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Explicit density-functional exchange potential with correct asymptotic behavior

Naoto Umezawa

National Institute for Materials Science, Advanced Electronic Materials Center, Namiki 1-1, Tsukuba, Ibaraki, 305-0044, Japan

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In this paper, a density-functional exchange potential is proposed. The suggested exchange potential reproduces the correct asymptotic behavior of finite systems: $-1/r$, without significant increase in computational costs over a local-density approximation. Our model exchange potential, which is an explicit functional of a density and the gradient of the density, is given by a hybridization procedure of a Hartree potential and the homogeneous electron gas limit of the exchange potential. Since the Hartree potential behaves as N/r in an asymptotic region with N number of electrons, it is utilized for achieving the correct $-1/r$ asymptotic behavior in our model exchange potential. We found that the suggested exchange potential can yield very good estimates for the ionization potential of atoms and ions from the highest occupied orbital energies.

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I. INTRODUCTION

The local-density approximation (LDA) in the density functional theory (DFT) [1,2] has been widely used in a variety of fields such as physics, chemistry, and materials science [3–5]. This is due to its simplicity and applicability to various systems with relatively less computational costs. Today, there is no doubt about usefulness of LDA in electronic structure calculations.

On the other hand, drawbacks of LDA have been also pointed out. One of the crucial disadvantages is underestimation of the band gap for insulators or semiconductors. A principal reason for this failure lies in the wrong asymptotic behavior of the LDA exchange-correlation potential $v_{\text{xc}}^{\text{LDA}}(\mathbf{r})$. Although the correct asymptotic behavior is $-1/r$, $v_{\text{xc}}^{\text{LDA}}(\mathbf{r})$ decreases exponentially [6]. This causes shallow energy levels of occupied states and that in turn results in the underestimation of the band gap, although DFT itself has difficulty in computing the band gap from the energy difference between the highest occupied and the lowest unoccupied Kohn-Sham eigenvalues [7,8]. Thus reproducing the correct asymptotic behavior of $v_{\text{xc}}(\mathbf{r})$ is an important issue for further development of DFT.

The wrong asymptotic behavior of $v_{\text{xc}}^{\text{LDA}}(\mathbf{r})$ originates from incomplete cancelation of the self-interactions included in a Hartree energy with those in an exchange energy. The self-interactions in the Hartree energy are completely canceled out if an exact exchange functional is adopted in the same way as the Hartree-Fock method. In LDA, however, since the homogeneous electron gas limit is used for the exchange energy functional as an approximation, the self-interactions in the Hartree energy cannot be completely removed. The remaining self-interactions cause the too rapid decay of $v_{\text{xc}}^{\text{LDA}}(\mathbf{r})$ leading to the wrong asymptotic behavior.

Perdew and Zunger have shown that the self-interaction correction (SIC) over the LDA exchange-correlation energy functional $E_{\text{xc}}^{\text{LDA-SIC}}$ is effective for improving the asymptotic behavior [9,10]. However, the SIC treatment accompanies orbital dependency in $E_{\text{xc}}^{\text{LDA-SIC}}$, which avoids the direct functional derivative of $E_{\text{xc}}^{\text{LDA-SIC}}$ with respect to the density. This is usually overcome by means of the optimized effective potential (OEP) method [11–13], although it requests one to solve an integral equation, which significantly increases computational cost over LDA.

The exact exchange (EXX) method [14–16] is of course a self-interaction-free approach reproducing the correct asymptotic behavior of the exchange potential. However, since the exact exchange energy functional $E_{\text{x}}^{\text{EXX}}$ is expressed as an orbital dependent two-body nonlocal functional, the OEP integral equation must be solved for computing the exchange potential. Some approximations [17–21] and a simple iterative approach [22] to the OEP method have been proposed, although they are still computationally demanding compared to LDA. Moreover, combination of $E_{\text{x}}^{\text{EXX}}$ with an LDA correlation energy functional is not always successful because of the lack of error cancelations between $E_{\text{x}}^{\text{EXX}}$ and the approximated correlation energy functional [13,23–26].

Generalized gradient approximation (GGA) is a well-known approach to go beyond LDA, in which the exchange-correlation energy functional explicitly depends on the gradient of a density as well as the density itself [27,28]. Recently, further developments over GGA have been made by incorporating another ingredient: the kinetic energy density, into the exchange-correlation energy functional [29,30]. This approach, known as meta-GGA, remarkably improves a variety of aspects over GGA. Unfortunately, however, neither GGA nor meta-GGA is capable of reproducing the correct asymptotic behavior of the exchange-correlation potential [31]. Becke pioneered the empirical mixing of the EXX functional with LDA or GGA exchange energy functionals [32] (B3). The hybrid functional has been successfully used with the Lee-Yang-Parr-type correlation energy functional [33] (B3LYP) especially in the field of quantum chemical calculation. Subsequently, a lot of hybrid functionals have been also suggested [34–39]. Since the B3 exchange functional contains the EXX term multiplied by an empirical parameter a_0, the asymptotic tail of $v_{\text{xc}}^{\text{B3LYP}}(\mathbf{r})$ is $-a_0/r$, which is still incorrect, although it is much better than the exponential decay of $v_{\text{xc}}^{\text{LDA}}(\mathbf{r})$. Besides that, both the meta-GGA and B3LYP are orbital-dependent functionals, and so they request the time-consuming OEP treatment for the self-consistent procedure.

