A proposal of an orbital-dependent correlation energy functional for energy-band calculations

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An explicitly orbital-dependent correlation energy functional is proposed, which is to be used in combination with the orbital-dependent exchange energy functional in energy-band calculations. It bears a close resemblance to the second-order direct and exchange perturbation terms calculated with Kohn-Sham orbitals and Kohn-Sham energies except that one of the two Coulomb interactions entering each term is replaced by an effective interaction which contains information about long-, intermediate-, and short-range correlations beyond second-order perturbation theory. Such an effective interaction can rigorously be defined for the correlation energy of the uniform electron liquid and is evaluated with high accuracy in order to apply to the orbital-dependent correlation energy functional. The coupling-constant-averaged spin-parallel and spin-antiparallel pair correlation functions are also evaluated with high accuracy for the electron liquid. The present orbital-dependent correlation energy functional with the effective interaction borrowed from the electron liquid is valid for tightly-binding electrons as well as for nearly-free electrons in marked contrast with the conventional local density approximation.

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I. INTRODUCTION

The band theory of solids has been developed with the help of the knowledge of exchange and correlation acquired from the study of the uniform electron liquid. The exchange difficulty arising from Hartree-Fock equations has been overcome by two different methods. One is the standard many-body theory which has established the quasi-particle picture through Dyson equations involving the self-energy operator responsible for all exchange and correlation effects on quasi-particles and clarified the importance of dynamically screening the exchange potential in the evaluation of the quasi-particle energy dispersion of the electron liquid \[ 1, 2 \]. The other is the Slater’s intuition \[ 3, 4 \] that the pathological behavior of the wavenumber-dependence of the Hartree-Fock exchange potential for the electron liquid around the Fermi wavenumber should be smoothed out by averaging the potential over all occupied states and that real many-electron systems may be regarded as a locally uniform electron liquid with the same local electron density to employ this averaged exchange potential. The Slater’s intuition has developed into a rigorously founded many-body theory valid for the ground state, namely, density-functional theory (DFT) \[ 5, 6 \].

In this paper we propose a new method for further developing the band theory along DFT. For this purpose we borrow detailed knowledge of long-, intermediate-, and short-range correlations from the electron liquid, not such averaged knowledge as the magnitude of its exchange-correlation energy on which the conventional local density approximation (LDA) is based. First we give a new expression for the correlation energy of the electron liquid since it is needed for a proposal of an orbital-dependent correlation energy functional for use in energy-band calculations. It resembles second-order direct and exchange perturbation terms, but one of the two Coulomb interactions entering each term is replaced by an effective interaction which contains all effects from the higher-order perturbation terms beyond second-order perturbation theory. The effective interaction thus defined is reduced in magnitude from the bare Coulomb interaction for all distances since it takes full account of long-, intermediate-, and short-range correlations in agreement with the Pauli principle. We evaluate the effective interaction with high accuracy over the entire region of metallic densities.

According to Moruzzi, Janak, and Williams \[ 7 \], the lowest possible uniform density realized in the interstitial region outside muffin-tin spheres of metals corresponds approximately to the critical density \[ (r_s = 5.25) \] where the compressibility of the electron liquid becomes divergent, indicative of an instability of this model. In the construction of an orbital-dependent correlation energy functional for energy-band calculations, we think it is physically sound to borrow the knowledge of the effective interaction from the electron liquid above the lowest critical density where the system remains thermodynamically stable. Note that the LDA regards real systems as a locally uniform electron liquid and borrows its exchange-correlation energy even below the critical density.

The orbital-dependent correlation energy functional we propose here consists of a direct and exchange pair of second-order perturbation like terms constructed with Kohn-Sham orbitals and Kohn-Sham energies, in which one of the two Coulomb interactions in each term is replaced by the effective interaction borrowed from the electron liquid. A combination of this orbital-dependent
correlation energy functional and the orbital-dependent exchange energy functional is of course reduced to the LDA in the limit of uniform density. The use of the orbital-dependent exchange energy functional in DFT makes it possible to cancel exactly the spurious self-interaction terms involved in the classical Hartree energy functional. Furthermore, the present orbital-dependent correlation energy functional cancels exactly higher-order self-interaction terms since it consists of a direct and exchange pair of terms. We would like to stress that the present orbital-dependent correlation energy functional reflects the anti-symmetric property of the many-electron wave function in a similar way as the Hartree and the exchange energy functionals in the Hartree-Fock approximation.

In order to obtain the exchange and correlation potential \( v_{xc}(\mathbf{r}) \) in DFT, it is necessary to evaluate the functional derivative of the exchange and correlation energy functional \( E_{xc} \) with respect to the electron density \( n(\mathbf{r}) \). However, the present correlation energy functional as well as the exact exchange energy functional is an explicit functional of Kohn-Sham orbitals, and hence is an implicit functional of \( n(\mathbf{r}) \). The method of evaluating the exchange potential through the functional derivative of the orbital-dependent exchange energy functional with respect to Kohn-Sham orbitals has been established and termed the optimized effective potential method (OEP) \( \mathcal{G} \).

The present correlation energy functional is given as a functional of both Kohn-Sham orbitals and the effective interaction borrowed from the electron liquid. Then, the OEP method can be applied to the evaluation of the correlation potential but the functional derivative of the effective interaction with respect to the electron density \( n(\mathbf{r}) \) has to be treated separately by resorting to an appropriate approximation.

Another problem is how to choose the density parameter for the effective potential we borrow from the electron liquid. In this respect we may utilize the fact that the compressibility of the electron liquid calculated for the uniform density in the interstitial region outside muffin-tin spheres is generally a good approximation to the compressibility of real metals. Hence it is a reasonable approximation to choose as the density parameter the value appropriate for the uniform electron density in the interstitial region of metals calculated from the LDA. The best choice of the density parameter is the optimization that minimizes the calculated ground state energy in the present theory as a function of the density parameter.

One of the remarkable merits of DFT is that the correlation-induced reconstruction of Kohn-Sham orbitals accompanied by a change in the electron density \( n(\mathbf{r}) \) of the system can in principle be described with the local correlation potential \( v_{c}(\mathbf{r}) \). This can be realized only when accurate information about orbital-dependent correlation energy functional \( E_{c}[\{\phi_i\}] \) and the potential \( v_{c}(\mathbf{r}) \) defined by \( \delta E_{c}[\{\phi_i\}]/\delta n(\mathbf{r}) \) is available in addition to the orbital-dependent exchange energy functional \( E_x[\{\phi_i\}] \) and the resulting exact exchange potential \( v_{x}(\mathbf{r}) \).

This reconstruction of Kohn-Sham orbitals is beyond the scope of the LDA since the LDA regards real systems as a locally uniform electron liquid and borrows its density dependence of the exchange-correlation energy. The presence of spurious self-interaction terms and the absence of the correlation-induced reconstruction of Kohn-Sham orbitals are the main two reasons why the LDA fails to give the correct evaluation of the band gap of semiconductors and the energy-band structure of the so-called strongly correlated electron systems.

In the present theory, the exchange and correlation energy functionals are both orbital-dependent and at the same time they are free from self-interaction errors. The present correlation potential \( v_{c}(\mathbf{r}) \) depends implicitly on the electron density \( n(\mathbf{r}') \) at the neighboring position \( \mathbf{r}' \) of \( \mathbf{r} \) through the orbital-dependence of \( E_{c}[\{\phi_i\}] \).

An important prediction the present theory makes is that correlation may reduce the screening of the nuclei at short distances to produce a shrinkage of the electron distribution around individual nuclei of the system and in accordance with this redistribution of the electron density Kohn-Sham orbitals may be reconstructed particularly in the neighborhood of the Fermi level or the energy gap.

An accurate description of exchange-correlation effects on the energy-band structure is expected from the present theory. Its orbital-dependent correlation energy functional, if applied to the so-called strongly correlated electron systems, will give rise to significant differences in the energy-band structure compared with the case of the orbital-dependent exchange energy functional alone, particularly in the neighborhood of the Fermi level or the energy gap.

Since the early stage of the development in DFT a number of authors \( \mathcal{G} \) have been interested in the relationship between Kohn-Sham equations and Dyson equations. DFT is an exact many-body theory for the ground state in the framework of the self-consistent one-electron theory. The Hohenberg-Kohn variational principle leads to a set of Kohn-Sham equations describing the reference non-interacting system with the same electron density as the real many-electron system. In this reference system electrons interact only through the local exchange-correlation potential \( v_{xc}(\mathbf{r}) \). On the other hand, the standard many-body theory is founded on the variational principle \( \mathcal{G} \) that the ground state energy defined as a functional of the many-body one-electron Green’s function \( G(\mathbf{r}, \mathbf{r}', \omega) \) is stationary with respect to any variation in \( G(\mathbf{r}, \mathbf{r}', \omega) \). This stationary property leads to Dyson equations for the one-electron Green’s function. The one-electron Green’s function has the well-founded physical meaning to give the concept of quasi-particles as low-lying elementary excitations of extended many-electron systems.

To make a comparison between Dyson equations and Kohn-Sham equations we have evaluated with high accu-
racy the quasi-particle energy dispersion of the electron liquid over the entire region of metallic densities. It is found that in the limit of uniform density energy spectra of Kohn-Sham equations are a rather good approximation to those of Dyson equations unless they exceed a critical energy beyond which screening no longer works around the Fermi energy plus the plasmon excitation energy.

In order to justify the application of Kohn-Sham equations to the band theory it is pointed out that the implicit dependence of the self-energy $\Sigma(r, r'; \omega; G)$ in Dyson equations on the self-consistent Green’s function $G$ is in one-to-one correspondence to the implicit dependence of exchange-correlation potential $v_{xc}(r; |n|)$ in Kohn-Sham equations on the self-consistent electron density $n(r)$.

The present paper is organized as follows. In Sec. II we give a detailed analysis of the dielectric formulation for the study of the electron liquid. This is a section requisite for the introduction of a new expression for the correlation energy. In Sec. III we calculate the effective interaction by interpolating between long-range correlation in the random phase approximation (RPA) and short-range correlation in the particle-particle ladder approximation such that the exchange counterparts are self-consistently included. We also calculate the coupling-constant-averaged spin-parallel and spin-antiparallel pair correlation functions as well as the correlation energy. In Sec. IV we propose an orbital-dependent correlation energy functional for use in energy-band calculations. Some characteristic properties of this correlation energy functional and how to use it in practical calculations are discussed. In Sec. V we show an accurate calculation of the quasi-particle energy dispersion of the electron liquid. In the last section we give some concluding remarks.

II. THEORY OF ELECTRON LIQUID

A. Exchange correction to the RPA

The random phase approximation (RPA) \[ \text{[12, 13, 14, 15]} \] is a good starting point to describe long-range correlation characteristic of the electron liquid, but it violates the Pauli principle since the second- and higher-order exchange counterparts of the RPA series of perturbation terms are missing. Hubbard \[ \text{[14]} \] was the first who made an attempt to allow for these exchange corrections. His approximation is an interpolation between long-range correlation in the RPA and short-range correlation in second-order perturbation theory, but all the coefficients of third- and higher-order exchange terms in his approximation are miscounted. The reason for this miscounting is that he failed to enumerate all the possible proper polarization diagrams leading to the same third- and higher-order exchange terms. This is not serious for his evaluation of the ground state energy $E_g$, but it is very serious for the purpose of evaluating the quasiparticle energy dispersion $E(p)$ and the Landau interaction function $f^{\sigma \sigma'}(p, p')$ which are closely related to the first and the second functional derivations of the ground state energy $E_g[G]$ with respect to the quasi-particle distribution function $n(p)$, respectively \[ \text{[14]} \].

By way of illustration we consider the exchange counterparts of the third-order PRA diagram (see Fig. 1). Three different exchange counterparts can be obtained by exchanging two incoming (or outgoing) particle or hole lines attached to one of the three Coulomb interaction lines in the RPA diagram. Additional three different exchange counterparts can also be obtained by doubly exchanging the PRA diagram. The last exchange counterpart can be obtained by exchanging all of the three interaction lines; this is a diagram with one interaction line inserted between a pair of particle and hole belonging to different bubbles in the second-order direct diagram. The Hubbard approximation miscounts the coefficients of singly and doubly exchanged perturbation terms and furthermore neglects the triply exchanged perturbation term. Besides the eight third-order diagrams we have just enumerated, there remain more vertex-type diagrams of the same order which are not derivable from the same order RPA diagram by exchanging, i.e., two diagrams with one Coulomb interaction line inserted between two particles or two holes in the second-order direct diagram and their exchange counterparts. Finally, there are third-order diagrams with a first-order self-energy correction.
inserted into the second-order direct and exchange diagrams.

Even if all the possible exchange counterparts of the RPA series are correctly calculated, another problem arises instead. The resulting approximation is unable to give the correct description of long-range correlation characteristic of the electron liquid.

The conserving approximation method by Baym and Kadanoff can raise levels of approximations maintaining the correct description of long-range correlation by improving the generating functional \( \Phi \) progressively. This method guarantees conservation of the local electron number, the local electron momentum and the local electron energy as well as the \( f \)-sum rule. However, it does not fulfill the Pauli principle unless the theory is exact. As a consequence the requirement of the Pauli principle in the framework of the conserving approximation method can be a guiding principle leading to the exact many-electron theory.

### B. Analysis of the dielectric formulation

The dielectric formulation is originally suitable for the description of long-range correlation of the electron liquid. It discriminates between proper and improper polarization functions. Improper polarization functions are responsible for long-range correlation and proper polarization functions for short-range correlation and exchange. By a diagrammatic analysis we shall investigate how the requirement of the Pauli principle should be fulfilled in the dielectric formulation and thereby give the integral equation for the particle-hole irreducible interaction in a diagrammatic representation (see Fig. 2).

We shall start with the following equations [19, 20, 21, 22, 27] for the spin-parallel and spin-antiparallel parts of the static structure factor \( S(q) \)

\[
S^{\uparrow\uparrow}(q) = \frac{1}{N} \sum_{\sigma} (\rho_{q\sigma}^{\uparrow} \rho_{-q\sigma}^{\uparrow}) = \frac{\hbar}{2\pi n} \int_0^\infty d\omega \text{Im} \left\{ \frac{1}{\epsilon(q)} \left( 1 - \frac{1}{\epsilon(q,\omega)} \right) + \pi_a(q,\omega) \right\}
\]

\[
= \frac{\hbar}{\pi n} \int_0^\infty d\omega \text{Im} \left\{ \pi_a(q,\omega) + \frac{1}{2} \pi_a(q,\omega) - 2 \pi_a(q,\omega) - \frac{\pi(q,\omega)\epsilon(q)(1+\pi(q,\omega))}{\epsilon(q,\omega)} \right\}, \tag{1}
\]

\[
S^{\uparrow\downarrow}(q) = \frac{1}{N} \sum_{\sigma} (\rho_{q\sigma}^{\uparrow} \rho_{-q\sigma}^{\downarrow}) = \frac{\hbar}{2\pi n} \int_0^\infty d\omega \text{Im} \left\{ \frac{1}{\epsilon(q)} \left( 1 - \frac{1}{\epsilon(q,\omega)} \right) - \pi_a(q,\omega) \right\}
\]

\[
= \frac{\hbar}{\pi n} \int_0^\infty d\omega \text{Im} \left\{ \frac{1}{2} \pi_b(q,\omega) - \frac{1}{2} \pi(q,\omega)\epsilon(q,\omega) \right\}, \tag{2}
\]

where \( \langle \cdots \rangle \) denotes the expectation value with respect to the exact ground state and \( \rho_{q\sigma}^{\uparrow} \) is the density fluctuation operator; the dielectric function \( \epsilon(q,\omega) \) is defined as \( \epsilon(q,\omega) = 1 + v(q)\pi(q,\omega) \) and \( v(q) = 4\pi e^2/q^2 \). The proper polarization function \( \pi_a(q,\omega) \) is divided into exchange and direct parts as \( \pi(q,\omega) = \pi_a(q,\omega) + \pi_b(q,\omega) \) (see Fig. 2 (a), (b) and (c)). The static structure factor \( S(q) \) that gives the description of charge-fluctuations is written as

\[
S(q) = S^{\uparrow\uparrow}(q) + S^{\uparrow\downarrow}(q)
\]

\[
= \frac{1}{N} \sum_{\sigma} (\rho_{q\sigma}^{\uparrow} + \rho_{q\sigma}^{\downarrow})(\rho_{-q\sigma}^{\uparrow} + \rho_{-q\sigma}^{\downarrow})
\]

\[
= \frac{\hbar}{\pi n} \int_0^\infty d\omega \text{Im} \left\{ \frac{1}{\epsilon(q)} \left( 1 - \frac{1}{\epsilon(q,\omega)} \right) \right\}. \tag{3}
\]

On the other hand, the exchange part of \( S(q) \), \( S_{\text{ex}}(q) \) that gives the description of spin-fluctuations is written as

\[
S(q) = S^{\uparrow\uparrow}(q) - S^{\uparrow\downarrow}(q)
\]

\[
= \frac{1}{N} \sum_{\sigma} (\rho_{q\sigma}^{\uparrow} + \rho_{q\sigma}^{\downarrow})(\rho_{-q\sigma}^{\downarrow} - \rho_{-q\sigma}^{\uparrow})
\]

\[
= \frac{\hbar}{\pi n} \int_0^\infty d\omega \text{Im} \{ \pi_a(q,\omega) \}. \tag{4}
\]

The exchange function \( \pi_a(q,\omega) \) comes from those diagrams in which two external points are connected through particle and hole lines; the function \( \pi_a(q,\omega) \) is spin-dependent and makes a direct contribution to \( S^{\uparrow\uparrow}(q) \) alone; it is reduced to the Lindhard function \( \pi_0(q,\omega) \) in the non-interacting limit. The direct function \( \pi_0(q,\omega) \), on the other hand, comes from those diagrams in which two external points are not connected through particle and hole lines; the function \( \pi_0(q,\omega) \) is spin-independent and makes a contribution to \( S^{\uparrow\downarrow}(q) \) and \( S^{\downarrow\uparrow}(q) \) equivalently. The improper polarization function, \( \pi(q,\omega)v(q)\pi(q,\omega)/\epsilon(q,\omega) \), whose diagrams can be separated into two pieces by cutting a single Coulomb interaction line in them, also makes a contribution to \( S^{\uparrow\uparrow}(q) \) and \( S^{\downarrow\uparrow}(q) \) equivalently.
where $G_\sigma(p, \epsilon)$ is the one-electron Green’s function and the proper vertex part $\Lambda(p, \epsilon; q, \omega)$ satisfies the following integral equation.

$$
\Lambda(p, \epsilon; q, \omega) = 1 + \frac{1}{2} \sum_{\sigma} \frac{\Omega}{(2\pi)^3} \int d^3 p' \int \frac{d\epsilon'}{2\pi i} I^{\sigma\sigma'}(p, \epsilon; p', \epsilon'; q, \omega) 
\times G_{\sigma'}(p', \epsilon') G_{\sigma'}(p' + q, \epsilon' + \omega) \Lambda(p', \epsilon'; q, \omega).
$$

The particle-hole irreducible interaction $I^{\sigma\sigma'}(p, \epsilon; p', \epsilon'; q, \omega)$ can be divided into two parts, direct and exchange (see Fig. 2 (c)). The function $\pi_a(q, \omega)$, apart from $\pi_0(q, \omega)$, is constructed only from exchange parts, whereas the function $\pi_b(q, \omega)$ is constructed from both direct and exchange parts but must include at least one direct part.

