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Orbital-dependent nonlocal correlation energy functional constructed from a Jastrow function: Application to atoms and ions

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An orbital-dependent nonlocal correlation energy functional has been derived from an energy formula defined in the transcorrelated method. The obtained functional explicitly depends on a Jastrow function, which has been successfully used for the electron gas and solids. We found that our correlation energy functional is successfully used with the exact exchange energy functional and gives relatively good estimates for the total energy and the ionization potential for atoms and ions.

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I. INTRODUCTION

Density-functional theory (DFT) [1,2] has become one of the standard methods to obtain electronic structures of a variety of systems. Since it was created, a lot of attention has been paid to improving the exchange-correlation energy functional E_{xc} since the functional form of E_{xc} is responsible for the quality of approximation in DFT. The most widely used functional is the local-density approximation (LDA) where E_{xc} is simply expressed as a functional of a local density. Although LDA has given a great number of successful results [3–5], it also has some problems: cohesive energy estimates for solids are overestimated, band gaps for insulators or semiconductors are underestimated, and so on [3–5]. These failures are considered to be due to the extremely simplified exchange-correlation energy functional E_{xc}^{LDA}, where nonlocal effects of the electron correlation are completely ignored. Therefore, it has been desired to go beyond LDA by constructing a nonlocal E_{xc}.

The generalized-gradient approximation (GGA) [6] is one of these attempts, in which E_{xc} is expressed as a functional of a gradient of the density as well as the density itself to incorporate the nonlocal effect of the electron correlation. GGA improves estimates of the total energy, the ionization potential, the electron affinity for atoms, and the atomization energy for molecules [7,8]. Moreover, GGA weaken the binding energy of solids, i.e., cohesive energy estimates are improved over LDA [9–11], though overcorrections are observed in some cases [12]. A different derivation of the gradient correction to the exchange energy was suggested by Becke [13]. The Becke's gradient correction has been combined with a correlation energy functional given by Lee, Yang, and Parr [14]. The hybrid functional named BLYP has been successfully applied to a wide range of quantum chemical calculations [15]. However, GGA or BLYP are not able to improve the underestimation of the band gaps over LDA. This is partly due to the wrong asymptotic behavior of the exchange-correlation potential in these gradient corrected functionals. It is known that any functional based on the gradient correction cannot satisfy the correct asymptotic behavior simultaneously for the exchange energy density $-1/2r$ and the exchange potential $-1/r$ [16]. Taking into account the Laplacian as well as the gradient of the density improves the asymptotic behavior [17]. Actually, the Laplacian of the density is known to be an important ingredient to go beyond GGA [18,19]. Unfortunately, both the LDA and GGA are not able to deal with van der Waals interactions [20–25].

The weighted density approximation (WDA) [26,27] is a well-known nonlocal density-functional approach. The formalism of WDA is based on the rigorous formula of E_{xc} written with a pair-correlation function. For approximation, some specific functions are adopted for the pair-correlation function with a weighted density, which is introduced so as to satisfy the sum rule for the exchange-correlation hole. WDA has been applied to a variety of systems: atoms [28,29], electron gas [30,31], surfaces [32,33], and solids [34–40]. However, some of the solid state calculations revealed that WDA has difficulty in going beyond LDA when it comes to computing physical constants such as the bulk modulus [40] and the band gap [39,40]. Furthermore, the exchange-correlation potential of WDA yields a wrong asymptotic behavior $-1/2r$ instead of the correct $-1/r$ [28].

There is another attempt to go beyond LDA by treating the exchange energy functional exactly in the Kohn-Sham formalism [2]. In this approach, which is called the exact exchange (EXX) method [41–47], the exchange energy E_x^{EXX} is expressed in the same way as the Hartree-Fock method, namely, the Fock term expressed as an orbital-dependent two-body functional. Since EXX is a self-interaction free method, it can reproduce the exact asymptotic behavior $-1/r$ of the exchange potential. A special treatment is required for the functional derivative of the orbital-dependent E_x^{EXX} functional with respect to the density, which is usually implemented by the optimized effective potential (OEP) method [48]. A useful approximation to the OEP method was suggested by Krieger, Li, and Iafrate (KLI) [49–51], which is applicable to any orbital-dependent exchange-correlation energy functional. The EXX method or its KLI approximation, where LDA or GGA correlation energy functional is usually employed in addition to E_x^{EXX}, have been proved to be successful especially for evaluating band gaps of semiconductors and insulators [44,45]. However, the other physical constants such as bulk moduli or lattice constants are not always improved over LDA [52]. This is also the case in estimations of the binding energy of molecules [47,50,53,54]. These failures are attributed to the absence of error cancellations between E_x^{EXX} and the correlation energy functional such as