Knowing the fact that these state-of-the-art exchange correlation energy functionals are orbital dependent, we con-

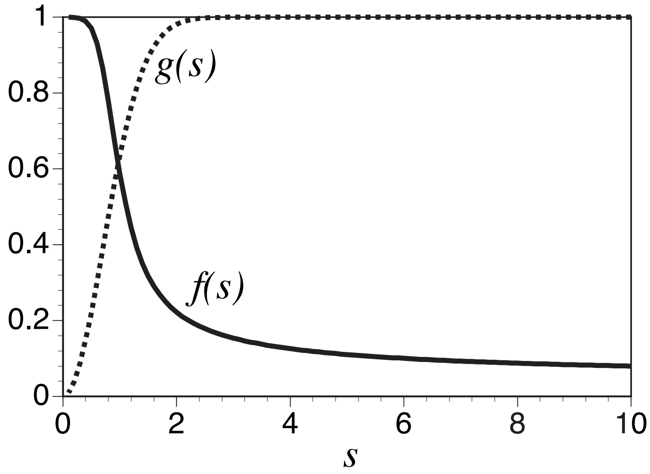

FIG. 1. The switching functions $f(s)$ and $g(s)$ used in Eq. (5).

sider that there is still room for improvement to the direction, which persists in explicit density dependence of E_{xc} and $v_{\mathrm{xc}}(\mathbf{r})$ with satisfaction of $-1/r$ asymptotic behavior of $v_{\mathrm{xc}}(\mathbf{r})$. The impression of the necessity for this kind of explicit density functionals originates from our experience on the solid state calculations for defects, where we had to compromise on the underestimation of the band gap and the quantitatively incorrect estimation of defect levels [40]. This is due to the restriction on practical computation time. Since this kind of calculation has to deal with nearly 100 atoms per simulation cell not only for the electronic structure calculation but also for demanding geometry optimizations, we are forced to use LDA or GGA, which of course cannot fulfill the correct asymptotic behavior of $v_{\mathrm{xc}}(\mathbf{r})$. The difficulty could be overcome by using the screened exchange (sX) method [41–44]. However, the sX functional is still orbital dependent and construction of an explicit density functional is still strongly desired to carry out large scale simulations such as time-dependent density functional calculations coupled with *ab initio* molecular dynamics [45–47].

Weighted density approximation (WDA) [48,49] is one of the explicit density-functional approaches with a relatively good asymptotic behavior $-0.5/r$ of $v_{\mathrm{xc}}^{\mathrm{WDA}}(\mathbf{r})$ [50]. A drawback of WDA is necessity of the time-consuming parameter optimization to satisfy the sum rule required for an exchange-correlation hole in every self-consistent iteration. Moreover, it is known that WDA does not always improve estimates for physical constants over LDA [51,52].

Van Leeuwen and Baerends have proposed a gradient correction to $v_{\mathrm{xc}}^{\mathrm{LDA}}(\mathbf{r})$ so as to reproduce the correct asymptotic behavior [6]. Their functional can yield fairly good estimates of the ionization potential for atoms and small molecules from the highest occupied orbital energies. The LB94 functional $v_{\mathrm{xc}}^{\mathrm{LB94}}(\mathbf{r})$ has been applied to a variety of systems especially in the framework of the time-dependent density-functional theory [53–56]. A convenience of $v_{\mathrm{xc}}^{\mathrm{LB94}}(\mathbf{r})$ lies in its explicit dependency on the local density $n(\mathbf{r})$ and the gradient of the local density $|\nabla n(\mathbf{r})|$. However, the convergence of $v_{\mathrm{xc}}^{\mathrm{LB94}}(\mathbf{r})$ into $-1/r$ as increase in r seems to be too slow compared to the exact asymptotic behavior. This notification motivated us to propose an alternative exchange potential, which rapidly approaches to $-1/r$ better than $v_{\mathrm{xc}}^{\mathrm{LB94}}(\mathbf{r})$. One of the possible solutions to this problem might be reached by the inclusion of Laplacian of the density: $\nabla^2 n(\mathbf{r})$, which is useful for achieving the $-1/r$ behavior of the exchange potential within the explicit density functional [57–59].

