Exchange-correlation energy functional constructed from orbital-dependent coupling-constant-averaged pair correlation functions

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Abstract

An exchange-correlation energy functional $E_{xc}$ and the resultant exchange-correlation potential $v_{xc}(\mathbf{r})$ in density-functional theory are proposed using orbital-dependent coupling-constant-averaged pair correlation functions, $ar{g}^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}')$ for electronic structure calculations of atoms, molecules, and solids. These orbital-dependent $ar{g}^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}')$ fulfill the symmetric property, the Pauli principle and the sum rules. In the limit of uniform density $ar{g}^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}')$ are reduced to the very accurate analogues of the electron liquid that are obtained from an interpolation between long- and short-range correlations involving the exchange corrections. The major contribution of $v_{xc}(\mathbf{r})$ is given in the form of the Coulomb interaction with the exchange-Coulomb hole around an electron. The present theory not only guarantees local charge neutrality, but also reproduces the exact asymptotic form of the exchange potential, $v_{x}(\mathbf{r}) = -e^2/\mathbf{r}$ for finite systems. The present method of dealing with correlations, if properly applied to finite systems, can give even the asymptotic form of the correlation potential $v_{c}(\mathbf{r})$ of order $r^{-4}$ as well as the van der Waals potential of order $r^{-6}$ for large $r$.

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I. INTRODUCTION

The most important subject in density-functional theory (DFT) [1,2] is the exploitation of an accurate exchange-correlation energy functional $E_{xc}$ and the corresponding exchange-correlation potential $v_{xc}(r)$ beyond the local-density approximation (LDA) and the generalized gradient expansion approximations (GGA’s). In a previous paper [3] we have proposed an orbital-dependent correlation energy functional $E_c[\{\varphi_i\}\{\varepsilon_i\}]$ which is to be used by the optimized potential method (OPM)[4] in combination with the exact orbital-dependent exchange energy functional $E_x[\{\varphi_i\}]$. It comprises a direct and exchange pair of second-order perturbation-like terms constructed from Kohn-Sham orbitals and Kohn-Sham energies, but one of the two Coulomb interactions entering each term is replaced by an effective interaction $v_{ef}(r)$ which can in principle contain all the effects of third- and higher-order perturbation terms. From the accurate knowledge of long-, intermediate-, and short-range correlations of the electron liquid, we have defined such effective interaction $v_{ef}(r)$ for the electron liquid in order to substitute it for the orbital-dependent correlation energy functional above. These orbital-dependent exchange and correlation energy functionals depend implicitly on the electron density $n(r)$ through Kohn-Sham orbitals and Kohn-Sham energies. The application of such implicit functionals to DFT is founded on the basic assumption that the correlation potential $v_c(r)$ as well as the exchange potential $v_x(r)$ will be evaluated by solving an integral equation which relates $v_{xc}(r)$ to $\delta E_{xc}/\delta \varphi_i(r)$ and $\delta E_{xc}/\delta \varepsilon_i$. The procedure for solving this integral equation has been called the optimized potential method (OPM) [4]. Actually, the OPM has been applied to the evaluation of the exchange potential $v_x(r)$ with great success [4,5,6,7].

Very recently, it has, however, been pointed out [8] that for finite systems the correlation potential $v_c(r)$ obtained from a direct application of the OPM to the lowest-order contribution of $E_c$, i.e., the second-order perturbation terms constructed from Kohn-Sham orbitals and Kohn-Sham energies, in fact, becomes divergent in the asymptotic region for large $r$. The unphysical behavior above is caused by the presence of unoccupied orbitals.
and unoccupied energies in the perturbation expression for \( E_c \). This implies that the OPM, though apparently most promising, might not be valid for the evaluation of the correlation potential \( v_c(r) \).

In this paper we propose an approximation method which enables one to avoid the above difficulty in the OPM in order to utilize the effective interaction of the electron liquid we have introduced for the evaluation of the correlation potential \( v_c(r) \) in DFT. For this purpose we transform the orbital-dependent exchange and the orbital-dependent second-order perturbation-like correlation energy functionals given in the previous paper [3] into another expression written in terms of the orbital-dependent coupling-constant-averaged pair correlation functions, \( \bar{g}(r, r') \)[9,10]. This transformation enables one to deal with \( E_{xc} \) as an explicit functional of the electron density \( n(r) \) and the major contribution of \( v_{xc}(r) \) is physically appealing since it is given in the form of the Coulomb interaction with the exchange-correlation hole around an electron at the position \( r \). The remaining terms involving the functional derivative, \( \delta \bar{g}(r', r'') / \delta n(r) \) probably will make a minor contribution to \( v_{xc}(r) \) since the six-fold integrations over \( r' \) and \( r'' \) may be expected to make only a secondary correction to the Hartree potential, giving a rather small and nearly uniform modification in the electron density \( n(r) \) of the system. Therefore we deal with these terms in the spirit of the local-density approximation (LDA), i.e., calculate these terms in the limit of uniform density and replace their density dependence by the local density \( n(r) \) of the system. It guarantees that the total \( v_{xc}(r) \) in the present theory is reduced to the LDA in the limit of uniform density.

