PHYSICAL REVIEW A VOLUME 54, NUMBER 5 NOVEMBER 1996

Kohn-Sham calculations with self-interaction-corrected local-spin-density exchange-correlation energy functional for atomic systems

Jiqiang Chen,* J. B. Krieger, and Yan Li
Department of Physics, Brooklyn College of the City University of New York, Brooklyn, New York 11210

G. J. Iafrate
U.S. Army Research Office, Research Triangle Park, North Carolina 27709-2211

(Received 27 June 1996)

We have investigated the accuracy of the local-spin-density approximation with orbital-density-dependent self-interaction correction (LSDSIC) as proposed by Perdew and Zunger within a Kohn-Sham approach in which electrons with a given spin projection all move in a single optimized effective potential (OEP). We have also studied the accuracy of the Krieger-Li-Iafrate (KLI) approximation to the OEP for the same energy functional in order to assess its applicability to systems in which the integral equation for the OEP cannot be reduced to a one-dimensional problem, e.g., molecules. Self-consistent Kohn-Sham LSDSIC calculations have been performed for atoms with atomic number $Z=1$–20 in the exchange-only case for the total energy, the highest-occupied orbital energy ϵ_m, and the expectation value of r^2. In addition, the structure of the resulting exchange potential is examined and compared with the exact exchange-only density-functional theory (OEP method with Hartree-Fock exchange-energy functional) results. Furthermore, we display ϵ_m, the ionization potential I, and the electron affinity A when both exchange and correlation energy effects are included. Finally, we also consider the results of evaluating the LSDSIC energy functional by employing the exact (in the central-field approximation) single particle orbitals as proposed by Harrison. We find that the LSDSIC energy functional generally leads to calculated values that are superior to those provided by the LSD approximation and that the KLI approximation yields results in excellent agreement with the corresponding exact OEP results for this energy functional. In particular, quantities strongly related to the behavior of the valence electrons are nearly identical in both the OEP and KLI calculations, i.e., the difference between the $\langle r^2\rangle$ and ϵ_m is less than 0.2% on average, while the difference between the calculated I is less than 0.2 millihartree on average with the corresponding difference of only 0.1 millihartree for A. [S1050-2947(96)08711-2]

PACS number(s): 31.10.+z, 31.15.Ew, 71.15.Mb

I. INTRODUCTION

One of the central issues in density-functional theory is how to better approximate the exchange-correlation energy functional $E_{\mathrm{xc}}[n]$, which is a functional of the ground-state electron-density distribution $n(\mathbf{r})$, but its explicitly exact form is not yet known [1]. In practice, the expression given by the local spin-density (LSD) approximation is often employed. However, the LSD lacks many of the known properties of the exact $E_{\mathrm{xc}}[n]$ [1,2]; for example, the highest-occupied Kohn-Sham orbital energy ϵ_m should be equal to the negative of the removal energy in an exact density-functional theory, while the LSD approximation often yields ϵ_m in error by 40–50 %. Also the exact exchange-correlation potential $V_{\mathrm{xc}}(\mathbf{r})$ approaches $-1/r$ as r approaches infinity while the LSD potential approaches zero exponentially fast. Furthermore, the LSD is not self-interaction free.

Although lacking properties of the exact $E_{\mathrm{xc}}[n]$, the LSD approximation provides a starting point for a better $E_{\mathrm{xc}}[n]$, as it is simple and sometimes very useful in predicting important electronic properties. Various modifications of the LSD have been proposed [1]. The LSD is derived from a uniform electron gas that should be a good approximation for a slowly varying many-electron system, but for real systems the electron densities could change rapidly. Therefore, gradient corrections to the LSD expression for $E_{\mathrm{xc}}[n]$ are the ones that have been carefully investigated [3,4]. Gradient corrections do improve the prediction for some quantities, however, none of the fundamental weaknesses of the LSD discussed above are eliminated.

An alternative approach to modifying the LSD is to incorporate orbital effects into the functional such as the local spin-density approximation with orbital-density-dependent self-interaction-correction (LSDSIC) proposed by Perdew and Zunger [5] that we shall employ in this work. With an orbital-dependent energy functional, the self-interaction correction could be easily implemented, a correct long-range behavior for the exchange-correlation potential could be obtained, and the highest-occupied orbital energy could also be better approximated. The difficulty is that there is no direct method of calculating the functional derivative of an orbital-dependent energy functional with respect to the density, and consequently the conventional Kohn-Sham procedure is not applicable with the LSDSIC. Perdew and Zunger performed LSDSIC calculations [5] but followed a Hartree-Fock-like procedure in which each electron moves in a different (but in this case, local) potential. Similar calculations have been performed for atoms [6], molecules [7,8], and small clusters [9].

