An Orbital-dependent Correlation Energy Functional in Density-functional Theory for the Study of Strongly-correlated Electronic Systems

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An orbital-dependent correlation energy functional E_c to be accompanied by the exact exchange energy functional E_x is proposed for applications of density-functional theory (DFT). The present E_c comprises spin-antiparallel and spin-parallel contributions, $E_c^{\sigma-\sigma}$ and $E_c^{\sigma\sigma}$. $E_c^{\sigma-\sigma}$ is a modification of the spin-antiparallel component of the Hartree energy functional with a factor of $\bar{g}^{\sigma-\sigma}(\mathbf{r}, \mathbf{r}') - 1$ and $E_c^{\sigma\sigma}$ a modification of the spin-parallel component of the same energy functional with $\bar{g}_c^{\sigma\sigma}(\mathbf{r}, \mathbf{r}')$ where $\bar{g}^{\sigma-\sigma}(\mathbf{r}, \mathbf{r}')$ (or $\bar{g}_c^{\sigma\sigma}(\mathbf{r}, \mathbf{r}')$) is the spin-antiparallel(or the correlational part of the spin-parallel) coupling-constant-averaged pair correlation function. The present orbital-dependent $\bar{g}^{\sigma-\sigma}(\mathbf{r}, \mathbf{r}')$ and $\bar{g}_c^{\sigma\sigma}(\mathbf{r}, \mathbf{r}')$ fulfill the symmetric property, the Pauli principle and the sum rules. In the limit of uniform density the two correlation functions are reduced to the very accurate analogues of the electron liquid that involve long-, intermediate-, and short-range correlations as well as their exchange counterparts. It is stressed that the correlation energy functional E_c in DFT should by its very nature be defined as a functional only of occupied Kohn-Sham orbitals and occupied Kohn-Sham energies for the purpose of employing the optimized potential method (OPM) to evaluate the correlation potential $v_c(\mathbf{r})$. The present scheme for E_c, if applied to finite systems after making a suitable change in the treatment of long-range correlation, can give the correct asymptotic form of $v_c(\mathbf{r})$ of order r^{-4} for large r as well as the van der Waals potential.

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1. Introduction

Density-functional theory (DFT)[1,2] is a rigorous approach to the many-body problem for the ground state in the framework of a highly self-consistent one-electron problem. DFT is based on the Hohenberg-Kohn variational principle that the ground state energy $E[n(\mathbf{r})]$ which is uniquely expressed as a functional of the electron density $n(\mathbf{r})$ takes its minimum for the exact $n(\mathbf{r})$ of the system. This can be restated in terms of Kohn-Sham (KS) equations that describe a reference non-interacting system with the same $n(\mathbf{r})$ as the real interacting system in the presence of an effective one-electron potential $v_s(\mathbf{r})$ consisting of the attractive nuclear potential $v_0(\mathbf{r})$, the Hartree potential $v_H(\mathbf{r})$, and the local exchange-correlation potential $v_{xc}(\mathbf{r})$ $(= v_x(\mathbf{r}) + v_c(\mathbf{r}))$. The kinetic energy T in DFT is separated into T_s, the kinetic energy of the reference non-interacting system and T_c, the correlational increase in T. The exchange-correlation energy $E_{xc}[n(\mathbf{r})]$ in DFT is the sum of E_x, the exchange energy and E_c, the net correlation-induced lowering in the electron-electron interaction energy that is partially cancelled by including T_c.

The local-density approximation (LDA)[2] to E_{xc} was proposed simultaneously with the advent of DFT. The LDA borrows the knowledge of the density-dependence of the exchange-correlation energy $E_{xc}(n)$ from the uniform electron liquid by regarding actual non-uniform systems as a locally uniform electron liquid. Twenty-five years ago DFT successfully explained the occurrence of ferromagnetism only in iron, cobalt, and nickel among all the metals with atomic number smaller than fifty using the LDA.[3]

Further development in DFT depends on the availability of a physically well-founded new form of $E_{xc}[n(\mathbf{r})]$ and $v_{xc}(\mathbf{r})$ $(= \delta E_{xc}/\delta n(\mathbf{r}))$ beyond the conventional approximations. First of all, the obscurities that the LDA and its modifications have hitherto brought in the treatment of exchange and correlation have to be clarified. A brief but sharp criticism of the LDA is needed for this purpose.

1.1 Criticism of the LDA

The LDA underestimates the magnitude of the exchange energy E_x and overestimates, by a factor of 2~2.5, the magnitude of the correlation energy E_c between electrons with localized orbitals in atomic cores.[4] The reason for these estimates is that E_x and the exchange potential $v_x(\mathbf{r})$ in the LDA fail to cancel the spurious self-interaction terms in the Hartree energy functional E_H and the Hartree potential $v_H(\mathbf{r})$, respectively and that the correlation energy borrowed from the electron liquid is increased in magnitude at high densities in contrast to the case in atomic cores. Therefore the LDA estimates the total energy of atoms higher than the Hartree-Fock theory in spite of the great overestimate of the correlation energy. This is because the exchange energy in atoms makes a much more important contribution to the total energy than the correlation energy; the latter constitutes only about 1% of the total energy in atoms. The ratio of the correlation energy to the exchange energy between conduction electrons in simple metals is an order of magnitude larger than that in atoms, but the absolute magnitude of the correlation energy is of the same order for both conduction electrons in metals and atomic electrons, *i.e.*, about 1 eV per electron.

In the evaluation of the cohesive energy the LDA takes advantage of the dangerous cancellation of the errors arising from atomic cores between an assembly of isolated atoms and the condensed state (a solid). In fact, the difference in the cohesive (or binding) energy between various possible crystalline (or molecular) structures is much smaller than the absolute errors arising from atomic cores. The too high location of occupied 3d levels relative to the Fermi level that

is observed in the band structure calculation of copper and zinc using the LDA is considered to be ascribed mainly to the self-interaction errors in E_x and $v_x(\mathbf{r})$.[3]

There is considerable cancellation between the underestimate of E_x and the overestimate of E_c for localized orbitals, which is favorable for the application of the LDA. This favorable cancellation probably will be most effective for the $4d$ levels in metals since they are less tightly bound.[3] By construction, the LDA is appropriate for use in the interstitial region outside muffin-tin spheres in metals; the electron density is uniform and the self-interaction errors in E_x become vanishingly small; the treatment of E_c in the LDA is most suitable.

A tendency of the LDA is to somewhat overestimate the cohesive energy of metals.[3] Probably, this overestimate will be more caused by a too highly estimated energy of an atom than by a too low estimated energy of a metal per atom. The reason for this statement is that the treatment of exchange and correlation in the LDA is expected to be better between conduction electrons participating in the metallic cohesion than between outermost electrons in an isolated atom and the core electrons. A second tendency of the LDA is to somewhat underestimate the lattice constant (or the equilibrium nucleus-nucleus separation).[3] This tendency of the LDA probably will come from too strong screening of each nucleus in its immediate vicinity. Accordingly, even in simple metals for which the LDA seems to be most suitable, the electron density $n(\mathbf{r})$ is not enhanced at the location of each nucleus, compared with the case of an isolated atom. This is in contradiction with the Reuderberg's assertion[5] that the metallic cohesion should involve an enhancement in the electron density $n(\mathbf{r})$ in the immediate vicinity of the nuclei in the same way as the situation that the binding of two hydrogen atoms into a hydrogen molecule involves a contraction of the electron density distribution near the nuclei to enhance $n(\mathbf{r})$ at the location of each nucleus. How to screen each nucleus at short distances in simple metals is beyond the description of the LDA. This is because such correlation effects as occur in the presence of the nuclei in the system cannot be properly allowed for in the LDA. In other words, the electron density in the regions close to the nuclei is far from being nearly uniform and the LDA cannot be applied in its strict sense.