The spin-parallel and spin-antiparallel pair correlation functions are given respectively as

$$
\begin{align*}
g_{^↑^↓}(r) &= 1 + \frac{2}{N} \sum_q (S^{↑↑}(q) - 1) e^{iq \cdot r}, \\
g_{^↑^↑}(r) &= 1 + \frac{2}{N} \sum_q S^{↑↑}(q) e^{iq \cdot r}.
\end{align*}
$$

The Pauli principle means that $g_{^↑^↓}(0) = 0$. This is satisfied only by $\pi_0(q, \omega)$ or its modification \[19\] in which two non-interacting one-electron Green’s functions are replaced by two exact one-electron Green’s functions. The Pauli principle then means that

$$
\sum_q \int_0^\infty d\omega \text{Im} \left\{ \pi_a(q, \omega) - \pi_0(q, \omega) + \frac{1}{2} \pi_b(q, \omega) \right\} = 0.
$$

We shall see how a direct term and its exchange counterpart which exactly cancel each other by integrating over $q$ and $\omega$ appear in pairs in the equation above. First of all, the quantity $\pi_a(q, \omega) - \pi_0(q, \omega)$ is nothing but the exchange counterpart of $\frac{1}{2}(\pi_b(q, \omega) - \pi(q, \omega)\nu(q)\pi(q, \omega)/\epsilon(q, \omega))$ (see Fig. 2 (d)). Consider in detail the interrelation between direct and exchange terms. For this purpose we shall define the order of $\pi_a(q, \omega)$ and $\pi_b(q, \omega)$ according to the number of irreducible particle-hole interactions included in them (see Fig. 2 (a), (b) and (c)). It can easily be seen that the exchange counterpart of the improper term $-\frac{1}{2} \pi(q, \omega)\nu(q)\pi(q, \omega)/\epsilon(q, \omega)$ is part of the first-order contribution of $\pi_a(q, \omega)$ that consists of a single exchange part of $I^{\sigma\sigma'}$. The exchange counterpart of $\frac{1}{2} \pi_b(q, \omega)$ is either the first- or higher-order contributions of $\pi_a(q, \omega)$. Consider the first-order contribution of $\frac{1}{2} \pi_b(q, \omega)$ that has a single direct part of $I^{\sigma\sigma'}$. The interaction in it can be separated into two parts: One is the doubly irreducible interaction and the other is the direct mate of all the second- and higher-order contributions of $\pi_a(q, \omega)$.
(see Fig. 2 (f)). By doubly irreducible we mean that the diagrams have no particle-hole pair in the intermediate states when they are seen not only from bottom to top, but also from left to right. All the second- and higher-order contributions of \( \frac{1}{2} \pi_\kappa (q, \omega) \) include at least one direct part of \( I^{\pi \sigma'} \). The exchange counterpart of all these contributions is part of the first-order contribution of \( \pi_\kappa (q, \omega) \).

We have seen how various parts of polarization functions, when integrated over \( \omega \) and \( q \), should be cancelled to fulfill the Pauli principle. From the analysis above we may conclude that the exchange part of \( I^{\pi \sigma'} \) consists of (i) the exchange counterpart of the interaction included in the improper polarization function, (ii) the exchange part of the doubly irreducible interaction, and (iii) the exchange counterpart of the interaction included in all the second- and higher-order contributions of \( \frac{1}{2} \pi_\kappa (q, \omega) \) (see Fig. 2 (e)). We may also conclude that the direct part of \( I^{\pi \sigma'} \) consists of (i) the direct part of the doubly irreducible interaction and (ii) the direct mate of the interaction included in all the second- and higher-order contributions of \( \pi_\kappa (q, \omega) \) (see Fig. 2 (f)). We have thus arrived at the same conclusion concerning the functional structure of the particle-hole irreducible interaction that Yasuhara and Takada \[24\] obtained from a diagrammatic analysis of polarization functions (see Fig. 2 (f)) is quite the same as the integral equation that Yasuhara and Takada \[24\] obtained from a diagrammatic analysis of the self-energy \( \Sigma_\sigma (p, \epsilon) \) as a functional of \( G_{\sigma'} (p', \epsilon') \) in their derivation of the symmetric expression for \( \Sigma_\sigma (p, \epsilon) \) in which each constituent \( G_{\sigma'} \) of \( \Sigma_\sigma (p, \epsilon) \) enters in an equivalent way (see Eq. (58)). According to many-body theory, this coincidence is natural since the particle-hole irreducible interaction \( I^{\pi \sigma} (p, \epsilon; p', \epsilon'; q, \omega) \) in the limit \( q = \omega = 0 \) is identical to the functional derivative \( \delta \Sigma_\sigma (p, \epsilon) / \delta G_{\sigma'} (p', \epsilon') \). Hence the functional structure of \( I^{\pi \sigma} (p, \epsilon; p', \epsilon'; q, \omega) \) is identical to that of \( \Sigma_\sigma (p, \epsilon) / \delta G_{\sigma'} (p', \epsilon') \).

The conserving approximation method by Baym and Kadanoff \[17, 18\] requires that an expression for \( \Sigma_\sigma (p, \epsilon) \) and the one for \( I^{\pi \sigma} (p, \epsilon; p', \epsilon'; q, \omega) \) to be used in the construction of an approximate proper polarization function \( \pi (q, \omega) \) be both \( \Phi \)-derivable. \( I^{\pi \sigma} (p, \epsilon; p', \epsilon'; q, \omega) \) has the same functional structure as \( \Sigma_\sigma (p, \epsilon) / G_{\sigma'} (p', \epsilon') \). The conserving approximation method then fulfills one of the rigorous self-consistent requirements imposed on the exact many-body theory.

With the exact generating functional \( \Phi \) one can obtain the exact self-energy and the exact particle-hole irreducible interaction from its first and second functional derivatives, respectively. The standard expression for the self-energy is given as

\[
\Sigma_\sigma (p, \epsilon) = \frac{1}{\Omega} \sum_q \int \frac{d\omega}{2\pi i} e^{i\omega \sigma} G_\sigma (p + q, \epsilon + \omega) - \frac{\nu (q)}{\epsilon (q, \omega)} \Lambda (p, \epsilon; q, \omega), \quad \delta \to +0.
\]

and the one-electron Green’s function \( G_\sigma (p, \epsilon) \) is related to the self-energy as

\[
\left[ G_\sigma (p, \epsilon) \right]^{-1} = \left[ G^0_\sigma (p, \epsilon) \right]^{-1} - \Sigma_\sigma (p, \epsilon),
\]

where \( G^0_\sigma (p, \epsilon) \) is the non-interacting one-electron Green’s function. Note that \( \pi (q, \omega) \) and \( \Lambda (p, \epsilon; q, \omega) \) in Eq. (10) satisfy Eqs. (5) and (6), respectively. We would like to stress here the importance of satisfying the integral equation for the particle-hole irreducible interaction \( I^{\pi \sigma} (p, \epsilon; p', \epsilon'; q, \omega) \) in the self-consistent evaluation of various quantities such as \( G_\sigma (p, \epsilon) \), \( \Sigma_\sigma (p, \epsilon) \), \( \Lambda (p, \epsilon; q, \omega) \), \( \pi (q, \omega) \) and \( \epsilon (q, \omega) \). The accurate knowledge of \( I^{\pi \sigma} (p, \epsilon; p', \epsilon'; q, \omega) \) makes it possible to evaluate all these quantities self-consistently in agreement with the Pauli principle. In this sense the integral equation for the particle-hole irreducible interaction is the crux of many-body theory.

We have thus clarified that the requirement of the Pauli principle in the framework of the dielectric formulation can lead to the exact integral equation for the particle-hole irreducible interaction \( I^{\pi \sigma} (p, \epsilon; p', \epsilon'; q, \omega) \) and that the same requirement imposed on the conserving approximation method can also lead to the exact many-body theory.

As can be seen in standard text books \[25, 26, 27, 28\] on many-body theory, there are two different expressions for the ground state energy: One is written in terms of the one-particle Green’s function \( G_\sigma (p, \epsilon) \) and the self-energy \( \Sigma_\sigma (p, \epsilon) \) and the other in terms of the dynamically screened Coulomb interaction \( \nu (q) / \epsilon (q, \omega) \) and the...
proper polarization function $\pi(q, \omega)$; the former can easily be transformed into the latter by definition of these quantities. The two expressions, if inspected into the innermost structure, can be represented with the same integral equation for the particle-hole irreducible interaction $I^{\sigma\sigma'}(p, e; p', e'; q, \omega)$. According to the symmetric expression for the self-energy $\Sigma_{\sigma}(p, e)$ by Yashihara and Takada [24], the knowledge of $I^{\sigma\sigma'}(p, e; p', e'; q, \omega)$ at $q = \omega = 0$ is sufficient for the evaluation of the ground state energy as well as the self-energy $\Sigma_{\sigma}(p, e)$.

It is important to recognize that the expansion of the self-energy $\Sigma_{\sigma}(p, e)$ or the proper polarization function $\pi(q, \omega)$ with respect to the screened Coulomb interaction converges very slowly since correlation is much complicated in the region of realistic metallic densities. It may then be naturally expected that the systematic inclusion of higher-order perturbation terms with respect to the screened Coulomb interaction is indispensable for the description of strongly correlated features of the electron liquid. In fact, there is a great deal of cancellation due to the Pauli principle occurring among various higher-order perturbation terms. For the evaluation of the quasi-particle energy dispersion $E(p)$ as well as the effective mass $m^*$, it is necessary to consider the integral equation for the particle-hole irreducible interaction which makes it possible to take systematically into account the cancellation between higher-order terms due to the Pauli principle.

Finally we give a brief survey of the present situation in the study of the electron liquid. (1) The numerical values of the correlation energy calculated from different theoretical methods [22, 24, 29, 31, 32, 33, 34, 35, 36] as well as from the Green's function Monte Carlo method [29, 30] agree within an accuracy of 0.5 mRy. per electron throughout the whole region of metallic densities. The compressibility and the spin-susceptibility are also evaluated with high accuracy. The RPA overestimates the correlation energy in magnitude by about 47% at a typical metallic density ($\rho_s \sim 4.0$) since it lacks higher-order particle-particle ladder interactions responsible for short-range correlation as well as exchange corrections. (2) Accurate evaluations of the spin-parallel and the spin-antiparallel pair correlation functions are performed [37, 38, 39]. (3) Physical quantities of quasi-particles such as the effective mass $m^*$ [10, 11, 11], the renormalization factor $\tilde{z}$ [12], the Landau interaction function $f^{\sigma\sigma'}(p, p'; q)$ [10] and the quasiparticle energy dispersion $E(p)$ [13, 14, 15, 16] (see Sec. V) are all evaluated with sufficient accuracy. (4) A self-consistent theory in which the integral equation for the particle-hole irreducible interaction can be fulfilled by iteration in the framework of the conserving approximation scheme has been presented by Takada [47] and successfully applied to the quantitative evaluation of the one-electron spectral function $A(p, e)$ [48] and the dynamical structure factor $S(q, \omega)$ [49] of the electron liquid at metallic densities.

### III. NEW EXPRESSION FOR CORRELATION ENERGY

#### A. Definition

In this section we define a new expression for the correlation energy of the electron liquid as follows:

$$E_c = \frac{1}{2} \left( \frac{1}{\Omega} \right)^2 \sum_{q, \sigma, \sigma', \rho, \rho'} f(p) f(p') \times v(q) \left\{ \frac{1 - f(p + q)}{\epsilon_p - \epsilon_{p+q} + \epsilon_{p'} - \epsilon_{p'-q}} \right\} \times \left\{ v_{eff}(q) - \delta_{\sigma\sigma'} v_{eff}(-p + p' - q) \right\},$$

(12)

where $f(p)$ is the Fermi distribution function at 0K and $\epsilon_p = \frac{\hbar^2 p^2}{2m}$. The expression bears second-order direct and exchange perturbation terms, but one of the two Coulomb interactions in each term is replaced by an effective interaction $v_{eff}(q)$ which contains information about third- and higher-order contributions in the perturbation expansion. In Sec. III B, C and D we evaluate the effective interaction $v_{eff}(q)$ by interpolating between long-range correlation in the RPA and short-range correlation in the particle-particle ladder approximation such that the exchange counterpart $v_{eff}(-p + p' - q)$ and its feedback effect on the direct interaction $v_{eff}(q)$ are evaluated in a self-consistent way. This expression for the correlation energy may be understood from intuition or from a diagrammatic consideration. Strictly, the effective interaction $v_{eff}(q)$ above should be defined as $v_{eff}(p, p'; q)$. Here we employ its averaged value over $p$ and $p'$ within the Fermi sphere.

First we shall see how the above expression for $E_c$ is related to the dielectric formulation we have described in Sec. II B. The direct term of $E_c$ comes from the direct part of the total polarization function $\pi_0(q, \omega) - \pi(q, \omega)\epsilon(q)\pi(q, \omega)/\epsilon(q, \omega)$ and the exchange term of $E_c$ from the exchange part of the total polarization function excluding the zeroth order Lindhard function $\pi_0(q, \omega) - \pi(q, \omega)$.

We start with the standard expression for the exchange-correlation energy, i.e., the integral of the potential energy over the coupling constant.

$$E_{xc} = \frac{n}{2} \sum_{\sigma} \frac{4\pi e^2}{\Omega^2} \left\{ \tilde{S}(q) - 1 \right\},$$

(13)

where $n$ is the electron density and $\tilde{S}(q)$ denotes the coupling-constant-averaged static structure factor defined as

$$\tilde{S}(q) = \frac{1}{e^2} \int_0^{e^2} d(e^2) S(q), \quad S(q) = \frac{1}{N} \langle \rho_{q\rho} - \rho \rangle.$$  

(14)

The integral over the coupling constant necessarily reduces the magnitude of the potential energy since it implies the addition of an increase in the kinetic energy.
caused by correlation to the potential energy. This correlation increase in the kinetic energy cannot be neglected since it cancels about one third of the correlational lowering in the potential energy at a typical metallic density, \( \rho_s = 4.0 \); in the limit \( \rho_s \to 0 \) the correlational lowering in the potential energy is by half cancelled by the correlational increase in the kinetic energy.

The function \( \tilde{S}(q) \) can be decomposed into two parts as \( \tilde{S}(q) = \tilde{S}^{HF}(q) + \tilde{S}_c(q) \). The Hartree-Fock contribution \( \tilde{S}^{HF}(q) \) is independent of the coupling constant. Then the correlation energy is given as

\[
E_c = \frac{n}{2} \sum_q \frac{4\pi e^2}{q^2} \tilde{S}_c(q),
\]

where \( \tilde{S}_c(q) \) can be decomposed into direct and exchange parts, \( \tilde{S}_c(q) = \tilde{S}_c^d(q) + \tilde{S}_c^{ex}(q) \).

Let us compare Eq. (15) with the new expression for \( E_c \) we have defined by Eq. (12). Then the functions \( \tilde{S}_c^d(q) \) and \( \tilde{S}_c^{ex}(q) \) may be identified as

\[
\tilde{S}_c^d(q) = \frac{1}{n} \left( \frac{1}{\Omega} \right)^2 \sum_{p,p',\sigma,\sigma'} f(p)f(p') \frac{\{1 - f(p + q)\}\{1 - f(p' - q)\}}{\epsilon_p - \epsilon_{p+q} + \epsilon_{p'} - \epsilon_{p'-q}} v_{eff}(q),
\]

\[
\tilde{S}_c^{ex}(q) = -\frac{1}{n} \left( \frac{1}{\Omega} \right)^2 \sum_{p,p',\sigma,\sigma'} f(p)f(p') \frac{\{1 - f(p + q)\}\{1 - f(p' - q)\}}{\epsilon_p - \epsilon_{p+q} + \epsilon_{p'} - \epsilon_{p'-q}} \delta_{\sigma\sigma'} v_{eff}(-p + p' - q).
\]

The spin-parallel and spin-antiparallel components of \( \tilde{S}_c(q) \) are defined as \( \tilde{S}_c^{\uparrow\uparrow}(q)/2 \) and \( \tilde{S}_c^{\uparrow\downarrow}(q)/2 + \tilde{S}_c^{\downarrow\uparrow}(q) \), respectively, and given as

\[
\tilde{S}_c^{\uparrow\uparrow}(q) = \frac{1}{2n} \left( \frac{1}{\Omega} \right)^2 \sum_{p,p',\sigma,\sigma'} f(p)f(p') \frac{\{1 - f(p + q)\}\{1 - f(p' - q)\}}{\epsilon_p - \epsilon_{p+q} + \epsilon_{p'} - \epsilon_{p'-q}} v_{eff}(q),
\]

\[
\tilde{S}_c^{\uparrow\downarrow}(q) = \frac{1}{2n} \left( \frac{1}{\Omega} \right)^2 \sum_{p,p',\sigma,\sigma'} f(p)f(p') \frac{\{1 - f(p + q)\}\{1 - f(p' - q)\}}{\epsilon_p - \epsilon_{p+q} + \epsilon_{p'} - \epsilon_{p'-q}} \delta_{\sigma\sigma'} v_{eff}(-p + p' - q).
\]

Note that this expression for \( \tilde{S}_c^{\uparrow\uparrow}(q) \) fulfills the Pauli principle. The coupling-constant-averaged spin-parallel pair correlation function is defined as

\[
\tilde{g}^{\uparrow\uparrow}(r) = 1 + \frac{2}{N} \sum_q \{ \tilde{S}^{\uparrow\uparrow}(q) - 1 \} e^{iqr}.
\]

Since \( S^{HF}(q) \) satisfies that \( \tilde{g}^{\uparrow\uparrow}(0) = 0 \), the relation that \( \sum_q \tilde{S}_c^{\uparrow\uparrow}(q) = 0 \) has to be satisfied. This identity can be easily checked by a simple transformation of the wavenumber variables in Eq. (10). The Pauli principle is automatically fulfilled in the present theory. Instead, we have to deal with much difficulty in the self-consistent determination of the effective interaction \( v_{eff}(q) \), as will be seen in Sec. III B, C and D.

