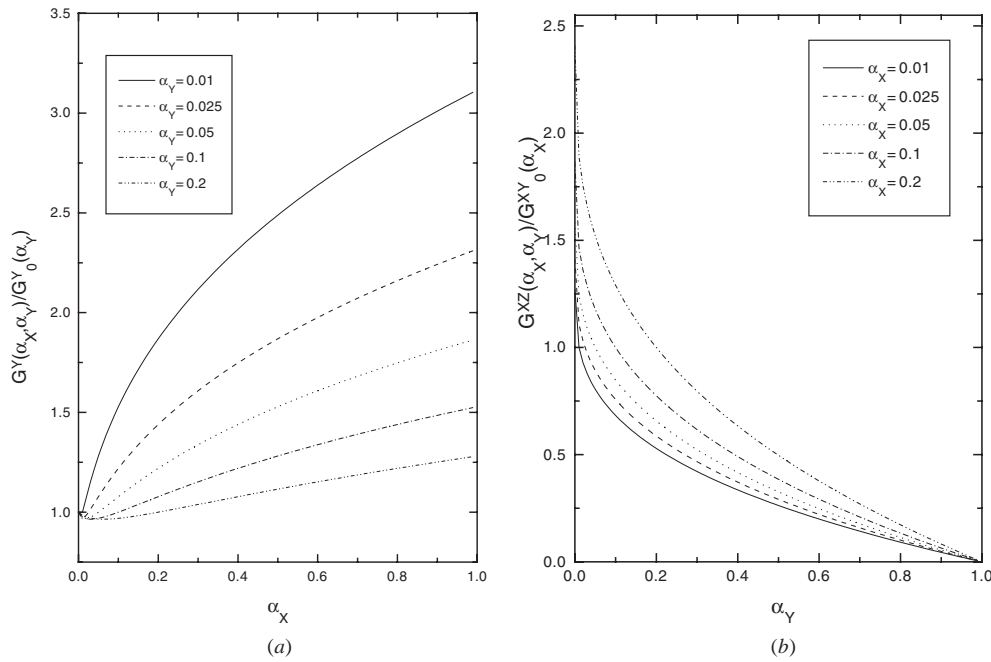
Figure 4. (a) The ratio of $G^Y[\alpha_X, \alpha_Y]/G_0^Y[\alpha_Y]$ as a function of α_X for a series of values of α_Y. (b) The ratio $G^{XZ}[\alpha_X, \alpha_Y]/G_0^{XY}[\alpha_X]$ as a function of α_Y at a series of values of α_X.

The above formula presumes two assumptions implicitly. First the system is partitionable and the density of a single particle can be calculated from its orbital. Second, the exchange-correlation energy for each single orbital has the same form and is identical to the exchange-correlation energy functional of the total system. In the following, we will presume the first assumption and discuss the feasibility of the second in our partitioning of the Dirac exchange energy. For doing it, we need to consider a two- and three-subsystem partitioning in which one of the subsystems contains only one orbital.

First let us consider the exchange energy of the highest occupied state in the system. This can be obtained from the partitioned exchange energy for the two-subsystem. Although the absolute values do not show a large difference between $G^Y[\alpha]$ and $G_0[\alpha]$, their ratio could deviate from 1 significantly. In fact their derivatives at the point of $\alpha = 1$ are 0 for $G_0[\alpha]$ and $-\frac{2}{3}$ for $G^Y[\alpha]$. This indicates that in a large system, the self-interaction of the highest occupied state can be much larger than it is calculated from the same functional form as the total exchange energy. Table 2 lists the values of $G^Y[\alpha]$ and $G_0[\alpha]$ for several chosen N. Although the ratio of $G^Y[\alpha]$ and $G_0[\alpha]$ is unlimited, it increases very slowly as the number of the electrons increases. At about a hundred electrons this ratio is only about three.