The proper allowance for short-range correlation between conduction or valence electrons in the presence of the nuclei probably will give less screening of each nucleus in its vicinity to enhance the electron density $n(\mathbf{r})$ at the location of the nuclei of the system. This cohesion-induced enhancement of $n(\mathbf{r})$ at the location of the nuclei is expected to lead to a small but significant increase in the lattice constant as a counterbalance, compared with the case in the LDA. A similar underestimate of the equilibrium nucleus-nucleus separations in molecules is regularly observed in the Hartree-Fock approximation. This is also because short-range correlation between valence electrons are not allowed for at all in this approximation and screening of each nucleus in its immediate vicinity becomes too strong as a result.

For atoms and molecules the LDA cannot give the exact asymptotic form of the correlation potential $v_c(\mathbf{r})$, $-r^{-4}/2\alpha$ for large r where α is the polarizability of the system.[6] The LDA by its very nature is intended for conduction electrons particularly in simple metals and hence cannot provide the proper description of such long-range correlation as is inherent in finite systems or insulators.

In conclusion, the unexpected success of the LDA may be ascribed to a great deal of cancellation between errors. This is a consequence of the long-range character of the Coulomb interaction.

1.2 Exact treatment of E_x

The exact treatment of the exchange energy functional E_x and the exchange potential $v_x(\mathbf{r})$ in DFT has been performed by the optimized potential method (OPM) for atoms and semiconductors.[7–10] The OPM enables one to derive the exact $v_x(\mathbf{r})$ from the functional derivative of E_x with respect to occupied KS orbitals by solving the OPM integral equation. The exact $v_x(\mathbf{r})$ thus derived is completely free from the self-interaction errors and describes the correct asymptotic form of finite systems, $-e^2/r$ for large r. The exchange only OPM in DFT and the usual Hartree-Fock theory are based on the same approximate total energy functional, but fulfill different variational calculations. The ground state energy in the DFT version of the Hartree-Fock theory is, by only a slight amount, higher than the usual Hartree-Fock ground state energy because of an additional condition imposed on the exchange potential, $i.e.$, the local $v_x(\mathbf{r})$. A slight difference between the two schemes should also be observed in the electron density $n(\mathbf{r})$. It has been shown that the two schemes based on the same total energy functional yield the same highest occupied energy level, though there is a significant difference between the two in the lower occupied and the unoccupied energy levels.

The exchange energy functional E_x can be rewritten in terms of the Hartree-Fock spin-parallel pair correlation function $g_{HF}^{\sigma\sigma}(\mathbf{r},\mathbf{r}')$ constructed from occupied KS orbitals alone. Its expression is a modification of the spin-parallel component of the Hartree energy functional with a factor of $g_{HF}^{\sigma\sigma}(\mathbf{r},\mathbf{r}') - 1$. The functional derivative of this expression with respect to $n(\mathbf{r})$ gives two distinct contributions. One is a modification of the spin-parallel component of the Hartree potential with $g_{HF}^{\sigma\sigma}(\mathbf{r},\mathbf{r}') - 1$; it has been termed the screening potential part of $v_x(\mathbf{r})$ that is responsible for the exact asymptotic form of the exchange potential for finite systems, $-e^2/r$ for large r. The other involves $\delta g_{HF}^{\sigma\sigma}(\mathbf{r}',\mathbf{r}'')/\delta n(\mathbf{r})$ in the expression; it has been termed the screening response potential part of $v_x(\mathbf{r})$. For atoms this part of $v_x(\mathbf{r})$ exhibits the step structure[11] that is responsible for the discontinuity Δ_x of the total exchange potential as a function of electron number. A new step appears as a new outer shell is started to be filled. The exchange only OPM and its approximation called the KLI[7] have both succeeded in making clearly visible the intershell peaks and the step structure in $v_x(\mathbf{r})$ for atoms as well as in describing the exact asymptotic form of $v_x(\mathbf{r})$ for large r.

The generalized gradient approximation (GGA)[12,13] was designed for the construction of an improvement over the LDA by the gradient expansion method with the help of the exact scaling properties of the exchange-correlation energy functional, but it fails to reproduce even the exact asymptotic form of $v_x(\mathbf{r})$ for finite systems. No systematic improvements

over the LDA can be seen from the GGA. Hence the GGA may be considered to be a semiempirical and pragmatic method using fitting parameters.

1.3 Purpose

DFT is a powerful method for studying the electronic structure of atoms, molecules, clusters, and solids. If the local correlation potential $v_c(\mathbf{r})$ as well as E_c is available with high accuracy, DFT enables one to evaluate exactly the electron density, the ground state energy, and the ionization energy that is proved to be equivalent to the magnitude of the highest occupied KS energy.[6] Furthermore, it should be stressed that KS eigenvalues are practically a good approximation of quasi-particle energies that are eigenvalues of Dyson equations.

A separate and accurate treatment of E_x and E_c ($v_x(\mathbf{r})$ and $v_c(\mathbf{r})$) is indispensable to further development in DFT. No one has, however, proposed a physically well-founded orbital-dependent correlation energy functional E_c which is to be accompanied by the exact exchange energy functional E_x and to be employed to evaluate the correlation potential $v_c(\mathbf{r})$ by the OPM.

In this paper we propose a correlation energy functional $E_c[\{\varphi_a\}, \{\varepsilon_a\}]$ which is a functional only of occupied KS orbitals and occupied KS energies and stress that E_c in DFT should by its very nature be defined as such a functional for the purpose of employing the OPM to evaluate the correlation potential $v_c(\mathbf{r})$. In general E_c can be defined as $E_c[\{\varphi_a\}, \{\varepsilon_a\}]$, which avoids the divergence of $v_c(\mathbf{r})$[14] caused by the presence of excited orbitals and excited energies in the usual perturbation expression for E_c. The highly self-consistent scheme we propose in the present paper may seem to be very demanding for practical calculations, but we think it will be needed in the near future for developing the study of the electronic structure of atoms, molecules, and solids in cooperation with the diffusion Monte Carlo method.[15]

It is important to gain a physically clear understanding of what role the correlation potential $v_c(\mathbf{r})$ plays in the determination of the electron density, the equilibrium nucleus-nucleus separation, and the electronic structure of many-electron systems. In this respect, several authors[6,16] have already made an excellent study by extracting information on $v_c(\mathbf{r})$ from available accurate trial wavefunctions chemists have invented for light atoms or ions. In the present paper we try to interpret such inductive information in terms of a physically well-founded form of orbital-dependent correlation energy functional E_c we have constructed by a deductive method.

It is important to recognize that the exact $v_c(\mathbf{r})$ of many-electron systems can be locally positive in contrast with the LDA correlation potential which is negative everywhere, and that the exact $v_c(\mathbf{r})$ is always negative at the location of the nuclei and has a steep positive slope with increasing distance from them, which we think is responsible for the Reuderberg's assertion[5] that the binding of molecules and the cohesion of solids involve a contraction of the electron density distribution near individual nuclei to enhance the electron density at the location of individual nuclei, compared with the case of constituent atoms or ions that are isolated.

In other words, the correlation potential $v_c(\mathbf{r})$ has the effect to further enhance inhomogeneity in the electron density in the immediate vicinity of individual nuclei in many-electron systems to attain the lowest possible ground state energy, compared with the case of the exchange only DFT. This enhancement involves a reduction in the electron density elsewhere and a small but significant increase in the equilibrium separations as a counterbalance for molecules and solids.