As known for almost two decades, with the Hartree-Fock energy functional that is orbital-dependent, Kohn-Sham calculations can be carried out by employing the optimized effective potential (OEP) method [10]. The OEP method de-

---

*Author to whom correspondence should be addressed.

mands the local effective potential from which the Kohn-Sham orbitals are obtained such that the resulting total energy of the system is minimized. This method is general for any orbital-dependent energy functional but poses great computational difficulties for systems with less symmetry than spherically symmetric atoms. Recently, Krieger, Li, and Iafrate (KLI) [11] proposed an approximation to the OEP for any $E_{\mathrm{xc}}[\phi_{i\sigma}]$ for arbitrary symmetry and demonstrated that this approximation is extremely close to the OEP with the Hartree-Fock exchange-energy functional. Thus the KLI approximation opens up the possibility of performing orbital-dependent exchange-correlation energy functional Kohn-Sham calculations for complex systems such as molecules [12,13] and solids [14].

Some atomic calculations with the OEP-LSDSIC (OEP method with the LSDSIC energy functional) [15] and KLI-LSDSIC (KLI method with the LSDSIC energy functional) [2] have been reported. The OEP-LSDSIC exchange potential for the beryllium atom is presented in Ref. [15] and shown to be very similar to the one obtained from an OEP-HF calculation. This is an encouraging result because the LSD produces the potential that lacks most of the exact structural behavior. However, the general properties of the LSDSIC Kohn-Sham potential remain to be examined as the beryllium atom is a simple light atom, and we should know what the situation will be for heavier atoms. The KLI-LSDSIC calculations presented in Ref. [2] yield results that are significantly closer to experimental observables than those obtained from LSD calculations. It should be of interest to compare them with their OEP-LSDSIC counterparts and see how accurately the KLI approximates the OEP. In the present paper, we will present results for atoms $Z=1$–20 and show (1) how the exact LSDSIC Kohn-Sham (i.e., OEP) results behave; (2) how the KLI-LSDSIC approximates the OEP-LSDSIC, and (3) how different they are from the OEP-HF calculation that is regarded as the exact exchange-only density-functional theory [16].

As discussed by Harrison [17], how the central-field approximation should be implemented to a self-consistent LSDSIC calculation is an interesting issue. While our focus will be on how the LSDSIC works with both the total density and individual orbital densities spherically averaged before substitution into the energy functional, i.e., as initially done by Perdew and Zunger (we will label this as LSDSICA), we will follow Harrison to consider the effects of this averaging by substituting the exact nonspherical orbital densities (in the central field approximation) into the LSDSIC energy functional and then performing the angular integrations to obtain a radially dependent energy functional (we will label this as LSDSICE). Harrison reported his Hartree-Fock-like LSDSICE calculation that shows a great improvement for the total energies for atoms with $Z=2$–18, compared to the results provided by the LSDSICA. In addition, we intend to provide some information on other important quantities such as the removal energies and electron affinities and the properties of the Kohn-Sham LSDSICE potential by performing a Kohn-Sham LSDSICE calculation for some atomic systems and comparing them with the corresponding LSDSICA counterparts.

In Sec. II we will briefly review the relevant parts of the orbital-dependent density-functional theory, and then in Sec. III we discuss the exchange potentials from OEP-LSDSICA, KLI-LSDSICA, OEP-HF, and LSD calculations, and in Sec. IV we discuss other quantities such as the total energies, the highest-occupied orbital energies, the electron-density distributions, the removal energies, and electron affinities. In Sec. V we will present some LSDSICE results and compare them with the LSDSICA, and finally in Sec. VI we present our conclusions.

II. OPTIMIZED EFFECTIVE POTENTIAL METHOD AND KLI APPROXIMATION

For a given exchange-correlation energy functional E_{xc}, the conventional Kohn-Sham procedure requires performing a functional derivative with respect to the spin density, $n_\sigma(\mathbf{r})$, to derive the local effective exchange-correlation potential, $V_{\mathrm{xc}\sigma}(\mathbf{r})=\delta E_{\mathrm{xc}}/\delta n_\sigma$. It is a trivial problem if the E_{xc} is explicitly expressed as a functional of the spin densities. However, there is no known direct method of performing $\delta E_{\mathrm{xc}}[\phi_{i\sigma}(\mathbf{r})]/\delta n_\sigma$ if it is known only in terms of orbitals such as the Hartree-Fock exchange-energy functional

$$E_x^{\mathrm{HF}}[\phi_{i\sigma}]=-\tfrac{1}{2}\sum_{ij\sigma}\int d\mathbf{r}\int d\mathbf{r}'\times\frac{\phi_{i\sigma}^*(\mathbf{r})\,\phi_{i\sigma}(\mathbf{r}')\,\phi_{j\sigma}^*(\mathbf{r}')\,\phi_{j\sigma}(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} \tag{1}$$

or the Perdew-Zunger self-interaction-corrected local-density approximation [5]

$$E_{\mathrm{xc}}^{\mathrm{LSDSIC}}[\phi_{i\sigma}]=E_{\mathrm{xc}}^{\mathrm{LSD}}[n_\alpha,n_\beta]-\sum_{i\sigma}E_{\mathrm{xc}}^{\mathrm{LSD}}[n_{i\sigma},0]-\tfrac{1}{2}\sum_{i\sigma}\int d\mathbf{r}\int d\mathbf{r}'\,\frac{n_{i\sigma}(\mathbf{r})n_{i\sigma}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}, \tag{2}$$

where $E_{\mathrm{xc}}^{\mathrm{LSD}}$ is the exchange-correlation functional in the local-density approximation, and $n_{i\sigma}(\mathbf{r})$ is the orbital density, $n_{i\sigma}(\mathbf{r})=|\phi_{i\sigma}(\mathbf{r})|^2$ with $n_\sigma(\mathbf{r})=\Sigma_i n_{i\sigma}(\mathbf{r})$ and $n(\mathbf{r})=\Sigma_\sigma n_\sigma(\mathbf{r})$.