In the present work, we rather take a different way to propose an exchange potential. The suggested model exchange potential $v_{\mathrm{x}}^{\mathrm{model}}(\mathbf{r})$ is explicitly written as a local functional of $n(\mathbf{r})$ and $|\nabla n(\mathbf{r})|$. Moreover, it rapidly approaches to the correct asymptotic behavior: $-1/r$. The model potential is constructed from two exact limits of $v_{\mathrm{x}}(\mathbf{r})$, i.e., a He atom $v_{\mathrm{x}}^{\mathrm{He}}(\mathbf{r})$ and the homogeneous electron gas $v_{\mathrm{x}}^{\mathrm{homo}}(\mathbf{r})$. In the case of the He atom, $v_{\mathrm{x}}^{\mathrm{He}}(\mathbf{r})$ is identical with the negative half of the Hartree potential: $v_{\mathrm{x}}^{\mathrm{He}}(\mathbf{r}) = -v_{\mathrm{H}}^{\mathrm{He}}(\mathbf{r})/2$, which of course approaches to $-1/r$ in the asymptotic region. On the analogy of this case, we assume that $-v_{\mathrm{H}}(\mathbf{r})/N$ can be conveniently used in our model exchange potential so as to satisfy the $-1/r$ asymptotic behavior, where N is the number of electrons. Moreover, $v_{\mathrm{x}}^{\mathrm{model}}(\mathbf{r})$ is tuned such that it can reproduce the exact limit of the homogeneous electron gas. It was found that the model exchange potential gives accurate ionization potential estimates for atoms and ions from the highest occupied Kohn-Sham orbital energies.

The layout of this paper is as follows. In Sec. II, the exchange potential will be proposed. In Sec. III, we will show the results for atoms and ions in comparison with those obtained from other potentials. 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 homogeneous electron gas, the exchange potential is written as a function of a density n:

$$v_{\mathrm{x}}^{\mathrm{homo}}[n] = -\frac{k_{\mathrm{F}}}{\pi}, \tag{1}$$

where $k_{\mathrm{F}}=(3\pi^2 n)^{1/3}$ is the Fermi number. In the local-density approximation (LDA), this functional form is universally used for general inhomogeneous systems:

$$v_{\mathrm{x}}^{\mathrm{LDA}}(\mathbf{r}) = v_{\mathrm{x}}^{\mathrm{homo}}[n(\mathbf{r})] = -\frac{k_{\mathrm{F}}(\mathbf{r})}{\pi}. \tag{2}$$

Thus $v_{\mathrm{x}}^{\mathrm{LDA}}(\mathbf{r})$ can be rigorous in the limit of the homogeneous electron gas, although it decreases too rapidly as $v_{\mathrm{x}}^{\mathrm{LDA}}(r) \propto e^{-\alpha r/3}$ $(r\to\infty)$ because of the exponential decay of the density: $n(r)\to Ce^{-\alpha r}$ $(r\to\infty)$ for finite systems.

On the other hand, the exchange potential for a He atoms is given by [60]

$$v_{\mathrm{x}}^{\mathrm{He}}(\mathbf{r}) = -\frac{1}{2}\int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' = -\frac{1}{2}v_{\mathrm{H}}^{\mathrm{He}}(\mathbf{r}), \tag{3}$$

where $v_{\mathrm{H}}^{\mathrm{He}}(\mathbf{r})$ is the Hartree potential for a He atom. This relation between $v_{\mathrm{x}}^{\mathrm{He}}(\mathbf{r})$ and $v_{\mathrm{H}}^{\mathrm{He}}(\mathbf{r})$ originates from the fact that the 1s Kohn-Sham orbital for a He atom is described as