In II we give two distinct expressions for the correlation energy functional E_c to discuss the relationship between them. A highly self-consistent scheme for DFT is presented in III. Concluding remarks are given in IV.

2. Two Expressions for E_c

2.1 Expression in terms of $\bar{g}(\mathbf{r}, \mathbf{r}')$

Let us start with the general expression for the exchange-correlation energy functional E_{xc} that Harris and Jones[17] have first introduced in DFT. It gives a clear physical meaning of E_{xc}.

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

The coupling-constant-averaged pair correlation function $\bar{g}(\mathbf{r}, \mathbf{r}')$ in eq. (1) 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 $\bar{g}(\mathbf{r}, \mathbf{r}')$ thus defined exhibits the 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 $g(\mathbf{r}, \mathbf{r}')$; it is noticeable particularly for small separations. The reason for this difference is that a lowering in the electron-electron interaction energy due to the presence of the usual pair correlation function $g(\mathbf{r}, \mathbf{r}')$ from the Hartree energy functional is partially cancelled by such an increase in the kinetic energy as is caused by correlation and is beyond the description of T_s.

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 between electrons and the effect to enhance the contribution from long separations as a counterbalance. Correlation does not only give 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. It is important to recoginize that correlation in the real electronic systems induces a change in the electron density to further stabilize the ground state energy in contrast with correlation in the uniform electron liquid.[18,19]

Next we decompose eq. (1) into the spin-dependent contributions as,

$$E_{xc} = \frac{1}{2} \sum_{\sigma,\sigma'} \iint d\mathbf{r} d\mathbf{r}' \frac{e^2 n_\sigma(\mathbf{r}) n_{\sigma'}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} (\bar{g}^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}') - 1). \quad (2)$$

The function $\bar{g}^{\sigma\sigma}(\mathbf{r}, \mathbf{r}')$ can be split into the Hartree-Fock and the correlational contributions as

$$\bar{g}^{\sigma\sigma}(\mathbf{r},\mathbf{r}') = g_{HF}^{\sigma\sigma}(\mathbf{r},\mathbf{r}') + \bar{g}_c^{\sigma\sigma}(\mathbf{r},\mathbf{r}'). \quad (3)$$

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

$$E_x = \frac{1}{2}\sum_\sigma \iint d\mathbf{r}d\mathbf{r}' \frac{e^2 n_\sigma(\mathbf{r})n_\sigma(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}(g_{HF}^{\sigma\sigma}(\mathbf{r},\mathbf{r}')-1), \quad (4)$$

$$g_{HF}^{\sigma\sigma}(\mathbf{r},\mathbf{r}') = 1 - \frac{1}{n_\sigma(\mathbf{r})n_\sigma(\mathbf{r}')}\left|\sum_i^{occ.} \varphi_{i\sigma}^*(\mathbf{r})\varphi_{i\sigma}(\mathbf{r}')\right|^2. \quad (5)$$

The function $g_{HF}^{\sigma\sigma}(\mathbf{r},\mathbf{r}')$ is constructed from occupied KS orbitals alone.

On the other hand, the correlation energy functional E_c consists of the spin-antiparallel and spin-parallel contributions as,

$$E_c = \sum_\sigma (E_c^{\sigma-\sigma} + E_c^{\sigma\sigma}), \quad (6)$$

$$E_c^{\sigma-\sigma} = \frac{1}{2}\iint d\mathbf{r}d\mathbf{r}' \frac{e^2 n_\sigma(\mathbf{r})n_{-\sigma}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}(\bar{g}^{\sigma-\sigma}(\mathbf{r},\mathbf{r}')-1), \quad (7)$$

$$E_c^{\sigma\sigma} = \frac{1}{2}\iint d\mathbf{r}d\mathbf{r}' \frac{e^2 n_\sigma(\mathbf{r})n_\sigma(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\bar{g}_c^{\sigma\sigma}(\mathbf{r},\mathbf{r}'), \quad (8)$$

where $\bar{g}^{\sigma-\sigma}(\mathbf{r},\mathbf{r}')$ is the spin-antiparallel coupling-constant-averaged pair correlation function and $\bar{g}_c^{\sigma\sigma}(\mathbf{r},\mathbf{r}')$ denotes the correlational part of the spin-parallel coupling-constant-averaged pair correlation function.

In the limit of uniform density $\sum_\sigma E_c^{\sigma-\sigma}$ amounts to about 70% of the total correlation energy E_c and $\sum_\sigma E_c^{\sigma\sigma}$ amounts to about 30% throughout the entire region of metallic densities.[19] Probably, this ratio will apply to all the valence electrons that are participating in the cohesion of real metals.

2.2 Second-order perturbation-like expression

Consider the second-order perturbation-like expression for E_c we have defined in previous papers.[18,19]

$$E_c = \frac{1}{2}\sum_{a,b}^{occ.}\sum_{r,s}^{unocc.}\left\{\frac{\langle\varphi_a\varphi_b|v(r_{12})|\varphi_r\varphi_s\rangle\langle\varphi_r\varphi_s|v_{eff}(r_{12})|\varphi_a\varphi_b\rangle}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s} - \frac{\langle\varphi_a\varphi_b|v(r_{12})|\varphi_r\varphi_s\rangle\langle\varphi_r\varphi_s|v_{eff}(r_{12})|\varphi_b\varphi_a\rangle}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s}\right\}, \quad (9)$$

$$\langle\varphi_a\varphi_b|v(r_{12})|\varphi_r\varphi_s\rangle = \iint d\mathbf{r}_1 d\mathbf{r}_2 \varphi_a^*(\mathbf{r}_1)\varphi_b^*(\mathbf{r}_2)v(r_{12})\varphi_r(\mathbf{r}_1)\varphi_s(\mathbf{r}_2), \quad (10)$$

$$\langle\varphi_r\varphi_s|v_{eff}(r_{12})|\varphi_a\varphi_b\rangle = \iint d\mathbf{r}_1 d\mathbf{r}_2 \varphi_r^*(\mathbf{r}_1)\varphi_s^*(\mathbf{r}_2)v_{eff}(r_{12})\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2), \quad (11)$$

where φ_a, φ_r, and $\varepsilon_a, \varepsilon_r$ are KS orbitals and KS energies, respectively. In eq. (9), $v(r_{12}) = e^2/|\mathbf{r}-\mathbf{r}'|$ and $v_{eff}(r_{12})$ denotes the effective interaction into which all the contributions from the third and higher order perturbation terms are transformed. The effective interaction $v_{eff}(r_{12})$ thus defined represents long-, intermediate-, and short-range correlations beyond second-order perturbation theory. Such an effective interaction can be rigorously defined for the uniform electron liquid and has actually been evaluated with high accuracy throughout the entire region of metallic densities. Strictly, the effective interaction should be defined so as to depend on two occupied states, a and b, i.e., like $v_{eff}^{ab}(r_{12})$ in eq. (9), but for simplicity we employ its averaged value over all occupied states, $v_{eff}(r_{12})$.