The optimized effective potential method [10] takes an indirect approach to obtain $V_{\mathrm{xc}\sigma}(\mathbf{r})$ with an orbital-dependent energy functional. This is achieved by minimizing the total energy of a system of interest

$$E=E[\phi_{i\sigma}]=T[\phi_{i\sigma}]+E_H[n]+E_{\mathrm{xc}}[\phi_{i\sigma}]+\sum_\sigma\int d\mathbf{r}\;V_{\mathrm{ext}\sigma}(\mathbf{r})n_\sigma(\mathbf{r}), \tag{3}$$

where

$$T[\phi_{i\sigma}]=\sum_{i,\sigma}\langle\phi_{i\sigma}|-\tfrac{1}{2}\nabla^2|\phi_{i\sigma}\rangle,$$

$$E_H[n]=\tfrac{1}{2}\int d\mathbf{r}\,d\mathbf{r}'\,\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}, \tag{4}$$

by varying the Kohn-Sham local effective potential $V_\sigma(\mathbf{r})$ from which the Kohn-Sham orbitals, $\phi_{i\sigma}$, are obtained:

$$-\tfrac{1}{2}\nabla^2\phi_{i\sigma}(\mathbf{r})+V_\sigma(\mathbf{r})\phi_{i\sigma}(\mathbf{r})=\epsilon_{i\sigma}\phi_{i\sigma}(\mathbf{r}),$$

$$V_\sigma(\mathbf{r})=V_{\mathrm{ext}\sigma}(\mathbf{r})+V_{\mathrm{xc}\sigma}(\mathbf{r})+\int d\mathbf{r}'\,\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}. \tag{5}$$

This leads to the following integral equation for searching for the "best" $V_{\mathrm{xc}\sigma}(\mathbf{r})$;

$$\int d\mathbf{r}'H_\sigma(\mathbf{r},\mathbf{r}')V_{\mathrm{xc}\sigma}(\mathbf{r}')=Q_\sigma(\mathbf{r}),$$

$$H_\sigma(\mathbf{r},\mathbf{r}')=\sum_i \phi^*_{i\sigma}(\mathbf{r})G_{i\sigma}(\mathbf{r},\mathbf{r}')\phi_{i\sigma}(\mathbf{r}'),$$

$$Q_\sigma(\mathbf{r})=-\sum_i\int d\mathbf{r}'\,\phi^*_{i\sigma}(\mathbf{r})G_{i\sigma}(\mathbf{r},\mathbf{r}')v_{\mathrm{xc}i\sigma}(\mathbf{r}')\phi_{i\sigma}(\mathbf{r}'), \tag{6}$$

where

$$v_{\mathrm{xc}i\sigma}(\mathbf{r})=\frac{\delta E_{\mathrm{xc}}[\phi_{i\sigma}]}{\phi_{i\sigma}\delta\phi^*_{i\sigma}}, \tag{7}$$

which is the single-particle potential that normally appears in a multiple potential theory and differs from orbital to orbital, and

$$G_{i\sigma}(\mathbf{r}',\mathbf{r})=\sum_{j\neq i}\frac{\phi^*_{j\sigma}(\mathbf{r}')\phi_{j\sigma}(\mathbf{r})}{\epsilon_{j\sigma}-\epsilon_{i\sigma}}, \tag{8}$$

which can be obtained by solving the equation

$$\begin{aligned}&[-\tfrac{1}{2}\nabla^2+V_\sigma(\mathbf{r})-\epsilon_{i\sigma}]G_{i\sigma}(\mathbf{r},\mathbf{r}')\\&\quad=\delta(\mathbf{r}-\mathbf{r}')-\phi_{i\sigma}(\mathbf{r})\phi^*_{i\sigma}(\mathbf{r}').\end{aligned} \tag{9}$$

Self-consistently solving the integral equation Eq. (6) would produce the exact Kohn-Sham results with an orbital-dependent energy functional. This computational scheme is manageable for systems with a high symmetry such as atoms, but becomes difficult for complex systems.