E_c^{LDA} or E_c^{GGA}. Since the exchange energy functional is treated exactly in the EXX method, errors included in E_c^{LDA} or E_c^{GGA} cannot be canceled out. Whereas the error cancellation usually occurs when LDA (GGA) is employed both for the exchange and the correlation energy functionals E_{xc}^{LDA} (E_{xc}^{GGA}) [3,4]. This is the reason why the EXX method is not successful with E_c^{LDA} or E_c^{GGA} and rather worsen the results given by E_{xc}^{LDA} in some cases. Therefore, the construction of a correlation energy functional, which is successfully used with E_x^{EXX}, is desired. Grabo and Gross have applied a correlation energy functional proposed by Colle and Salvetti (CS) [55] to atomic systems [50,51] using E_x^{EXX} and obtained very good results. However, since parameters in the CS functional are determined by a fitting procedure for a He atom using Hartree-Fock orbitals, it is hardly expected to be applicable to solid state calculations. It is actually known that the CS functional fails to reproduce the dissociation energies of molecules [50]. A simple remedy for coupling E_{xc}^{LDA} with E_x^{EXX} was suggested by Becke [56] where the LDA exchange-correlation potential is utilized for the coupling procedure with semiempirical parameters. Recently, another nonlocal correlation energy functional, which is successfully used with E_x^{EXX}, was suggested [57]. In their work, the long-range electron-electron correlation is treated by the random-phase approximation (RPA) and the short-range correlation is represented by LDA or GGA. It was shown that this method can improve the binding energy estimates for molecules over LDA or GGA [58].

In this paper, we propose a new correlation energy functional, which is completely different from these conventional functionals. Our correlation energy functional is derived from an energy formula defined in the transcorrelated (TC) method [60–69] and explicitly depends on a Jastrow factor [59]. Such an attempt has been made by Imamura and Scuseria [64] where Jastrow parameters are determined so as to reproduce atomic energies. Thus, the obtained functional is hardly expected to be applicable to extended system such as electron gas or solid. Moreover, three-body interactions emerged in the formula of the transcorrelated energy were completely ignored in their work. On the other hand, our correlation energy functional does not contain any fitting parameter and the three-body interactions are fully taken into account. The Jastrow factor adopted in the present work has been successfully used in the quantum Monte Carlo calculations for electron gas and solids. Thus, the obtained functional is expected to be useful for extended systems. Actually, we have reported that our correlation energy functional well reproduces correlation energies of the homogeneous electron gas [67]. In the present work, we apply this new correlation energy functional to atomic systems in order to assess the usefulness of it for inhomogeneous systems.

The layout of this paper is as follows. In Sec. II, a new orbital-dependent nonlocal correlation energy functional will be proposed. In Sec. III, we will show the results for atoms and ions in comparison with those obtained from other nonlocal density-functional approaches. Charge densities and correlation potentials are also depicted for atoms. In Sec. IV, we will give our conclusions.

II. THEORY

The Hartree atomic units ($m=e^2=\hbar=1$) are used in the following. In the transcorrelated method, an energy formula is derived from a stationary condition to a variance with respect to a parameter E:

$$\frac{\partial}{\partial E}\int |\mathcal{H}_{\mathrm{TC}}D - ED|^2 dx^{3N} = 0, \qquad (1)$$

where D is a single Slater determinant. $\mathcal{H}_{\mathrm{TC}}$ is the transcorrelated Hamiltonian defined by a similarity transformation of a Hamiltoniam $\mathcal{H}$ with respect to a Jastrow factor F:

$$\mathcal{H}_{\mathrm{TC}} = \frac{1}{F}\mathcal{H}F. \qquad (2)$$

Equation (1) results in the following energy formula:

$$E_{\mathrm{TC}} = \mathrm{Re}\langle D|\mathcal{H}_{\mathrm{TC}}|D\rangle = \frac{1}{2}\langle D|\mathcal{H}_{\mathrm{TC}} + \mathcal{H}_{\mathrm{TC}}^{\dagger}|D\rangle, \qquad (3)$$