There is a close resemblance between the present second-order perturbation-like expression and the well-known expression[20] for the correlation energy that is defined in the configuration interaction representation by the difference in the ground state energy between the exact theory and the usual Hartree-Fock theory.

$$E_c = \sum_{a>b}^{occ.}\sum_{r>s}^{unocc.} C_{ab}^{rs}\langle\Phi_{HF}|H|\Phi_{ab}^{rs}\rangle \quad (12)$$

The exact many-electron wavefunction Ψ can in principle be expanded by a complete set of configuration functions (or Slater determinants) that are constructed from an infinite set of the Hartree-Fock occupied and unoccupied orbitals.

$$\Psi = \Phi_{HF} + \sum_a^{occ.}\sum_r^{unocc.} C_a^r\Phi_a^r + \sum_{a>b}^{occ.}\sum_{r>s}^{unocc.} C_{ab}^{rs}\Phi_{ab}^{rs} + \ldots, \quad (13)$$

where Ψ is normalized such that $\langle\Psi|\Phi_{HF}\rangle = 1$. The leading term in the expansion is the Hartree-Fock Slater determinant, Φ_{HF}. The second is the sum of all the possible determinants with an excited orbital (r) substituted for an occupied orbital (a) in the leading determinant, Φ_a^r's. The third is the sum of all the possible determinants with two excited orbitals (r, s) substituted for two occupied orbitals (a, b), Φ_{ab}^{rs}'s and so on. Note that C_{ab}^{rs} in eq. (12) is the coefficient attached to each Slater determinant Φ_{ab}^{rs}'s entering the third term in the expansion. Owing to the Brillouin's theorem,[20] the second term representing one-pair-excited configurations in eq. (13) has no contribution to the correlation energy. Equation (12) states that the correlation energy is determined by two-electron-excited configurations alone. This statement corresponds to the assertion that all the contributions of the third and higher order perturbation terms can be transformed into the effective interaction $v_{eff}(r)$ entering the present second-order perturbation-like expression.

We have stated in 1.2 that there is a slight difference between the ground state energy in the usual Hartree-Fock approximation and that in its DFT version; the latter is by only a slight amount higher. The correlation energy defined in DFT is slightly different from that in the standard many-body theory, accordingly. Consider a similar configuration

expansion of the exact ground state wavefunction in which KS orbitals are used in place of Hartree-Fock orbitals. The second term in such an expansion can have a slight contribution to the correlation energy. For simplicity we shall exclude such a slight contribution.

Consider the second-order perturbation-like expression for E_c in the limit of uniform density. Then, the correlation energy of the uniform electron liquid can be exactly expressed as,

$$
\begin{aligned}
E_c = \frac{1}{2}\left(\frac{1}{\Omega}\right)^2 & \sum_{\mathbf{p},\sigma,\mathbf{p}',\sigma'} f_\sigma(\mathbf{p})f_{\sigma'}(\mathbf{p}') \\
& \times \sum_{\mathbf{q}} v(\mathbf{q}) \frac{(1-f(\mathbf{p}+\mathbf{q}))(1-f(\mathbf{p}'-\mathbf{q}))}{\varepsilon_\mathbf{p} - \varepsilon_{\mathbf{p}+\mathbf{q}} + \varepsilon_{\mathbf{p}'} - \varepsilon_{\mathbf{p}'-\mathbf{q}}} \\
& \times (v_{\text{eff}}(\mathbf{q}) - \delta_{\sigma\sigma'}v_{\text{eff}}(-\mathbf{p}+\mathbf{p}'-\mathbf{q})),
\end{aligned} \tag{14}
$$

where $f_\sigma(\mathbf{p})$ is the Fermi distribution function at zero temperature and $\varepsilon_\mathbf{p} = \hbar^2 \mathbf{p}^2/2m$; Ω being the volume of the system. In eq. (14), 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 $v_{\text{eff}}(\mathbf{q})$; strictly, the effective interaction $v_{\text{eff}}(\mathbf{q})$ should be defined as $v_{\text{eff}}(\mathbf{p},\mathbf{p}';\mathbf{q})$. We have evaluated the averaged effective interaction over $\mathbf{p}$ and $\mathbf{p}'$, $v_{\text{eff}}(\mathbf{q})$ by making a sophisticated interpolation between long-range correlation in the random-phase approximation (RPA)[21] and short-range correlation in the particle-particle ladder approximation[22–24] such that the corresponding exchange interaction $v_{\text{eff}}(-\mathbf{p}+\mathbf{p}'-\mathbf{q})$ and its feedback effect on the direct interaction $v_{\text{eff}}(\mathbf{q})$ are allowed for in a self-consistent way. The new expression for E_c using $v_{\text{eff}}(\mathbf{q})$ does not only reproduce the most accurate numerical values.[25,26] 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 separately spin-antiparallel and spin-parallel components of the total correlation energy.

For a later discussion it is useful to define a different expression for the correlation energy of the electron liquid, in which wavenumbers smaller than the Fermi wavenumber p_F alone appear. This can be easily done by introducing the following quantity:

$$
\begin{aligned}
F_c(\mathbf{p},\mathbf{p}';& \varepsilon_\mathbf{p},\varepsilon_{\mathbf{p}'}) \\
= & \left(\frac{1}{\Omega}\right)^2 \sum_{\mathbf{q}} v(\mathbf{q}) \frac{(1-f(\mathbf{p}+\mathbf{q}))(1-f(\mathbf{p}'-\mathbf{q}))}{\varepsilon_\mathbf{p} - \varepsilon_{\mathbf{p}+\mathbf{q}} + \varepsilon_{\mathbf{p}'} - \varepsilon_{\mathbf{p}'-\mathbf{q}}} \\
& \times (v_{\text{eff}}(\mathbf{q}) - \delta_{\sigma\sigma'}\mathbf{v}_{\text{eff}}(-\mathbf{p}+\mathbf{p}'-\mathbf{q})),
\end{aligned} \tag{15}
$$

where the sum over $\mathbf{q}$ means the sum over excited states. Then the correlation energy can be expressed by the total sum of separate pair contributions over occupied states,

$$
E_c = \frac{1}{2}\sum_{\mathbf{p},\sigma,\mathbf{p}',\sigma'} f_\sigma(\mathbf{p})f_{\sigma'}(\mathbf{p}')F_c(\mathbf{p},\mathbf{p}';\varepsilon_\mathbf{p},\varepsilon_{\mathbf{p}'}). \tag{16}
$$

It is important to notice that an exact expression for E_c can be defined without any explicit representation of excited states and excited energies. The physical meaning of $F_c(\mathbf{p},\mathbf{p}';\varepsilon_\mathbf{p},\varepsilon_{\mathbf{p}'})$ can be interpreted as a kind of correlation

potential operating between two occupied states, $\mathbf{p}\sigma$, and $\mathbf{p}'\sigma'$. We add that detailed information on $F_c(\mathbf{p},\mathbf{p}';\varepsilon_\mathbf{p},\varepsilon_{\mathbf{p}'})$ will require the original form of effective interaction $v_{\text{eff}}(\mathbf{p},\mathbf{p}';\mathbf{q})$ before averaging over $\mathbf{p}$ and $\mathbf{p}'$.

Consider the real-space Fourier transform $v_{\text{eff}}(\mathbf{r})$ of the interaction $v_{\text{eff}}(\mathbf{q})$ we have evaluated for the electron liquid. The effective interaction $v_{\text{eff}}(\mathbf{r})$ thus obtained is in magnitude reduced from the bare Coulomb interaction e^2/r for any r. This is because long-, intermediate-, and short-range correlations beyond second order perturbation theory are all involved in $v_{\text{eff}}(\mathbf{r})$. We think that it is appropriate to employ this $v_{\text{eff}}(\mathbf{r})$ for the effective interaction entering the present orbital-dependent expression defined in eq. (9). Then, the correlation energy may be much better estimated even for localized orbitals in atomic cores without any overestimate and furthermore is reduced to the accurate value in the limit of uniform density.