The KLI approximation [11] to the OEP is made by transforming the OEP integral equation to a simpler form and omitting some terms whose average values over the $i\sigma$ state are zero, thus obtaining the following equation for constructing the Kohn-Sham effective exchange-correlation potential in a much simpler way:

$$V_{\mathrm{xc}\sigma}(\mathbf{r})=V^S_{\mathrm{xc}\sigma}(\mathbf{r})+\sum_{i\neq m}\frac{n_{i\sigma}(\mathbf{r})}{n_\sigma(\mathbf{r})}(\overline{V}_{\mathrm{xc}i\sigma}-\overline{v}_{\mathrm{xc}i\sigma}), \tag{10}$$

where the sum does not include the highest-occupied orbital $m\sigma$, and

$$V^S_{\mathrm{xc}\sigma}(\mathbf{r})=\sum_i\frac{n_{i\sigma}(\mathbf{r})}{n_\sigma(\mathbf{r})}v_{\mathrm{xc}i\sigma}(\mathbf{r}), \tag{11}$$

which is essentially the exact Slater (i.e., average Fock) potential when the Hartree-Fock exchange-energy functional is taken for $E_{\mathrm{xc}}[\phi_{i\sigma}(\mathbf{r})]$. $\overline{V}_{\mathrm{xc}i\sigma}$ and $\overline{v}_{\mathrm{xc}i\sigma}$ are the expectation values of $V_{\mathrm{xc}i\sigma}(\mathbf{r})$ and $v_{\mathrm{xc}i\sigma}(\mathbf{r})$ with respect to the $i\sigma$ orbital.

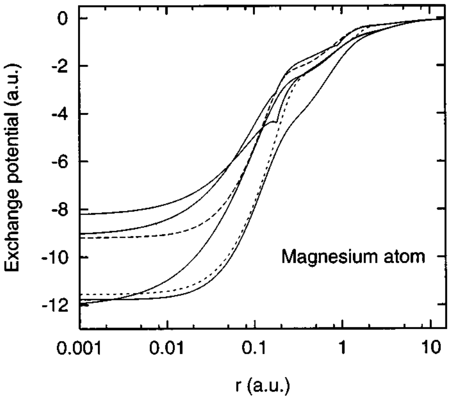

FIG. 1. The $v_{xi}(\mathbf{r})$, $V^S_x(\mathbf{r})$, and $V_x(\mathbf{r})$ for the magnesium atom resulting from the exchange-only self-consistent KLI-LSDSICA calculation. The solid lines are $v_{xi}(\mathbf{r})$, and they are $v_{x2s}(\mathbf{r})$, $v_{x3s}(\mathbf{r})$, $v_{x1s}(\mathbf{r})$, and $v_{x2p}(\mathbf{r})$ from above to below according to their values at $r=0.001$ a.u. in contrast to the order of the eigenvalues $\epsilon_{1s}<\epsilon_{2s}<\epsilon_{2p}<\epsilon_{3s}$. The short-dashed line is $V^S_x(\mathbf{r})$ and the long-dashed line is $V_x(\mathbf{r})$.

The KLI $V_{\mathrm{xc}\sigma}(\mathbf{r})$ is much easier to construct than is the exact OEP. For a given $E_{\mathrm{xc}}[\phi_{i\sigma}(\mathbf{r})]$ such as the expression (1) or (2), Eqs. (5), (7), (10), and (11) can be solved self-consistently. Also the KLI method explicitly demonstrates how the Kohn-Sham local effective potential can be constructed from an orbital-dependent possibly nonlocal energy functional. As an example, in Fig. 1 we show the final convergent results for $v_{xi}(r)$, $V^S_x(r)$, and $V_x(r)$ for the magnesium atom, from an exchange-only KLI calculation with the LSDSICA energy functional. The magnesium atom is a spin-unpolarized system, so we have ignored the spin coordinate. It is seen that $v_{xi}(r)$ $(i=1s,\,2s,\,3s,$ and $2p)$ somehow cross each other, and their depths at small r are not in the same order as that of the corresponding energy eigenvalues. For $i=2s$ and $3s$, the $v_{xi}(r)$ has cusps that are located at the zeros of the $2s$ and $3s$ orbital wave functions. The KLI approach first samples the $v_{xi}(r)$ according to the weight of the ith orbital density in the total density $n(r)$ to construct the Slater potential $V^S_x(r)$; consequently, $V^S_x(r)$ tends to $v_{xi}(r)$ in a region where $n_i(r)$ is dominant in the total density $n(r)$. In particular, we see that $V^S_x(r)$ is very close to $v_{x1s}(r)$ at small r and assumes the same long-range tail of $v_{x3s}(r)$ at large r that corresponds to the highest-occupied orbital that is most extended for this system. Obviously the $V^S_x(r)$ has the $-1/r$ long-range behavior because

$$\begin{aligned}V^S_x(\mathbf{r})&=\sum_i\frac{n_i(\mathbf{r})}{\frac{1}{2}\,n(\mathbf{r})}v^{\mathrm{LSDSIC}}_{xi}(\mathbf{r})\rightarrow v^{\mathrm{LSDSIC}}_{3s}(\mathbf{r})\\&=V^{\mathrm{LSD}}_x[\tfrac{1}{2}\,n(\mathbf{r}),\tfrac{1}{2}\,n(\mathbf{r})]-V^{\mathrm{LSD}}_x[n_{3s}(\mathbf{r}),0]\\&\quad-\int d\mathbf{r}\,\frac{n_{3s}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\rightarrow-\frac{1}{r}\quad(r\rightarrow\infty),\end{aligned} \tag{12}$$

where the LSDSIC energy functional, the expression Eq. (2), has been employed, and $V^{\mathrm{LSD}}_x[n_\alpha,n_\beta]$ is the expression for the LSD exchange potential. From Eq. (10) it can be seen that