In section II we give an approximate expression for the orbital-dependent spin-parallel and spin-antiparallel coupling-constant-averaged pair correlation functions for use in the exchange and correlation functionals in DFT. We show that these pair correlation functions not only fulfill the inherent symmetric property as well as the requirement due to the Pauli principle, but also satisfy the basic sum rules. In section III we give an approximate form of exchange and the correlation potentials for practical use. The last section is devoted to conclusions and discussions.
II. ORBITAL-DEPENDENT COUPLING-CONSTANT-AVERAGED PAIR CORRELATION FUNCTIONS

Let us start with the general expression for $E_{xc}(\mathbf{r})$ that Harris and Jones [9] have first introduced in DFT. This expression gives a clear physical meaning of exchange and correlation in DFT.

$$E_{xc} = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{e^2 n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} (\bar{g}(\mathbf{r}, \mathbf{r}') - 1)).$$

(1)

In Eq.(1), the coupling-constant-averaged pair correlation function $\bar{g}(\mathbf{r}, \mathbf{r}')$ is defined using the technique that the electron density $n(\mathbf{r})$ in the real interacting system is maintained while the Coulomb interaction among electrons is adiabatically switched on as a perturbation. The function thus defined, $\bar{g}(\mathbf{r}, \mathbf{r}')$ exhibits general behaviors analogous to those of the usual pair correlation function $g(\mathbf{r}, \mathbf{r}')$ as a function of $|\mathbf{r} - \mathbf{r}'|$. The difference of $\bar{g}(\mathbf{r}, \mathbf{r}')$ from unity is, however, generally reduced in magnitude compared with that of $g(\mathbf{r}, \mathbf{r}')$, which is noticeable particularly for small separations. This is because a lowering in the electron-electron interaction energy due to the presence of $g(\mathbf{r}, \mathbf{r}')$ from its value in the Hartree approximation is partially cancelled by an increase in the kinetic energy which is caused by correlation and at the same time cannot be described in terms of $T_s$, the kinetic energy of the reference non-interacting system with the same $n(\mathbf{r})$ as the real interacting system, through the coupling-constant-averaged pair correlation function $\bar{g}(\mathbf{r}, \mathbf{r}')$ introduced in DFT. From Eq.(1) it is evident that exchange and correlation have the effect to reduce the contribution of the Hartree energy functional from short separations and the effect to enhance the contribution from long separations as a counteraction. Correlation between electrons not only gives the net reduction in the electron-electron interaction energy that is gained at the cost of an inevitable increase in the kinetic energy, but also plays an important role in the determination of the electron density $n(\mathbf{r})$ of real many-electron systems that are for the most part stabilized under the influence of the presence of nuclei. Correlation in real systems gives rise to a change in the electron density $n(\mathbf{r})$ in contrast with correlation in the uniform electron liquid.
In addition to the effective interaction $v_{\text{eff}}(r)$ we have also calculated with high accuracy the spin-parallel and spin-antiparallel coupling-constant-averaged pair correlation functions for the electron liquid, $\bar{g}^{\sigma\sigma}(|\mathbf{r} - \mathbf{r}'|)$ and $\bar{g}^{\sigma-\sigma}(|\mathbf{r} - \mathbf{r}'|)$. We have then ascertained that the difference of $\bar{g}^{\sigma\sigma}(|\mathbf{r} - \mathbf{r}'|)$ from the Hartree-Fock correlation function $g_{HF}^{\sigma\sigma}(|\mathbf{r} - \mathbf{r}'|)$ is significantly reduced in comparison with that of $g^{\sigma\sigma}(|\mathbf{r} - \mathbf{r}'|)$ and that the difference of $\bar{g}^{\sigma-\sigma}(|\mathbf{r} - \mathbf{r}'|)$ from unity is appreciably reduced in comparison with that of $g^{\sigma\sigma}(|\mathbf{r} - \mathbf{r}'|)$.

These reductions are due to the correlational increase in the kinetic energy, which is by definition involved in the coupling-constant-averaged pair correlation functions. It should, however, be noted that these coupling-constant-averaged pair correlation functions for the electron liquid are inappropriate for use in Eq.(1) since no orbital-dependent features can be involved in these functions.