Finally, we transform the second-order perturbation-like expression for E_c we have given in eq. (9) in the form of $E_c[\{\varphi_{a\sigma}\},\{\varepsilon_{a\sigma}\}]$ by performing first the sum over the excited states in it. Let us introduce the following quantity:

$$
\begin{aligned}
& F_c(\varphi_{a\sigma},\varphi_{b\sigma'};\varepsilon_{a\sigma},\varepsilon_{b\sigma'}) \\
& = \sum_{r,s}^{\text{unocc.}} \left\{ \frac{\langle\varphi_{a\sigma}\varphi_{b\sigma'}|v(r_{12})|\varphi_{r\sigma}\varphi_{s\sigma'}\rangle\langle\varphi_{r\sigma}\varphi_{s\sigma'}|v_{\text{eff}}(r_{12})|\varphi_{a\sigma}\varphi_{b\sigma'}\rangle}{\varepsilon_{a\sigma} + \varepsilon_{b\sigma'} - \varepsilon_{r\sigma} - \varepsilon_{s\sigma'}} \right. \\
& \left. -\delta_{\sigma\sigma'} \frac{\langle\varphi_{a\sigma}\varphi_{b\sigma'}|v(r_{12})|\varphi_{r\sigma}\varphi_{s\sigma'}\rangle\langle\varphi_{r\sigma}\varphi_{s\sigma'}|v_{\text{eff}}(r_{12})|\varphi_{b\sigma'}\varphi_{a\sigma}\rangle}{\varepsilon_{a\sigma} + \varepsilon_{b\sigma'} - \varepsilon_{r\sigma} - \varepsilon_{s\sigma'}} \right\},
\end{aligned} \tag{17}
$$

where spin orientations are explicitly given. The physical meaning of $F_c(\varphi_{a\sigma},\varphi_{b\sigma'};\varepsilon_{a\sigma},\varepsilon_{b\sigma'})$ can be interpreted as a kind of correlation potential operating between two occupied states, $\varphi_{a\sigma}$ and $\varphi_{b\sigma'}$. Thus, E_c can be redefined as a functional only of occupied states and occupied energies.

$$
E_c[\{\varphi_{a\sigma}\},\{\varepsilon_{a\sigma}\}] = \frac{1}{2}\sum_{a\sigma,b\sigma'}^{\text{occ.}} F_c(\varphi_{a\sigma},\varphi_{b\sigma'};\varepsilon_{a\sigma},\varepsilon_{a\sigma'}). \tag{18}
$$

For the application of the OPM beyond E_x it is indispensable to define the functional $E_c[\{\varphi_{a\sigma}\},\{\varepsilon_{a\sigma}\}]$ in DFT.

2.3 Symmetric expression for $\bar{g}^{\sigma-\sigma}(\mathbf{r},\mathbf{r}')$ and $\bar{g}_c^{\sigma\sigma}(\mathbf{r},\mathbf{r}')$

In 2.1 and 2.2 we have given a separate description of two distinct expressions for E_c. The two have to be the same so far as we exclude the slight difference we have mentioned before. From such a comparison of the two expressions for E_c we may easily obtain an explicit expression for $\bar{g}^{\sigma-\sigma}(\mathbf{r},\mathbf{r}')$ and $\bar{g}_c^{\sigma\sigma}(\mathbf{r},\mathbf{r}')$ which fulfill the symmetric property, the sum rules, and the requirement due to the Pauli principle.Consider the second-order perturbation-like expression for E_c. It comprises a couple of direct and exchange terms. Each term has a single Coulomb interaction and an effective interaction in it. Let us focus attention on the single Coulomb interaction entering the direct or exchange term to identify it as the same Coulomb interaction entering the other expression for E_c explicitly written in terms of $\bar{g}^{\sigma-\sigma}(\mathbf{r},\mathbf{r}')$ or $\bar{g}_c^{\sigma\sigma}(\mathbf{r},\mathbf{r}')$. Thus, we obtain the following expression:

$$\bar{g}^{\sigma-\sigma}(\mathbf{r}, \mathbf{r}') - 1$$

$$= \frac{1}{n_\sigma(\mathbf{r})n_{-\sigma}(\mathbf{r}')} \sum_{a,b}^{\text{occ.}} \sum_{r,s}^{\text{unocc.}} \frac{\varphi^*_{a\sigma}(\mathbf{r})\varphi^*_{b-\sigma}(\mathbf{r}')\varphi_{r\sigma}(\mathbf{r})\varphi_{s-\sigma}(\mathbf{r}')}{\varepsilon_{a\sigma} + \varepsilon_{b-\sigma} - \varepsilon_{r\sigma} - \varepsilon_{s-\sigma}}$$

$$\times \iint d\mathbf{r}_1 d\mathbf{r}_2 \varphi^*_{r\sigma}(\mathbf{r}_1)\varphi^*_{s-\sigma}(\mathbf{r}_2)v_{\text{eff}}(r_{12})\varphi_{a\sigma}(\mathbf{r}_1)\varphi_{b-\sigma}(\mathbf{r}_2), \tag{19}$$

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

$$= \frac{1}{n_\sigma(\mathbf{r})n_\sigma(\mathbf{r}')} \sum_{a,b}^{\text{occ.}} \sum_{r,s}^{\text{unocc.}} \frac{\varphi^*_{a\sigma}(\mathbf{r})\varphi^*_{b\sigma}(\mathbf{r}')\varphi_{r\sigma}(\mathbf{r})\varphi_{s\sigma}(\mathbf{r}')}{\varepsilon_{a\sigma} + \varepsilon_{b\sigma} - \varepsilon_{r\sigma} - \varepsilon_{s\sigma}}$$

$$\times \iint d\mathbf{r}_1 d\mathbf{r}_2 \varphi^*_{r\sigma}(\mathbf{r}_1)\varphi^*_{s\sigma}(\mathbf{r}_2)v_{\text{eff}}(r_{12})\{\varphi_{a\sigma}(\mathbf{r}_1)\varphi_{b\sigma}(\mathbf{r}_2)$$

$$- \varphi_{b\sigma}(\mathbf{r}_1)\varphi_{a\sigma}(\mathbf{r}_2)\}. \tag{20}$$

These correlation functions are constructed from both occupied and unoccupied KS orbitals and KS energies in contrast with the function $g_{\text{HF}}^{\sigma\sigma}(\mathbf{r}, \mathbf{r}')$ that has no explicit dependence on the Coulomb interaction.

In the limit of uniform density, *i.e.*, if KS orbitals and KS energies in eqs. (19) and (20) are replaced by plane waves and free electron energies shifted by μ_{xc}, the exchange-correlation contribution of the chemical potential for the uniform electron liquid, respectively, these correlation functions are reduced to the very accurate analogues of the electron liquid because of the effective interaction $v_{\text{eff}}(\mathbf{r})$ we have borrowed from the electron liquid.

From eqs. (19) and (20) it is evident that the present $\bar{g}^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}')$ fulfills the symmetric property inherent in the pair correlation function as well as the requirement due to the Pauli principle.

$$\bar{g}^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}') = \bar{g}^{\sigma'\sigma}(\mathbf{r}', \mathbf{r}), \tag{21}$$

$$\bar{g}_c^{\sigma\sigma}(\mathbf{r}, \mathbf{r}) = 0. \tag{22}$$

Note that the well-known sum rule concerning the exchange-correlation hole is in fact fulfilled by the Hartree-Fock exchange hole alone.

$$\int d\mathbf{r}' n_\sigma(\mathbf{r}')(g_{\text{HF}}^{\sigma\sigma}(\mathbf{r}, \mathbf{r}') - 1) = -1. \tag{23}$$

This can easily be checked from the orthogonality between occupied KS orbitals. The Coulomb hole caused by spin-antiparallel correlation and the change in the Fermi hole due to the Coulomb interaction separately have to integrate to zero, accordingly.