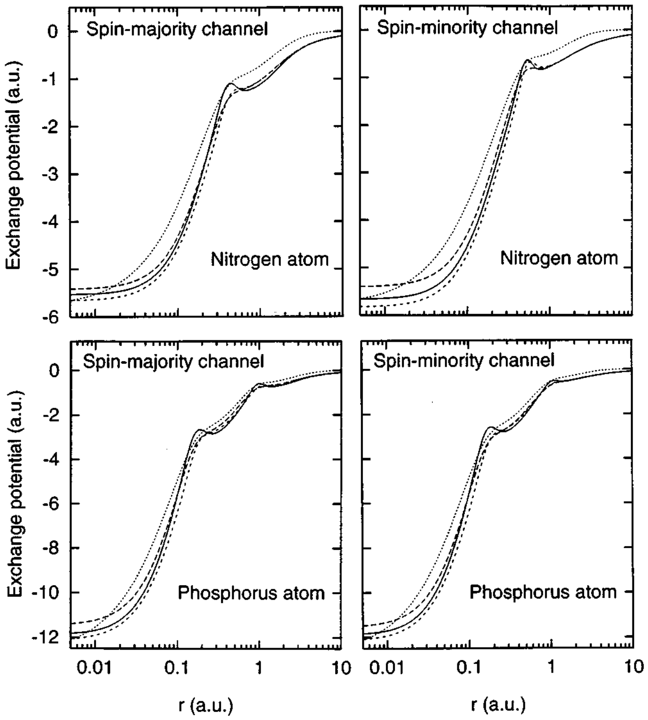

FIG. 2. The exchange potentials from exchange-only Kohn-Sham calculations for the nitrogen and phosphorus atoms. The solid line is the result of the OEP calculation with the Hartree-Fock exchange-energy functional, the long and short dashed lines are, respectively, results of OEP and KLI calculations with the LSDXSICA exchange-energy functional, and the dotted line is the result of the LSD exchange-energy functional calculation.

$$V_x(\mathbf{r})\to V_x^S(\mathbf{r})\to -\frac{1}{r} \quad (r\to\infty), \tag{13}$$

which is the correct behavior for the exchange potential. However, $V_x^s(r)$ is too deep at small r. The second term in the KLI equation (10) adjusts the depth using again the weight of the orbital densities in total density for the expectation values of the $v_{xi}(r)$ and $V_x(r)$. The resulting $V_x(r)$ is smooth, with no cusps, lies far above $V_x^S(r)$ at small r, and quickly goes to $V_x^S(r)$ when r becomes large.

III. KOHN-SHAM EXCHANGE POTENTIAL

To show how the LSDSIC energy functional works, in this section we present the Kohn-Sham exchange potentials from various exchange-only calculations. We will refer to the exchange-only LSD and LSDSIC as LSDX and LSDXSIC, respectively. Figure 2 shows our results for the nitrogen and phosphorus atoms, each atom having three p electrons with parallel spins in its highest-energy subshell and an empty p shell with opposite spin projection. The OEP-LSDXSICA and OEP-HF potentials represent the exact Kohn-Sham results for the LSDXSICA and HF energy functionals, respectively, and the latter is defined as the exact exchange-only Kohn-Sham potential. It is seen from Fig. 2 that besides a correct long-range behavior, the OEP-LSDXSICA potential is substantially better than that of LSDX compared to the OEP-HF, showing that the LSDXSICA exchange-energy functional represents a significant improvement over the LSDX. Figure 2 also shows that the KLI-LSDXSICA potential is a very good approximation to the OEP-LSDXSICA, a large difference occurs only deep in the core region where the electron radial density is small, and therefore the consequence should be minor. A more encouraging result is that as far as an approximation to the OEP-HF exchange-potential is concerned, KLI-LSDXSICA is equally accurate as the OEP-LSDXSICA, showing the strong computational ability of the KLI to produce an accurate Kohn-Sham potential with an orbital-dependent energy functional.

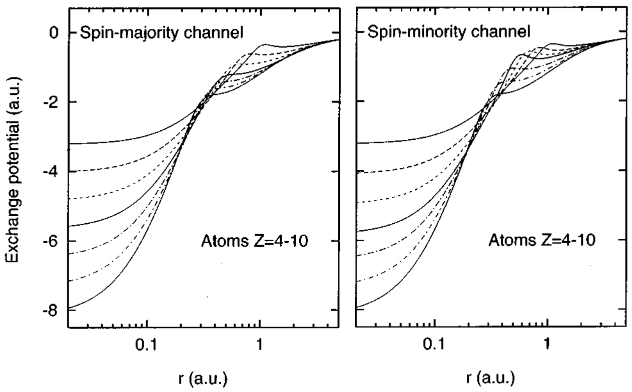

FIG. 3. The exchange potential from exchange-only OEP-LSDSICA calculation for atoms $Z=4$–10. According to their values at small r, the shallowest one is for $Z=4$, and then for $Z=5$, 6, 7, 8, 9, and the deepest one is for $Z=10$.