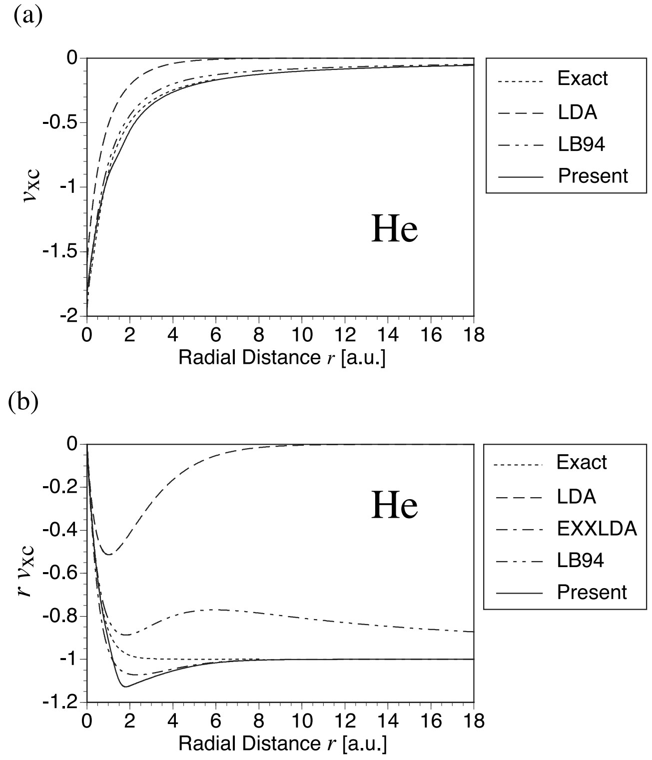

FIG. 2. Exchange-correlation potentials (a) $v_{\mathrm{xc}}(r)$ and (b) $rv_{\mathrm{xc}}(r)$ for a He atom given by the preset model potential of Eq. (12), the local-density approximation (LDA)[9], and the LB94-type gradient corrected functional of Eq. (16) [6] are shown. For the sake of comparison, the result obtained from the exact exchange plus LDA correlation energy functional (EXXLDA) is also shown in (b). The present model potential rapidly approaches to the exact result from Ref. [60].

$\phi_{1s}(\mathbf{r})=\sqrt{n(\mathbf{r})/2}$. From Eq. (3), it is understood that $v_{\mathrm{x}}^{\mathrm{He}}(\mathbf{r})$ approaches to $-1/r$ at the asymptotic region. Although Eq. (3) is a rigorous expression only for a H atom, a He atom or their isoelectronic series, we suppose that it could be utilized for general finite systems to satisfy the asymptotic behavior. Thus we define a potential representing the asymptotic tail:

$$v_{\mathrm{x}}^{\mathrm{asymp}}(\mathbf{r})=-\frac{1}{N}v_{\mathrm{H}}(\mathbf{r}), \tag{4}$$

where N is the number of electrons. Obviously, $v_{\mathrm{x}}^{\mathrm{asymp}}(\mathbf{r})$ asymptotically decreases as $-1/r$. Combing Eq. (2) with Eq. (4), we propose a model exchange potential:

$$v_{\mathrm{x}}^{\mathrm{model}}(\mathbf{r})=f(s)v_{\mathrm{x}}^{\mathrm{LDA}}(\mathbf{r})+g(s)v_{\mathrm{x}}^{\mathrm{asymp}}(\mathbf{r}), \tag{5}$$

$$f(s)=\frac{1}{\ln(1+s^5)+1}, \tag{6}$$

$$g(s)=1-e^{-s^2}, \tag{7}$$

$$s=\gamma\frac{|\nabla n(\mathbf{r})|}{n(\mathbf{r})^{4/3}}, \tag{8}$$

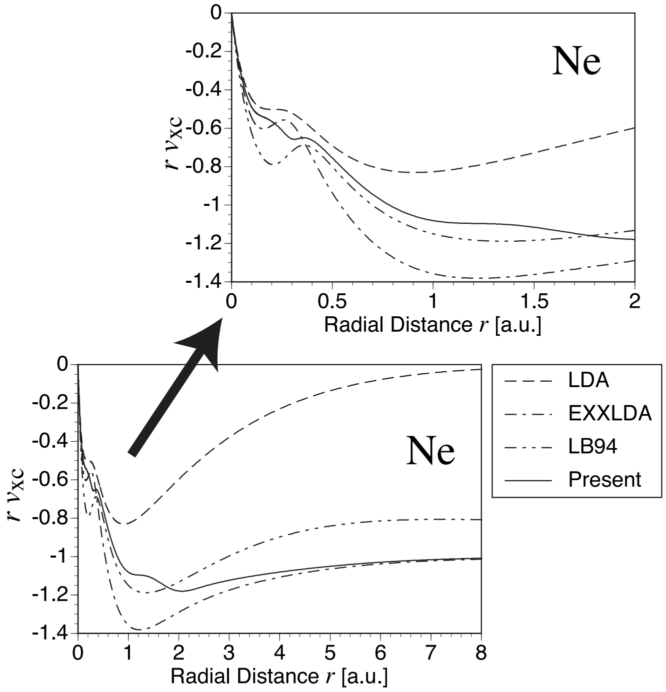

FIG. 3. Exchange-correlation potentials multiplied by r: $rv_{\mathrm{xc}}(r)$ for a Ne atom given by the preset model potential of Eq. (12), the local-density approximation (LDA) [9], the exact exchange plus LDA correlation energy functional (EXXLDA), and the LB94-type gradient corrected functional of Eq. (16) [6] are shown. The present model potential rapidly approaches to the correct $-1/r$ asymptotic behavior.