Consider the second-order perturbation-like expression we have proposed in the previous paper for the orbital-dependent correlation energy functional [3]:

$$E_c = \frac{1}{2} \sum_{i,j} \sum_{\text{occ.},\text{unocc.}} \left\{ \frac{\langle \varphi_i \varphi_j | v(r_{12}) | \varphi_a \varphi_b \rangle \langle \varphi_a \varphi_b | v_{\text{eff}}(r_{12}) | \varphi_i \varphi_j \rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} - \frac{\langle \varphi_i \varphi_j | v(r_{12}) | \varphi_a \varphi_b \rangle \langle \varphi_a \varphi_b | v_{\text{eff}}(r_{12}) | \varphi_j \varphi_i \rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \right\},$$

$$\langle \varphi_i \varphi_j | v(r_{12}) | \varphi_a \varphi_b \rangle = \int \int d\mathbf{r}_1 d\mathbf{r}_2 \varphi_i^*(\mathbf{r}_1) \varphi_j^*(\mathbf{r}_2) v(r_{12}) \varphi_a(\mathbf{r}_1) \varphi_b(\mathbf{r}_2), \quad (2)$$

$$\langle \varphi_i \varphi_j | v_{\text{eff}}(r_{12}) | \varphi_a \varphi_b \rangle = \int \int d\mathbf{r}_1 d\mathbf{r}_2 \varphi_i^*(\mathbf{r}_1) \varphi_j^*(\mathbf{r}_2) v_{\text{eff}}(r_{12}) \varphi_a(\mathbf{r}_1) \varphi_b(\mathbf{r}_2),$$

where $\varphi_i$, $\varphi_a$ and $\varepsilon_i$, $\varepsilon_a$ are Kohn-Sham orbitals and Kohn-Sham energies, respectively. In Eq.(2), $v(r_{12}) = e^2/|\mathbf{r}_1 - \mathbf{r}_2|$ and the effective interaction $v_{\text{eff}}(\mathbf{r})$ is the real-space Fourier transform of the interaction $v_{\text{eff}}(\mathbf{q})$ we have defined by an exact expression for the correlation energy of the electron liquid as

$$E_c = \frac{1}{2} \left( \frac{1}{\Omega} \right)^2 \sum_{\mathbf{q},\sigma,\sigma'} f(\mathbf{p}) f(\mathbf{p}') v(\mathbf{q}) \frac{(1 - f(\mathbf{p} + \mathbf{q}))(1 - f(\mathbf{p}' - \mathbf{q}))}{\varepsilon_\mathbf{p} - \varepsilon_\mathbf{p} + \mathbf{q} + \varepsilon_\mathbf{p}' - \varepsilon_\mathbf{p}' - \mathbf{q}} \times (v_{\text{eff}}(\mathbf{q}) - \delta_{\sigma\sigma'} v_{\text{eff}}(-\mathbf{p} + \mathbf{p}' - \mathbf{q})),$$ \quad (3)$$

where $f(\mathbf{p})$ is the Fermi distribution function at zero temperature and $\varepsilon_\mathbf{p} = \hbar^2 \mathbf{p}^2/2m$; $\Omega$ being the volume of the system. In Eq.(3), long-, intermediate-, and short-range correlations arising from all the higher-order perturbation terms beyond the second are taken into
account in the form of $v_{\sigma}(\mathbf{q})$. We have evaluated the effective interaction $v_{\sigma}(\mathbf{q})$ by making a sophisticated interpolation between long-range correlation in the random-phase approximation (RPA) [11] and short-range correlation in the particle-particle ladder approximation [12,13,14] such that the corresponding exchange interaction $v_{\sigma}(\mathbf{q})$ and its feedback effect on the direct interaction $v_{\sigma}(\mathbf{q})$ are allowed for in a self-consistent way. The new expression for $E_c$ given by Eq.(3) not only reproduces available most accurate numerical values [15] of the correlation energy within an accuracy of 0.5 mRy. per electron throughout the entire region of metallic densities, but also has the merit of giving spin-antiparallel and spin-parallel contributions of the correlation energy separately. It is important to realize that the spin-antiparallel contribution occupies about 70% of the total correlation energy and the spin-parallel contribution does occupy as much as about 30% throughout the entire region of metallic densities. Probably, this ratio will apply to all the valence electrons that take part in cohesion of real metals.