where Re denotes the real part. Detailed derivation of Eq. (3) is given in Ref. [66]. If we treat the nuclei classically and adopt the Born-Oppenheimer approximation for $\mathcal{H}$, $\mathcal{H}_{\mathrm{TC}}$ and its Hermitian conjugate $\mathcal{H}_{\mathrm{TC}}^{\dagger}$ are explicitly written as

$$\mathcal{H}_{\mathrm{TC}} = \sum_{i=1}^{N}\left(-\frac{1}{2}\nabla_i^2 - \frac{1}{2}\frac{\nabla_i^2 F}{F} - \frac{\boldsymbol{\nabla}_i F}{F}\cdot\boldsymbol{\nabla}_i\right) + U + V, \qquad (4)$$

$$\mathcal{H}_{\mathrm{TC}}^{\dagger} = \sum_{i=1}^{N}\left[-\frac{1}{2}\nabla_i^2 + \frac{1}{2}\frac{\nabla_i^2 F^*}{F^*} + \frac{\boldsymbol{\nabla}_i F^*}{F^*}\cdot\boldsymbol{\nabla}_i - \left(\frac{\boldsymbol{\nabla}_i F^*}{F^*}\right)^2\right] + U + V, \qquad (5)$$

where F^* denotes the complex conjugate of F. U and V are potential energies for electron-electron and electron-nucleus interactions, respectively. Obviously, Eq. (5) is different from Eq. (4) and so $\mathcal{H}_{\mathrm{TC}}$ is a non-Hermitian operator. Using Eqs. (3)–(5), E_{TC} is explicitly written as

$$E_{\mathrm{TC}} = \langle D|\mathcal{H}|D\rangle - \frac{1}{2}\langle D|\sum_{i=1}^{N}\left[\frac{1}{2}\left(\frac{\nabla_i^2 F}{F} - \frac{\nabla_i^2 F^*}{F^*}\right) + \left(\frac{\boldsymbol{\nabla}_i F}{F} - \frac{\boldsymbol{\nabla}_i F^*}{F^*}\right)\cdot\nabla_i + \left(\frac{\boldsymbol{\nabla}_i F^*}{F^*}\right)^2\right]|D\rangle. \qquad (6)$$

The first term in Eq. (6) corresponds to the total energy formula of the Hartree-Fock method. Therefore, the second term of Eq. (6) could be a correlation energy functional E_{c}. If we assume F to be a real function, E_{c} is written as

$$E_{\mathrm{c}} = -\frac{1}{2}\left\langle D\left|\sum_{i=1}^{N}\left(\frac{\boldsymbol{\nabla}_i F}{F}\right)^2\right|D\right\rangle. \qquad (7)$$

It is interesting to notice that E_{c} is negative definite, and so, it is guaranteed that E_{TC} gives a smaller value than a total energy calculated from the Hartree-Fock method if Eq. (3) is minimized over D.

The Jastrow factor F is usually written as

$$F = \exp\left(\sum_{i=1}^{N} \chi_{\sigma_i}(\mathbf{r}_i) - \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1(\neq i)}^{N} u_{\sigma_i\sigma_j}(\mathbf{r}_i,\mathbf{r}_j)\right). \tag{8}$$

Here, $\chi_\sigma(\mathbf{r})$ and $u_{\sigma\sigma'}(\mathbf{r},\mathbf{r}')$ are the one-body and the two-body Jastrow factor, respectively. For the two-body term, we have adopted the following simple function:

$$u_{\sigma\sigma'}(\mathbf{r},\mathbf{r}') = u_{\sigma\sigma'}(R) = \frac{A}{R}(1 - e^{-\beta_{\sigma\sigma'}R}), \tag{9}$$

where $R=|\mathbf{r}-\mathbf{r}'|$. This type of function has been used in the quantum Monte Carlo calculations for the electron gas and solids [59,67,70,71]. In the present work, the parameters in Eq. (9) are determined by the following two conditions. One is the cusp conditions [59,72,73]:

$$\left.\frac{du_{\sigma\sigma'}(R)}{dR}\right|_{R=0} = -\alpha_{\sigma\sigma'}, \tag{10}$$

where $\alpha_{\uparrow\uparrow}=1/4$ and $\alpha_{\uparrow\downarrow}=1/2$, which restrict short-range interactions between two electrons. Substituting Eq. (9) into Eq. (10), the following equation is derived:

$$\beta_{\sigma\sigma'} = \sqrt{\frac{2\alpha_{\sigma\sigma'}}{A}}, \tag{11}$$

where $\beta_{\sigma\sigma'}$ is assumed to be a positive value. The second condition is based on the random-phase approximation (RPA) [59,74], which restricts the long range electron interactions in a high density electron gas. From the result of the RPA, the parameter A in Eq. (9) is determined by

$$A = \frac{1}{\omega_p} = \frac{1}{\sqrt{4\pi n}}, \tag{12}$$

where ω_p is the plasma frequency and n is the density of the homogeneous electron gas. In the case of inhomogeneous systems, we suppose that an averaged density

$$\bar{n} = \frac{1}{N}\int n(\mathbf{r})n(\mathbf{r})d\mathbf{r} \tag{13}$$

is reasonably used in Eq. (12).