### B. New expression for the RPA correlation energy

In this subsection we calculate the effective interaction \( v_{eff}(q) \) appropriate for the RPA. The correlation contribution of the static structure factor in the RPA is given as

\[
S_c^{RPA}(q) = -S^{HF}(q) + \frac{\hbar}{\pi n} \int_0^\infty dw \text{Im} \frac{\pi_0(q, \omega)}{1 + v(q)\pi_0(q, \omega)},
\]

where \( \pi_0(q, \omega) \) is the Lindhard function. The coupling constant integral of \( S_c^{RPA}(q) \) can be easily performed as

\[
S_c^{RPA}(q) = -S^{HF}(q) + \frac{\hbar}{\pi n} \left( \frac{\hbar}{2v(q)} \tan^{-1} \frac{v(q)\text{Im}[\pi_0(q, \omega)]}{1 + v(q)\text{Re}[\pi_0(q, \omega)]} \right).
\]

This expression contains contributions of one-pair excitations and those of plasmon excitations. The frequency integral in Eq. (22) can be numerically performed to obtain \( S_c^{RPA}(q) \). The effective interaction in the RPA, \( v_{eff}^{RPA}(q) \) is then defined as

\[
\tilde{S}_c^{RPA}(q) = \frac{1}{n} \left( \frac{1}{\Omega} \right)^2 \sum_{p,p',\sigma,\sigma'} f(p)f(p') \frac{\{1 - f(p + q)\}\{1 - f(p' - q)\}}{\epsilon_p - \epsilon_{p+q} + \epsilon_{p'} - \epsilon_{p'-q}} v_{eff}^{RPA}(q).
\]

The integral over \( p \) and \( p' \) in the prefactor has been analytically performed by Kimball [53]. With the interaction \( v_{eff}^{RPA}(q) \) thus calculated we can give a new expression for the RPA correlation energy as

\[
E_c^{RPA} = \frac{1}{2} \left( \frac{1}{\Omega} \right)^2 \sum_{q,p,p',\sigma,\sigma'} f(p)f(p') \frac{\{1 - f(p + q)\}\{1 - f(p' - q)\}}{\epsilon_p - \epsilon_{p+q} + \epsilon_{p'} - \epsilon_{p'-q}} v_{eff}^{RPA}(q).
\]
Note that the exchange term is missing in the RPA. The ratio of the effective interaction \( v_{eff}^{RPA}(q) \) to the bare Coulomb interaction \( v(q) \) is reduced in magnitude from the bare Coulomb interaction \( v(q) \) on the small side of wavenumbers under the influence of dynamical screening in the RPA. In fact, the effective interaction \( v_{eff}(q) \) is also reduced in magnitude from \( v(q) \) on the large side of wavenumbers under the strong influence of short-range correlation at metallic densities; it is not so drastic for small \( q \) but essential for large \( q \).

Consider those perturbation terms which consist only of an infinite series of particle-particle ladder interactions \([51, 52, 53, 54, 55]\) via the bare Coulomb interaction. Fig. 3 gives a diagrammatic representation of those perturbation terms. The correlation energy contribution from those diagrams is written as follows:

\[
E_{c}^{\text{ladd}(d)} = \frac{1}{2} \left( \frac{1}{\Omega} \right)^2 \sum_{q, p, p'} \sum_{\sigma, \sigma'} f(p) f(p') v(q) \frac{1 - f(p + q)}{\epsilon_p - \epsilon_{p+q} + \epsilon_{p'} - \epsilon_{p'-q}} I(p, p'; q),
\]

where the particle-particle ladder interaction \( I(p, p'; q) \) is the solution of the following integral equation:

\[
\begin{align*}
I(p, p'; q) &= v(q) \\
&+ \frac{1}{\Omega} \sum_{k} v(q - k) \frac{1 - f(p + k)}{\epsilon_p - \epsilon_{p+k} + \epsilon_{p'} - \epsilon_{p'-k}} \\
&\quad \times I(p, p'; k).
\end{align*}
\]

(27)

The spin-antiparallel and spin-parallel pair correlation functions, \( g_{ladd}^{\uparrow\downarrow}(r) \) and \( g_{ladd}^{\uparrow\uparrow}(r) \) derived from \( E_{c}^{\text{ladd}(d)} \) and \( E_{c}^{\text{ladd(ex)}} \) are given respectively as

\[
\begin{align*}
g_{ladd}^{\uparrow\downarrow}(r) &= \left( \frac{2}{N} \right)^2 \sum_{p, p'} f(p) f(p') \\
&\quad \times \left[ 1 + \frac{1}{\Omega} \sum_{q} \frac{1 - f(p + q)}{\epsilon_p - \epsilon_{p+q} + \epsilon_{p'} - \epsilon_{p'-q}} \right] I(p, p'; q) e^{iq\cdot r} \right|^2, \quad (28)
\end{align*}
\]

\[
\begin{align*}
g_{HF,ladd}^{\uparrow\downarrow}(r) &= g_{HF}^{\uparrow\downarrow}(r) + \Delta g_{ladd}^{\uparrow\downarrow}(r) \\
&= \left( \frac{2}{N} \right)^2 \sum_{p, p'} f(p) f(p') \frac{1}{2} \left( 1 - e^{i(p-p')\cdot r} \right) \\
&\quad + \frac{1}{\Omega} \sum_{q} \frac{1 - f(p + q)}{\epsilon_p - \epsilon_{p+q} + \epsilon_{p'} - \epsilon_{p'-q}} \right] I(p, p'; q) e^{iq\cdot r} \right|^2. \quad (29)
\end{align*}
\]

Eq. (29) includes the Hartree-Fock contribution. Both of \( g_{ladd}^{\uparrow\downarrow}(r) \) and \( g_{HF,ladd}^{\uparrow\downarrow}(r) + \Delta g_{ladd}^{\uparrow\downarrow}(r) \), so far as their behaviors at short distances are concerned, are physically sound and reasonable throughout the entire region of metallic densities in contrast with the RPA in which both of the pair correlation functions become negative.

Consider the general properties of \( I(p, p'; q) \). It is reduced to the bare Coulomb interaction \( v(q) \) in the limit of small \( q \). On the other hand, it tends approximately to \( v(q)|g_{ladd}^{\uparrow\downarrow}(0)|^{1/2} \) in the limit of large \( q \). The ratio \( I(p, p'; q)/v(q) \) starts from unity at \( q = 0 \) and decreases monotonically with increasing \( q \). Thus, \( I(p, p'; q) \) is reduced in magnitude from \( v(q) \) on the large side of wavenumbers under the strong influence of short-range correlation at metallic densities. The inclusion of an infinite series of particle-particle ladder interactions has the effect to reduce the contribution from large wavenumber components of one of the two Coulomb interactions entering the second-order direct perturbation term.

A very good analytic expression for \( g_{ladd}^{\uparrow\downarrow}(r) \) at short distances was given by one of the authors (H.Y.) \([51]\). The magnitude of \( g_{ladd}^{\uparrow\downarrow}(0) \) is remarkably reduced from unity as the electron density is lowered to metallic levels. The inclusion of particle-particle ladder interactions \( (25) \) much reduces the ratio \( v_{eff}(q)/v(q) \) from unity on the
large side of wavenumbers, compared with the case of the RPA.

It should be indicated that among all many-body perturbation terms only particle-particle ladder interacting parts (via the bare Coulomb interaction) can make a contribution to the predominant asymptotic form of $S^\uparrow\downarrow_{\ell}(q)$ of order $q^{-4}$ for large $q$. The predominant asymptotic form of $S^\uparrow\downarrow_{\ell}(q)$, on the other hand, is of order $q^{-6}$ for large $q$ as a consequence of the cancellation between a direct and exchange pair of particle-particle ladder interactions.

Consider the iterative solution of the integral equation for $I(p, p'; q)$. The $n$-th iterative term involves $n + 1$ different wavenumber components of the Coulomb interactions. Each wavenumber can vary in magnitude from zero to infinity under the condition that the total sum of $n + 1$ different wavenumbers amounts to $q$. In this sense the mixing of different wavenumber components in $I(p, p'; q)$ is most complete among all types of interactions. It is this property of the particle-particle ladder interactions that is responsible for the description of local density fluctuations. The particle-particle ladder approximation is in marked contrast with the RPA appropriate for the description of long-range correlation associated with small wavenumber components of the Coulomb interaction. The RPA amounts to an infinite summation for the description of long-range correlation associated with short-range Coulomb repulsion.

We make a smooth interpolation between long-range correlation in the RPA and short-range correlation in the particle-particle ladder approximation by replacing even interactions shown in Fig. 3 will be considered in Sec. III D, combined with other exchange counterparts associated with small and intermediate wavenumbers.

### D. Allowance for the exchange correction

In this subsection we allow for the exchange correction, starting with the interpolated effective interaction we have obtained above. First of all, we would like to remind the reader of the detailed analysis of the dielectric formulation we have made in terms of the exchange and direct parts of the proper polarization function, $\pi_a(q, \omega)$ and $\pi_0(q, \omega)$ in Sec. II.B. So far we have treated the Lindhard function $\pi_0(q, \omega)$ that is the non-interacting contribution of $\pi_a(q, \omega)$, the main contribution of the direct part $\pi_0(q, \omega)$ involving an infinite series of particle-particle ladder interactions and the corresponding improper polarization function, leaving the interacting exchange part $\pi_a(q, \omega) - \pi_0(q, \omega)$ out of account. In Sec. II. B we have stressed that the exchange part $\pi_a(q, \omega)$ has an influence on $S^{\uparrow\uparrow}(q)$ and $S^{\downarrow\downarrow}(q)$ indirectly through the improper polarization function common to the two. This means that the two functions $S^{\uparrow\uparrow}(q)$ and $S^{\downarrow\downarrow}(q)$ are interconnected through $\pi_a(q, \omega)$ in the improper polarization function and have to be determined in a self-consistent way. For convenience we term the requirement of this self-consistency through the improper polarization function the indirect, or feedback effect of exchange.

In order to allow for the indirect effect of exchange as well as the direct one we employ an iterative method. First, we start with an exchange interaction of $v_{eff}^{RPA+\text{ladd}(d)}(-p + p' - q)$, which is obtained by replacing $q$ in $v_{eff}^{RPA+\text{ladd}(d)}(q)$ by the variable $-p + p' - q$ appropriate for the exchange term. Secondly, we define the local field factor from exchange $G(q)$ as follows:

$$S^{\text{RPA+}\text{ladd}(d)}_{\ell}(q) = -S^{HF}(q) + \frac{\hbar}{\pi n} \int_0^\infty d\omega \frac{1}{v(q)(1 - C(q))} \times \tan^{-1} \left( \frac{v(q)(1 - C(q)) \text{Im} [\pi_0(q, \omega)]}{1 + v(q)(1 - C(q)) \text{Re} [\pi_0(q, \omega)]} \right).$$

It is evident from the interpolation that this expression is reduced to $S_{\ell}^{\text{RPA}}(q)$ for small $q$ and tends to $S^{\text{ladd}(d)}_{\ell}(q)$ for large $q$. Following the same procedure as in the RPA, we have evaluated the effective interaction appropriate for the interpolation. The ratio of the interpolated effective interaction $v_{eff}^{RPA+\text{ladd}(d)}(q)$ to $v(q)$ is quadratic for small $q$ in a similar way as in the RPA, increases monotonically with $q$ and tends to a constant of $[g^{\text{ladd}(d)}(0)]^{1/2}$ which is remarkably smaller than unity at metallic densities. The value of $[g^{\text{ladd}(d)}(0)]^{1/2}$ is estimated to be 0.547 at $r_s = 2$ and 0.326 at $r_s = 4$, in the particle-particle ladder approximation [51].

The exchange counterpart of particle-particle ladder interactions shown in Fig. 3 will be considered in Sec. III D, combined with other exchange counterparts associated with small and intermediate wavenumbers.
Thirdly, we replace every factor of \( v(q)(1-C(q)) \) appearing in Eq. (29) by \( v(q)(1-C(q) - G(q)/2) \) to allow for the feedback effect of exchange; a factor of 1/2 is to be attached because the local field correction from exchange occurs between electrons with the same spin orientations alone. The resulting expression is given as

\[
\tilde{S}^{\text{RPA+ladd(d)+ex}}_c(q) = -S^{HF}(q) \\
+ \frac{\hbar}{\pi n} \int_0^\infty d\omega \frac{1}{v(q)(1-C(q) - G(q)/2)} \\
\times \tan^{-1} \frac{v(q)(1-C(q) - G(q)/2) \text{Im}[\pi_0(q,\omega)]}{1 + v(q)(1-C(q) - G(q)/2) \text{Re}[\pi_0(q,\omega)]}.
\]

(32)

Fourthly, we evaluate a new effective interaction \( v_{\text{eff}}^{\text{NEW}}(q) \) from the direct part of \( S_c^{\text{RPA+ladd(d)+ex}}(q) \), i.e., \( S_c^{\text{RPA+ladd(d)+ex}}(q) - \tilde{S}^{\text{ex}}_c(q) \) as

\[
\tilde{S}_c^{\text{RPA+ladd(d)+ex}}(q) - \tilde{S}^{\text{ex}}_c(q) \\
= \frac{1}{n} \left( \frac{1}{\Omega} \right)^2 \sum_{\mathbf{p},\mathbf{p}',\mathbf{s},\mathbf{s}'} f(\mathbf{p}) f(\mathbf{p}') \times \left\{ 1 - f(\mathbf{p}+\mathbf{q}) \right\} \left\{ 1 - f(\mathbf{p}'-\mathbf{q}) \right\} v_{\text{eff}}^{\text{NEW}}(q).
\]

(33)

The interaction \( v_{\text{eff}}^{\text{NEW}}(q) \) thus defined includes the feedback effect of exchange. From \( v_{\text{eff}}^{\text{NEW}}(q) \) we construct the exchange interaction \( v_{\text{eff}}^{\text{NEW}}(-\mathbf{p} + \mathbf{p}' - \mathbf{q}) \) to calculate a new value of the local field factor from exchange \( G(q) \). We have repeated the iterative process above until we reach the convergent result of the local field factor \( G(q) \) and the effective interaction \( v_{\text{eff}}(q) \).

It should be noted that the above self-consistent determination of the exchange correction corresponds to seeking an approximate solution to the integral equation for the particle-hole irreducible interaction within the present form of the correlation energy.

The ratio of the self-consistently determined effective interaction \( v_{\text{eff}}(q) \) to the bare Coulomb interaction \( v(q) \) is shown for various values of \( r_s \) in Fig. 4. A remarkable change in the ratio \( v_{\text{eff}}(q)/v(q) \) from its interpolated value in Sec. III C can be seen over a wide range of intermediate wavenumbers. The feedback effect of exchange makes the ratio \( v_{\text{eff}}(q)/v(q) \) have a broad peak around \( q/p_F = 1.4 \), though its limiting value for large \( q \) remains unchanged.

The difference of the ratio \( v_{\text{eff}}(q)/v(q) \) from unity can be interpreted to be a measure of how third- and higher-order perturbation terms effectively reduce in magnitude in one of the two Coulomb interactions entering the second-order direct perturbation term. The feedback effect of exchange enhances the effective interaction over a wide range of intermediate wavenumbers, particularly around \( q/p_F = 1.4 \) almost independently of \( r_s \) throughout the entire region of metallic densities. The origin of the broad peak around \( q/p_F = 1.4 \) can be traced back to the interacting exchange part \( \pi_a(q,\omega) - \pi_0(q,\omega) \). This can easily be seen from the starting expression for the function \( S^{\uparrow\downarrow}(q) \) in Sec. II B.

\[
S^{\uparrow\downarrow}(q) = \frac{\hbar}{2\pi n} \int_0^\infty d\omega \text{Im} \left\{ \frac{1}{v(q)} \left( 1 - \frac{1}{\epsilon(q,\omega)} \right) - \pi_a(q,\omega) \right\} \\
= \frac{1}{2} S_c(q) - \frac{\hbar}{2\pi n} \int_0^\infty d\omega \text{Im}[\pi_a(q,\omega) - \pi_0(q,\omega)] \\
= \frac{1}{2} (S_c(q) - \tilde{S}_c(q)).
\]

(34)

The broad peak in the ratio \( v_{\text{eff}}(q)/v(q) \) comes from the peak of \( \tilde{S}_c(q) \) or \( S_c(q) \) located at the almost same wavenumber.

### E. Coupling-constant-averaged spin-parallel and spin-antiparallel pair correlation functions

An exact expression for the exchange and correlation energy functional in DFT is given in terms of the coupling-constant-averaged pair correlation function \( g(r, r') \) whose behaviors are analogous to those of the usual spin-averaged pair correlation function \( g(r, r') \).

\[
E_{xc} = \frac{1}{2} \int d\mathbf{r} d\mathbf{r'} \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \{ g(\mathbf{r}, \mathbf{r}') - 1 \}.
\]

(35)

This is the inhomogeneous version of the formula for the exchange and correlation energy of the uniform electron liquid. Similarly, the integral over the coupling constant...
implies the addition of the correlational increase in the kinetic energy to the correlational lowering in the potential energy between electrons. The function $\tilde{g}(r, r')$ is defined such that the presence of a coupling-constant dependent fictitious one-electron potential introduced in a starting reference Hamiltonian maintains the electron density $n(r)$ of the real interacting system while the Coulomb interaction among electrons is adiabatically switched on as a perturbation. This artifice reflects that correlation among electrons in inhomogeneous systems necessarily causes a change in the electron density $n(r)$ in contrast with the uniform electron liquid.

The magnitude of the pair correlation function $g(r, r')$ at short separations depends on whether one-electron orbitals concerned are extended or localized. Probably, the lowering of $g(r, r')$ from 1/2 at short separations will be greater for nearly free electrons than for atomic electrons tightly bound to the nucleus. This property will also apply to the function $g(r, r')$.

In this subsection we shall first discuss what effect the correlation energy functional generally has on the electron density $n(r)$ of non-uniform electron systems with the help of the expression for $E_{xc}$ above. The sum of the Hartree energy functional and the above $E_{xc}$ gives the total electron-electron interaction energy functional in the ground state energy functional in DFT. The general properties of $\tilde{g}(r, r')$ are quite analogous to those of the usual spin-averaged pair correlation function $g(r, r')$, though the quantity $\tilde{g}(r, r') - 1$ is somewhat reduced in magnitude under the influence of the correlational increase in the kinetic energy.