It is important to notice that Eq.(2) can be transformed into the correlation part of Eq.(1). For this purpose we shall start with the spin-dependent version of Eq.(1), which enables one to deal with the exchange and the correlation energy functionals, $E_x$ and $E_c$, separately.

$$E_{xc} = \frac{1}{2} \sum_{\sigma,\sigma'} \int \int d\mathbf{r} d\mathbf{r}' e^{2n_{\sigma}(\mathbf{r})n_{\sigma'}(\mathbf{r}')} \frac{|\mathbf{r} - \mathbf{r}'|}{|\mathbf{r} - \mathbf{r}'|} \left( \bar{g}_{\sigma\sigma}^{\sigma\sigma}(\mathbf{r}, \mathbf{r}') - 1 \right), \quad \text{(4)}$$

where the spin-parallel coupling-constant-averaged pair correlation function $\bar{g}_{\sigma\sigma}^{\sigma\sigma}(\mathbf{r}, \mathbf{r}')$ may be split into the Hartree-Fock and the correlational contributions as

$$\bar{g}_{\sigma\sigma}^{\sigma\sigma}(\mathbf{r}, \mathbf{r}') = g_{\sigma\sigma}^{\sigma\sigma}(\mathbf{r}, \mathbf{r}') + \bar{g}_{\sigma\sigma}^{\sigma\sigma}(\mathbf{r}, \mathbf{r}'). \quad \text{(5)}$$

Then the exchange energy functional $E_x$ can be written in terms of the Hartree-Fock spin-parallel pair correlation function $g_{\sigma\sigma}^{\sigma\sigma}(\mathbf{r}, \mathbf{r}')$ as

$$E_x = \frac{1}{2} \sum_{\sigma} \int \int d\mathbf{r} d\mathbf{r}' e^{2n_{\sigma}(\mathbf{r})n_{\sigma}(\mathbf{r}')} \frac{|\mathbf{r} - \mathbf{r}'|}{|\mathbf{r} - \mathbf{r}'|} \left( g_{\sigma\sigma}^{\sigma\sigma}(\mathbf{r}, \mathbf{r}') - 1 \right), \quad \text{(6)}$$

where
The two correlation functions, \( \bar{g} \), by paying special attention to a single Coulomb interaction entering each of direct and exchange terms as

\[
g_{\text{HF}}^\sigma(r, r') = 1 - \frac{1}{n_\sigma(r)n_{-\sigma}(r')} \left| \sum_i \varphi^*_i(r)\varphi_{i\sigma}(r') \right|^2. \tag{7}
\]

This function is constructed from occupied Kohn-Sham orbitals alone. On the other hand, the correlation energy functional \( E_c \) consists of the spin-antiparallel and spin-parallel contributions as

\[
E_c = \sum_\sigma \left( E^{\sigma-\sigma}_c + E^{\sigma\sigma}_c \right), \tag{8}
\]

\[
E^{\sigma-\sigma}_c = \frac{1}{2} \int dr dr' \frac{e^2 n_\sigma(r)n_{-\sigma}(r')}{|r-r'|} (\bar{g}^{\sigma-\sigma}(r, r') - 1), \tag{9}
\]

\[
E^{\sigma\sigma}_c = \frac{1}{2} \int dr dr' \frac{e^2 n_\sigma(r)n_{\sigma}(r')}{|r-r'|} \bar{g}_c^{\sigma\sigma}(r, r'), \tag{10}
\]

where \( \bar{g}^{\sigma-\sigma}(r, r') \) is the spin-antiparallel coupling-constant-averaged pair correlation function and \( \bar{g}_c^{\sigma\sigma}(r, r') \) denotes the correlational part of spin-parallel coupling-constant-averaged pair correlation function. An inspection of these two contributions of \( E_c \) manifests that development of the Coulomb hole and further lowering of the Fermi hole at short separations both make a contribution to the correlation energy.

Now we can easily transform the second-order perturbation-like expression given by Eq. (2) into the above spin-dependent expressions written in terms of \( \bar{g}^{\sigma-\sigma}(r, r') \) and \( \bar{g}_c^{\sigma\sigma}(r, r') \) by paying special attention to a single Coulomb interaction entering each of direct and exchange terms in it. The two correlation functions, \( \bar{g}^{\sigma-\sigma}(r, r') \) and \( \bar{g}_c^{\sigma\sigma}(r, r') \) may be identified, respectively, as

\[
\bar{g}^{\sigma-\sigma}(r, r') - 1 = \frac{1}{n_\sigma(r)n_{-\sigma}(r')} \sum_{i,j} \sum_{a,b} \varphi^*_i(r)\varphi_{j-\sigma}(r')\varphi_{a\sigma}(r)\varphi_{b-\sigma}(r') \\
\quad \times \oint dr_1 dr_2 \varphi^*_a(r_1)\varphi_{b-\sigma}(r_1)\varphi_{a\sigma}(r_2)v_{\sigma\sigma}(r_1)\varphi_{j-\sigma}(r_2), \tag{11}
\]

\[
\bar{g}_c^{\sigma\sigma}(r, r') = \frac{1}{n_\sigma(r)n_{\sigma}(r')} \sum_{i,j} \sum_{a,b} \varphi^*_i(r)\varphi_{j\sigma}(r')\varphi_{a\sigma}(r)\varphi_{b\sigma}(r') \\
\quad \times \oint dr_1 dr_2 \varphi^*_a(r_1)\varphi_{b\sigma}(r_2)v_{\sigma\sigma}(r_1) \{ \varphi_{i\sigma}(r_1)\varphi_{j\sigma}(r_2) - \varphi_{j\sigma}(r_1)\varphi_{i\sigma}(r_2) \}, \tag{12}
\]
where the electron density with spin $\sigma$ is given by

$$n_\sigma(r) = \sum_{i} |\psi_{i\sigma}(r)|^2.$$  \hspace{1cm} (13)