The one-body term in Eq. (8) $\chi_\sigma(\mathbf{r})$ is known to be an important ingredient because it suppresses unfavorable changing of charge density caused by the two-body term [59,75]. Recently, a simple remedy is suggested for producing $\chi_\sigma(\mathbf{r})$ from the two-body term as [76]

$$\chi_\sigma(\mathbf{r}) = \frac{N-1}{2N}\sum_{\sigma'}\int n^{\sigma'}(\mathbf{r}')u_{\sigma\sigma'}(\mathbf{r},\mathbf{r}')d\mathbf{r}'. \tag{14}$$

The essence of Eq. (14) is understood from the fact that the main role of $\chi_\sigma(\mathbf{r})$ is to cancel out the unfavorable effect caused by $u_{\sigma\sigma'}(\mathbf{r},\mathbf{r}')$ [59,75,77]. Now all the functions in Eq. (8) are completely determined without any variational parameters.

Using Eq. (8), the correlation energy functional E_{c} defined by Eq. (7) is explicitly written as

$$E_{\mathrm{c}} = E_{\mathrm{c}}^{(1)} + E_{\mathrm{c}}^{(2)} + E_{\mathrm{c}}^{(3)}, \tag{15}$$

$$E_{\mathrm{c}}^{(1)} = -\frac{1}{2}\sum_{\sigma}\sum_{i}\int|\phi_{i\sigma}(\mathbf{r})|^2|\nabla\chi_\sigma(\mathbf{r})|^2 d\mathbf{r}, \tag{16}$$

$$\begin{aligned}E_{\mathrm{c}}^{(2)} = \frac{1}{2}\sum_{\sigma}\sum_{ij}\int\Bigg[&\frac{1}{2}|S_{ij}^{\sigma}(\mathbf{r},\mathbf{r}')|^2 h_{\uparrow\uparrow}^{(2)}(\mathbf{r},\mathbf{r}')\\ &+|\phi_{i\sigma}(\mathbf{r})\phi_{j-\sigma}(\mathbf{r}')|^2 h_{\uparrow\downarrow}^{(2)}(\mathbf{r},\mathbf{r}')\Bigg]d\mathbf{r}d\mathbf{r}',\end{aligned} \tag{17}$$

$$\begin{aligned}E_{\mathrm{c}}^{(3)} = -\frac{1}{2}\sum_{\sigma}\sum_{ijk}\int\Bigg[&\frac{1}{6}|R_{ijk}^{\sigma}(\mathbf{r},\mathbf{r}',\mathbf{r}'')|^2 h_{\uparrow\uparrow\uparrow}^{(3)}(\mathbf{r},\mathbf{r}',\mathbf{r}'')\\ &+\frac{1}{2}|S_{ij}^{\sigma}(\mathbf{r},\mathbf{r}')\phi_{k-\sigma}(\mathbf{r}'')|^2 h_{\uparrow\uparrow\downarrow}^{(3)}(\mathbf{r},\mathbf{r}',\mathbf{r}'')\\ &+\frac{1}{2}|S_{ki}^{\sigma}(\mathbf{r}'',\mathbf{r})\phi_{j-\sigma}(\mathbf{r}')|^2 h_{\uparrow\downarrow\uparrow}^{(3)}(\mathbf{r},\mathbf{r}',\mathbf{r}'')\\ &+\frac{1}{2}|S_{jk}^{-\sigma}(\mathbf{r}',\mathbf{r}'')\phi_{i\sigma}(\mathbf{r})|^2 h_{\uparrow\downarrow\downarrow}^{(3)}(\mathbf{r},\mathbf{r}',\mathbf{r}'')\Bigg]d\mathbf{r}d\mathbf{r}'d\mathbf{r}'',\end{aligned} \tag{18}$$