In the Hartree-Fock approximation, $\tilde{g}(r, r) = 1/2$ and $1/2 < \tilde{g}(r, r') < 1$. Generally, correlation reduces the value of $\tilde{g}(r, r')$ on the short-distance side of $|r - r'|$ and reversely enhances the value of $\tilde{g}(r, r')$ on the long-distance side such that the total electron charge involved is conserved; at zero separation $0 < \tilde{g}(r, r) < 1/2$ and the function $\tilde{g}(r, r')$ increases with $|r - r'|$, exceeds unity and forms a broad peak around the average inter-electron separation and thereafter asymptotically approaches to unity. The function $\tilde{g}(r, r')$ can be rewritten as $\tilde{g}(\bar{r}, \bar{R})$ with $\bar{r} = r - r'$ and $\bar{R} = (r + r')/2$ and its value at zero separation $\tilde{g}(0, \bar{R})$ should vary rather slowly from place to place in solids.

Repelling of other electrons from the immediate neighborhood of an electron in question, when it approaches each nucleus in solids, makes it "feel" the attractive potential from the nucleus significantly stronger because of less screening than in the Hartree-Fock approximaton in DFT. Hence the electron density $n(r)$ is enhanced in the immediate neighborhood of the nuclei. Generally, correlation causes an enhancement in the electron density $n(r)$ at the positions of individual nuclei in solids.

Next we shall mention the general properties of the coupling-constant-averaged spin-parallel and spin-antiparallel pair correlation functions for the uniform electron liquid, $\bar{g}^{\uparrow\uparrow}(r)$ and $\bar{g}^{\uparrow\downarrow}(r)$ and their Fourier transforms $\bar{S}^{\uparrow\uparrow}(\mathbf{q})$ and $\bar{S}^{\uparrow\downarrow}(\mathbf{q})$ before we show their numerical results calculated from the present theory. The coupling-constant-averaged pair correlation functions $\bar{g}^{\sigma\sigma'}(r)$ are defined as

$$
\bar{g}^{\sigma\sigma'}(r) = \frac{1}{e^2} \int_0^2 d(e^2) g^{\sigma\sigma'}(r).
$$

The integral over the coupling constant generally reduces both the shift of $\bar{g}^{\uparrow\uparrow}(r)$ from unity and the shift of $\bar{g}^{\uparrow\downarrow}(r)$ from its Hartree-Fock value over all distances since the correlational increase in the kinetic energy is involved. The reduction is conspicuous particularly at short distances. The cusp condition on $\bar{g}^{\sigma\sigma'}(r)$ is modified as

$$
\bar{g}^{\uparrow\uparrow}(r) = \left\{ 1 + \frac{r}{a_0} \left( 1 - \int_0^2 d(e^2) e^2 \right) \right\} \bar{g}^{\uparrow\uparrow}(0) + \cdots,
$$

$$
\bar{g}^{\uparrow\downarrow}(r) = \frac{r^2}{2} \left\{ 1 + \frac{r}{2a_0} \left( 1 - \frac{1}{(e^2)^2} \int_0^2 d(e^2) e^2 \right) \right\}
\times \frac{d^2\bar{g}^{\uparrow\downarrow}(r)}{dr^2} \bigg|_{r=0} + \cdots.
$$

The difference between $g^{\sigma\sigma'}(r)$ and $\bar{g}^{\sigma\sigma'}(r)$ in the cusp condition is the presence of the coupling constant integral operators in the case of $\bar{g}^{\sigma\sigma'}(r)$. The cusp conditions on $g^{\uparrow\uparrow}(r)$ and $g^{\uparrow\downarrow}(r)$ are fulfilled in the particle-particle ladder approximation and in the Hartree-Fock plus particle-particle particle-ladder approximation, respectively. We have already given the expression for $g^{\uparrow\uparrow}(r)$ and $g^{\uparrow\downarrow}(r)$ in these approximations in Eqs. \[\text{25}\] and \[\text{26}\], respectively. These cusp conditions hold also for inhomogeneous electron systems if one averages the value of $g^{\sigma\sigma'}(r, r')$ on the sphere centered at $R = (r + r')/2$ with a small radius $|r - r'|$.

In Fig. 5 the value of $\bar{g}^{\uparrow\downarrow}(r)$ calculated from the present theory is drawn for various values of $r_s$. We have ascer-tained that the value of $\bar{g}^{\uparrow\downarrow}(r)$ is significantly enhanced at short distances, compared with the value of $g^{\uparrow\downarrow}(r)$ calculated in the particle-particle ladder approximation. As is obvious from Fig. 6, the present $\bar{g}^{\uparrow\downarrow}(r)$ fulfills the Pauli principle. We have also observed that the shift of $\bar{g}^{\uparrow\downarrow}(r)$ from its Hartree-Fock value is reduced at short and intermediate distances, compared with the case of $g^{\uparrow\downarrow}(r)$ calculated in the same approximation. Perdew and Wang \[\text{67}\] have also calculated the spin-averaged $\bar{g}(r)$ of the electron liquid by interpolating between the RPA and the particle-particle ladder approximation, but they have left the interacting exchange part $\pi_0(n, \omega) - \pi_0(n, \omega)$ out of account.

Fig. 7 shows the functions $\bar{S}^{\uparrow\uparrow}_{\uparrow}(\mathbf{q})$ and $\bar{S}^{\uparrow\downarrow}_{\downarrow}(\mathbf{q})$ in the present theory. For comparison the same functions in the RPA are also drawn in the figure. These functions are both reduced in magnitude from the corresponding functions without bars for the same reason as in the case of $g^{\sigma\sigma'}(r)$. The difference between $\bar{S}^{\uparrow\downarrow}(\mathbf{q})$ and $\bar{S}^{\uparrow\downarrow}(\mathbf{q})$ is given by $\bar{S}_{\downarrow}(\mathbf{q})$. For lack of the second- and higher-order
exchange corrections the RPA fails to discriminate between the two functions. As is obvious from Fig. 7, the inclusion of exchange corrections shifts the two functions in opposite directions for small $q$. This splitting is evident from the very definition of $S_{↑↑}(q)$ and $S_{↑↓}(q)$ that we have given in Sec. II B. The interacting exchange part of proper polarization function $\pi_\alpha(q, \omega) - \pi_\alpha(0, \omega)$ is responsible for this splitting of $\bar{S}_{↑↑}(q)$ and $\bar{S}_{↑↓}(q)$ for small $q$. In this connection we mention that the accurate description of $S(q)$ in the RPA for small $q$ does not imply that it also can give the accurate description of $\bar{S}(q)$ for small $q$.

The function $\bar{S}_{↑↑}(q)$ becomes positive for $q \gtrsim 1.5p_F$ while the function $\bar{S}_{↑↓}(q)$ stays negative for any $q$. This is because the exchange contribution overcomes in magnitude the direct contribution for intermediate and large wavenumbers. The following asymptotic forms of $\bar{S}_{↑↑}(q)$ and $\bar{S}_{↑↓}(q)$ for large $q$ are an alternative representation of the cusp conditions \cite{55} on $g_{↑↓}(r)$ and $g_{↑↑}(r)$.

$$S_{↑↑}(q) = \frac{4}{3} \left( \frac{\alpha r_s}{\pi} \right) \left( \frac{p_F}{q} \right)^4 g_{↑↑}(0) + \cdots, \quad (39)$$

$$S_{↑↑}(q) = 4 \left( \frac{\alpha r_s}{\pi} \right) \left( \frac{p_F}{q} \right)^6 q^2 g_{↑↑}(r) + \cdots. \quad (40)$$

It is straightforward to derive the corresponding asymptotic forms of $\bar{S}_{↑↑}(q)$ and $\bar{S}_{↑↑}(q)$ for large $q$. 

FIG. 5: The coupling-constant-averaged spin-antiparallel pair correlation function for the electron liquid, $\bar{g}_{↑↓}(r)$ calculated from the present theory as a function of $p_F r$ for various values of $r_s$.

FIG. 6: The coupling-constant-averaged spin-parallel pair correlation function for the electron liquid, $\bar{g}_{↑↑}(r)$ calculated from the present theory as a function of $p_F r$ for various values of $r_s$.

FIG. 7: (a) and (b) The coupling-constant-averaged spin-parallel and spin-antiparallel correlation functions of the static structure factor, $S_{↑↑}(q)$ and $S_{↑↓}(q)$ as functions of $q/p_F$ for $r_s = 2.0$ and $4.0$; the dotted line in each figure represents the value of the two functions in the RPA.
In Figs. 8 and 9 $S^{\uparrow\uparrow}_c(q)$ and $\bar{S}^{\uparrow\uparrow}_c(q)$ are drawn for various values of $r_s$, respectively. The correlation energy of the electron liquid can be evaluated by integrating $S^{\uparrow\uparrow}_c(q)$ and $\bar{S}^{\uparrow\uparrow}_c(q)$ over $q$, or equivalently by the area of the two curves drawn in Figs. 8 and 9 relative to the horizontal axis. The value of the correlation energy calculated from the present theory agrees with the most reliable values out the entire region of metallic densities (see Table I). However, one must not forget that the accuracy of the correlation energy is not necessarily the best criterion for the validity of a theory. For example, the self-consistent GW approximation gives a very accurate evaluation of the correlation energy of the electron liquid, but it makes the value of $g(r)$ negative at short distances.

The present theory gives an accurate description of both $S^{\uparrow\uparrow}_c(q)$ and $\bar{S}^{\uparrow\uparrow}_c(q)$, or equivalently their Fourier transforms. Furthermore, it gives with high accuracy spin-parallel and spin-antiparallel components of the correlation energy $\epsilon_c$ over the entire region of metallic densities. Fig. 10 shows the ratios of $\epsilon^{\uparrow\downarrow}_c/\epsilon_c$ and $\epsilon^{\uparrow\uparrow}_c/\epsilon_c$ as functions of $r_s$. In the high density region, the two ratios are analytically given as

$$\frac{\epsilon^{\uparrow\downarrow}_c}{\epsilon_c} = \frac{1}{2} - \frac{1}{2} \frac{c_{2x}}{0.0622 \ln(r_s)} + \cdots,$$
$$\frac{\epsilon^{\uparrow\uparrow}_c}{\epsilon_c} = \frac{1}{2} + \frac{1}{2} \frac{c_{2x}}{0.0622 \ln(r_s)} + \cdots,$$
$$\epsilon_c = 0.0622 \ln(r_s) + c_{RPA} + c_{2x} + \cdots \text{Ry.},$$
$$c_{RPA} = -0.1422, \ c_{2x} = 0.04836. \quad (41)$$

where $c_{RPA}$ is the constant from the RPA and $c_{2x}$ is the value of the second-order exchange energy. It is important to recognize that $\epsilon^{\uparrow\downarrow}_c$ and $\epsilon^{\uparrow\uparrow}_c$ occupy nearly 70% and 30% of the total correlation energy throughout almost the entire region of metallic densities, respectively; these ratios probably will apply to all valence electrons participating in cohesion of solids. The component $\epsilon^{\uparrow\uparrow}_c$ of $\epsilon_c$ comes from the deepened Fermi hole at short and intermediate distances from its Hartree-Fock value, as can be seen from $\bar{g}^{\uparrow\uparrow}(r)$. The component $\epsilon^{\uparrow\downarrow}_c$, on the other hand, comes from the developed Coulomb hole. The parallel and antiparallel components equivalently contribute to the leading logarithmic term in the high density limit. This is because $S^{\uparrow\downarrow}_c(q)$ and $\bar{S}^{\uparrow\uparrow}_c(q)$ become equivalent in the limit $r_s \to 0$. This tendency can be observed from the two functions drawn in Figs. 8 and 9 for $r_s = 0.1$. In the language of the pair correlation functions, the leading logarithmic term comes from such distances as $1 \ll p_F r_s \ll r_s^{-1/2}$ where $g^{\uparrow\downarrow}(r) - 1$ and $g^{\uparrow\uparrow}(r) - g^{\uparrow\downarrow}(r)$ both behave like $-r_s/(p_F r_s)^2$; the screening length is proportional to $r_s^{-1/2}/p_F$ for small $r_s$. [55].

FIG. 8: The function $S^{\uparrow\uparrow}_c(q)$ for various values of $r_s$.

FIG. 9: The function $\bar{S}^{\uparrow\uparrow}_c(q)$ for various values of $r_s$.

FIG. 10: The ratios of $\epsilon^{\uparrow\downarrow}_c/\epsilon_c$ and $\epsilon^{\uparrow\uparrow}_c/\epsilon_c$ as functions of $r_s$. The curves drawn in Figs. 8 and 9 relative to the horizontal axis. The value of the correlation energy calculated from the present theory agrees with the most reliable values out the entire region of metallic densities (see Table I). However, one must not forget that the accuracy of the correlation energy is not necessarily the best criterion for the validity of a theory. For example, the self-consistent GW approximation gives a very accurate evaluation of the correlation energy of the electron liquid, but it makes the value of $g(r)$ negative at short distances. The present theory gives an accurate description of both $S^{\uparrow\uparrow}_c(q)$ and $\bar{S}^{\uparrow\uparrow}_c(q)$, or equivalently their Fourier transforms. Furthermore, it gives with high accuracy spin-parallel and spin-antiparallel components of the correlation energy $\epsilon_c$ over the entire region of metallic densities. Fig. 10 shows the ratios of $\epsilon^{\uparrow\downarrow}_c/\epsilon_c$ and $\epsilon^{\uparrow\uparrow}_c/\epsilon_c$ as functions of $r_s$. In the high density region, the two ratios are analytically given as

$$\frac{\epsilon^{\uparrow\downarrow}_c}{\epsilon_c} = \frac{1}{2} - \frac{1}{2} \frac{c_{2x}}{0.0622 \ln(r_s)} + \cdots,$$
$$\frac{\epsilon^{\uparrow\uparrow}_c}{\epsilon_c} = \frac{1}{2} + \frac{1}{2} \frac{c_{2x}}{0.0622 \ln(r_s)} + \cdots,$$
$$\epsilon_c = 0.0622 \ln(r_s) + c_{RPA} + c_{2x} + \cdots \text{Ry.},$$
$$c_{RPA} = -0.1422, \ c_{2x} = 0.04836. \quad (41)$$

where $c_{RPA}$ is the constant from the RPA and $c_{2x}$ is the value of the second-order exchange energy. It is important to recognize that $\epsilon^{\uparrow\downarrow}_c$ and $\epsilon^{\uparrow\uparrow}_c$ occupy nearly 70% and 30% of the total correlation energy throughout almost the entire region of metallic densities, respectively; these ratios probably will apply to all valence electrons participating in cohesion of solids. The component $\epsilon^{\uparrow\uparrow}_c$ of $\epsilon_c$ comes from the deepened Fermi hole at short and intermediate distances from its Hartree-Fock value, as can be seen from $\bar{g}^{\uparrow\uparrow}(r)$. The component $\epsilon^{\uparrow\downarrow}_c$, on the other hand, comes from the developed Coulomb hole. The parallel and antiparallel components equivalently contribute to the leading logarithmic term in the high density limit. This is because $S^{\uparrow\downarrow}_c(q)$ and $\bar{S}^{\uparrow\uparrow}_c(q)$ become equivalent in the limit $r_s \to 0$. This tendency can be observed from the two functions drawn in Figs. 8 and 9 for $r_s = 0.1$. In the language of the pair correlation functions, the leading logarithmic term comes from such distances as $1 \ll p_F r_s \ll r_s^{-1/2}$ where $g^{\uparrow\downarrow}(r) - 1$ and $g^{\uparrow\uparrow}(r) - g^{\uparrow\downarrow}(r)$ both behave like $-r_s/(p_F r_s)^2$; the screening length is proportional to $r_s^{-1/2}/p_F$ for small $r_s$. [55].
| r_{\text{A}} | RPA | STLS | C-A | VWN | EPX | Present |
|-------|------|------|-----|-----|-----|--------|
| 1.0   | -157.6 | -123 | -119.6 | -120.6 | -119 | -120.7 |
| 2.0   | -123.6 | -91.4 | -90.2 | -89.6 | -89.1 | -89.9 |
| 3.0   | -105.5 | -74.8 | -73.8 | -73.7 | -73.7 | -73.7 |
| 4.0   | -93.6 | -64.0 | -63.6 | -63.3 | -63.3 | -63.3 |
| 5.0   | -85.0 | -56.3 | -56.3 | -56.3 | -56.3 | -56.3 |
| 6.0   | -78.2 | -50.5 | -50.7 | -50.7 | -50.7 | -50.1 |

TABLE I: Values of the correlation energy calculated from a variety of approximations and methods for the electron liquid, RPA, STLS, C-A, VWN, EPX and the present interpolation method; C-A and VWN stand for the original values Ceperley and Alder obtained from the Green’s function Monte Carlo method (GFMC) and the values from an interpolation formula using their GFMC data, respectively; EPX stands for the effective potential expansion method proposed by Takada.

The approximation method of replacing $\bar{g}(r, r')$ in the exact formula for $E_{xc}$ in Eq. (35) by its analogue of the uniform electron liquid has been proposed by a number of authors [71, 72, 73, 74, 75, 76]. This method has the merit of giving the nonlocal effect of exchange functions in a local density. In this case it will be appropriate to approximate $\bar{g}(r, r')$ by $\bar{g}(r - r')$ at the neighboring position $r'$ of $r$. As for the density parameter to be used in the function $\bar{g}(r - r')$ of the electron liquid, we think that the uniform electron density in the interstitial region outside muffin-tin spheres for metals or the averaged density of the system as a whole is rather better than the local density. In this case it will be appropriate to approximate the functional derivative $\delta \bar{g}(r - r')/\delta n(r)$ as $\delta (r - (r' + r''))/2)\delta \bar{g}(r' - r'')/dn$ where $\delta \bar{g}(r' - r'')/dn$ should be evaluated at the same density parameter as in $\bar{g}(r - r')$.

F. Some criticisms on the interpolation

Finally, we offer some criticisms of the present interpolation method for its possible development in the future. We have first interpolated between long-range correlation in the RPA and short-range correlation in the particle-particle ladder approximation in Sec. III C and then allowed self-consistently for the exchange correction together with its feedback effect on the direct interaction by iteration in Sec. III D. Once the local field factor from short-range Coulomb repulsion $C(q)$ introduced in Sec. III C is given, there is no problem in the present method of evaluating the exchange correction; the local field factor from exchange $G(q)$ is uniquely determined.

The present theory depends on the accuracy of the starting interpolation, i.e., the local field factor from short-range Coulomb repulsion $C(q)$. One of the authors (H.Y.) [51] gave an analytic solution to the ladder interaction $I(p, p'; q)$ averaged over $p$ and $p'$ within the Fermi sphere. We have employed this analytic solution for the determination of the factor $C(q)$ primarily for $q > p_F$ and made a smooth extrapolation to smaller wavenumbers assuming an appropriate form quadratic in the limit $q \to 0$.