Note that these correlation functions are constructed from both unoccupied and occupied Kohn-Sham orbitals and Kohn-Sham energies. It is important to notice that these correlation functions in the limit of uniform density, i.e., if Kohn-Sham orbitals and Kohn-Sham energies in Eqs. (11) and (12) are replaced by plane waves and free electron energies, respectively, they are reduced to the accurate analogues of the electron liquid because of the very definition of the effective interaction $v_{\sigma\sigma}(r)$ that we have introduced.

It is evident from Eqs. (11) and (12) that the present theory satisfies the symmetric property inherent in the pair correlation function as well as the requirement due to the Pauli principle.

$$\bar{g}^{\sigma\sigma'}(r, r') = \bar{g}^{\sigma'\sigma}(r', r),$$

$$\bar{g}^{\sigma\sigma'}_c(r, r) = 0.$$  \hspace{1cm} (14)

It is important to realize that the well-known sum rule concerning the exchange-Coulomb hole is in fact exhausted by the Hartree-Fock exchange hole alone.

$$\int dr' n_{\sigma}(r') (g_{\text{HF}}^{\sigma\sigma}(r, r') - 1) = -1.$$  \hspace{1cm} (16)

This is evident from the orthogonality between occupied Kohn-Sham orbitals. As a consequence, the Coulomb hole due to correlation between electrons with opposite spin and the correlational change in the Fermi hole separately have to integrate to zero. In other words, correlation due to the Coulomb interaction occurs among electrons, for either of two spin orientations, such that local charge neutrality is maintained at every position $r$ of the system. The present theory has the striking merit that the requirements above are fulfilled, as is evident from the orthogonality between occupied and unoccupied Kohn-Sham orbitals appearing in Eqs.(11) and (12).
\[ \int d\mathbf{r}' n_{-\sigma}(\mathbf{r}') \left( \tilde{g}^{\sigma-\sigma}(\mathbf{r},\mathbf{r}') - 1 \right) = 0, \]  
(17)

\[ \int d\mathbf{r}' n_{\sigma}(\mathbf{r}') \tilde{g}_{c}^{\sigma\sigma}(\mathbf{r},\mathbf{r}') = 0. \]  
(18)

**III. EXCHANGE AND CORRELATION POTENTIALS**

In order to obtain the exchange potential \( v_{x\sigma}(\mathbf{r}) \) we evaluate the functional derivative of \( E_{x} \) given by Eq.(6) with respect to \( n_{\sigma}(\mathbf{r}) \). The major contribution of \( v_{x\sigma}(\mathbf{r}) \) is given as

\[ \int d\mathbf{r}' e^{2} n_{\sigma}(\mathbf{r}') \left| \mathbf{r} - \mathbf{r}' \right| \left( \tilde{g}_{HF}^{\sigma\sigma}(\mathbf{r},\mathbf{r}') - 1 \right). \]  
(19)

This is nothing but the Coulomb interaction with the bare Fermi hole around an electron located at the position \( \mathbf{r} \). In the limit of uniform density it is reduced to \( 3/2 \mu_{x\sigma} [16] \) where \( \mu_{x\sigma} \) denotes the exchange contribution to the chemical potential of the uniform electron liquid. The remaining term of \( v_{x\sigma}(\mathbf{r}) \) is written as

\[ \frac{1}{2} \int \int d\mathbf{r}' d\mathbf{r}'' e^{2} n_{\sigma}(\mathbf{r}') n_{\sigma}(\mathbf{r}'') \frac{\delta g_{HF}^{\sigma\sigma}(\mathbf{r}',\mathbf{r}'')}{\delta n_{\sigma}(\mathbf{r})}. \]  
(20)

The functional derivative entering Eq.(20) cannot possibly be evaluated for arbitrary electronic systems, but Eq.(20) can be analytically evaluated in the limit of uniform density. It amounts to be \(-1/2 \mu_{x\sigma}[16]\). It is not likely that Eq.(20) may produce such an important contribution to \( v_{x\sigma}(\mathbf{r}) \) as is comparable to Eq.(19) because of the six-fold integration over \( \mathbf{r}' \) and \( \mathbf{r}'' \). Then we approximate this term by \(-1/2 \mu_{x\sigma}(n_{\sigma}(\mathbf{r})) \) following the spirit of the LDA.