where

$$h_{\sigma\sigma'}^{(2)}(\mathbf{r},\mathbf{r}') = -|\nabla u_{\sigma\sigma'}(|\mathbf{r}-\mathbf{r}'|)|^2 + 2\nabla\chi_\sigma(\mathbf{r})\cdot\nabla u_{\sigma\sigma'}(|\mathbf{r}-\mathbf{r}'|), \tag{19}$$

$$h_{\sigma\sigma'\sigma''}^{(3)}(\mathbf{r},\mathbf{r}',\mathbf{r}'') = \nabla u_{\sigma\sigma'}(|\mathbf{r}-\mathbf{r}'|)\cdot\nabla u_{\sigma\sigma''}(|\mathbf{r}-\mathbf{r}''|), \tag{20}$$

$$S_{ij}^{\sigma}(\mathbf{r},\mathbf{r}') = \phi_{i\sigma}(\mathbf{r})\phi_{j\sigma}(\mathbf{r}') - \phi_{i\sigma}(\mathbf{r}')\phi_{j\sigma}(\mathbf{r}), \tag{21}$$

$$R_{ijk}^{\sigma}(\mathbf{r},\mathbf{r}',\mathbf{r}'') = \begin{vmatrix}\phi_{i\sigma}(\mathbf{r}) & \phi_{j\sigma}(\mathbf{r}) & \phi_{k\sigma}(\mathbf{r})\\ \phi_{i\sigma}(\mathbf{r}') & \phi_{j\sigma}(\mathbf{r}') & \phi_{k\sigma}(\mathbf{r}')\\ \phi_{i\sigma}(\mathbf{r}'') & \phi_{j\sigma}(\mathbf{r}'') & \phi_{k\sigma}(\mathbf{r}'')\end{vmatrix}. \tag{22}$$

$E_{\mathrm{c}}^{(2)}$ and $E_{\mathrm{c}}^{(3)}$ are calculated from the Monte Carlo sampling as addressed in our previous paper [69] where required integrations are up to three-body even for many-body systems.

Although Eqs. (17) and (18) are not explicitly written as functionals of the density but functionals of orbitals, they are implicitly functionals of the density analogous to the exact exchange energy functional [41–43]. Thus, in the present work, the KLI approximation [49,50] is adopted for implementing the functional derivative of Eqs. (17) and (18) with respect to the density in the same way as the exact exchange energy. The total energy is then given by Eq. (6) with the second term replaced by Eq. (15). The Kohn-Sham equation is self-consistently solved for atoms and ions within the KLI approximation both for the exact exchange and the correlation energy functional. The averaged density $\bar{n}$ defined by Eq. (13) is fixed during the functional derivative, although $\bar{n}$ is updated every time when the density is updated while solving the Kohn-Sham equation.

The computational cost for the calculation of $E_{\mathrm{c}}^{(3)}$ scales as N^3 as understood from Eq. (18), which is larger than that of the exact exchange term N^2 or the LDA exchange-correlation energy N. Thus, application of the present method

TABLE I. Ground state total energy estimates for Helium-isoelectronic series (H^-, He, Li^+, and Be^{2+}) and atoms from Li to Ne, given by the present method, the exact exchange method with an LDA correlation energy functional [78] (EXXLDA) within the KLI approximation [50,51], GGA given by Perdew and Wang (PW91) [8,50], and the weighted density approximation from Ref. [28] (WDA1) and [29] (WDA2). Exact values are from [80,81]. × and blanks indicate no bound state and no data, respectively. $\bar{\Delta}$ denotes the mean absolute deviation from the exact data for atoms from Li to Ne. All energies are in Hartree atomic units ($m=e^2=\hbar=1$).

	EXXLDA	PW91	WDA1	WDA2	Present	Exact
H^-	−0.5630	×			−0.5095	−0.5278
He	−2.9742	−2.9000	−2.945	−2.909	−2.8929	−2.9037
Li^+	−7.3705	−7.2676			−7.2728	−7.2799
Be^{2+}	−13.7610	−13.6340			−13.6514	−13.6556
Li	−7.5937	−7.4742	−7.535	−7.473	−7.4737	−7.4781
Be	−14.7964	−14.6479	−14.725	−14.605	−14.6311	−14.6674
B	−24.8233	−24.6299	−24.775	−24.583	−24.6077	−24.6539
C	−38.0628	−37.8265	−37.895	−37.779	−37.7930	−37.8450
N	−54.8623	−54.5787	−54.61	−54.530	−54.5451	−54.5893
O	−75.3592	−75.0543	−75.195	−75.011	−75.0125	−75.067
F	−100.0502	−99.7316	−99.97	−99.695	−99.6850	−99.734
Ne	−129.2851	−128.9466	−129.265	−128.914	−128.9066	−128.939
$\bar{\Delta}$	0.232	0.012	0.125	0.048	0.040	

to the systems that contain a larger number of electrons would be difficult. Moreover, statistical errors caused by the Monte Carlo sampling are inevitable for computing the three-body integrals in $E_c^{(3)}$ [69]. In the present work, we set the sampling number ($10^4\times 3$) so that the statistical error is negligible.