There remains some arbitrariness in the choice of the local field factor $C(q)$ around intermediate wavenumbers. Those proper polarization functions of the direct type $\pi_0(q, \omega)$ which involve second- and higher-order particle-particle ladder interactions make the predominant contribution to $S^{++}(q)$ and $S^{++}(q)$ for intermediate and large wavenumbers. It should, however, be pointed out that those proper polarization functions of the same direct type which involve particle-hole and hole-hole ladder interactions can make an appreciable contribution for intermediate wavenumbers (see (3h) and (3j) in Fig. 1). By its strict definition, the local field factor from short-range Coulomb repulsion $C(q)$ should be determined from all the proper polarization functions of the direct type $\pi_0(q, \omega)$.

Since the first attempt by Hubbard [14, 15], a number of interpolation methods have been proposed with the local field correction to the RPA for the study of the electron liquid in the region of metallic densities. The present theory is the most sophisticated among these attempts. Here we have managed to circumvent the treatment of multi-pair excitations [22, 23] by evaluating the coupling-constant-averaged static structure factor $\bar{S}(q)$ instead of the static structure factor $S(q)$. If one starts with $\bar{S}(q)$ in his interpolation, one cannot avoid treating multi-pair excitations and thereafter has to perform the integral over the coupling constant to enumerate correctly the many-body perturbation terms involving particle-particle ladder interactions. Instead, we have started with the exact ground state energy contribution from an infinite series of particle-particle ladder diagrams in order to interpolate between the RPA and the ladder approximation in the form of the coupling-constant-averaged static structure factor $\bar{S}(q)$.

IV. ORBITAL-DEPENDENT CORRELATION ENERGY FUNCTIONAL

A. Orbital-dependent exchange energy functional

According to the optimized-effective-potential method (OEP) [8] in DFT, the ground state energy functional of many-electron systems can be written as

$$
E_g = \sum_{i=1}^{N} \int d\varphi_i^*(r) \left( -\frac{\hbar^2}{2m} \nabla^2 \right) \varphi_i(r) + \int drv_{\text{ext}}(r)n(r) + \frac{1}{2} \int dr \int dr' \frac{n(r)n(r')}{|r - r'|} - \frac{1}{2} \sum_{i,j} \int dr \varphi_i^*(r)\varphi_j^*(r')\varphi_j(r)\varphi_i(r')|r - r'| + E_c(\{\varphi_i\})
$$

(42)
The first term is the kinetic energy functional of the reference noninteracting system with the same electron density \( n(r) \) as the real system; this term is usually denoted by \( T_0 \). The second is the electron-nucleus interaction energy functional. The third and the fourth are the Hartree and the exchange energy functionals, respectively. The exchange energy functional \( E_x[\{\varphi_i\}] \) is represented as an explicit functional of Kohn-Sham orbitals and hence \( E_x[\{\varphi_i\}] \) is an implicit functional of the electron density \( n(r) \); \( i \) and \( j \) have the same spin orientations. The sum of the third and fourth terms amounts to the electron-electron interaction energy partially confined in DFT amounts to the net correlational lowering the reference noninteracting system as

\[
\delta E \equiv \delta E[n]/\delta n(r) = 0 \quad \text{can be expressed in terms of a self-consistent set of Kohn-Sham equations describing the reference noninteracting system as}
\]

\[
\left\{ -\frac{\hbar^2}{2m} \nabla^2 + v_s(r) \right\} \varphi_i(r) = \epsilon_i \varphi_i(r),
\]

\[
v_s(r) = v_{ext}(r) + v_H(r) + v_x(r) + v_c(r),
\]

\[
v_H(r) = \int d\mathbf{r}' \frac{n(r')}{|r - r'|},
\]

\[
n(r) = \sum_i |\varphi_i(r)|^2,
\]

where \( v_s(r) \) denotes the total single electron potential; \( v_{ext}(r) \) is the Coulomb potential from the nuclei and \( v_H(r) \) is the Hartree potential; \( v_x(r) \) and \( v_c(r) \) denote the exchange and the correlation potentials defined by \( v_x(r) = \delta E_x[\{\varphi_i\}]/\delta n(r) \) and \( v_c(r) = \delta E_c[\{\varphi_i\}]/\delta n(r) \), respectively.

In this subsection we mention only the exchange energy functional \( E_x[\{\varphi_i\}] \) and its functional derivative \( v_x(r) \) since it is a starting point fundamental to the introduction of an orbital-dependent correlation energy functional in DFT. An excellent review on the theoretical treatment of an orbital-dependent correlation energy functional in DFT and its numerical results for atoms, molecules and solids has recently been given by Grabo, Kreibich, Kurth and Gross.

If one employs the orbital-dependent exchange energy functional, one has to evaluate \( v_x(r) \) as follows:

\[
v_x(r) = \delta E_x[\{\varphi_i\}]/\delta n(r) = \sum_i \int d\mathbf{r}' d\mathbf{r}'' \left\{ \delta E_x[\{\varphi_i\}] \frac{\delta \varphi_i(r')}{\delta \varphi_i(r'')} + c.c. \right\} \frac{\delta v_x(r'')}{\delta n(r)},
\]

where \( \delta v_x(r')/\delta n(r) \) is the inverse of the static density response function of the reference noninteracting system, \( \chi^{-1}(r, r') \). The functional derivative \( \delta \varphi_i(r')/\delta v_x(r') \) and the response function \( \chi(r, r') \) can both be expressed in terms of Kohn-Sham orbitals and Kohn-Sham energies. After a few manipulations one can obtain the integral equation which determines the exchange potential \( v_x(r) \).

\[
\begin{align*}
&\sum_i \int d\mathbf{r}' \left\{ \varphi_i^+(r') G_{si}(r', r) \varphi_i(r) + c.c. \right\} v_x(r') \\
&= \sum_i \int d\mathbf{r}' \left\{ \varphi_i^+(r') \frac{1}{\varphi_i(r')} \delta E_x[\{\varphi_i\}] G_{si}(r', r) \varphi_i(r) + c.c. \right\},
\end{align*}
\]

\[
G_{si}(r, r') = \sum_{i, j} \infty \varphi_j(r) \varphi_i^+(r') \epsilon_i - \epsilon_j.
\]

It is straightforward to generalize this integral equation to include the correlation potential \( v_c(r) \) as well if an orbital-dependent correlation energy functional \( E_c[\{\varphi_i\}] \) is available.

An alternative method can lead to the same integral equation for the exchange-correlation potential \( v_{xc}(r) = v_x(r) + v_c(r) \). Consider the ground state energy functional \( E_g \) in Eq. (42) under the condition that \( \varphi_i(r) \)'s are the solutions of Eq. (44) with an unknown one-electron potential \( v_s(r) \). Then, \( E_g \) can be considered to be a functional of \( v_s(r) \) and there arises a variational problem of how to optimize \( v_s(r) \) in the minimization of \( E_g \), i.e., \( \delta E_g[v_s(r)]/\delta v_s(r) = 0 \). The potential \( v_s(r) \) thus calculated is named the optimized-effective-potential (OEP). From this optimization one can also derive the same integral equation that we have just mentioned above. Hence it is termed the OEP integral equation. In fact, the optimization \( \delta E_g[v_s(r)]/\delta v_s(r) = 0 \) is equivalent to the Hohenberg-Kohn variational principle \( \delta E_g[n(r)]/\delta n(r) = 0 \). We summarize the conclusions obtained from the so-called exchange-only OEP method in the following:

1. The exchange-only OEP method gives the exact exchange potential \( v_x(r) \) that completely cancels the self-interaction terms involved in the Hartree potential.
2. The derivative discontinuity in \( E_x[\{\varphi_i\}] \), or the discontinuity of \( v_x(r) \) can be correctly described.
3. The Hartree-Fock ground state energy in the framework of DFT is by only a slight amount higher than the usual Hartree-Fock ground state energy. This is because in DFT the additional condition of a local form is imposed on the exchange potential in the minimization of the same ground state energy functional.
4. Instead, the electron density \( n(r) \) calculated from DFT might be by only a slight amount better than the one calculated from the usual Hartree-Fock theory owing to the variational principle.

However, it is important to recognize that the exchange-only OEP integral equation is identical to the
Fock theory significantly distorts the electron density of its essential properties are kept unchanged. The integral equation in which the complexity of the original have proposed a simple approximate solution to the OEP to the exchange potential, Krieger et al (KLI) [81, 82, 83] in the SUHF. Along the spirit of the Slater approximation it is evident that the difference in the electron density \( n(r) \) between the two methods will be only a slight amount just like the difference in the ground state energy.

(5) Li, Krieger and Iafrate [79] have applied the exchange-only spin-unrestricted OEP method to atoms \((Z=3\sim56\text{(Li}\sim\text{Ba)}, 79\text{ and } 80\text{ (Au and Hg)})\) to make a comparison with the spin-unrestricted Hartree-Fock method (SUHF). Their calculations are very accurate; the virial theorem and the related identity \((V_{ee} + \int r \partial v_e(r) \cdot \text{grad} v_e(r) = 0)\) for the exchange energy functional \(E_x(= V_x)\) and the exchange potential \(v_e(r)\) due to Levy and Perdew [84] are satisfied to four or five significant figures.

The ground state energy calculated from the exchange-only OEP method is at most by 40ppm higher than that from the Hartree-Fock method and the difference decreases with increasing Z. They report that the electron density \(n(r)\) calculated from the exchange-only spin-unrestricted OEP method is close to the SUHF value. Interestingly, they observe a few reversals of the order of the state yielding the highest occupied eigenvalue between the ns and \((n-1)d\) states in the transition series of atoms. The Kohn-Sham exchange potential \(v_e(r)\) always raises the energy levels of the inner shell states compared with those of the SUHF; the same trend can also be seen from a comparison between the Hartree-Fock energy levels of occupied states of the electron liquid and the corresponding Kohn-Sham energy levels. The reversals occur only when the ns and \((n-1)d\) energy levels are very close in the SUHF. Along the spirit of the Slater approximation to the exchange potential, Krieger et al (KLI) [81, 82, 83] have proposed a simple approximate solution to the OEP integral equation in which the complexity of the original OEP integral equation is significantly reduced but many of its essential properties are kept unchanged.

(6) Buijse and Baerends [84] write that the Hartree-Fock theory significantly distorts the electron density distribution \(n(r)\) of atoms to the extent that often the largest absolute errors in the total Hartree-Fock energy occur for the electron-nucleus interaction energy and the kinetic energy rather than for the electron-electron interaction energy and that the Slater approximation for the exchange potential gives rather better results for the electron density \(n(r)\) of atoms. However, the largest relative error, i.e., the largest ratio of each error to the corresponding Hartree-Fock value probably will occur for the electron-electron interaction energy.

(7) Hartree-Fock calculations make higher 4s orbitals occupy prior to lower 3d orbitals in 3d transition atoms. This reversal of the occupied states has been supposed to be ascribed to the variational principle \(\delta E_{\text{HF}}^{\text{ex}}(\{\varphi_i\})/\delta \varphi_i = 0\). The reversal has been interpreted to be a consequence of the strategy that the total energy will not be raised due to the electron-electron interaction energy in \(E_{\text{HF}}^{\text{ex}}(\{\varphi_i\})\). On the other hand, no reversal of occupied states should occur if one accurately solves the exchange-only OEP integral equation in DFT. This is because Kohn-Sham equations by definition are intended for the reference non-interacting system. This problem may be closely related to the central field approximation conventionally applied to atoms. However, no systematic method has yet been developed to solve the OEP integral equation appropriately for a nonspherically symmetric system. Strictly, the degeneracy of 3d or 4d orbitals should be lifted for lack of spherical symmetry and ns and \((n-1)d\) orbitals should be mixed as a result.

(8) As for the energy gap of semiconductors, the exchange-only OEP method gives a good result [77, 85].

(9) Strictly, the Hartree-Fock theory and its density-functional version by the x-only OEP method generally give different results of the ground state energy \(E_g\), the electron density \(n(r)\) and the ionization potential \((or)\) the chemical potential \((or)\); for the uniform electron liquid the two give the same result of these quantities.

B. Correlation-induced reconstruction of Kohn-Sham orbitals

In this subsection we propose an explicitly orbital-dependent correlation energy functional beyond the Hartree-Fock approximation for the study of the electronic structure in atoms, molecules and solids in DFT. It is to be employed in combination with the orbital-dependent exchange energy functional.

In Sec.III we have defined a new expression for the correlation energy of the electron liquid. It is a modification of second-order perturbation terms, in which one of the two Coulomb interactions in each term is replaced by an effective interaction containing information about long-, intermediate-, and short-range correlations. Similarly, we propose here a second-order perturbation like expression [87] which is constructed from Kohn-Sham orbitals, Kohn-Sham energies, and the effective interaction borrowed from the electron liquid.
where $i,j$ and $a,b$ represent occupied and unoccupied Kohn-Sham states, respectively and the states $i,j$ in the second-order exchange like term have the same spin orientations; $v(r_{12})$ is the Coulomb interaction for $r_{12} = |r_1 - r_2|$. The effective interaction $v_{\text{eff}}(r_{12})$ in Eq. (43) is the real-space Fourier transform of the interaction $v_{\text{eff}}(q)$ we have evaluated for the electron liquid in Sec.III. How to choose in practical calculations the density parameter for the effective interaction we borrow from the electron liquid will be discussed in detail in Sec. IV C.

Here we note that a fully orbital-dependent correlation energy functional, or equivalently an orbital-dependent effective interaction in the present scheme can in principle be obtained if one follows the same procedure as in the electron liquid with Kohn-Sham orbitals and Kohn-Sham energies in place of planewaves and free electron energies.

From a comparison with a general expression for the exchange-correlation energy functional using the coupling-constant-averaged pair correlation function $\tilde{g}(\mathbf{r}, \mathbf{r'})$ (see Eq. (43)) it may be naturally expected that the present correlation energy functional has also the effect to reduce the Hartree-Fock electron-electron interaction energy in its contributions from short distances. Let us characterize the present orbital-dependent correlation energy functional.

(1) The exact many-electron wavefunction fulfills the requirement of antisymmetry. In accordance with this antisymmetry, the electron-electron interaction energy functional in DFT should be constructed from direct and exchange pairs of terms. The present orbital-dependent correlation energy functional as well as a direct and exchange pair of electron-electron interaction energy functionals in the Hartree-Fock approximation reflects the requirement of antisymmetry.

(2) In the limit of uniform density the present theory is reduced to the local density approximation (LDA) as it should be. The self-interaction terms involved in the Hartree energy are exactly cancelled by the orbital-dependent exchange energy functional. Furthermore, higher-order self-interaction terms are, from the beginning, eliminated from the present $E_{\text{c}}(\{\varphi\})$ since it consists of a direct and exchange pair of terms. Therefore the present theory is completely free from self-interaction errors. This is indispensable for the treatment of exchange and correlation between electrons with localized orbitals. The LDA estimates the location of the occupied 3d-bands in copper and zinc too highly because of self-interaction errors. The overestimation as large as about 18% in the neck cross section of the Fermi surface of copper in the [111] direction, which is considered to be ascribed to the too high 3d-bands in the LDA, will be for the most part improved by removing self-interaction errors.

(3) One of the remarkable merits of the present theory is that the physical meaning of correlation is clarified by the present representation of the functional $E_{\text{c}}(\{\varphi\})$. According to the virial theorem, the correlation energy of atoms, molecules and solids under no constraint of any external force amounts to a half of the lowering in the total potential energy since it is by half cancelled by the correlational increase in the kinetic energy. In this sense the partitioning of the ground state energy functional in DFT is helpful in understanding the meaning of the correlation energy since it is an exact many-body theory assuming the self-consistent one-electron formalism. The total potential energy consists of three terms. The first is the electron-electron interaction energy and the second the electron-nucleus interaction energy. The third is the nucleon-nucleus interaction energy. Usually, the first and second potential energies are both lowered at the cost of increasing the corresponding two kinetic energies, $T_e$ and $T_n$. Here we assume the Born-Oppenheimer approximation.

It is important to notice that correlation usually changes the magnitude of the nucleon-nucleus interaction energy from its Hartree-Fock value. The Hartree-Fock approximation regularly underestimates the equilibrium length between the nuclei in molecules. The LDA that borrows knowledge of the exchange-correlation energy from the uniform electron liquid has a tendency to underestimate the Wigner-Seitz radius of metals or the lattice constant of solids. Probably, these shortcomings will be closely related to the fact that both approximations overestimate the screening of the nuclei at short distances.

By definition, the functional $E_{\text{c}}(\{\varphi\})$ in DFT represents the net lowering of the electron-electron interaction energy partially cancelled by the correlational increase in the kinetic energy $T_e$. From a comparison with the Hartree-Fock total energy functional it is evident that
the direct term in Eq. (15) has the effect to reduce the Hartree energy and its exchange counterpart has the effect to reduce in magnitude the exchange energy in a well-balanced way through the same effective interaction \( v_{ef}(r) \) that contains accurate information about long-, intermediate-, and short-range correlations beyond second-order perturbation theory.

Furthermore, it is important to recognize that the presence of \( E_c(\{\varphi_i\}) \) in the total energy functional not only has the effect to reduce the net electron-electron interaction energy in its contributions from short distances but also causes a change in the electron density \( n(r) \) such that the total energy is further stabilized by a lowering in the only negative energy, i.e., the electron-nucleus interaction energy though it inevitably increases the kinetic energy of the reference non-interacting system \( T_e \). The partitioning of the ground state energy functional in DFT has the merit of connecting the net lowering in the electron-electron interaction energy (in its contributions from short distances) with the further lowering in the electron-nucleus interaction energy through Kohn-Sham equations that minimize the total energy functional.

(4) The present theory is expected to give an accurate evaluation of the correlation energy even of the most localized electrons such as atomic electrons in which the LDA makes the most serious errors because of its failure to cancel self-interaction terms and its overestimation of the correlation energy. Then we may expect that the present \( E_c(\{\varphi_i\}) \) is valid for tightly binding electrons as well as for nearly free electrons. These two different types of electrons are both participating in the cohesion of transition metals. An accurate evaluation of the ground state energy of atoms, molecules and solids may be generally expected from the present theory if the density parameter for the effective interaction borrowed from the electron liquid is suitably chosen. The optimization of the density parameter will be discussed in detail in Sec. IV C.