However, the LSDXSICA does not generally produce the Kohn-Sham potential with all structural behaviors of the exact exchange-only density-functional theory such as ''bumps.'' Bumps are a characteristic of the exact exchange potential for atomic systems and they exist as a barrier separating shells [18,19]. For example, there is a bump for the nitrogen atom between the $n=1$ and 2 shells, and there are two bumps for the phosphorus atom, one between the $n=1$ and 2, and the other between $n=2$ and 3. Figure 2 shows that the OEP-LSDSICA spin-minority potential for the nitrogen atom does have a bump similar to that in the corresponding OEP-HF counterpart, however, there are no bumps for all other cases for the nitrogen and phosphorus atoms but plateaus instead.

As we mentioned earlier, the OEP-LSDXSICA Kohn-Sham exchange potential for the beryllium atom is presented in Ref. [15] and the potential appears to have all the exact structural behaviors. Clearly it is not a general result. To see more about this, we plot in Fig. 3 the OEP-LSDSICA potentials for atoms $Z=4$–10. For the beryllium atom, or the spin-minority channel of the atoms $Z=5$–7, there is a bump in the corresponding exchange potential. We notice that in all these cases there are no more than two electrons in a given spin channel and when there are more electrons in a spin channel, the bump in the exchange potential of this channel will quickly be smoothed out. Therefore, generally speaking, there are no bumps in the LSDXSICA Kohn-Sham exchange potential except for a few light atoms. The beryllium atom is the only closed-shell atom whose exchange potential has a bump.

TABLE I. Total energies in atomic units for atoms $Z=1$–20 from various exchange-only Kohn-Sham calculations.

Z	OEP-HF	OEP-LSDXSICA	KLI-LSDXSICA	LSDX
1	-0.5000	-0.5000	-0.5000	-0.4571
2	-2.8617	-2.8617	-2.8617	-2.7236
3	-7.4325	-7.4347	-7.4342	-7.1934
4	-14.5724	-14.5795	-14.5784	-14.2233
5	-24.5283	-24.5502	-24.5490	-24.0636
6	-37.6889	-37.7462	-37.7450	-37.1119
7	-54.4034	-54.5075	-54.5064	-53.7093
8	-74.8121	-74.9635	-74.9624	-73.9919
9	-99.4092	-99.6361	-99.6351	-98.4740
10	-128.5454	-128.8595	-128.8586	-127.4907
11	-161.8566	-162.2181	-162.2170	-160.6443
12	-199.6116	-200.0285	-200.0273	-198.2488
13	-241.8733	-242.3425	-242.3409	-240.3561
14	-288.8507	-289.3795	-289.3775	-287.1820
15	-340.7150	-341.3014	-341.2989	-338.8885
16	-397.5016	-398.1510	-398.1483	-395.5190
17	-459.4776	-460.1997	-460.1966	-457.3435
18	-526.8122	-527.6028	-527.5994	-524.5174
19	-599.1591	-600.0133	-600.0094	-596.7115
20	-676.7519	-677.6797	-677.6756	-674.1601

TABLE II. Values of the negative of the highest occupied orbital energies in atomic units for atoms $Z=1$–20 from various exchange-only Kohn-Sham calculations.

Z	OEP-HF	OEP-LSDXSICA	KLI-LSDXSICA	LSDX
1	0.5000	0.5000	0.5000	0.2469
2	0.9180	0.9180	0.9180	0.5170
3	0.1963	0.1958	0.1957	0.1004
4	0.3092	0.3081	0.3082	0.1700
5	0.3108	0.2893	0.2897	0.1201
6	0.4358	0.4118	0.4124	0.1960
7	0.5714	0.5357	0.5363	0.2763
8	0.5083	0.4778	0.4788	0.2097
9	0.6734	0.6438	0.6452	0.3259
10	0.8507	0.8062	0.8078	0.4431
11	0.1821	0.1862	0.1864	0.0967
12	0.2530	0.2560	0.2561	0.1421
13	0.2094	0.1914	0.1915	0.0862
14	0.2970	0.2744	0.2747	0.1436
15	0.3920	0.3579	0.3582	0.2033
16	0.3636	0.3433	0.3438	0.1742
17	0.4734	0.4467	0.4473	0.2542
18	0.5907	0.5486	0.5493	0.3338
19	0.1477	0.1536	0.1537	0.0805
20	0.1956	0.2004	0.2005	0.1114

IV. ENERGIES, DENSITY DISTRIBUTIONS, AND ENERGY DIFFERENCES

In Sec. III we compared the exchange potentials from exchange-only OEP-LSDSICA, KLI-LSDSICA, OEP-HF, and LSD calculations, and discussed their common features and differences. In this section, we present some calculated physical properties of the atomic systems for $Z=1$–20 from those Kohn-Sham approaches with exchange-only and exchange-correlation energy functionals and discuss their merits and defects.