$$\int d\mathbf{r}' n_{-\sigma}(\mathbf{r}')(\bar{g}^{\sigma-\sigma}(\mathbf{r}, \mathbf{r}') - 1) = 0, \tag{24}$$

$$\int d\mathbf{r}' n_\sigma(\mathbf{r}')\bar{g}_c^{\sigma\sigma}(\mathbf{r}, \mathbf{r}') = 0. \tag{25}$$

It is important to notice that eqs. (24) and (25) are both fulfilled by the present expression for $\bar{g}^{\sigma-\sigma}(\mathbf{r}, \mathbf{r}')$ and $\bar{g}_c^{\sigma\sigma}(\mathbf{r}, \mathbf{r}')$ given in eqs. (19) and (20). This can be easily checked from the orthogonality between occupied and unoccupied KS orbitals. The two identities above imply that correlation due to the Coulomb interaction, for both spin orientations, occurs among electrons such that local charge neutrality is maintained at any position $\mathbf{r}$ of the system. It should be stressed that the maintenance of local charge

neutrality in the theoretical treatment of correlation is indispensable for the quantitative evaluation of the ground state energy of many-electron systems. Actually, the success of the LDA in the evaluation of metallic properties depends on its basic assumption of rigid charge neutrality.[3] This means that the total charge of an electron and its surrounding exchange-correlation hole assumed to be spherically symmetric is set to zero anywhere in the system.

Finally, we return to the expression for $\bar{g}^{\sigma-\sigma}(\mathbf{r}, \mathbf{r}')$ and $\bar{g}_c^{\sigma\sigma}(\mathbf{r}, \mathbf{r}')$ given in eqs. (19) and (20). It is important to notice that if the sum over the excited states is first performed both of the expressions can be redefined as the total sum of separate pair contributions over occupied states.

3. Exchange and Correlation Potentials

3.1 Exchange potential $v_{\text{x}\sigma}(\mathbf{r})$

In the application of the OPM to the exact exchange energy functional E_{x} there is no problem in contrast with the case of E_{c}. This is because E_{x} is originally a functional of occupied KS orbitals alone.

$$E_{\text{x}}[\{\varphi_{a\sigma}\}] = -\frac{1}{2} \sum_{a,b,\sigma}^{\text{occ.}} \iint d\mathbf{r}d\mathbf{r}' \frac{e^2 \varphi^*_{a\sigma}(\mathbf{r})\varphi_{b\sigma}(\mathbf{r})\varphi^*_{b\sigma}(\mathbf{r}')\varphi_{a\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \tag{26}$$

The functional derivative $\delta E_{\text{xc}}/\delta n_\sigma(\mathbf{r})$, or the exchange potential $v_{\text{x}\sigma}(\mathbf{r})$ can be indirectly evaluated from the functional derivative $\delta E_{\text{x}}/\delta \varphi_{a\sigma}$ by solving the OPM integral equation.

According to the expression for E_{x} given in terms of the spin-parallel Hartree-Fock pair correlation function (see eq. (4)), the functional derivative of E_{x} with respect to $n_\sigma(\mathbf{r})$ yields two components of $v_{\text{x}\sigma}(\mathbf{r})$, *i.e.*, $v_{\text{x}\sigma}(\mathbf{r}) = v_{\text{x}\sigma}^{\text{scr}}(\mathbf{r}) + v_{\text{x}\sigma}^{\text{resp}}(\mathbf{r})$ where $v_{\text{x}\sigma}^{\text{scr}}(\mathbf{r})$ is the screening potential part and $v_{\text{x}\sigma}^{\text{resp}}(\mathbf{r})$ the screening response part. The screening potential part $v_{\text{x}\sigma}^{\text{scr}}(\mathbf{r})$ is written as,

$$v_{\text{x}\sigma}^{\text{scr}}(\mathbf{r}) = \int d\mathbf{r}' \frac{e^2 n_\sigma(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}(g_{\text{HF}}^{\sigma\sigma}(\mathbf{r}, \mathbf{r}') - 1). \tag{27}$$

This is nothing but the Coulomb interaction between an electron at the position $\mathbf{r}$ and the surrounding positively charged bare Fermi hole; $g_{\text{HF}}^{\sigma\sigma}(\mathbf{r}, \mathbf{r}') < 1$ for any $\mathbf{r}$ and $\mathbf{r}'$. The screening potential part $v_{\text{x}\sigma}^{\text{scr}}(\mathbf{r})$ is responsible for the exact asymptotic form of $v_{\text{x}\sigma}(\mathbf{r})$ for finite systems, $-e^2/r$ for large r. In the limit of uniform density $v_{\text{x}\sigma}^{\text{scr}}(\mathbf{r})$ is reduced to $3/2\mu_{\text{x}\sigma}$[27,28] where $\mu_{\text{x}\sigma}$ denotes the exchange contribution to the chemical potential of the electron liquid. On the other hand, the screening response part $v_{\text{x}\sigma}^{\text{resp}}(\mathbf{r})$ is given as,

$$v_{\text{x}\sigma}^{\text{resp}}(\mathbf{r}) = \frac{1}{2} \iint d\mathbf{r}'d\mathbf{r}'' \frac{e^2 n_\sigma(\mathbf{r}')n_\sigma(\mathbf{r}'')}{|\mathbf{r}' - \mathbf{r}''|} \frac{\delta g_{\text{HF}}^{\sigma\sigma}(\mathbf{r}', \mathbf{r}'')}{\delta n_\sigma(\mathbf{r})}. \tag{28}$$

It has been recognized that for atoms $v_{\text{x}\sigma}^{\text{resp}}(\mathbf{r})$ exhibits the step structure that is responsible for the discontinuity in $v_{\text{x}\sigma}(\mathbf{r})$ as a function of electron number. A new step Δ_x arises from $v_{\text{x}\sigma}^{\text{resp}}(\mathbf{r})$ when a new outer shell is started to be filled. In the limit of uniform density $v_{\text{x}\sigma}^{\text{resp}}(\mathbf{r})$ is reduced to $-1/2\mu_{\text{x}\sigma}$.[27,28]

3.2 Correlation potential $v_{\text{c}\sigma}(\mathbf{r})$

A serious problem arises if one straightforwardly applies

the OPM to the second-order perturbation functional of E_c in its original form. The resulting correlation potential $v_{c\sigma}(\mathbf{r})$ for finite systems is divergent in its asymptotic form for large r.[14] This divergence of $v_{c\sigma}(\mathbf{r})$ can be traced back to the presence of excited orbitals and excited energies in the perturbation functional for E_c. Actually, Benetti, Engel, Schmid, and Dreizler[14] have managed to avoid this divergence by resorting to the closure approximation that forces the excited states in the expression to disappear.

In this subsection we stress that the divergence of $v_{c\sigma}(\mathbf{r})$ above can in principle be avoided by redefining a new correlation energy functional E_c which is a functional only of occupied orbitals and occupied energies, $E_c[\{\varphi_{a\sigma}\}, \{\varepsilon_{a\sigma}\}]$. Our assertion is that the orbital-dependent correlation energy functional E_c to be employed in the OPM should be redefined so as to depend only on occupied orbitals and occupied energies. This can be done as follows: First perform the sum over excited states (r, s) in eq. (9) and one can obtain a new correlation energy functional which depends only on occupied orbitals and occupied energies without any representation of excited states. The application of the OPM to E_c can thus be justified by imposing the conditional summation on eq. (9), *i.e.*, the requirement that the sum over the excited states be first performed in eq. (9) in order to redefine the functional $E_c[\{\varphi_{a\sigma}\}, \{\varepsilon_{a\sigma}\}]$.