A similar approximation method may be applied to the correlation potential \( v_{c\sigma}(\mathbf{r}) \). The potential \( v_{c\sigma}(\mathbf{r}) \) in the present theory consists of the major functional derivative of \( E_{c} \) given by Eqs.(8), (9) and (10) with respect to \( n_{\sigma}(\mathbf{r}) \) and the minor correction as

\[ v_{c\sigma}(\mathbf{r}) = \int d\mathbf{r}' e^{2} n_{-\sigma}(\mathbf{r}') \left( \tilde{g}^{\sigma-\sigma}(\mathbf{r},\mathbf{r}') - 1 \right) + \int d\mathbf{r}' e^{2} n_{\sigma}(\mathbf{r}') \tilde{g}_{c}^{\sigma\sigma}(\mathbf{r},\mathbf{r}') + \Delta \mu_{c\sigma}(n_{\sigma}(\mathbf{r})). \]  
(21)

The first term is given in the form of the Coulomb interaction with the Coulomb hole around an electron located at the position \( \mathbf{r} \) and the second term in the form of the Coulomb interaction with a correlation-induced change in the Fermi hole around the electron. From these
expressions it is then evident that the first and second terms have the effect to significantly reduce the contribution of the Hartree potential from short separations, which is important to the accurate evaluation of the electron density $n(r)$ of the system. This is because the screening of each attractive nuclear potential by valence electrons is expected to be significantly reduced at short distances by the first and second terms in Eq.(21) and the electron density of $n(r)$ may be somewhat enhanced in the immediate vicinity of each nucleus. On the other hand, it is not likely that the remaining terms of $v_{c\sigma}(r)$ may make such an important contribution as is comparable to the first and second terms because of the six-fold integrations involved. Then we approximate the remaining terms of $v_{c\sigma}(r)$ in the spirit of the LDA. The last term $\Delta \mu_{c\sigma}(n_{\sigma}(r))$ in Eq.(21) denotes such an approximation to those terms which involve the functional derivatives, $\delta \tilde{g}^{\sigma-\sigma}(r', r'')/\delta n_{\sigma}(r)$ and $\delta \tilde{g}^{\sigma\sigma}_c(r', r'')/\delta n_{\sigma}(r)$.

The coefficient $\Delta$ should be determined such that in the limit of uniform density the total correlation potential $v_{c\sigma}(r)$ is reduced to the correlation contribution to the chemical potential of the electron liquid, $\mu_{c\sigma}$. We think that the contribution of $v_{c\sigma}(r)$ involving the six-fold integrations will form a background-like potential against the Hartree potential and plays a secondary role in the occurrence of a correlation-induced change in the electron density $n(r)$ of the system. Then we have treated that contribution following the spirit of the local-density approximation (LDA).

For the practical application of the present scheme, it is a delicate problem how to choose the density parameter in the effective interaction $v_{\text{eff}}(r)$ we have borrowed from the electron liquid. The best choice of the density parameter will be such an optimization as gives the minimum value of the calculated ground state energy. Another choice will be the effective average density of valence electrons that take part in binding of molecules or in cohesion of solids; for metals it will correspond to the nearly uniform density realized in the interstitial region outside muffin-tin spheres.

Now all quantities requisite for DFT are available. The exchange energy functional $E_x$ is exactly given in terms of the Hartree-Fock spin-parallel pair correlation function $g_{HF}^{\sigma\sigma}(r, r')$ and the correlation energy functional $E_c$ in terms of the spin-antiparallel coupling-
constant-averaged pair correlation function \( \bar{g}^{\sigma-\sigma}(\mathbf{r}, \mathbf{r}') \) and the correlation-induced spin-parallel coupling-constant-averaged pair correlation function \( \bar{g}^{\sigma\sigma}_c(\mathbf{r}, \mathbf{r}') \). Correspondingly, the exchange potential \( v_{x\sigma}(\mathbf{r}) \) and the correlation potential \( v_{c\sigma}(\mathbf{r}) \) are also given in terms of \( g^{\sigma\sigma}_{HF}(\mathbf{r}, \mathbf{r}') \), \( \bar{g}^{\sigma-\sigma}(\mathbf{r}, \mathbf{r}') \), and \( \bar{g}^{\sigma\sigma}_c(\mathbf{r}, \mathbf{r}') \), though the minor contribution of \( v_{x\sigma}(\mathbf{r}) \) and \( v_{c\sigma}(\mathbf{r}) \) is approximately treated in a similar way as in the LDA. We have thus avoided the difficulty that is encountered in dealing with the correlation potential \( v_{c\sigma}(\mathbf{r}) \) according to the OPM by transforming the exchange and correlation energy functionals into the expression given by Eq.(4) and making some approximations.