Tables I and II present, respectively, the total energies E_t and the highest-occupied orbital energies ϵ_m from exchange-only calculations. We first compare results from the KLI-LSDXSICA and OEP-LSDXSICA. The KLI-LSDXSICA total energy is slightly higher than that of OEP-LSDXSICA, but the difference is two orders of magnitude smaller than the corresponding highest-occupied orbital energy, which is a good approximation to the removal energy. For example, $\epsilon_m \approx -0.200$ a.u. for $Z=20$ while the energy difference is 0.004 a.u. Comparing the highest-occupied orbital energies, the greatest difference is 0.0016 a.u. at $Z=10$, which is about 0.2% of the OEP orbital energy, and for $Z=20$, the difference is 0.0001 a.u. The average difference between the ϵ_m for these twenty atoms is <0.0005 a.u. These results support our earlier assessment that the deviation of the KLI exchange potential from the OEP at small r has small effects on observable quantities, especially those related to the valence electrons.

Comparing the LSDXSICA with the OEP-HF, all the LSDXSICA total energies listed in Table I are lower while all the LSDX counterparts are higher. However, the deviation of the Kohn-Sham LSDXSICA total energy, either the OEP-LSDXSICA or the KLI-LSDXSICA, is about $\frac{1}{3}$ smaller than that of the LSDX. The LSDXSICA orbital energy in most cases is above that of the OEP-HF, so is the LSDX. However, the LSDXSICA deviation from the OEP-HF is less than 10%, but the LSDX orbital energy is about 40–50 % in error. The results show that the LSDXSICA functional substantially reduces the error in the total energy and the highest-occupied orbital energy. The excellent prediction for ϵ_m clearly originates from the correct $-1/r$ long-range tail in the LSDXSICA exchange potential.

The expectation values of r^2 provide a measure for evaluating the accuracy of an electron-density distribution, particularly in the valence electron region. In Table III we present $\langle r^2 \rangle$ from the exchange-only Kohn-Sham calculations. It is shown that the density distributions from the OEP-LSDXSICA and KLI-LSDXSICA are very close, but they are clearly distinct from the LSDX. In all of the cases given in Table III, the LSDXSICA densities are more contracted than the LSDX. However, the LSDXSICA densities generally are not contracted enough compared with the OEP-HF results. The exceptions are those atoms for which the highest-occupied orbital is s type such as atoms $Z=11$, 12, 19, and 20. Examination of the expectation values of r^2 with respect to individual orbitals shows that the s orbital is the only orbital that makes the reverse of the contraction of the total density distribution. As shown in Table II, it is these atoms whose LSDXSICA ϵ_m is below the corresponding OEP-HF orbital energy.

Correlation interaction has to be included in order to compare with experimental results. In Tables IV and V we present our Kohn-Sham results from LSD and LSDSICA calculations with the Perdew-Wang LSD correlation functional [20]; we denote them LSDXC and LSDXCSICA [20], respectively. We compare them with experiments on energy differences for a neutral atom of N electrons such as the

TABLE III. Expectation values of r^2 in atomic units for atoms $Z=1$–20 from various exchange-only Kohn-Sham calculations.

Z	OEP-HF	OEP-LSDXSICA	KLI-LSDXSICA	LSDX
1	3.0000	3.0000	3.0000	3.4998
2	1.1848	1.1848	1.1848	1.3275
3	6.2145	6.2224	6.2350	6.4685
4	4.3316	4.3442	4.3457	4.4809
5	3.1690	3.1931	3.1999	3.3918
6	2.2967	2.3161	2.3194	2.4543
7	1.7253	1.7486	1.7504	1.8461
8	1.4032	1.4228	1.4252	1.5108
9	1.1386	1.1538	1.1554	1.2211
10	0.9372	0.9513	0.9524	1.0036
11	2.4708	2.3895	2.3820	2.4506
12	2.4693	2.4177	2.4129	2.4575
13	2.5772	2.6014	2.5984	2.6668
14	2.3042	2.3373	2.3354	2.3788
15	2.0174	2.0570	2.0557	2.0856
16	1.8269	1.8566	1.8552	1.8847
17	1.6265	1.6520	1.6508	1.6744
18	1.4465	1.4709	1.4699	1.4889
19	2.6939	2.5777	2.5732	2.6087
20	2.8282	2.7320	2.7289	2.7503

removal energy (or ionization energy) $I=E_t[N-1]-E_t[N]$ and the electron affinity $A=E_t[N]-E_t[N+1]$, where $E_t[M]$ is the ground-state total energy of the M-electron system. In Tables IV and V we also list the highest-occupied orbital energies for the corresponding atomic systems for comparison because for an accurate exchange-correlation energy functional, $-\epsilon_m$ should be very close to the energy difference.

For all the systems considered here, the removal energies predicted from the KLI-LSDXCSICA have almost no difference with the corresponding OEP-LSDXCSICA counterparts. For the twenty atoms considered the average difference between the OEP and KLI values of the ionization energy is less than 0.0002 a.u. and the greatest deviation is 0.0006 a.u. Similarly, the average difference between the OEP and KLI values of the electron affinities given in Table V is only 0.0001 a.u. with the maximum discrepancy of 0.0003 a.u. It is indeed encouraging as it is well known that to obtain accurate results for negative ions is particularly difficult.