(5) One of the greatest merits of DFT lies in the fact that one can describe all correlation effects on one-electron states with the local correlation potential \( v_c(r) \) in the framework of self-consistent one-electron theory, without being troubled with the treatment of the non-local, energy-dependent, and complex self-energy operator involving many-body background excitations. This merit is acquired only when accurate information about the potential \( v_c(r) \) is available. The total single electron potential \( v_s(r) \) in Kohn-Sham equations determines the electron density \( n(r) \) of the system. Its accuracy depends entirely on the exchange-correlation potential \( v_{xc}(r) \). The exchange potential \( v_x(r) \) can be exactly treated by the exchange-only OEP method. Consider what effect the correlation potential \( v_c(r) \) has on the electron density \( n(r) \) of the system.

The correlated motion of valence electrons in solids, though it inevitably increases the kinetic energy, more lowers the electron-electron interaction energy in its contributions from short distances. The simultaneous change in the electron density \( n(r) \), i.e., the shrinkage of the electron distribution around the nuclei arising from less screening of the nuclei due to short-range correlation, further lowers the only negative electron-nucleus interaction energy at the cost of increasing the kinetic energy of the reference non-interacting system \( T_e \). Then the lowest possible ground state energy is realized such that the nucleus-nucleus interaction energy is lowered by somewhat increasing the lattice constant as a counteraction of the shrinkage of the electron distribution around the nuclei and the increase in \( T_e \) is to some extent relaxed accordingly.

Thus, correlation in real solids is necessarily accompanied by a change in the electron density \( n(r) \) in contrast with the case of the uniform electron liquid. It may be generally expected that correlation induces inhomogeneity in the electron density distribution \( n(r) \) of the system against the Hartree-Fock approximation in DFT.

In the neighborhood of individual nuclei of the system, the total single electron potential \( v_s(r) \) in Kohn-Sham equations can be written in terms of the coupling-constant-averaged pair correlation function \( \tilde{g}(r, r') \) as

\[
v_s(r) = -\frac{Ze^2}{|r|} + \int dr' \frac{n(r')}{|r - r'|} \left\{ \tilde{g}(r, r') - 1 \right\} + \frac{1}{2} \int dr'dr'' \frac{n(r')n(r'')}{|r' - r''|} \frac{\delta\tilde{g}(r', r'')}{\delta n(r)}.
\]

(51)

The screening of individual nuclei at short-, intermediate-, and long-distances can be properly described by the second and third terms; for isolated systems like atoms these two terms give the correct asymptotic form \( v_s(r) = -e^2/r \) for large \( r \) since the following sum rule holds:

\[
\int dr'n(r') \left\{ \tilde{g}(r, r') - 1 \right\} = -1.
\]

(52)

The last term in Eq. (51) probably will not give a significant \( r \)-dependence for any \(|r|\) and plays a background-like role in \( v_s(r) \) since the integrand including the functional derivative \( \delta\tilde{g}(r', r'')/\delta n(r) \) is integrated over \( r' \) and \( r'' \). Consider the physical role of \( \tilde{g}(r, r') \) in the sum of the second and third terms when the distance \(|r - r'|\) is decreased. Since the inequality that \( 0 < \tilde{g}(r, r') < 1/2 \) holds for \(|r - r'|\) less than the average inter-electron separation, it is evident that the Hartree or Hartree-Fock screening of individual nuclei is significantly reduced at short distances due to the presence of \( \tilde{g}(r, r') \). In other words, short-range correlation yields less screening of the attractive nuclear potential at short distances. It is this less screening of the nuclear potential that shrinks the electron distribution in the vicinity of the nuclei to enhance the electron density \( n(r) \) at the positions of individual nuclei.

If \( r \) and \( r' \) are both in the interstitial region outside muffin-tin spheres of metals, the function \( \tilde{g}(r, r') \) is very well approximated by the corresponding function of the
uniform electron liquid we have calculated in Sec. III E
and hence causes no change in the electron density. On
the other hand, if \( \mathbf{r} \) and \( \mathbf{r}' \) are both inside a muffin-tin
sphere, the probability of \( \tilde{g}(\mathbf{r}, \mathbf{r}') \) is concerned with not
only valence electrons but also core electrons. The mag-
nitude of \( \tilde{g}(\mathbf{r}, \mathbf{r}') \) at short separations within the muffin-
tin sphere is less than 1/2 due to short-range correla-
tion, though it may be somewhat greater than in the
interstitial region. Short-range correlation in this essen-
tially nonuniform density region reduces the Hartree or
Hartree-Fock screening of the nuclei and hence causes the
shrinkage of the electron density distribution around the
nuclei to lower the electron-nucleus interaction energy
more than its Hartree-Fock value.

(6) Most importantly, the present orbital-dependent
correlation energy functional \( E_c[\{\varphi_i\}] \) hybridizes
Hartree-Fock Kohn-Sham orbitals in order to produce self-consistently reconstructed Kohn-Sham orbitals
through its functional derivative \( \delta E_c[\{\varphi_i\}]/\delta n(\mathbf{r}) \),
i.e., the correlation potential \( v_c(\mathbf{r}) \). Naturally, this
correlation-induced reconstruction of Kohn-Sham or-
bital gives a further stabilization of the ground state
energy as well as a redistribution of the electron density
\( n(\mathbf{r}) \) of the system. The present correlation potential
\( v_c(\mathbf{r}) \) is expected to produce less screening of the
attractive nuclear potential at short distances to give a
shrinkage of \( n(\mathbf{r}) \) around individual nuclei, thereby
leading to a lowering in the electron-nucleus interaction
energy.

The Hartree-Fock approximation, in its original
version or its DFT version, overestimates the effect of
the electron-electron interaction on the screening of the
nuclei at short distances as well as the magnitude of the
electron-electron interaction energy. Variation of the ex-
pectation value of the total Hamiltonian within a sin-
gle Slater determinant overestimates the influence of
the interaction on occupied orbitals in the form of self-
consistent Coulomb and (nonlocal or local) exchange po-
tentials. The Hartree-Fock orbitals are then spread too
far away from the nuclei and hence the kinetic and the
electron-nucleus interaction energies in this approxima-
tion are both underestimated in magnitude.

From these peculiarities it is evident that this approxi-
mation tends to underestimate nucleus-nucleus separa-
tions in order to get a sufficient lowering in the only
negative electron-electron interaction energy for the sta-
bilization of molecules. There are some cases such as
\( \text{F}_2 \), in which the Hartree-Fock approximation is unable
to stabilize molecules and the redistribution of the elec-
tron density due to correlation is indispensable to the
formation of molecules.

The LDA is exact in the limit of uniform density but,
when applied to nonuniform electronic systems, it cannot
describe properly such exchange-correlation effects as are
peculiar to nonuniform systems. The most important of
these effects is correlation-induced less screening of the
nuclei at short distances. The LDA tends to underesti-
mate the lattice constant of solids for lack of this effect
and furthermore tends to overestimate the magnitude of
the cohesive energy because of a rather too uniform spa-
tial variation of the exchange-correlation potential \( v_{xc}(\mathbf{r}) \).
Notice that the LDA considerably smooths out the spa-
tial variation of \( v_{xc}(\mathbf{r}) \) since it borrows the knowledge of
\( \mu_{xc}(n(\mathbf{r})) \) from the uniform electron liquid; \( \mu_{xc}(n(\mathbf{r})) \) is
the exchange-correlation contribution of the chemical po-
tential of the uniform electron liquid appropriate for the
electron density \( n(\mathbf{r}) \).

(7) On the basis of the virial theorem and his own
partitioning of the total energy, Ruedenberg has gained
a profound insight into the binding nature of molecules
[89, 90]. He has emphasized that the binding of molecules
or the cohesion of solids (including metals) is essentially
stabilized by shrinking the electron density distribution
in the immediate vicinity of the nuclei to enhance the
electron density \( n(\mathbf{r}) \) at the positions of individually isolated
atoms.

According to Moruzzi, Janak and Williams [9], on the
other hand, the electron density in simple metals is re-
versely reduced in the immediate vicinity of the nuclei.
This is because the LDA fails to give the proper descrip-
tion of the correlation-induced less screening of individ-
ual nuclei at short distances. In the LDA the Hartree
screening of the nuclear potential is simply shifted by
an amount of \( \mu_{xc}(n(\mathbf{r})) \). The density dependence of
\( \mu_{xc}(n(\mathbf{r})) \) appropriate for the electron liquid is abso-
lutely insufficient for describing the correlation-induced
less screening of nuclei. It is beyond the scope of the
LDA since the electron density \( n(\mathbf{r}) \) in the vicinity of the
nuclei in metals is far from being slowly varying.

The present theory is promising for the realization of
the enhancement of the electron density in the vicinity
of the nuclei as a consequence of less screening of the
nuclear potential. This is because the present \( E_c[\{\varphi_i\}] \)
involve all unoccupied excited states that are needed to
redistribute the electron density \( n(\mathbf{r}) \) in this region; the
resulting \( v_c(\mathbf{r}) \) is expected to have much larger negative
values than the LDA correlation potential in this region.

Kohn-Sham one-electron states have to be recon-
structed while atoms condense into solids. We think that
the reconstruction of Kohn-Sham one-electron states asso-
ciated with the cohesion of solids can also be well de-
scribed by the present correlation energy functional pro-
vided the density parameter in the effective potential is
appropriately chosen.

In connection with the considerations above we men-
tion a noteworthy fact. According to Boyd and his cowor-
kers [91, 92, 93], Hund’s multiplicity rule can be as-
cribed to a gain in the electron-nucleus potential en-
ergy caused by correlation-induced less screening of the
nuclei in contrast with the traditionally accepted inter-
pretation due to the exchange energy. On the contrary,
the electron-electron interaction energy is greater in a high
spin state for all neutral atoms and molecules calculated
with requisite accuracy. They have arrived at this con-
clusion from accurate configuration interaction calcula-
tions of low-lying excitation energies of light atoms and
molecules, in which the virial theorem is of course satisfied.

(8) There is a strong possibility that the electronic structure of the so-called strongly correlated electron systems may be interpreted in terms of the correlation-induced reconstruction of Kohn-Sham orbitals. The energy-band structure of solids calculated in the LDA is approximately equivalent to the band-structure that is calculated in the Hartree approximation and shifted to the low energy side by an amount of \( \mu_{xc} \) of the uniform electron liquid with the averaged electron density of solids. In marked contrast to the LDA, the present orbital-dependent correlation energy functional hybridizes Hartree-Fock Kohn-Sham one-electron states with different orbital characters, particularly in the neighborhood of the Fermi level or the energy gap, in order to produce self-consistently reconstructed Kohn-Sham one-electron states. The occurrence of such reconstruction of one-electron states is peculiar to non-uniform real systems, quite absent in the uniform electron liquid which consists of electrons with the same character.

Consider the energy denominator in the present \( E_{ee}(\{\varphi_i\}) \). Evidently, the functional \( E_{ee}(\{\varphi_i\}) \) can gain its magnitude if the density of states is sharply enhanced in the immediate neighborhood of the Fermi level under the influence of self-consistently reconstructed Kohn-Sham energies. Such an enhancement in the density of states should be accompanied by a considerable change in the electron density \( n(r) \) particularly for strongly anisotropic systems.

Our scenario of heavy fermions is as follows: As a consequence of strong hybridization between conduction electrons and f electrons, the occupied and unoccupied states will probably be reconstructed such that they enhance the density of states in the immediate neighborhood of the Fermi level as sharply as possible in order to gain the magnitude of the functional \( E_{ee}(\{\varphi_i\}) \), which is balanced against a simultaneous increase in the kinetic energy of the reference non-interacting system.

For the study of the electronic structure of heavy fermion systems it is of course indispensable to adopt the fully relativistic one-electron Dirac equations \( \Phi \) in the framework of DFT.

(9) Almbladh and von Barth \cite{96} have studied the relations between Kohn-Sham eigenvalues and exact excitation energies. From exact asymptotic results for the spin density far away from a finite system, they have shown that the uppermost Kohn-Sham eigenvalue equals the ionization potential, not only for extended systems but also for finite systems like solids, but also for finite systems like atoms.

From available accurate wavefunctions for a number of light atoms (the He isoelectronic series, Li and Be), Almbladh and Pedroza \cite{96} have constructed \( E_{ee}, v_{ee}(r) \) and \( v(r) \) to evaluate the Kohn-Sham eigenvalues. They have then found that the uppermost (or highest occupied) Kohn-Sham eigenvalue reproduces the exact ionization potential and that the eigenvalues for deeper shells lie above the corresponding exact excitation energies, while the Hartree-Fock eigenvalues lie below.

The correlation potential \( v_e(r) \) they have constructed for He, Li\(^+\) and Be\(^{++}\) takes large negative values in the immediate vicinity of the nucleus reflecting that the exact electron density is slightly higher than the Hartree-Fock value in this region and on the other hand becomes positive at large \( r \) from the nucleus, forms a broad peak and tends to zero with increasing \( r \). This is quite different from the potential \( v_e(r) \) in the LDA since it is always negative and increases monotonically with increasing \( r \).

Generally, the Koopmans theorem gives a fairly good evaluation of the ionization potential for atoms and molecules, though Hartree-Fock eigenvalues take no account of both correlation and relaxation \cite{97}. This is because a great amount of cancellation occurs between the extra correlation energy of the \( N \)-body ground state relative to the \( (N-1) \)-body excited state and the relaxation energy (which is also a kind of correlation energy) of the \( (N-1) \)-body excited state produced by removing an electron from the Hartree-Fock \( N \)-body ground state.

This cancellation is not complete, however, and the Koopmans theorem usually overestimates the ionization potential, or equivalently the Hartree-Fock theory tends to evaluate the highest occupied eigenvalue (negative) too low. This implies that the relaxation energy is usually somewhat larger than the extra correlation energy in magnitude; for much localized orbitals like the He atom it is so large that the Koopmans theorem cannot be applied. Thus, the correlation correction to the ionization potential is usually negative for molecules; the Hartree-Fock Kohn-Sham equations with the optimized local exchange potential will lead to the same conclusion. The presence of nuclei in atoms and molecules is responsible for the occurrence of relaxation. If an electron is removed, the remaining \( N-1 \) electrons have to readjust themselves to the attractive nuclei.

It is very reasonable that the correlation potential \( v_e(r) \) for He, Li\(^+\) and Be\(^{++}\) takes positive values at large distances from the nucleus if one considers that the expectation value of \( v_e(r) \) with respect to the highest occupied state has to give a correction with the positive sign.

On the other hand, the solutions of Hartree-Fock or Hartree-Fock Kohn-Sham equations for the uniform electron liquid are plane waves and hence there occur no relaxation of orbitals. Then, only the extra correlation energy is missing in this case. The correlation contribution to the chemical potential, \( \mu_e \) for the uniform electron liquid is thus negative. \cite{98,99}

Averill and Painter \cite{98,99}, and Levy and Perdew \cite{80} have given an expression for the virial theorem in terms of density-functional theory. Their expression for the virial theorem at the equilibrium positions of the nuclei is split into two parts, i.e., the reference one-electron (non-interacting) and the correlational parts.

\[ 2T_e + V_{ee} + \int d\rho_e(r) \cdot \text{grad}v_e(r) = 0. \] (53)

This is the correlational part of the virial theorem that
relates also to atoms, molecules and solids. It vanishes to second order in particle states with opposite spins makes a contribution \(2T_c + V_{ee}^c\). This equation is helpful to discuss the general shape of \(v_c(r)\).

Let us first consider the quantity \(2T_c + V_{ee}^c\) in Eq. (53). It vanishes to second order in \(e^2\) for atoms and molecules. It also vanishes for the electron liquid in the high density region where the correlation energy is given by the leading logarithmic and the subsequent constant terms. Consider the contribution to \(2T_c + V_{ee}^c\) from very large momentum transfer interactions in the electron liquid at metallic densities, or very short-range parts of the Coulomb interaction. It also vanishes since the relation \(2T_c + V_{ee}^c = 0\) holds for this case [54]. The reason for this cancellation is that the particle-particle ladder interaction \(J(p,p';q)\), or multiple scattering between two particle states with opposite spins makes a contribution to both \(T_c\) and \(V_{ee}^c\) in a way analogous to second-order perturbation theory. This type of cancellation between \(2T_c\) and \(V_{ee}^c\) associated with short-range correlation, applies also to atoms, molecules and solids.

From these considerations, \(2T_c + V_{ee}^c\) is a rather small but negative quantity. It is negative for the electron liquid at metallic densities. Second-order perturbation theory for atoms and molecules, by which \(2T_c + V_{ee}^c\) vanishes, tends to overestimate the magnitude of the correlation energy and hence the total higher-order contribution to \(2T_c + V_{ee}^c\) is expected to be negative. We may then conclude from Eq. (53) that the integral \(\int d\mathbf{r} n_c(r) \cdot \mathbf{grad} v_c(r)\) is a small positive quantity for atoms, molecules and solids (including metals).

Correlation changes the electron density \(n(r)\) in atoms, molecules and solids. The correlation potential \(v_c(r)\) is responsible for this change in \(n(r)\). Short-range correlation rectifies the overestimated screening of the nuclei in the Hartree- or Hartree-Fock approximation and enhances the electron density \(n(r)\) in the immediate vicinity of the nuclei as a result. Correspondingly, the potential \(v_c(r)\) takes large negative values in this region. As the distance from the nucleus \(r\) increases, the value of \(v_c(r)\) increases with a steep positive slope. In order to conserve total electronic charge, the potential \(v_c(r)\) for an atom has to become positive for larger \(r\) from the nucleus, forms a broad peak and tends to zero with increasing \(r\). The correlation potential \(v_c(r)\) that Ahnbladh and Pedroza have constructed from a few accurate many-electron wavefunctions actually shows such a non-monotonic behavior.

Similarly, the correlation potential \(v_c(r)\) for metals will probably take large negative values in the immediate vicinity of each nucleus and steeply increase with the distance from the nucleus. It is expected to exceed \(\mu_s(r_s^*)\) (instead of zero) within the muffin-tin sphere as the distance from the nucleus \(r\) is increased, form a broad peak and tend to \(\mu_s(r_s^*)\) as \(r\) approaches the muffin-tin sphere radius; \(\mu_s(r_s^*)\) is the correlation contribution of the chemical potential of the uniform electron liquid with the density parameter \(r_s^*\) appropriate for the interstitial region of metals. It should be noted that the potential \(v_c(r)\) in the immediate vicinity of nuclei probably will take larger negative values for metals than for isolated atoms, reflecting that the electron density in this region should be enhanced under the influence of cohesion.

The tendency of the LDA to overestimate the cohesive energy of metals in magnitude and to underestimate the lattice constant of metals probably will be ascribed to the failure of its correlation energy functional to give the above nonmonotonic behavior of the correlation potential \(v_c(r)\) as well as to the failure of its exchange energy functional to cancel spurious self-interaction terms.