For considering the self-interaction of the intermediate states, we need to consider the three-subsystem partitioning. The ratio $G^Y[\alpha_X, \alpha_Y]/G_0^Y[\alpha_Y]$ (see figure 4(a)) shows the deviation of the real self-interaction from the SIC. For a N-electron system, $\alpha_Y = 1/N$ and α_X relates to the position of the state. If $\alpha_X \to 1$, then the higher occupied states are under consideration and if $\alpha_X \to 0$, then the lower occupied states are under consideration. Figure 4(a) shows that while the state moves from the lower occupation to the higher, the deviation from SIC becomes larger.

Table 2. The exchange energy of the highest occupied state for system with N electrons, calculated from the two-subsystem partitioning.

	1	2	3	4	5	10	20	50	100
$G_0^Y[\alpha]$	1	0.397	0.231	0.157	0.117	0.046	0.018	0.0054	0.0022
$G^Y[\alpha]$	1	0.397	0.249	0.181	0.143	0.069	0.034	0.0134	0.0067
$\dfrac{G^Y[\alpha]}{G_0^Y[\alpha]}$	1	1	1.078	1.152	1.220	1.485	1.840	2.472	3.105
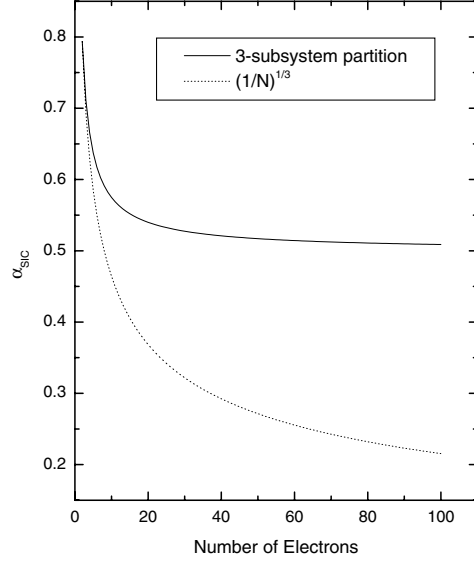
Figure 5. The calculated SIC coefficient as a function of the number of electrons, in comparison with the typical value of $\left(\frac{1}{N}\right)^{1/3}$.

For the free-electron gas, one way to correct the self-interaction is to subtract the exchange energy of each orbital. Because the energy density is uniform in real space, a universal coefficient α_{SIC} can be defined to fulfil the correction. As will be shown this coefficient only depends on N, i.e. the number of electrons concerned. If the traditional SIC is used, then the exchange energy density of each orbital is $\left(\frac{1}{N}\right)^{4/3}$ no matter which state is occupied. The summation of the exchange energy of each orbital offers a correction coefficient $\alpha_{\text{SIC}} = N\left(\frac{1}{N}\right)^{4/3} = \left(\frac{1}{N}\right)^{1/3}$. So that the larger the system, the smaller the SIC correction. It is more reliable to use the exchange energy of each orbital obtained from the above three-subsystem partitioning. Assuming there are M states in the lower occupied subsystem and one state in the intermediate subsystem for a three-subsystem partitioning of N electrons, the self-interaction correction coefficient is then

$$\alpha'_{\text{SIC}} = \sum_{M=0}^{N-1} \left[\left(\frac{M+1}{N}\right)^{1/3} \left(\frac{1-M}{N}\right) + \left(\frac{M}{N}\right)^{4/3} \right]. \tag{25}$$

Figure 5 shows α_{SIC} and α'_{SIC} as a function of the number of electrons. In contrast to α_{SIC}, α'_{SIC} becomes $\frac{1}{2}$ at the limit of infinite N.