where $\gamma=0.125$. Determination of this parameter will be discussed later. Here, $f(s)$ and $g(s)$ are switching functions that moderately adjust the mixing ratio of $v_{\mathrm{x}}^{\mathrm{LDA}}(\mathbf{r})$ and $v_{\mathrm{x}}^{\mathrm{asymp}}(\mathbf{r})$ according to the value of s. These functions are depicted in Fig. 1. The function $f(s)$ slowly decreases from 1 to 0 as an increase in the value of s, while $g(s)$ rapidly rises from 0 to 1. This indicates that in Eq. (5), $v_{\mathrm{x}}^{\mathrm{LDA}}(\mathbf{r})$ is slowly switched off and $v_{\mathrm{x}}^{\mathrm{asymp}}(\mathbf{r})$ is rapidly switched on in the asymptotic region because the s value exponentially diverges as an increase in r due to $n(r)\to Ce^{-\alpha r}$ $(r\to\infty)$. This rapid switching of $v_{\mathrm{x}}^{\mathrm{asymp}}(\mathbf{r})$ contributes to the quick convergence of $v_{\mathrm{x}}^{\mathrm{model}}(\mathbf{r})$ into $-1/\mathbf{r}$. Moreover, $v_{\mathrm{x}}^{\mathrm{model}}(\mathbf{r})$ can be rigorous in the limit of the homogeneous electron gas because in this case $(s=0)$, values of $f(s)$ and $g(s)$ are 1 and 0, respectively, and so, $v_{\mathrm{x}}^{\mathrm{model}}=v_{\mathrm{x}}^{\mathrm{LDA}}$. Obviously, the model exchange potential of Eq. (5) satisfies the scaling relation required for the exchange potential [61]:

$$v_{\mathrm{x}}^{\mathrm{model}}([n_\lambda];\mathbf{r})=\lambda^3 v_{\mathrm{x}}^{\mathrm{model}}([n];\lambda\mathbf{r}), \tag{9}$$

where n_λ is the scaling density:

$$n_\lambda(\mathbf{r})=\lambda^3 n(\lambda\mathbf{r}). \tag{10}$$

For the correlation energy functional, we have adopted an LDA functional proposed by Perdew and Zunger [9], $v_{\mathrm{c}}^{\mathrm{PZ}}(\mathbf{r})$. Hence in the present work, the exchange-correlation potential is given by

$$v_{\rm xc}^{\rm model}(\mathbf{r}) = v_{\rm x}^{\rm model}(\mathbf{r}) + v_{\rm c}^{\rm PZ}(\mathbf{r}). \tag{11}$$

The parameter $\gamma = 0.125$ in Eq. (8) was determined such that the self-consistent solution of $v_{\rm xc}^{\rm model}(\mathbf{r})$ for a He atom can be close as much as possible to the exact $v_{\rm xc}(\mathbf{r})$ shown in Ref. [60]. In the spin polarized case, Eq. (11) could be written as

$$v_{\rm xc}^{\sigma{\rm model}}(\mathbf{r}) = v_{\rm x}^{\sigma{\rm model}}(\mathbf{r}) + v_{\rm c}^{\sigma{\rm PZ}}(\mathbf{r}), \tag{12}$$

$$v_{\rm x}^{\sigma{\rm model}}(\mathbf{r}) = f(s_\sigma) v_{\rm x}^{\rm LDA}(\mathbf{r}) + g(s_\sigma) v_{\rm x}^{\rm asymp}(\mathbf{r}), \tag{13}$$

$$s_\sigma = \gamma \frac{|\nabla n_\sigma(\mathbf{r})|}{n_\sigma(\mathbf{r})^{4/3}}. \tag{14}$$

The Kohn-Sham equation is self-consistently solved by using the model exchange-correlation potential Eq. (12). Note that since Eq. (12) contains neither orbital dependent functional nor nonlocal potential except for the Hartree potential, computational cost for solving the Kohn-Sham equation is not significantly increased over LDA and almost comparable to that of GGA. This is a great advantage of using this potential.

In the present work, since an exchange potential is defined first, the exchange energy must be calculated from the Levy-Perdew relation [61]:

$$E_{\rm x}^{\rm model}[n] = -\sum_\sigma \int n_\sigma(\mathbf{r})\mathbf{r} \cdot \nabla v_{\rm x}^{\sigma{\rm model}}(\mathbf{r}) d\mathbf{r}. \tag{15}$$

We will show the results for atoms and ions in the following section.

For the sake of comparison, corresponding calculations have been also done with the gradient corrected exchange-correlation potential proposed by van Leeuwen and Baerends (LB) [6]:

$$v_{\rm xc}^{\sigma{\rm LB94}}(\mathbf{r}) = v_{\rm x}^{\sigma{\rm LB94}}(\mathbf{r}) + v_{\rm c}^{\sigma{\rm PZ}}(\mathbf{r}), \tag{16}$$

$$v_{\rm x}^{\sigma{\rm LB94}}(\mathbf{r}) = v_{\rm x}^{\rm LDA}(\mathbf{r}) - \beta n_\sigma^{1/3}(\mathbf{r}) \frac{x_\sigma^2}{1 + 3\beta x_\sigma \ln(x_\sigma + \sqrt{x_\sigma^2 + 1})}, \tag{17}$$

$$x_\sigma = \frac{|\nabla n_\sigma(\mathbf{r})|}{n_\sigma(\mathbf{r})^{4/3}}. \tag{18}$$