3.3   Highly self-consistent scheme for DFT

In this subsection we write down a set of equations describing a highly self-consistent DFT scheme which is constructed from a combination of the exact orbital-dependent exchange energy functional $E_x[\{\varphi_{a\sigma}\}]$ and the well-founded orbital-dependent correlation energy functional $E_c[\{\varphi_{a\sigma}\}, \{\varepsilon_{a\sigma}\}]$ we have defined in 2.2. An accurate correlation potential $v_{c\sigma}(\mathbf{r})$ as well as the exact exchange potential $v_{x\sigma}(\mathbf{r})$ can be evaluated from the present $E_x[\{\varphi_{a\sigma}\}]$ and $E_c[\{\varphi_{a\sigma}\}, \{\varepsilon_{a\sigma}\}]$ by solving the OPM integral equation.

Let us start with the present ground state energy functional for DFT.

$$
E[\{\varphi_{a\sigma}\}, \{\varepsilon_{a\sigma}\}] = T_s + \int d\mathbf{r}\, n(\mathbf{r}) v_0(\mathbf{r}) \\
+ E_H + E_x[\{\varphi_{a\sigma}\}] + E_c[\{\varphi_{a\sigma}\}, \{\varepsilon_{a\sigma}\}]
\tag{29}
$$

where T_s is the kinetic energy of the reference non-interacting system with the same electron density $n(\mathbf{r})$ as the real interacting system; $v_0(\mathbf{r})$ is the Coulomb potential from the nuclei; E_H is the Hartree energy.

$$
T_s = -\frac{\hbar^2}{2m} \sum_{i,\sigma}^{\text{occ.}} \int d\mathbf{r}\, \varphi_{i\sigma}^*(\mathbf{r}) \nabla^2 \varphi_{i\sigma}(\mathbf{r}),
\tag{30}
$$

$$
E_H = \frac{1}{2} \sum_{\sigma,\sigma'} \iint d\mathbf{r} d\mathbf{r}'\, \frac{e^2 n_\sigma(\mathbf{r}) n_{\sigma'}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|},
\tag{31}
$$

$$
E_x = -\frac{1}{2} \sum_{a,b,\sigma}^{\text{occ.}} \iint d\mathbf{r} d\mathbf{r}'\, \frac{e^2 \varphi_{a\sigma}^*(\mathbf{r}) \varphi_{b\sigma}(\mathbf{r}) \varphi_{b\sigma}^*(\mathbf{r}') \varphi_{a\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|},
\tag{32}
$$

$$
E_c[\{\varphi_{a\sigma}\}, \{\varepsilon_{a\sigma}\}] = \frac{1}{2} \sum_{a\sigma,b\sigma'}^{\text{occ.}} F_c(\varphi_{a\sigma}, \varphi_{b\sigma'}; \varepsilon_{a\sigma}, \varepsilon_{a\sigma'}),
\tag{33}
$$

where the correlation potential $F_c(\varphi_{a\sigma}, \varphi_{b\sigma'}; \varepsilon_{a\sigma}, \varepsilon_{a\sigma'})$ operating between two occupied states, $\varphi_{a\sigma}$ and $\varphi_{b\sigma'}$ is defined in eq. (17).

The Hohenberg-Kohn variational principle $\delta E / \delta n_\sigma(\mathbf{r}) = 0$ can be restated in terms of KS equations as,

$$
\left[-\frac{\hbar^2}{2m} \nabla^2 + v_{s\sigma}(\mathbf{r}) \right] \varphi_{i\sigma}(\mathbf{r}) = \varepsilon_{i\sigma} \varphi_{i\sigma}(\mathbf{r}),
\tag{34}
$$

$$
v_{s\sigma}(\mathbf{r}) = v_0(\mathbf{r}) + \sum_{\sigma'} \int d\mathbf{r}'\, \frac{e^2 n_{\sigma'}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{x\sigma}(\mathbf{r}) + v_{c\sigma}(\mathbf{r})
\tag{35}
$$

$$
n_\sigma(\mathbf{r}) = \sum_{i}^{\text{occ.}} |\varphi_{i\sigma}(\mathbf{r})|^2, \quad n(\mathbf{r}) = \sum_\sigma n_\sigma(\mathbf{r}).
\tag{36}
$$

The exchange-correlation potential, $v_{x\sigma}(\mathbf{r}) + v_{c\sigma}(\mathbf{r})$ is defined as,

$$
v_{x\sigma}(\mathbf{r}) + v_{c\sigma}(\mathbf{r}) = \sum_{\sigma'} \int d\mathbf{r}'\, \frac{\delta v_{s\sigma'}(\mathbf{r}')}{\delta n_\sigma(\mathbf{r})} \sum_a \left\{ \int d\mathbf{r}'' \left[\frac{\delta \varphi_{a\sigma'}(\mathbf{r}'')}{\delta v_{s\sigma'}(\mathbf{r}')} \frac{\delta(E_x + E_c)}{\delta \varphi_{a\sigma'}(\mathbf{r}'')} + \text{c.c.} \right] + \frac{\delta \varepsilon_{a\sigma'}}{\delta v_{s\sigma'}(\mathbf{r}')} \frac{\delta E_c}{\delta \varepsilon_{a\sigma'}} \right\}.
\tag{37}
$$

Following Engel and Dreizler[29] one can transform the above equation into the OPM integral equation:

$$
\int d\mathbf{r}'\, \chi_{s\sigma}(\mathbf{r}, \mathbf{r}')(v_{x\sigma}(\mathbf{r}) + v_{c\sigma}(\mathbf{r})) = \Lambda_{xc\sigma}(\mathbf{r}),
\tag{38}
$$

$$
\Lambda_{xc\sigma}(\mathbf{r}) = -\sum_a^{\text{occ.}} \int d\mathbf{r}' \left[\varphi_{a\sigma}^*(\mathbf{r}) G_{a\sigma}(\mathbf{r}, \mathbf{r}') \frac{\delta(E_x + E_c)}{\delta \varphi_{a\sigma}(\mathbf{r}')} + \text{c.c.} \right] + \sum_a^{\text{occ.}} \varphi_{a\sigma}^*(\mathbf{r}) \varphi_{a\sigma}(\mathbf{r}) \frac{\delta E_c}{\delta \varepsilon_{a\sigma}},
\tag{39}
$$

$$
\chi_{s\sigma}(\mathbf{r}, \mathbf{r}') = -\sum_a^{\text{occ.}} \varphi_{a\sigma}^*(\mathbf{r}) G_{a\sigma}(\mathbf{r}, \mathbf{r}') \varphi_{a\sigma}(\mathbf{r}') + \text{c.c.},
\tag{40}
$$

$$
G_{a\sigma}(\mathbf{r}, \mathbf{r}') = \sum_{i \neq a} \frac{\varphi_{i\sigma}(\mathbf{r}) \varphi_{i\sigma}^*(\mathbf{r}')}{\varepsilon_{i\sigma} - \varepsilon_{a\sigma}},
\tag{41}
$$

where we have used the following relations,[29]

$$
\frac{\delta \varphi_{a\sigma}(\mathbf{r})}{\delta v_{s\sigma}(\mathbf{r}')} = -\varphi_{a\sigma}(\mathbf{r}') G_{a\sigma}(\mathbf{r}, \mathbf{r}'), \quad \frac{\delta \varepsilon_{a\sigma}}{\delta v_{s\sigma}(\mathbf{r}')} = \varphi_{a\sigma}^*(\mathbf{r}') \varphi_{a\sigma}(\mathbf{r}').
\tag{42}
$$

Thus we have written down a set of equations for a developed stage of DFT in which the potential $v_{x\sigma}(\mathbf{r}) + v_{c\sigma}(\mathbf{r})$ can be determined from $E_x[\{\varphi_{a\sigma}\}] + E_c[\{\varphi_{a\sigma}\}, \{\varepsilon_{a\sigma}\}]$ by solving the OPM integral equation. The present scheme, though still being formal, is the first example in which a well-founded form of orbital-dependent correlation energy functional, $E_c[\{\varphi_{a\sigma}\}, \{\varepsilon_{a\sigma}\}]$ is proposed for practical use in DFT.