(10) The correlation energy defined in DFT, \(E_{cDFT}\), is in magnitude slightly larger than the usual correlation energy, \(E_c\) defined by the difference between the usual Hartree-Fock and the exact ground state energies (see IV A. (3)). According to the virial theorem, \(E_{cDFT} = -(T_s - T_s^{HF}) - T_c = (V_{ee} + V_{ee} + V_{ee}^c) - \frac{1}{2}(V_{ee} + V_{ee}^c)^{DHF}\) where \(V_{ee}\) is the total classical electrostatic energy that consists of the nucleus-electron, the Hartree, and the nucleus-nucleus interaction energies; \(V_{ee}\) and \(V_{ee}^c\) are the exchange and correlation contributions to the electron-electron interaction energy, respectively. The inequalities that \(T_s > T_s^{HF} > T_s^{HF}\) hold since two different virial theorems with the same formal expression are satisfied for the usual Hartree-Fock approximation and its density-functional version (see Eq. (27)). The quantity \(T_s^{HF}\) stands for the kinetic energy of the usual Hartree-Fock theory.

We give an explanation of the correlation energy defined in DFT, \(E_{cDFT}\). The first term, \(-(T_s - T_s^{HF})\) is the negative of an increase in the kinetic energy of the reference non-interacting system, which is primarily associated with a correlation-induced enhancement in the electron density in the immediate vicinity of nuclei, giving a correlational lowering in the nucleus-electron and nucleus-nucleus interaction energies. The second term, \(-T_c\), on the other hand, is the negative of an increase in the kinetic energy arising from the correlated motion of many electrons, which is primarily associated with a correlational lowering in the electron-electron interaction energy.

C. Density parameter appropriate for the effective interaction

In Sec. III B we have mentioned that a fully orbital-dependent correlation energy functional, or an orbital-dependent effective interaction can in principle be obtained if one makes a similar interpolation between long- and short-range correlations involving exchange effects with Kohn-Sham orbitals and Kohn-Sham energies in place of planewaves and free-electron energies for the electron liquid. At present, such a sophisticated interpolation is exceedingly difficult to perform. Instead, we borrow the knowledge of the effective interaction from
the electron liquid. In this case there arises a problem of how to choose the density parameter for the effective interaction. We must then resolve this problem to make the present theory applicable to practical calculations. For this purpose we adopt the following method.

Moruzzi, Janak and Williams [7] were the first who successfully applied DFT to energy-band calculations of metals with the atomic number less than 50 using the LDA. One of the most important conclusions they have obtained from their systematic study is that the compressibility of real metals. This general trend can be observed over a wide variety of metals covering simple, transition and noble metals. The value of the inverse compressibility 1/κ for transition metals is generally a good approximation to the compressibility of real metals. This general trend becomes divergent and the system can no longer be stable thermodynamically. This critical density corresponds to about rs = 5.25. It has been generally observed that the uniform electron density in the interstitial region of metals is somewhat enhanced in comparison with the averaged density of valence electrons as a whole. Let us describe the uniform electron density in the interstitial region by the effective density parameter rs*. Then, rs* < rs for almost all metals. The values of rs* for sodium, potassium, and rubidium are about 3.66, 4.36, and 4.67, respectively, while those of rs are 3.96, 4.87, and 5.18, respectively. For cesium with the lowest observable metallic density, the usual density parameter rs = 5.57 is beyond 5.25, but its effective density parameter rs* is considered to be less than 5.25.

In fact, the LDA has borrowed the knowledge of the exchange-correlation energy from the electron liquid beyond its applicability. One can practically calculate its ground state energy beyond the critical density resorting to a variety of approximation methods, but this does not imply that the system stays stable. According to many-body theoretic techniques, the exact theory should maintain the internal consistency between self-energy and vertex parts and fulfill the Pauli principle. Since the vertex part is closely related to the compressibility κ of the system, this internal consistency can no longer be maintained when it is divergent. In this sense the electron liquid is no longer stable for rs > 5.25.

In accordance with the situation above, we borrow the knowledge of the effective interaction from the electron liquid for rs < 5.25. A practical choice of the density parameter for the effective interaction probably will be the parameter rs* appropriate for the uniform electron density in the interstitial region of metals calculated from the LDA. The best choice of the density parameter is the optimization that minimizes the calculated ground state energy in the present theory as a function of the density parameter; rs* will be a good approximation to the optimized density parameter.

The present correlation energy functional borrows the effective interaction from the electron liquid. Therefore we have to treat separately the functional derivative δv_{eff}(r)/δn(r) when we solve the OEP integral equation in order to evaluate the exchange-correlation potential v_{xc}(r) = v_{x}(r) + v_{c}(r). An approximation appropriate for this purpose will be that δv_{eff}(r)/δn(r) = δ(r − r')dv_{eff}(r)/dn. The derivative dv_{eff}(r)/dn should be evaluated at the same density parameter as in the effective interaction v_{eff}(r).

So far we have discussed how to choose the density parameter for the effective interaction v_{eff}(r) when it is intended for use in metals. Originally, the knowledge of the correlation energy of the electron liquid should be applied to the study of the electronic structure of metals. The LDA, if applied to atoms, underestimates the exchange energy in magnitude by 14 ~ 8% and reversely overestimates the correlation energy by a factor of 2 ~ 2.5 [99, 100]. This is because the spurious self-interaction terms are not cancelled and because the correlation energy of the uniform electron liquid increases its magnitude like ln rs, Ry. per electron at high densities.

In reality, the correlation energy of atoms is in magnitude comparable with that of conduction electrons in metals, i.e., about 75 ~ 66 mRy. per electron. However, the ratio of the correlation energy to the exchange energy is an order of magnitude larger in conduction electrons than in atomic electrons; in atoms the accurate evaluation of the exchange energy is indispensable before the correlation energy is allowed for.

The present theory gives the exact evaluation of the exchange energy and moreover does not overestimate the correlation energy of atoms at all since it borrows the knowledge of the effective interaction from the electron liquid, not of the density dependence of the correlation energy. It should, however, be noted that the effective interaction v_{eff}(r) of the electron liquid, if applied to atoms, probably will lead to an underestimation at long distances. This is because the screening in atoms is not perfect in contrast to the electron liquid. If one defines the effective interaction properly for atoms in a similar way as in the electron liquid, the ratio of the Fourier transformed effective interaction v_{eff}(q) to the bare Coulomb should tend to a finite value of order 1/ε_0, not to zero in the limit q → 0 where ε_0 is the static dielectric constant of atoms. Fortunately, the small-wavenumber components of v_{eff}(q) are not expected to make an important contribution to the correlation energy.
of atoms since the predominant part of the correlation energy comes from virtual transitions to unoccupied localized orbitals with discrete spectra. Similarly, the ratio of the effective interaction properly defined for insulators and semiconductors should have a finite value in the limit \( q \to 0 \) owing to the presence of the energy gap.

On the other hand, no qualitative difference in the intermediate- and short-wavenumber components of \( HF \) is attached to the corresponding Hartree-Fock val-

To conclude, the best choice of the density parameter for the effective interaction in the present theory is the optimization that minimizes the calculated ground state energy as a function of the density parameter, irrespective of the difference between metals, insulators and atoms. It is noteworthy that in the limit of uniform density Kohn-Sham orbitals are reduced to plane waves and the resulting ground state energy in the present theory takes its minimum when the density parameter for the effective interaction amounts approximately to \( r_s = 4.2 \).

There is another method of choosing the density parameter for \( v_{\text{eff}}(r) \). It utilizes the reference one-electron part of the virial theorem in terms of DFT \[54, 61, 98\].

\[
2T_e + V_{ee} + V_{xc} - \int d\mathbf{r} n(\mathbf{r}) \mathbf{r} \cdot \nabla \psi(\mathbf{r}) = 0, \quad (54)
\]

where \( V_{ee} = V_{ee} + V_{eh} + V_{en} \) is the total classical electrostatic energy functional that consists of the nucleus-electron interaction energy \( V_{ne} \), the Hartree energy \( V_{eh} \) and the nucleus-nucleus interaction energy \( V_{nn} \); \( V_{xc} \) stands for the exchange energy functional \( V_{xc}^e = E_x \). The density parameter for \( v_{\text{eff}}(r) \) can in principle be determined from the requirement that Eq. (54) be satisfied. The minimization of the exact ground state energy expression and the virial theorem should be fulfilled simultaneously at the exact equilibrium inter-nucleus separation.

It should be noticed that the usual expression for the virial theorem, \( 2T + V = 0 \) can be obtained from Eqs. (54) and (55): \( T = T_e + T_s \) and \( V \) stands for the total potential energy of the system.

In the electron liquid with the neutralizing uniform positive background correlation shifts the equilibrium density parameter from \( r_s = 4.83 \) to 4.2. Correspondingly, the ground state energy is lowered from \(-0.095\) to about \(-0.154 \text{ Ry. per electron.} \) From the virial theorem with and without correlation it follows that \( 2(T - T^{HF}) + (V_{ee} - V_{ee}^{HF}) = 0 \) where \( T \) and \( V_{ee} \) are the exact kinetic and electron-electron interaction energies of the electron liquid, respectively; the superscript \( HF \) is attached to the corresponding Hartree-Fock values.

There is a second-order perturbation like relation \[54\] between large wave number components of \( T \) associated with the one-electron momentum distribution function \( n_k \) and those of \( V_{ee} \) associated with the static structure factor \( S(k) \) due to short-range correlation, i.e. \( 2T(k) + V_{ee}(k) = 0 \) for \(|k| \gg p_F\).

In real molecules and solids, on the other hand, the Hartree-Fock model generally gives a fairly good approximation to the equilibrium nucleus-nucleus separation. Correlation tends to increase the equilibrium separation by only a small amount. The Hartree-Fock potential curve of diatomic molecules as a function of the nucleus-nucleus separation, if shifted nearly uniformly downward by an amount of the correlation energy, leads to the exact potential curve in the neighborhood of the equilibrium separation. This implies that \( 2(T - T^{HF}) + (V_{ee} - V_{ee}^{HF}) + (V_{ne} - V_{ne}^{HF}) \) (or equivalently \( -(V_{nn} - V_{nn}^{HF}) \)) nearly vanishes or is a small positive value where \( V_{ne} \) and \( V_{nn} \) denote the electron-nucleus and nucleus-nucleus interaction energies, respectively.

Besides the net correlational lowering in the electron-electron interaction energy partially cancelled by the correlational increase in the kinetic energy, the correlation-induced less screening of the nuclei produces a further lowering in the electron-nucleus potential energy by shrinking the electron distribution in the vicinity of the nuclei and accordingly the lattice is somewhat expanded to reduce the nucleus-nucleus interaction energy, relaxing the simultaneous increase in the kinetic energy of the reference non-interacting system \( T_e \) to some extent.

Thus, the correlational lowering in the electron-nucleus potential energy, which is absent in the uniform electron liquid and hence cannot be properly described in the LDA, plays a significant role in the accurate evaluation of the equilibrium nucleus-nucleus separation as well as the electron density \( n(r) \).

V. RELATIONSHIP BETWEEN KOHN-SHAM EQUATIONS AND DYSON EQUATIONS

In this section we first evaluate the quasiparticle energy dispersion of the electron liquid with high accuracy. Next we give a detailed discussion about the relationship between Kohn-Sham equations and Dyson equations in order to justify the application of Kohn-Sham equations to the energy-band theory.

A. Symmetric expression for the self-energy

Sham and Kohn \[54\] were the first who discussed the relationship between Kohn-Sham equations and Dyson equations. In the system where the electron density is slowly varying, they have found that in the neighborhood of the Fermi level \( \mu \) the quasiparticle energy dispersion \( E(p) - \mu \) can be related to the Kohn-Sham energy dispersion \( \epsilon^{KS}(p) - \mu \) as

\[
E(p) - \mu = \frac{\epsilon^{KS}(p) - \mu}{\int d\mathbf{r} m^{*} |\chi_{p}(\mathbf{r})|^{2}},
\]

\[55\]
where $m^*(n(r))$ denotes the effective mass of the uniform electron liquid appropriate for the local density $n(r)$ and $φ_p(r)$ is the Kohn-Sham orbital specified by wavenumber $p$.

It is very difficult to give a qualitatively reliable evaluation of the effective mass $m^*$ of the electron liquid over the entire region of metallic densities. This is because the expansion of the self-energy with respect to the screened Coulomb interaction converges very slowly in this region. The effective mass ratio $m^*/m$ calculated to the first order in the RPA screened interaction, giving the leading term in the high density expansion of $m^*/m$ for small $r_s$ [101], takes the minimum around $r_s = 0.7$, exceeds unity around $r_s = 2.3$ and thereafter slowly increases with $r_s$. The ratio $m^*/m$ calculated to the second order stays less than unity until $r_s = 6$, but it has also the minimum around $r_s = 1$ and thereafter increases slowly with $r_s$. The very slow convergence of the effective mass ratio $m^*/m$ reflects that correlation is much complicated in the region of metallic densities.

In the language of many-body perturbation theory, this implies that the determination of the quasiparticle energy dispersion requires the accurate knowledge of the self-energy $Σ_σ(p, ε)$ as a functional of the one-electron Green’s function $G_σ(p, ε')$ rather than a few lowest order expansion of $Σ_σ(p, ε)$ in the screened Coulomb interaction, though screening is of course necessary to overcome the exchange difficulty. As is proved in a celebrated book by Noziers, any variation in the self-energy $Σ_σ(p, ε)$ occurs only through a variation in each constituent $G_σ(p', ε')$ of the self-energy $Σ_σ(p, ε)$. This is the reason why the accurate knowledge of $Σ_σ(p, ε)$ as a functional of $G_σ(p', ε')$ is essential for the evaluation of the quasiparticle energy dispersion.

Yasuhara and Takada [24] have introduced the very expression for the self-energy $Σ_σ(p, ε)$ that is symmetric with respect to each constituent $G$ in it.

$$Σ_σ(p, ε; [G]) = \sum_σ I^{(n)σσ'}(p, ε; p', ε'; [G])G_σ(p', ε'),$$

$$I^{σσ'}(p, ε; p', ε'; [G]) = \sum_{n=1}^\infty \frac{1}{2n-1} \frac{1}{(2π)^d} \int dε' \int dε \int \frac{dε}{(2π)^d} G^{0}_σ(p', ε')G^{0}_σ(p', ε'),$$

where $I^{(n)σσ'}(p, ε; p', ε'; [G])$ denotes the contribution to the particle-hole irreducible interaction from all the possible $n$-th order skeleton diagrams. According to this symmetric expression, one can easily check that the functional derivative $\delta Σ_σ(p, ε; [G])/δG_σ(p', ε')$ is equivalent to the particle-hole irreducible interaction $I^{σσ'}(p, ε; p', ε'; [G])$, as is proved in standard textbooks on many-body theory. The interaction $I^{σσ'}(p, ε; p', ε'; [G])$ is the value of the full particle-hole irreducible interaction $I^{σσ'}(p, ε; p', ε'; q, ω; [G])$ in the limit of $q = ω = 0$. The symmetric expression has the striking merit of visualizing that a great deal of cancellation occurs systematically between higher-order contributions due to the Pauli principle. This is indispensable to the qualitative and quantitative evaluation of the quasiparticle energy dispersion as well as the effective mass of the electron liquid in the strongly correlated density region.

A great deal of cancellation can also be observed between the wavenumber dependence and the energy dependence of the self-energy $Σ(p, ε; [G])$ in the determination of the quasiparticle energy dispersion $E(p)$. This can be traced back to the dynamical nature of screening in the electron liquid. Both of the wavenumber dependence and the energy dependence are comparatively large in magnitude, but they cancel each other for the most part in the determination of $E(p)$ and $m^*$.

Since the early stage of the study of the electron liquid [102, 103], it has been recognized that the first iterative solution for the quasiparticle energy dispersion, i.e., $E(p) = ε(p) + Σ_σ(p, ε(p); [G^0])$ is a good approximation to the solution of the fully self-consistent equation, $E(p) = ε(p) + Σ_σ(p, E(p); [G])$. This is because there is a great deal of cancellation between the higher-order iterative correction and the correction made by replacing $Σ_σ(p, ε; [G^0])$ with $Σ_σ(p, ε; [G])$: the partially self-consistent solution with $Σ_σ(p, ε; [G^0])$, the solution of $ε = ε(p) + Σ_σ(p, ε; [G^0])$ becomes worse. Almost no difference can be expected between the first iterative and the fully self-consistent solutions around the Fermi level since the electron liquid is a many-body system which consists of electrons with the same character.

The self-energy as a functional of $G^0$, $Σ_σ(p, ε; [G^0])$ can be written as [25]

$$Σ_σ(p, ε; [G^0]) = \frac{\langle ε^2 \rangle_σ}{2} \int dε' (ε'^2)^{-2} \times \sum_{σ'} \int \frac{dε'}{(2π)^d} \int dε' I^{σσ'}(p, ε; p', ε'; [G^0])G^{0}_{σ'}(p', ε'),$$

where the sum over $n$ with the factor $1/(2n - 1)$ in Eq. 56 is transformed into the coupling constant integral since $G^0$ does not depend on the coupling constant. All diagrams for the particle-hole irreducible interaction $I^{σσ'}(p, ε; p', ε'; [G^0])$ can be classified into three different types, improper, doubly irreducible, and proper and reducible [24] (see Fig. 2). From this classification it is evident that there is a great deal of systematic cancellation among higher order contributions of $I^{σσ'}(p, ε; p', ε'; [G^0])$ due to the Pauli principle. In the practical calculations we have employed an approximate form of $I^{σσ'}(p, ε; p', ε'; [G^0])$, in which the above cancellation due to the Pauli principle is allowed for systematically up to higher orders; on the other hand, we have put the contribution from $I^{σσ'}(p, ε; p', ε'; [G^0])$ as a constant since it is rather small; we have chosen the constant by fitting the value of $Σ(p, ε(p); [G^0])$ at $p = p_F$ to the exchange-correlation contribution of the chemical potential $μ_{xc}$. 


Fig. 11 shows the real part of the self-energy correction calculated from the present theory, $\text{Re} \Sigma(p, \epsilon(p); [G^0])$ in units of the Fermi energy $\epsilon_F$ as a function of $q/p_F$ for various values of $r_s$. For comparison the correction calculated from the GW approximation is also drawn.

The real part of the self-energy correction calculated from the present theory, $\text{Re} \Sigma(p, \epsilon(p); [G^0])$ in units of the Fermi energy $\epsilon_F$ as a function of $q/p_F$ for various values of $r_s$. For comparison the correction calculated from the GW approximation is also drawn.