Although in the original paper of van Leeuwen and Baerends [6], the second term of Eq. (17) is considered to be a gradient correction both for the exchange and correlation potentials, we here suppose that it is the correction only for the exchange potential. Thus the exchange energy is calculated from the Levy-Perdew relation [61] in the same way as Eq. (15) with $v_{\rm x}^{\sigma{\rm model}}(\mathbf{r})$ replaced by $v_{\rm x}^{\sigma\ {\rm LB94}}(\mathbf{r})$. Moreover, we adopted the Perdew-Zunger-type LDA correlation energy functional [9] instead of the Vosko-Wilk-Nusair-type functional [62] used in Ref. [6]. This treatment of LB94 is for fair comparison with our model exchange-correlation potential.

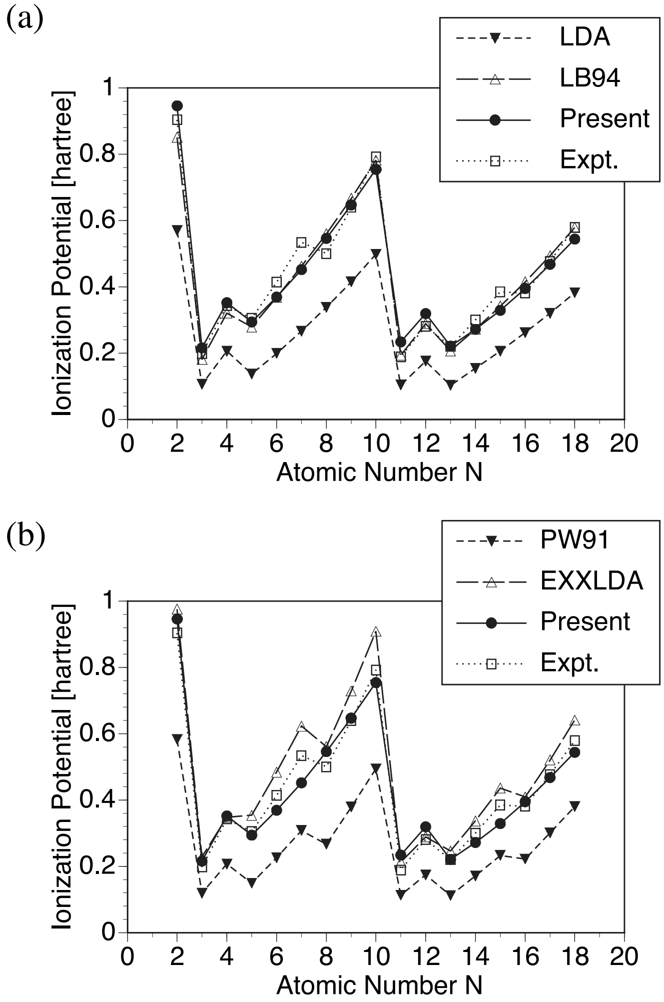

FIG. 4. (a) Ionization potential estimates calculated from absolute eigenvalues of the highest occupied states for atoms from He to Ar, given by the present method, the local-density approximation (LDA), and the LB94-type gradient corrected functional [6]. (b) Corresponding results calculated from the generalized gradient approximation given by Perdew and Wang (PW91) [13,63] and the exact exchange plus LDA correlation energy functional (EXXLDA) are depicted. Experimental values for atoms from He to Ar are from Refs. [13,67].

III. RESULTS

Here, we show the results for atoms and ions given by the model exchange potential proposed in the previous section. In Fig. 2(a), the exchange-correlation potential for a He atom given by the present model functional is shown in comparison with that obtained from the other functionals. It is shown that both the present model functional $v_{\rm xc}^{\rm model}(r)$ and $v_{\rm xc}^{\rm LB94}(r)$ asymptotically approach the exact exchange-correlation potential, while $v_{\rm xc}^{\rm LDA}(r)$ decays too rapidly. The differences of these potentials are more clearly observed in $rv_{\rm xc}(r)$ as shown in Fig. 2(b). It is understood that the present model potential quickly approaches -1, which is the exact asymptotic value of $rv_{\rm xc}(r)$. Moreover, this behavior of $rv_{\rm xc}^{\rm model}(r)$ is very close to that of the exact exchange plus Perdew-Zunger-type LDA correlation energy functional

TABLE I. Ionization potential estimates calculated from absolute eigenvalues of the highest occupied states for helium-isoelectronic series (H^-, Li^+, and Be^{2+}), and atoms from He to Ar, given by the present method, the Hartree-Fock method (HF), the exact exchange plus LDA correlation energy functional [9] (EXXLDA) within the Krieger-Li-Iafrate approximation [13,17,65], the generalized gradient approximation given by Perdew and Wang (PW91) [13,63], the weighted density approximation (WDA) [50], and the gradient corrected functional given by van Leeuwen and Baerends (LB94) shown in Eq. (16) [6]. Exact values for the helium-isoelectronic series are from data in [66] and the experimental values for atoms from He to Ar are from Ref. [67]. Here, × indicates no bound state, and $\bar{\Delta}$ denotes the mean absolute deviation from the exact or experimental data for the atoms from He to Ar. All energies are in the Hartree atomic units ($m=e^2=\hbar=1$).