III. RESULTS

Here, we show the results for atoms and ions given by the correlation energy functional proposed in the previous section. In Table I, total energy estimates for atoms and ions given by the present correlation energy functional are listed in comparison with those obtained from various nonlocal density-functional approaches. It is shown that the present method gives relatively good estimates for the atomic total energy. It is especially remarkable that the present method can reproduce a bound state for the negatively ionized hydrogen, which is known to be very difficult to be achieved. The results given by the exact exchange method with an LDA [78] correlation energy functional (EXXLDA) contain largest deviations from exact values among the methods listed in Table I. The reason for this large deviation is the lack of the error cancellation between exchange and correlation energies as discussed before. The present correlation energy functional certainly improves this issue over EXXLDA.

In Table II, correlation energy estimates are listed compared to the exact values for atoms and ions. Here, the correlation energy is defined by the difference between a total energy estimate and the Hartree-Fock energy. Although the absolute values of the correlation energy are still underestimated in the present method, one can observe significant improvements in the present results over EXXLDA, WDA1, and WDA2. The percentages of the correlation energy reproduced in these estimates are depicted in Fig. 1. It is understood that the present method can reproduce 60–90 % of the correlation energies for these atoms. The failure in the error cancellation is again observed in the results of EXXLDA, where absolute values of the correlation energy estimates are largely overestimated. The present method certainly improves this aspect. The disagreements between WDA1 and WDA2 are originated from the different functional forms in the exchange-correlation energy functional. It is clearly shown that both the WDA methods are behind the present method in terms of the correlation energy estimates. Nevertheless, PW91 yields slightly better results than the present method. The underestimation of the absolute correlation energy estimates in the present method infers that more sophisticated Jastrow factors are required to achieve accurate estimation of the atomic correlation energies.

In Table III, ionization potentials given by the present work and the other methods are listed for atoms and ions. These values are calculated from the highest occupied orbital energies $\varepsilon_{\mathrm{HO}}$. It is well known that the ground state total energy difference of a neutral atom and a cation ΔE gives a fairly good estimate of the ionization potential even in LDA or GGA. On the other hand, the absolute value of $\varepsilon_{\mathrm{HO}}$, which is in principle identical with ΔE [79], yields poor estimates of the ionization potential in LDA and GGA because of the wrong asymptotic behavior of the exchange-correlation

TABLE II. Correlation energy estimates for Helium-isoelectronic series (H^-, He, Li^+, and Be^{2+}) and atoms from Li to Ne, given by the present method, the exact exchange method with an LDA correlation energy functional [78] (EXXLDA) within the KLI approximation [50,51], GGA given by Perdew and Wang (PW91) [8,50], and the weighted density approximation from Ref. [28] (WDA1) and [29] (WDA2). Exact values are from subtractions of the exact total energies [80,81] and the Hartree-Fock energies [82,83]. × and blanks indicate no bound state and no data, respectively. All energies are in Hartree atomic units ($m=e^2=\hbar=1$).

	EXXLDA	PW91	WDA1	WDA2	Present	Exact
H^-	−0.0751	×			−0.0216	−0.0399
He	−0.1125	−0.0383	−0.083	−0.0473	−0.0312	−0.042
Li^+	−0.1341	−0.0312			−0.0364	−0.0435
Be^{2+}	−0.1497	−0.0227			−0.0401	−0.0443
Li	−0.1609	−0.0414	−0.1022	−0.0402	−0.0409	−0.0453
Be	−0.2234	−0.0749	−0.152	−0.032	−0.0581	−0.0944
B	−0.294	−0.1006	−0.2457	−0.0537	−0.0784	−0.1246
C	−0.3728	−0.1365	−0.205	−0.089	−0.103	−0.155
N	−0.4577	−0.1741	−0.2054	−0.1254	−0.1405	−0.1847
O	−0.5456	−0.2407	−0.3814	−0.1974	−0.1989	−0.2534
F	−0.6394	−0.3208	−0.5592	−0.2842	−0.2742	−0.3232
Ne	−0.738	−0.3995	−0.7179	−0.3669	−0.3595	−0.3919