It can be easily ascertained that the present scheme is

reduced to the LDA in the limit of uniform density. First, calculate the present $E_x[\{\varphi_{a\sigma}\}] + E_c[\{\varphi_{a\sigma}\}, \{\varepsilon_{a\sigma}\}]$ with plane waves and free electron energies shifted by μ_{xc}, the exchange-correlation contribution of the chemical potential for the uniform electron liquid. Next, replace the density dependence of $E_x(n) + E_c(n)$ thus obtained by the local density $n(\mathbf{r})$ in the system and the LDA results. This is because we have borrowed the knowledge of the effective interaction $v_{eff}(\mathbf{r})$ from the electron liquid.

3.4 van der Waals potential energy

In the construction of the second-order perturbation-like correlation energy functional given in eq. (9) we have borrowed the knowledge of $v_{eff}(\mathbf{r})$ from the uniform electron liquid. The effective interaction $v_{eff}(\mathbf{r})$ thus defined is evidently most suitable for conduction electrons in metals since perfect screening is realized, but it is also expected to give a reasonable estimate of the correlation energy even for core electrons in atoms because of the second-order perturbation-like orbital-dependent form.

It is important to notice that the present $v_{eff}(\mathbf{r})$ we have borrowed from the electron liquid cannot give an appropriate description of such long-range correlation as is inherent in atoms, molecules, and insulators. There is an essential difference in the long-range behavior of $v_{eff}(\mathbf{r})$ between metals and non-metals or finite systems, though no qualitative difference can be seen in the intermediate- and short-range behavior of $v_{eff}(\mathbf{r})$. In this sense the long-range behavior of the effective interaction $v_{eff}(\mathbf{r})$ we have introduced for the definition of E_c will be a good indicator to discriminate between metals and non-metals. Screening is not perfect in non-metals and the long-range behavior of $v_{eff}(\mathbf{r})$ for non-metals is qualitatively different from that for metals.

In this subsection we note that the effective interaction $v_{eff}(\mathbf{r})$ entering the present E_c, if appropriately changed in its long-range behavior, can reproduce the correct asymptotic form of the correlation potential $v_c(\mathbf{r})$ for finite systems, $-r^{-4}/2\alpha$ for large r where α is the polarizability of the system. This change of $v_{eff}(\mathbf{r})$ in the present E_c can also give an appropriate description of the van der Waals potential energy in DFT.

Engel and Dreizler[29] have demonstrated that the second-order perturbation functional involving two Coulomb interactions, $E_c^{(2)}$ gives the leading term of the van der Waals potential energy. They have considered two neutral atoms, A and B, whose centers are separated by a large distance, R, so that the KS orbitals are localized around the two atomic centers and the overlap between the two orbitals vanishes exponentially with R. Then $E_c^{(2)}$ can be decomposed into two atomic contributions and the interacting contribution, $E_c^{(2)} \rightarrow E_{cA}^{(2)} + E_{cB}^{(2)} + E_{cint}^{(2)}$. For an appropriate choice of coordinates the two Coulomb interactions entering $E_{cint}^{(2)}$ can be expanded in inverse powers of R and the correct asymptotic order of R^{-6} appropriate for the van der Waals potential is obtained as a result.

In order to reproduce the van der Waals potential energy we have to change the long-range behavior of the effective interaction $v_{eff}(\mathbf{r})$ so as to be appropriate for finite systems. This can be done phenomenologically by replacing $v_{eff}(\mathbf{r})$ in

the present E_c with $e^2/\varepsilon_0 r$ for large r where ε_0 is a kind of dielectric constant which can be defined through the present expression for E_c.

A completely orbital-dependent form of correlation energy functional can in principle be defined by introducing an orbital-dependent form of effective interaction $v_{eff}^{ab}(\mathbf{r})$. This can be done if the same procedure as in the case of the electron liquid is followed with KS orbitals and KS energies in place of plane waves and free electron energies, *i.e.*, by such a sophisticated interpolation of the RPA (for long-range correlation) and the particle-particle ladder approximation (for short-range correlation) as self-consistently involves the corresponding exchange counterparts. The orbital-dependent effective interaction $v_{eff}^{ab}(\mathbf{r})$ determined by such a completely self-consistent method should by itself exhibit the correct long-range behavior for large r, depending on whether the system is metallic or not.

4. Concluding Remarks

We have proposed a well-founded correlation energy functional $E_c[\{\varphi_{a\sigma}\}, \{\varepsilon_{a\sigma}\}]$ to be employed by the OPM in combination with the exact exchange energy functional $E_x[\{\varphi_{a\sigma}\}]$. The present $E_c[\{\varphi_{a\sigma}\}, \{\varepsilon_{a\sigma}\}]$ is an explicit functional only of occupied KS orbitals and occupied KS energies without any explicit representation of excited KS states. For the application of the OPM beyond E_x it is indispensable to define the functional $E_c[\{\varphi_{a\sigma}\}, \{\varepsilon_{a\sigma}\}]$. Note that $E_c[\{\varphi_{a\sigma}\}, \{\varepsilon_{a\sigma}\}]$ is an implicit functional of excited KS states.

We have borrowed accurate knowledge of long-, intermediate-, and short-range correlations from the electron liquid in the construction of the effective interaction $v_{eff}(\mathbf{r})$ entering the original second-order perturbation like expression for E_c and performed the sum over the excited states in it in order to redefine the present $E_c[\{\varphi_{a\sigma}\}, \{\varepsilon_{a\sigma}\}]$.

The present scheme guarantees local charge neutrality, or fulfillment of the sum rules for the orbital-dependent coupling-constant-averaged pair correlation functions $\bar{g}^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}')$ as well as the symmetric property of $\bar{g}^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}')$. The present functions $\bar{g}^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}')$ are guaranteed to reproduce the very accurate analogues of the uniform electron liquid in the limit of uniform density.

The correlation potential $v_c(\mathbf{r})$ that can in principle be derived from the present $E_c[\{\varphi_{a\sigma}\}, \{\varepsilon_{a\sigma}\}]$ by the OPM is expected to yield less screening of the nuclei at short distances. This is because short-range correlation between valence electrons is allowed for through $\bar{g}^{\sigma\sigma'}(\mathbf{r}, \mathbf{r}')$ or $v_{eff}(\mathbf{r})$. The present scheme is expected to give an accurate evaluation of the correlation potential $v_c(\mathbf{r})$ particularly for metals. A suitable change which is made in the long-range part of $v_{eff}(\mathbf{r})$ to be appropriate for finite systems or insulators can give a description of the van der Waals potential as well as the correct asymptotic form of $v_c(\mathbf{r})$ of order r^{-4} for large r. The present scheme by construction is expected to give an appropriate description of correlation-induced reconstruction of KS orbitals in the vicinity of the Fermi level or the energy gap, which we think is indispensable for the interpretation of the electronic structure of the so-called strongly correlated electronic systems.

A very high degree of self-consistency is required to

perform the present scheme since the OPM is employed to evaluate $v_{x\sigma}(\mathbf{r})$ and $v_{c\sigma}(\mathbf{r})$ from $E_x[\{\varphi_{a\sigma}\}]$ and $E_c[\{\varphi_{a\sigma}\}, \{\varepsilon_{a\sigma}\}]$. The KLI method[7] that amounts to approximately solving the OPM integral equation along the lines of Slater's idea will be promising.

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