	HF	LDA	EXXLDA	PW91	WDA	LB94	Present	Exact[a]/Expt.[b]
H^-	×	×	0.0785	×		0.0319	0.0773	0.0278[a]
Li^+	2.792	2.190	2.864	2.227		2.653	2.797	2.7799[a]
Be^{2+}	5.667	4.806	5.748	4.870		5.450	5.643	5.6556[a]
He	0.918	0.570	0.976	0.583	0.624	0.851	0.946	0.9037[a]
Li	0.196	0.106	0.228	0.119	0.128	0.181	0.216	0.198[b]
Be	0.309	0.206	0.348	0.207	0.225	0.321	0.352	0.343[b]
B	0.311	0.137	0.354	0.149	0.215	0.279	0.294	0.305[b]
C	0.435	0.199	0.484	0.226	0.230	0.368	0.369	0.414[b]
N	0.571	0.266	0.623	0.308	0.301	0.462	0.452	0.534[b]
O	0.509	0.338	0.561	0.267	0.376	0.560	0.546	0.500[b]
F	0.674	0.415	0.729	0.379	0.456	0.667	0.647	0.640[b]
Ne	0.850	0.498	0.909	0.494	0.542	0.782	0.754	0.792[b]
Na	0.182	0.104	0.213	0.113		0.194	0.234	0.189[b]
Mg	0.253	0.176	0.289	0.174		0.289	0.319	0.281[b]
Al	0.210	0.103	0.246	0.112		0.207	0.221	0.220[b]
Si	0.297	0.154	0.337	0.171		0.272	0.272	0.300[b]
P	0.392	0.206	0.436	0.233		0.342	0.329	0.385[b]
S	0.364	0.262	0.409	0.222		0.415	0.395	0.381[b]
Cl	0.473	0.320	0.521	0.301		0.494	0.468	0.477[b]
Ar	0.591	0.382	0.641	0.380		0.579	0.544	0.579[b]
$\bar{\Delta}$	0.018	0.176	0.051	0.177		0.028	0.031	

[a] Reference [66].

[b] Reference [67]

(EXXLDA), even though our model functional does not contain any orbital dependency. On the other hand, the convergence of $rv_{xc}^{LB94}(r)$ into -1 is found to be very slow. It could be a disadvantage of LB94.

In Fig. 3, the exchange-correlation potentials multiplied by r: $rv_{xc}(r)$ for a Ne atom are depicted. Again, the convergence of $rv_{xc}^{LB94}(r)$ into -1 is very slow, and it is almost impossible to confirm the correct asymptotic behavior of $rv_{xc}^{LB94}(r)$ from Fig. 3. In contrast, the present model potential $rv_{xc}^{model}(r)$ quickly approaches to -1 similar to $rv_{xc}^{EXXLDA}(r)$. The nice behavior of $v_{xc}^{model}(r)$ in the asymptotic region could be a great benefit of the model potential. However, intershell structure of the present model potential is found to be weak compared to that of EXXLDA or LB94 as shown in upper panel of Fig. 3. It might indicate that the hybridization of two potentials in Eq. (5) is not suitable in the core region. This aspect should be improved in the future.

In Figs. 4(a) and 4(b), ionization potentials (IP) calculated from a variety of functionals are plotted for atoms from He to Ar. These values are calculated from the highest occupied orbital energies ε_{HO}. Compared to the experimental results, it is clearly shown that the present model potential gives very good IP estimates for these atoms, which are almost comparable to those given by LB94-type gradient corrected functional in accuracy [Fig. 4(a)]. On the other hand, LDA or generalized gradient approximation (GGA) proposed by Perdew and Wang (PW91) [63] significantly underestimate IP. It is well-known that the ground state total energy difference of a neutral atom and a cation ΔE gives a fairly good estimate for IP even in LDA or GGA. While the absolute value of ε_{HO}, which is in principle identical with ΔE [64], yields poor estimates for the IP in LDA or GGA due to the wrong asymptotic behavior of the exchange-correlation potential as shown in Figs. 2 and 3. Unfortunately, both the present model and LB94 potentials cannot reproduce the half occupied shell structures observed as the decrease in IP from N to O atom and P to S atom. These shell structures are well reproduced in the EXXLDA method as shown in Fig. 4(b). Nevertheless, the present values are still better than those of EXXLDA on average. These results are very encouraging for applying the model potential to other systems.