4. Conclusions

In this article, we partitioned the classical TF and Weizsäcker kinetic-energy functionals and the Dirac exchange functional into the functionals of the densities of the subsystems. The variation of the functionals with the subsystem densities is discussed in detail. The partitioning of the TF functional lifts up the kinetic energy of the valence electrons while the partitioning of the Weizsäcker kinetic functional does not. The partitioning of the Dirac exchange functional reveals that the exchange energy of a subsystem strongly depends on the position of the system in the state space and is largely influenced by the other subsystems. The corresponding self-interaction correction is different from previous results.

Acknowledgments

Appendix A. Partitioning of the exchange functional through partitioning of density matrices

Considering a non-degenerate ground state described by a single determinant of the lowest single-particle orbitals, and its spinless first order reduced matrix (RM)

$$n_1(r, r') = 2 \sum_{i=1}^{occ} \psi_i(r)\psi_i^*(r') \tag{26}$$

one can write the exchange-energy functional as

$$K[n(r)] = \frac{1}{4} \int \frac{1}{|r - r'|} |n(r, r')|^2 \, \mathrm{d}r \, \mathrm{d}r'. \tag{27}$$

For a free-uniform gas, the single-particle orbitals are the plane waves or confined waves in a box and the corresponding first-order RM is

$$
\begin{aligned}
n_1(r, r') &= \frac{1}{4\pi^3} \int_0^{k_F} k^2 \, \mathrm{d}k \int_0^\pi \sin\theta \mathrm{e}^{ikr_{12}\cos\theta} \, \mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\phi \\
&= n(r)\left[\frac{\sin t - t\cos t}{t^3}\right] = n_1(r, s)
\end{aligned} \tag{28}
$$

in which $t = k_F(r)s$. Suppose that the system is partitioned into two subsystems X and Y, and subsystem X only occupies the lowest orbitals. Then the two subsystems are orthogonal and their first-order RMs are

$$
\begin{aligned}
n_1^X(r, r') &= 3n^X(r)\left[\frac{\sin t_P - t_P\cos t_P}{t_P^3}\right] \\
n_1^Y(r, r') &= 3n(r)\left[\frac{\sin t - t\cos t}{t^3}\right] - 3n^X(r)\left[\frac{\sin t_P - t_P\cos t_P}{t_P^3}\right]
\end{aligned} \tag{29}
$$

in which

$$t_P = k_P(r)s = [3\pi^2 n^X(r)]^{1/3}s = \alpha^{1/3}k_F(r)s = \alpha^{1/3}t. \tag{30}$$

The exchange energy functional is now

$$K_D[n(r)] = \frac{1}{4} \int\int \frac{1}{s} \left[n_1^X + n_1^Y \right]^2 \, dr \, ds$$

$$= \pi \int\int \left(\left| n_1^X \right|^2 + \left| n_1^Y \right|^2 + 2 \left| n_1^X \right| \left| n_1^Y \right| \right) s \, dr \, ds$$

$$= K_D^X + K_D^Y + K_D^{XY}. \tag{31}$$

Noticing that an orthogonal condition between the two RMs is assumed. It is easy to obtain the first term which is the exchange energy for X subsystem

$$K_D^X = C_x \int n^X(r)^{4/3} \, dr$$

$$= C_x \int \alpha^{4/3}(r) n(r)^{4/3} \, dr$$

$$= C_x \int G^X[\alpha(r)] \, n(r)^{4/3} \, dr \tag{32}$$

in which

$$C_X = \frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} = 0.7386. \tag{33}$$

The exchange energy between the two subsystems is

$$K_D^{XY} = 2\pi \int\int \left| n_1^X \right| \left| n_1^Y \right| s \, dr \, ds = 2\pi \int\int \left| n_1^X \right| \left(|n_1| - \left| n_1^Y \right| \right) s \, dr \, ds$$

$$= 2\pi \int\int \left| n_1^X \right| |n_1| s \, dr \, ds - 2 K_D^X. \tag{34}$$

Since

$$\int_0^\infty \frac{\sin t - t \cos t}{t^3} \frac{\sin t_P - t_P \cos t_P}{t_P^3} t \, dt_P = \int_0^\infty \frac{\sin t - t \cos t}{t^3} \frac{\sin t_P - t_P \cos t_P}{t_P^3} t_P \, dt$$