For $p > p_F + q_c$, on the other hand, the self-energy correction $\text{Re} \Sigma_s(p, \epsilon(p); [G^0])$ behaves approximately like $-1/p$ in a quite different way from for $0 < p < p_F + q_c$. The critical wavenumber near $p_F + q_c$ is the cutoff wavenumber of plasmon excitations.

The GW approximation gives a fairly good evaluation of the magnitude of the self-energy correction, but it fails to give a qualitatively correct description of its derivative for $0 < p < p_F + q_c$ over almost the entire region of metallic densities. The appearance of a dip around $p_F + q_c$ in both cases is ascribed to the use of $\text{Re} \Sigma_s(p, \epsilon; [G^0])$ in place of $\text{Re} \Sigma_s(p, \epsilon; [G])$. The dip should be destroyed under the influence of a coupling between plasmon excitations and multipair excitations.

From these observations we may conclude that the self-energy correction to the quasiparticle energy dispersion $E(p)$ is fairly well approximated by its value at the Fermi wavenumber $p_F$ for a range of wavenumbers $0 < p < p_F + q_c$ throughout the entire region of metallic densities. In the limit of uniform density the Kohn-Sham energy dispersion becomes $\epsilon^{KS}(p) = \epsilon(p) + \mu^{xc}$. The ratio $\{\text{Re} \Sigma(p, \epsilon(p); [G^0]) - \mu^{xc}\}/\mu^{xc}$ is less than about 10% for $0 < p < p_F + q_c$. Therefore we may say that Kohn-Sham energies are a rather good approximation to quasiparticle energies so far as excitation energies relative to the Fermi level are less than about $\hbar \omega_{pl}$.

The conclusion above will probably apply to real metals. This is because the large cancellation between the wavenumber dependence and the energy dependence of the self-energy $\Sigma(p, \epsilon; [G])$ in the determination of the quasiparticle energy dispersion $E(p)$ below the critical energy near $\mu + \hbar \omega_{pl}$ can be traced back to the dynamical nature of screening that is associated with the presence of the Fermi surface.

An energy-band calculation of sodium performed in the Yasuhara-Takada approximation much more advanced than the usual GW approximation has actually revealed that the occupied band width of sodium is increased by an amount less than 10%, compared with the conventional LDA result.

Very recently, R. Maezono, M.D. Towler, Y. Lee, and R. J. Needs have performed the diffusion Monte Carlo (DMC) energy-band calculation of sodium to find confidently that its occupied band width is increased to the almost same extent as the present result. It seems that the exchange difficulty of Hartree-Fock equations associated with metals as well as the electron liquid has long been believed to be resolved completely by the RPA, but in fact it is not the case, i.e., the RPA only removes the infinite derivative at $p_F$. It is concluded that the present many-body theoretic study and the above DMC calculation have cooperated to resolve in a truly complete sense the exchange difficulty of the Hartree-Fock theory at realistic metallic densities.

B. Relation between $\Sigma(r, r', \epsilon)$ and $\nu_{xc}(r)$

Dyson equations and Kohn-Sham equations are derived from two different variational principles concerning the same ground state energy $E_g$ and $\delta E_g/\delta G(r, r', \epsilon) = 0$ and $\delta E_g/\delta n(r) = 0$, respectively, where $E_g$ can be considered to be a functional of the one-electron Green’s functional $G(r, r', \epsilon)$ or another functional of the electron density $n(r)$. The two different types of equations can in
principle give the same exact electron density \( n(r) \), chemical potential and ground state energy of a many-electron system.

Sham and Schluter have derived an exact expression for the exchange-correlation energy functional \( E_{xc} \) by means of many-body theoretical technique based on the Green’s function formalism and related the exchange-correlation potential \( v_{xc}(r) \) in DFT to the self-energy \( \Sigma(r, r', e; [G]) \). This Sham-Schulter equation implies that the electron density \( n^KS(r) \) evaluated from the Kohn-Sham Green’s function \( G^{KS}(r, r', e) \) as the unperturbed Green’s function in the many-body perturbation expansion is identical to the electron density \( n(r) \) calculated from the exact one-electron Green’s function \( G(r, r', e) \).

Grabo, Kreibich, Kurth and Gross have discussed the OEP method from the viewpoint of many-body perturbation theory. They have then pointed out that the higher order contribution of the exchange-correlation energy functional beyond the Hartree-Fock approximation, \( E_{xc}^{(n)}(n \geq 2) \) depends not only on occupied and unoccupied Kohn-Sham orbitals and Kohn-Sham energies but also on the exchange-correlation potential \( v_{xc}(r) \). This implies that the resulting OEP integral equation involves the functional derivative \( \delta v_{xc}(r)/\delta n(r') \) as well as the potential \( v_{xc}(r) \) and is much more difficult to solve as a result.

Casida has started with an approximate expression for the ground state energy functional. In the expansion of the self-energy functional using skeleton diagrams he has omitted those terms which arise from the coupling constant integral of the constituent renormalized Green’s functions, or equivalently those terms which vanish if the exact one-electron Green’s function \( G \) is replaced by the unperturbed Kohn-Sham Green’s function \( G^{KS} \) in the exact ground state energy functional for the variational principle. Using this approximate ground state energy functional \( E_0[G^{KS}] + \Phi[G^{KS}] \), Casida has generalized the exchange-only OEP method by Sharp and Horton to include correlation. The resulting OEP integral equation has turned out to be identical to the first iterative form of the Sham-Schulter equation (see Eq. (35)). Casida has thus shown that the exchange-correlation potential \( v_{xc}(r) \) in DFT can be interpreted to be the variationally best optimized local approximation to the exchange-correlation part of the self-energy \( \Sigma(r, r', e; [G]) \).

We would like to stress here that Casida’s expression for the ground state energy functional \( E_0[G^{KS}] + \Phi[G^{KS}] \) is a sufficiently accurate approximation for the practical purpose of studying the electronic structure of solids. This may be understood from the fact that the same approximation, if applied to the uniform electron liquid, gives an excellent description of long-, intermediate-, and short-range correlations and furthermore obeys the Pauli principle; it can also give a highly accurate evaluation of the ground state energy for the electron liquid. This is because the self-energy functional employed is exact.

We may say that Kohn-Sham equations assume the complete cancellation between the nonlocality (or the wavenumber dependence) and the energy dependence of \( \Sigma(r, r', e; [G]) \) in the evaluation of quasiparticle energies. This assumption is rather good, as we have already discussed in Sec. V A.

As for the energy gap of semiconductors, the gap of Kohn-Sham equations is related to that of Dyson equations as \( E_{gap} + \Delta_{xc} = E_{gap} \) where \( \Delta_{xc} \) denotes the discontinuity of the exchange-correlation potential \( v_{xc}(r) \). According to an accurate Hartree-Fock calculation in DFT, the relation \( E_{HF KS}^{gap} + \Delta_x = E_{HF}^{gap} \) has been ascertained for silicon within an accuracy of 3%. It has been reported that the value of \( E_{HF KS}^{gap} \) is a good approximation of the experimental gap and the discontinuity \( \Delta_x \) amounts to about twice the experimental gap. This implies that \( \Delta_x \) must be for the most part cancelled by \( \Delta_c \). According to standard many-body perturbation theory, the well-known overestimation in the gap of semiconductors calculated from usual Hartree-Fock equations can be remedied by the screened exchange potential. In the framework of DFT, on the other hand, the same screening effect can be represented by a great deal of cancellation between \( \Delta_x \) and \( \Delta_c \). Probably, the total discontinuity \( \Delta_{xc}(= \Delta_x + \Delta_c) \) will be small but positive by analogy with the difference in the energy dispersion of the electron liquid between Dyson equations and Kohn-Sham equations. Kohn-Sham equations overestimate the density of states at the Fermi level by less than 10% through the scaling factor \( m/m^* \).

**C. Correspondence between two self-consistencies**

In an attempt to interpret the extraordinarily enhanced effective mass of heavy fermion systems using the Hubbard model, a number of authors have exaggerated the role of the energy dependence of the self-energy in the determination of the quasiparticle energy dispersion around the Fermi level, neglecting its wavenumber dependence. In fact, there is a great deal of cancellation between the wavenumber dependence and the energy dependence of the self-energy. The former somewhat overcomes the latter in magnitude as we have elucidated in Sec. V A. This characteristic of the self-energy can be traced back to the dynamical nature of screening and hence is expected to apply to all metals as far as the Fermi surface is well defined. Then we have to ascribe the origin of the extraordinarily enhanced effective mass to a different characteristic of the self-energy in Dyson equations.

In this subsection we would like to point out a characteristic of the self-energy peculiar to nonuniform real metals as a promising candidate for the origin of the extraordinarily enhanced effective mass. In transition metals and rare earth metallic compounds the Fermi surface is constructed from a few kinds of electrons with different orbital characters, in contrast with the electron liquid
which consists of a single kind of electrons with the same character.

Consider the self-energy \( \Sigma_{\sigma}(\mathbf{r}, \mathbf{r}'; \epsilon; [G]) \) entering Dyson equations. It is a nonlocal and energy-dependent operator, but it is, at the same time, a functional of the self-consistent Green’s function \( G \). In the uniform electron liquid there is no essential difference in the neighborhood of the Fermi level between the first iterative and the fully self-consistent solutions for the quasiparticle energy dispersion. In the case of rare earth metallic compounds, on the other hand, there is a very strong possibility that being a functional of the self-consistent Green’s function \( G \) may cause a drastic change in the quasiparticle energy dispersion particularly in the immediate vicinity of the Fermi level due to the presence of \( f \) electrons and gives an extraordinarily sharp enhancement in the density of states. Probably, such a drastic change in the dispersion will be caused by the correlation-induced reconstruction of quasiparticle states in the immediate vicinity of the Fermi level and of course involve a significant change in the electron density \( n(\mathbf{r}) \) of the system.

According to Casida, the exchange-correlation potential \( v_{xc}(\mathbf{r}) \) in Kohn-Sham equations can be interpreted to be the variationally best optimized local approximation to the self-energy \( \Sigma(\mathbf{r}, \mathbf{r}', \epsilon; [G]) \). Kohn-Sham equations assume the complete cancellation between the wavenumber dependence (non-locality) and the energy dependence of the self-energy, but still maintain its essential property as a functional of the self-consistent \( G \) in the form of the exchange-correlation potential \( v_{xc}(\mathbf{r}) \) as a functional of the self-consistent electron density \( n(\mathbf{r}) \). In other words, the implicit dependence of \( \Sigma(\mathbf{r}, \mathbf{r}', \epsilon; [G]) \) on the self-consistent \( G \) is in one-to-one correspondence to the implicit dependence of \( v_{xc}(\mathbf{r}; [n]) \) on the self-consistent \( n(\mathbf{r}) \) in the sense that the latter occurs only from the former. This may be seen from the first iterative form of the Sham-Schluter equation which is identical to the OEP integral equation.

\[
\int \, d\mathbf{y} \int \, d\mathbf{y}' \frac{d\omega}{2\pi} G^{KS}(\mathbf{r}, \mathbf{y}, \omega) \delta(\mathbf{y} - \mathbf{y}')
\times v_{xc}(\mathbf{y}; [n]) G^{KS}(\mathbf{y}', \mathbf{r}, \omega)
= \int \, d\mathbf{y} \int \, d\mathbf{y}' \frac{d\omega}{2\pi} G^{KS}(\mathbf{r}, \mathbf{y}, \omega) \Sigma(\mathbf{y}, \mathbf{y}', \omega; [G^{KS}])
\times G^{KS}(\mathbf{y}', \mathbf{r}, \omega),
\]

where \( G^{KS}(\mathbf{r}, \mathbf{y}, \omega) \) denotes the unperturbed Kohn-Sham Green’s function in the many-body perturbation expansion.

We may therefore expect that such a correlation effect on quasiparticle energies as involves a change in the electron density \( n(\mathbf{r}) \) of the system probably will be for the most part taken into account in the framework of Kohn-Sham equations in DFT. This is parallel to the expectation that there will probably be no significant difference between the Kohn-Sham Fermi surface and the true Fermi surface, though strictly speaking the two Fermi surfaces are not identical. The one-to-one correspondence between the two self-consistencies, i.e., \( \Sigma(\mathbf{r}, \mathbf{r}', \epsilon; [G^{KS}]) \) as a functional of the self-consistent \( G^{KS} \) and \( v_{xc}(\mathbf{r}; [n]) \) as a functional of the self-consistent \( n(\mathbf{r}) \) will persist even for strongly anisotropic systems such as heavy fermion systems.

In Sec. IV we have predicted that the correlation-induced reconstruction of Kohn-Sham orbitals in the vicinity of the Fermi level or the energy gap will be essential to the theoretical interpretation of the electronic structure of the so-called strongly correlated electron systems. This prediction is based on the one-to-one correspondence between the two self-consistencies we have just mentioned above.

To conclude, if the correlation energy functional to be used is sufficiently accurate, Kohn-Sham equations are expected to give a good approximation to quasiparticle energies as far as they do not exceed a critical energy near \( \mu + \hbar \omega_{\mu} \). The orbital-dependent correlation energy functional we have proposed in Sec. IV B to be used in combination with the orbital-dependent exchange energy functional probably will be sufficiently accurate to promote development in the band theory of solids.

**VI. CONCLUDING REMARKS**

One of the most important subjects in solid state physics at present is exploitation of more accurate methods for treating correlation in the theoretical study of the electronic structure of solids. For this purpose we have constructed a density-functional theory (DFT) with the help of detailed knowledge of long-, intermediate-, and short-range correlations of the electron liquid, not its density dependence of the correlation energy. This is a sophisticated but feasible method which may develop the band theory to a new advanced stage beyond the LDA. The present correlation energy functional \( E_{c}([\varphi_1]) \) is valid for tightly binding electrons as well as for nearly free electrons.

Generally, effects of correlation on the electronic structure of solids are so complicated and delicate that in order to obtain a reliable conclusion one has to take account of various aspects of correlation systematically starting from the original Coulomb interaction between valence electrons participating in cohesion of solids instead of resorting to intuitive simplifications such as the Hubbard model.

Two aspects of long-range correlation arising from long-range parts of the Coulomb interaction in the electron liquid, i.e., the existence of plasmons as a collective excitation and screening of the Coulomb interaction between individual excitations (quasiparticles) as its complementary effect in the lower energy region apply to real metals though both are somewhat modified by band structure effects. The RPA is the simplest approxima-
tion to describe these aspects and its screening is indispensable to overcome the exchange difficulty. However, it is important to recognize that the qualitative and quantitative evaluation of the quasiparticle energy dispersion $E(p)$ and the effective mass $m^*$ in the region of metallic densities requires a systematic inclusion of higher-order perturbation terms obeying the Pauli principle in the expansion of the self-energy operator in the screened Coulomb interaction. This is because long-, intermediate-, and short-range correlations occurring in this region are very much complicated under the constraint of the Pauli principle, in marked contrast to the situation in the high density region where long-range correlation in the RPA is predominant. In the evaluation of $E(p)$ and $m^*$ of the electron liquid, a great deal of cancellation is observed between the wavenumber dependence and the energy dependence of the self-energy operator. This can be interpreted as the dynamical nature of screening and hence we may expect that this cancellation will be observed in real metals so far as the Fermi surface is well defined.

No qualitative difference may be expected in the neighborhood of the Fermi level or the energy gap between the quasiparticle energy dispersion calculated from Dyson equations and the one-electron energy dispersion from Kohn-Sham equations. The quantitative difference is less than 10% so far as we know. Then we may conclude that the use of Kohn-Sham equations will be valid for further development of the band theory.

The reason for the unexpected success of the LDA may be ascribed to the long-range nature of the Coulomb interaction between electrons, which tends to cancel the difference between a real metal and its locally uniform electron liquid model in the quantitative evaluation of various electron-electron interaction effects.

Except for the correlated properties coming from the electron liquid, what new correlation is the most important in real metals at all? We answer this question from the viewpoint of DFT. The present $E_c[\{\phi_i\}]$ is valid for both nearly-free and tightly-binding electrons since it assumes an orbital-dependent second-order perturbation like form in which all effects of higher-order perturbation terms are represented by an effective interaction defined for the electron liquid in the region of metallic densities. A striking merit of the present $E_c[\{\phi_i\}]$ is that it makes the meaning of correlation clear against the Hartree-Fock approximation in the framework of DFT and that it suggests how the electron density $n(r)$ of the system may be redistributed under the influence of correlation. The present $E_c[\{\phi_i\}]$ hybridizes Hartree-Fock Kohn-Sham orbitals in order to produce self-consistently reconstructed Kohn-Sham orbitals through the correlation potential $v_c(r)$. The important point is that the present $v_c(r)$ probably gives rise to less screening of the attractive nuclear potential at short distances to enhance the electron density $n(r)$ in the immediate vicinity of individual nuclei in solids.

The electronic structure of the so-called strongly correlated electron systems such as heavy fermions and Mott insulators might be interpreted in terms of self-consistently reconstructed Kohn-Sham orbitals in the neighborhood of the Fermi level or the energy gap.

The expression "strongly correlated" has been extensively used in the sense that the electronic structure is beyond the scope of the LDA. In fact, the magnitude of the spin-antiparallel pair correlation function $g^{\uparrow \downarrow}(r,r')$ for conduction electrons in cesium will be most reduced at short separations. Correctly, we should state that the LDA fails to give the proper description of correlation-induced reconstruction of Kohn-Sham orbitals. This reconstruction may be interpreted as a natural consequence of the fact that short-range correlation between valence electrons participating in cohesion of solids induces inhomogeneity in the electron density $n(r)$ associated with the presence of the nuclei, or equivalently short-range correlation between valence electrons significantly reduces the Hartree- or Hartree-Fock screening of the attractive nuclear potential at short distances to enhance the electron density $n(r)$ at the positions of individual nuclei in solids. This correlation-induced reconstruction of Kohn-Sham orbitals involving the enhancement of $n(r)$ at the positions of individual nuclei is precisely the most important correlation that the LDA fails to describe.

The present theoretical treatment of correlation will manifest the true value of DFT in the study of the electronic structure of solids. The present theory requires highly complicated self-consistency because of the orbital-dependence of the exchange-correlation energy functional $E_{xc}(= E_x + E_c)$. Much technical difficulty is expected in its practical application. The most difficult problem will be the accuracy required in solving the OEP integral equation to evaluate the exchange-correlation potential $v_{xc}(r) = v_x(r) + v_c(r)$. The KLI method of approximately solving the OEP integral equation may be hopefully applied to the present orbital-dependent correlation energy functional. It is not so difficult to construct the spin-polarized version of the present theory.

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