In the present scheme, the major contribution of \( v_{x\sigma}(\mathbf{r}) \) and \( v_{c\sigma}(\mathbf{r}) \) as well as \( E_x \) and \( E_c \) depends implicitly on Kohn-Sham orbitals and Kohn-Sham energies through the coupling-constant-averaged pair correlation functions \( \bar{g}^{\sigma\sigma}_c(\mathbf{r}, \mathbf{r}') \). The present \( v_{c\sigma}(\mathbf{r}) \), when applied to finite systems, is not divergent for large \( r \), however. This is evident from its expression (Eq.(21)) and the sum rules (Eqs. (17) and (18)). A much higher degree of self-consistency is required to perform the present scheme than in the LDA or GGA’s since the coupling-constant-averaged pair correlation functions involved are orbital- and energy-dependent.

**IV. CONCLUSIONS AND DISCUSSIONS**

Between metals and non-metals there is an essential difference in long-range correlation, or equivalently screening at long distances, depending on whether the Fermi surface exists or not. We have borrowed the knowledge of long-range correlation from the electron liquid in which perfect screening at long distances is realized in the presence of the Fermi surface. In this sense, the effective potential \( v_{\text{eff}}(\mathbf{r}) \) in the previous paper [3] is properly defined for metals. If one performs a similar interpolation between long-range correlation in the RPA and short-range correlation in the particle-particle ladder approximation for finite systems or semiconductors and insulators in order to properly define the effective interaction \( v_{\text{eff}}(\mathbf{r}) \) in the second-order perturbation-like correlation energy functional, the resulting effective potential \( v_{\text{eff}}(\mathbf{r}) \) takes the form of \( e^2/\varepsilon_0 r \) at large distances where \( \varepsilon_0 \) is a constant of order
of the static dielectric constant. On the other hand, there is no essential difference in short-range correlation, or the analytic form of \( v_{\sigma\sigma}(r) \) at short distances between metals and non-metals. The particle-particle ladder approximation [12,13,14] gives the adequate description of short-range correlation as well as of the cusp condition [17,18,19] on the many-body wavefunction, independent of whether the Fermi surface exists or not. Therefore the present interpolation method of dealing with correlations can give the correct asymptotic form of the correlation potential \( v_{\sigma\sigma}(r) \) of order \( r^{-4} \) for finite systems as well as the van der Waals potential of order \( r^{-6} \) [20], if the effective interaction \( v_{\sigma\sigma}(r) \) for finite systems is properly defined as \( \frac{e^2}{\varepsilon_0 r} \) for large \( r \).

From experiences it has been widely observed [10] that the LDA has the tendency to underestimate the nucleus-nucleus separation in the formation of solids and the tendency to overestimate the binding energy of solids. Probably, these shortcomings of the LDA will be, for the most part, ascribed to that the screening of each nucleus or ion by valence electrons is overestimated at short distances and that the ground state energy of the atomic state is evaluated too high in comparison with that of the solid state. In our view, the adequate inclusion of short-range correlation between valence electrons may correct the underestimate in the nucleus-nucleus separation in solids. It is important to notice that short-range correlation between valence electrons has the effect to give less screening of each nucleus or ion at short distances and therefore may significantly enhance the electron density \( n(r) \) in the immediate vicinity of each nucleus. As a counteraction of this enhancement, the nucleus-nucleus separation is expected to be somewhat increased.

The present approximation to \( E_{xc} \) in its construction is expected to provide a much more accurate evaluation of the ground state energy of both atoms and molecules or solids than the LDA and GGA’s. In the present \( E_{xc} \), the self-interaction errors arising from the Hartree energy functional are completely cancelled by the Hartree-Fock spin-parallel pair correlation function \( g^{\sigma\sigma}_{HF}(r, r') \), though the corresponding exchange potential \( v_{x\sigma}(r) \) involves a minor approximate part. Furthermore, the correlation energy functional \( E_c \) in the present scheme cannot be overestimated in magnitude since we borrow the knowledge of the effective
interaction $v_{\text{eff}}(\mathbf{r})$ from the electron liquid instead of the density dependence of the correlation energy. The LDA overestimates the correlation energy between nearly localized or tightly-binding electrons due to the occurrence of the locally high-density region caused by these electrons since the correlation energy of the uniform electron liquid increases its magnitude like $\ln r_s$ in the high-density region where $r_s$ is the usual density parameter.