$$= \frac{\alpha^{1/3}}{4} \tag{35}$$

the first term of K_D^{XY} can be obtained by inserting the first-order RMs n_1^X and n_1 as

$$2\pi \int\int \left| n_1^X \right| |n_1| s \, dr \, ds = 18\pi \int n^X(r) n(r) \frac{1}{k_P k_F} \, dr$$

$$\times \int_0^\infty \frac{\sin t - t \cos t}{t^3} \frac{\sin t_P - t_P \cos t_P}{t_P^3} t \, dt_P$$

$$= \frac{18\pi}{4} \int n^X(r) n(r) \frac{1}{k_F^2} \, dr = 2 C_x \int n^X(r) n^{1/3}(r) \, dr. \tag{36}$$

So that the exchange-energy functional can be obtained as

$$K_D^{XY} = 2 C_x \int n^X(r) n^{1/3}(r) \, dr - 2 C_x \int n^X(r)^{4/3} \, dr$$

$$= C_x \int [2\alpha(r) - 2\alpha^{4/3}(r)] \, n(r)^{4/3} \, dr$$

$$= C_x \int G^{XY}[\alpha(r)] \, n(r)^{4/3} \, dr \tag{37}$$

Further on, the exchange-energy functional of Y subsystem is

$$
\begin{aligned}
K_{\mathrm{D}}^{Y} &= K_{\mathrm{D}} - K_{\mathrm{D}}^{X} - K_{\mathrm{D}}^{XY} \\
&= C_x \int \left[1 - 2\alpha(r) + \alpha^{4/3}(r)\right] n(r)^{4/3} \, \mathrm{d}r \\
&= C_x \int G^{Y}[\alpha(r)] \, n(r)^{4/3} \, \mathrm{d}r.
\end{aligned}
\tag{38}
$$

Appendix B. Several limit cases of G functions

For three-subsystem partitioning, the exchange-energy density of the intermediate subsystem is corrected by G function,

$$
G^{Y} = (\alpha_X + \alpha_Y)^{1/3}(\alpha_Y - \alpha_X) + \alpha_X^{4/3}.
\tag{39}
$$

While α_Y is small compared to α_X, the G function can be significantly simplified. Notifying the expansion

$$
(1+b)^{1/3} = 1 + \frac{b}{3} - \frac{2}{9}b^2 + \cdots
\tag{40}
$$

and assuming

$$
b = \frac{\alpha_Y}{\alpha_X}
\tag{41}
$$

we will have

$$
\begin{aligned}
G^{Y} &= \alpha_X^{1/3}(1+b)^{1/3}(\alpha_Y - \alpha_X) + \alpha_X^{4/3} \\
&\approx \left(\alpha_X^{1/3} + \tfrac{1}{3}\alpha_Y \alpha_X^{-2/3}\right)(\alpha_Y - \alpha_X) + \alpha_X^{4/3} \\
&\approx \tfrac{2}{3}\alpha_X^{1/3}\alpha_Y.
\end{aligned}
\tag{42}
$$

Similarly, we can simplify the coefficient-correction function for the exchange energy between lower and upper subsystems X and Y while they are separated by a large intermediate system Y

$$
\begin{aligned}
G^{XZ} &= 2\alpha_X - 2\alpha_X \alpha_Y^{1/3}\left(\frac{\alpha_X}{\alpha_Y} + 1\right)^{1/3} \\
&\approx 2\alpha_X - 2\alpha_X \alpha_Y^{1/3}\left(1 + \frac{1}{3}\frac{\alpha_X}{\alpha_Y}\right) \\
&\approx 2\alpha_X - 2\alpha_X \alpha_Y^{1/3}.
\end{aligned}
\tag{43}
$$

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