potential. In Table III, it is clearly shown that the present correlation energy functional gives very good estimates of the ionization potential from $|\varepsilon_{\mathrm{HO}}|$ for atoms. The accuracy is almost comparable to that of the Hartree-Fock method, which is known to yield good ionization potential estimates for atoms. This is partly due to the fact that the exchange energy is treated exactly in the present work, and then, the correct asymptotic behavior of the exchange-correlation potential is reproduced. Moreover, the present method certainly improves the results of EXXLDA. Therefore, it was proved that the present correlation energy functional is successfully used with the exact exchange functional. On the other hand, PW91 and WDA fail to give accurate ionization potentials from the highest occupied orbital energies because these functionals do not reproduce the correct asymptotic behavior of the exchange-correlation potential.

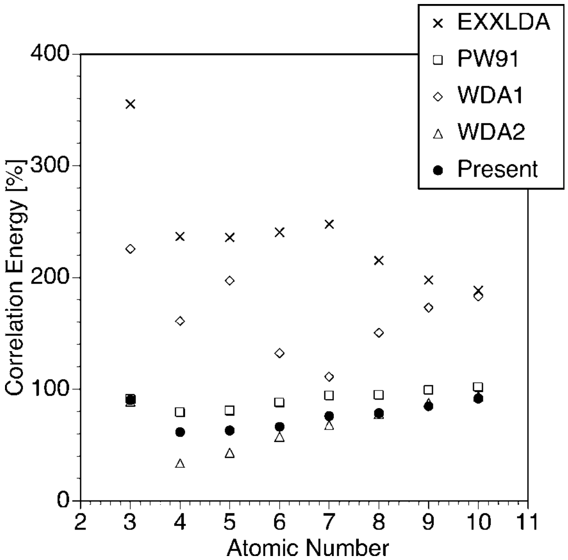

FIG. 1. Percentage of the correlation energy reproduced by the present method is shown in comparison with those obtained from the other density functional methods.

In Fig. 2, errors in charge densities given by the present work are shown for a He atom. The present correlation energy functional reproduces fairly good charge density compared to that obtained from LDA or GGA (PW91). However, the accuracy is comparable to that of the exact exchange method with an LDA correlation energy functional (EXXLDA) and still behind the Hartree-Fock (HF) method. Thus, our correlation energy functional should be further modified for improving the charge density over EXXLDA and the HF method.

In Fig. 3, the correlation potential $v_c(r)$ for a He atom obtained from the present correlation energy functional is depicted with those given by other correlation energy functionals. The exact result is taken from Ref. [85]. It is shown that $v_c(r)$s given by Colle-Salvetti functional and the gradient corrected functionals of BLYP and PW91 are all diverged at the origin. This is an unphysical behavior of $v_c(r)$. On the other hand, $v_c(r)$ given by the present functional becomes a finite value at the origin and this value is very close to that of the exact $v_c(r)$. Nevertheless, the detailed behaviors of the exact $v_c(r)$, i.e., turning from negative to positive value at about $r=0.5$ a.u. and reaches the maximum value at about $r=0.9$ a.u. are still not reproduced by the present correlation energy functional.

IV. CONCLUSIONS

In this work, an orbital-dependent nonlocal correlation energy functional was suggested. It was constructed from an

TABLE III. Ionization potential estimates calculated from absolute eigenvalues of the highest occupied states for Helium-isoelectronic series (H^-, He, Li^+, and Be^{2+}), and atoms from Li to Ne, given by the present method, the exact exchange method with an LDA correlation energy functional given by Perdew and Zunger [78] (EXXLDA) within the KLI approximation [50,51], GGA given by Perdew and Wang (PW91) [8,50], and the weighted density approximation from Ref. [28] (WDA). Exact values for the Helium-isoelectronic series are from data in Ref. [81] and the experimental values for atoms from Li to Ne are from Ref. [84]. × and blanks indicate no bound state and no data, respectively. $\bar{\Delta}$ denotes the mean absolute deviation from the exact or experimental data for the atoms from Li to Ne. All energies are in Hartree atomic units ($m=e^2=\hbar=1$).