A clear understanding of the difficulty [8] that is encountered in the evaluation of $v_{xc}(\mathbf{r})$ according to the OPM will require a detailed investigation of how to make OPM integral equations compatible with Kohn-Sham equations, i.e., how to combine the two different self-consistencies in a unified way. Probably, the unphysical behavior of $v_{c\sigma}(\mathbf{r})$ reported will indicate that the authors may have attempted to combine the two self-consistencies in a forced way. It will be closely related to the fact that the integral equation for $v_{xc\sigma}(\mathbf{r})$, if treated in a way consistent with Kohn-Sham equations, involves the functional derivative $\delta v_{xc\sigma}(\mathbf{r})/\delta n_{\sigma'}(\mathbf{r'})$ in it. The OPM integral equation in its exact form is equivalent to the Sham-Schluter equation [21]. This equation requires that the Kohn-Sham Green’s function $G^{KS}(\mathbf{r}, \mathbf{r'}, \varepsilon)$ defined for the Kohn-Sham reference non-interacting Hamiltonian and the standard many-body theoretical one-electron Green’s function $G(\mathbf{r}, \mathbf{r'}, \varepsilon)$ for the same many-electron system give the same electron density $n(\mathbf{r})$. This requirement can be fulfilled if and only if both $G^{KS}(\mathbf{r}, \mathbf{r'}, \varepsilon)$ and $G(\mathbf{r}, \mathbf{r'}, \varepsilon)$ are exact. According to a systematic perturbation expansion of the many-body Hamiltonian in which the Kohn-Sham noninteracting reference Hamiltonian is dealt with as the unperturbed system, the $n$-th order perturbation energy $E_{xc}^{(n)}$ for $n \geq 2$ has turned out to be a functional of not only occupied and unoccupied Kohn-Sham orbitals and Kohn-Sham energies, but also of $v_{xc\sigma}(\mathbf{r})$ itself [4]. Therefore the $n$-th order integral equation for $v_{xc\sigma}(\mathbf{r})$ involves the functional derivative $\delta v_{xc\sigma}(\mathbf{r})/\delta n_{\sigma'}(\mathbf{r'})$ and is extremely difficult to solve [4], if one goes beyond the first order perturbation $E_{xc}^{(1)}$ equivalent to $E_x$.

The correlation potential $v_{c\sigma}(\mathbf{r})$ is by definition a functional of $n_{\sigma'}(\mathbf{r'})$. It is very probable that the accurate spatial dependence of $v_{c\sigma}(\mathbf{r})$ cannot be obtained without the detailed knowledge of its functional derivative, $\delta v_{xc\sigma}(\mathbf{r})/\delta n_{\sigma'}(\mathbf{r'})$. The situation is analogous to the
fact that the $p$- and $\omega$- dependence of the self-energy operator $\Sigma_\sigma(p, \omega)$ essential to the accurate evaluation of the quasi-particle energy dispersion $E(p)$ for the electron liquid cannot be obtained without the detailed knowledge of its functional derivative with respect to the one-electron Green’s function $G_{\sigma'}(p', \omega')$, $\delta \Sigma_\sigma(p, \omega)/\delta G_{\sigma'}(p', \omega')$ [22,23,24]. This is because the variation of $\Sigma_\sigma(p, \omega)$ with respect to $p$ or $\omega$ occurs only through that of each constituent in it, $G_{\sigma'}(p', \omega')$ [25]. Similarly, the accurate $r$-dependence of $v_{xc}(r)$ will not be obtained without the detailed knowledge of $\delta v_{xc}(r)/\delta n_{\sigma'}(r') = \delta^2 E_{xc}/\delta n_{\sigma}(r)\delta n_{\sigma'}(r')$. Probably, the situation in DFT will be much more complicated than in the standard many-body formalism. This is because the simplicity of Kohn-Sham equations is established in DFT at the cost of the extreme complexity of how to obtain $E_{xc}$ and $v_{xc}(r)$. From a comparison with the second-order functional derivative of the Hartree energy functional, $e^2/|r - r'|$ it can be seen that the factor of $e^2(\tilde{g}^{\sigma\sigma'}(r, r') - 1)/|r - r'|$ entering the present $E_{xc}$ will form a physically appealing and important part of the second-order functional derivative, $\delta^2 E_{xc}/\delta n_{\sigma}(r)\delta n_{\sigma'}(r')$.

Finally we would like to stress that the present theory gives an adequate description of both the orbital-dependence and the non-local dependence of the basic two quantities $E_{xc}$ and $v_{xc}(r)$ in DFT through the orbital-dependent $\tilde{g}^{\sigma\sigma'}(r, r')$ we have constructed with the help of the knowledge of long-, intermediate-, and short-range correlations of the electron liquid at metallic densities and that it is a feasible scheme for practical calculations.

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