In Table I, these IP estimates are listed with the results calculated form the Hartree-Fock method and WDA [50]. As shown in Table I, both the LDA and PW91 largely underestimate IP due to the wrong asymptotic behavior of the exchange-correlation potential. On the other hand, the present model functional gives fairly good estimates of IP.

TABLE II. Ground state total energy estimates for helium-isoelectronic series (H^-, Li^+, and Be^{2+}) and atoms from He to Ar, given by the present method, the exact exchange plus LDA correlation energy functional [9] (EXXLDA) within the KLI approximation [13,17,65], the weighted-density approximation (WDA) [50], and the LB94-type gradient corrected functional. Exact values are from [66,68]. Here, × indicates no bound state, and $\bar{\Delta}$ denotes the mean absolute deviation from the exact data for atoms from He to Ne. All energies are in the Hartree atomic units ($m=e^2=\hbar=1$).

	LDA	EXXLDA	WDA	LB94	Present	Exact
H^-	×	−0.5630		−0.5880	−0.5423	−0.5278
Li^+	−7.1416	−7.3705		−7.2705	−7.1002	−7.2799
Be^{2+}	−13.4432	−13.7610		−13.5947	−13.3594	−13.6556
He	−2.8343	−2.9742	−2.945	−2.9394	−2.8333	−2.9037
Li	−7.3341	−7.5938	−7.535	−7.5278	−7.3538	−7.4781
Be	−14.4462	−14.7965	−14.725	−14.8032	−14.4883	−14.6674
B	−24.3432	−24.8233	−24.775	−24.9090	−24.4047	−24.6539
C	−37.4242	−38.0628	−37.895	−38.2134	−37.4774	−37.8450
N	−54.0225	−54.8623	−54.61	−55.0409	−54.0431	−54.5893
O	−74.4693	−75.3593	−75.195	−75.8801	−74.4923	−75.067
F	−99.0946	−100.0504	−99.97	−100.8700	−99.0801	−99.734
Ne	−128.2272	−129.2853	−129.265	−130.3514	−128.1522	−128.939
Na	−161.4333	−162.6639		−163.8847	−161.4031	−162.257
Mg	−199.1326	−200.4961		−202.0290	−199.1826	−200.059
Al	−241.3089	−242.8366		−244.5410	−241.3885	−242.356
Si	−288.1918	−289.8990	−289.815	−291.7341	−288.2540	−289.374
P	−339.9396	−341.8528		−343.7710	−339.9485	−341.272
S	−396.7091	−398.7303		−400.9784	−396.7442	−398.139
Cl	−458.6565	−460.8009		−463.3104	−458.6541	−460.196
Ar	−525.9375	−528.2330	−527.915	−530.9364	−525.8563	−527.604
$\bar{\Delta}$	0.802	0.364		1.446	0.787	

Moreover, it gives significantly better estimates than the other explicit density functional approach of WDA. The accuracy is almost comparable to that of LB94, although it is still slightly behind that of the Hartree-Fock method. It is interesting to note that the present potential improves these estimates over EXXLDA on average. This could be attributed to the failure of the error cancelation between exchange and correlation potentials in EXXLDA.

In Table II, total energy estimates for atoms and ions given by the present method are listed in comparison with those obtained from other functionals. It is shown that the present model potential yields slightly better accuracy than LDA, and much better results than LB94. This might indicate that the present potential has the advantage in computing the total energy over LB94. Nevertheless, comparative studies for various systems are still required to confirm this remark. It is surprising that the present method reproduces very good total energy for the hydrogen anion H^-, which is known to be very difficult to achieve. This indicates that the present model exchange potential of Eq. (5) is successfully used with the LDA correlation energy functional in this case. In contrast, total energies for cations (Li^+ and Be^{2+}) are not well-reproduced by the present method. Therefore there is still room for improvement in the proposed model exchange potential.

IV. CONCLUSIONS

In the present work, the exchange potential, which is explicitly written as a functional of the density and the gradient of the density, has been proposed. The suggested exchange potential can reproduce the correct asymptotic behavior required for finite systems: $-1/r$. This was achieved by making use of the Hartree potential in our model exchange potential without including any orbital dependent functionals. Thus the computational cost is not significantly increased over the local-density approximation. Moreover, the model potential can be rigorous in the limit of the homogeneous electron gas. It was clearly shown that the proposed exchange potential rapidly approaches to the correct asymptotic behavior: $-1/r$, and this contributes to reproducing very good ionization potentials from the highest occupied orbital energies for atoms. From these results, we conclude that our model exchange potential is promising for computing physical constants related to Kohn-Sham eigenvalues such as ionization potentials for finite systems and band gaps for solids.

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