	HF	EXXLDA	PW91	WDA	Present	Exact[a]/Expt.[b]
H^-	×	0.078	×		0.054	0.0278[a]
He	0.918	0.976	0.583	0.624	0.943	0.9037[a]
Li^+	2.792	2.864	2.227		2.824	2.7799[a]
Be^{2+}	5.667	5.748	4.870		5.703	5.6556[a]
Li	0.196	0.228	0.119	0.128	0.200	0.198[b]
Be	0.309	0.348	0.207	0.225	0.314	0.343[b]
B	0.311	0.354	0.149	0.215	0.316	0.305[b]
C	0.435	0.484	0.226	0.230	0.444	0.414[b]
N	0.571	0.623	0.308	0.301	0.584	0.534[b]
O	0.509	0.561	0.267	0.376	0.531	0.500[b]
F	0.674	0.729	0.379	0.456	0.703	0.640[b]
Ne	0.850	0.909	0.494	0.542	0.878	0.792[b]
$\bar{\Delta}$	0.025	0.064	0.197	0.157	0.038	

energy formula defined in the transcorrelation method, including two-body and three-body interactions originated from a Jastrow factor. We found that our correlation energy functional gives fairly good estimates for the total energy of atoms and ions compared to those obtained from other nonlocal correlation energy functionals. Moreover, it yields remarkably good ionization potential estimates from the highest occupied orbital energies. Our correlation energy functional also reproduces relatively good charge density for a He atom compared to LDA or GGA. However, the accuracy in the charge density is still behind the Hartree-Fock method. Furthermore, the correlation potential $v_c(r)$ for a He atom derived from our correlation energy functional was found to converge to a finite value at the origin, which is very close to the exact value, although detailed behavior of

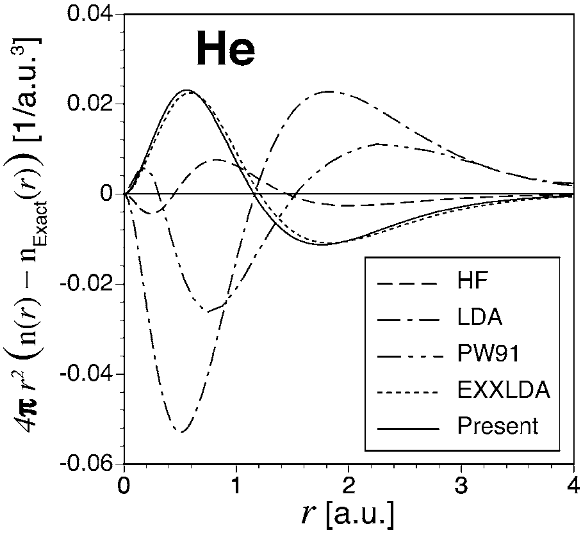

FIG. 2. Errors in the charge densities for a He atom given by the present method, the Hartree-Fock (HF) method, the local-density approximation (LDA) [78], the generalized gradient approximation suggested by Perdew and Wang (PW91) [8,50], the exact exchange method with an LDA correlation (EXXLDA).

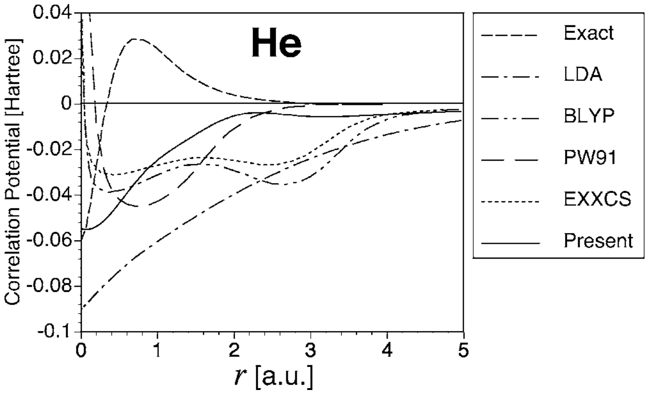

FIG. 3. Correlation potentials for a He atom given by the present method, the local-density approximation (LDA) [78], the gradient correction of BLYP [13,14], the generalized gradient approximation suggested by Perdew and Wang (PW91) [8,50], and the exact exchange method with Colle-Salvetti-type correlation functional [55] (EXXCS). The exact correlation potential is from Ref. [85].

$v_c(r)$ should be further improved. From these results, we conclude that the suggested correlation energy functional is successfully used with the exact exchange energy functional and our approach is promising for creating a new correlation energy functional.

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