Comparing I with $-\epsilon_m$, we see that the LSDSICA exchange-correlation energy functional satisfies the condition $-\epsilon_m=I$ to within a few percent while $-\epsilon_m\approx 0.60I$ when the LSD is employed. The same LSDSICA pattern holds for electron affinities. Due to error cancellation, the LSD predicts ionization energies with accuracy comparable to that of LSDSICA calculations. However, the LSD is not applicable to negative ion calculations as it does not yield bound states for such systems, so there are no LSD results given in Table V.

V. LSDSICE KOHN-SHAM POTENTIAL, ENERGY, AND ENERGY DIFFERENCE

In this section we present some results from LSDSICE Kohn-Sham calculations. We consider only those atoms

TABLE IV. Removal energies (the ionization energies) I and the highest occupied orbital energies ϵ_m for atoms $Z=1$–20 from experiments (exact) ($Z=2$–10 from [21], $Z=11$–18 from [22,23] and $Z=19$–20 from [24]) and various Kohn-Sham calculations. Atomic units are used.

	EXACT	OEP-LSDXCSICA		KLI-LSDXCSICA		LSDXC	
Z	$I(-\epsilon_m)$	I	$-\epsilon_m$	I	$-\epsilon_m$	I	$-\epsilon_m$
1	0.500	0.5000	0.5000	0.5000	0.5000	0.4787	0.2690
2	0.904	0.9198	0.9481	0.9198	0.9481	0.8927	0.5703
3	0.198	0.2005	0.1974	0.2001	0.1973	0.2011	0.1163
4	0.343	0.3348	0.3284	0.3346	0.3285	0.3318	0.2058
5	0.305	0.3259	0.3056	0.3265	0.3059	0.3151	0.1506
6	0.414	0.4447	0.4263	0.4451	0.4268	0.4323	0.2272
7	0.536	0.5643	0.5493	0.5646	0.5499	0.5510	0.3085
8	0.500	0.5195	0.5265	0.5198	0.5274	0.5108	0.2724
9	0.641	0.6730	0.6840	0.6732	0.6855	0.6637	0.3839
10	0.795	0.8244	0.8411	0.8245	0.8429	0.8152	0.4978
11	0.189	0.1952	0.1895	0.1951	0.1896	0.1972	0.1132
12	0.281	0.2842	0.2752	0.2842	0.2753	0.2839	0.1755
13	0.220	0.2220	0.2047	0.2219	0.2047	0.2204	0.1110
14	0.300	0.3070	0.2868	0.3069	0.2871	0.3039	0.1699
15	0.386	0.3918	0.3701	0.3916	0.3705	0.3870	0.2311
16	0.381	0.3939	0.3825	0.3940	0.3831	0.3877	0.2286
17	0.477	0.4946	0.4805	0.4946	0.4813	0.4870	0.3047
18	0.579	0.5947	0.5793	0.5946	0.5800	0.5857	0.3822
19	0.159	0.1646	0.1579	0.1646	0.1580	0.1664	0.0961
20	0.228	0.2278	0.2179	0.2278	0.2181	0.2285	0.1415

TABLE V. Electron affinities A and the highest occupied orbital energies of the corresponding negative ions ϵ_m for light atoms from experiments (exact) [24] and various Kohn-Sham calculations. Atomic units are used.

	EXACT	OEP-LSDXCSICA		KLI-LSDXCSICA	
Z	$A(-\epsilon_m)$	A	$-\epsilon_m$	A	$-\epsilon_m$
1	0.028	0.0263	0.0625	0.0263	0.0624
3	0.023	0.0205	0.0251	0.0207	0.0251
5	0.010	0.0243	0.0280	0.0246	0.0283
6	0.047	0.0621	0.0722	0.0623	0.0727
8	0.054	0.0649	0.0992	0.0650	0.1002
9	0.125	0.1376	0.1866	0.1377	0.1878
11	0.020	0.0214	0.0244	0.0214	0.0244
13	0.017	0.0233	0.0203	0.0233	0.0203
14	0.051	0.0584	0.0542	0.0584	0.0542
16	0.076	0.0915	0.0950	0.0915	0.0952
17	0.133	0.1467	0.1506	0.1467	0.1509
19	0.018	0.0203	0.0208	0.0203	0.0208

whose total electron densities are spherically symmetric so that the different treatments of the central-field approximation in LSDSICA and LSDSICE calculations are only due to the treatment of the nonspherical orbitals in the self-interaction correction part of the LSDSIC energy functional, thus some insights on SIC could be clearly obtained. The total densities of atoms for $Z=1$–4 are spherical, but there is no difference between LSDSICA and LSDSICE because the individual orbital densities of these atoms are all spherically symmetric. We list atomic systems in Table VI for $Z\leqslant 20$ for which its total density is spherical except $Z\leqslant 4$.

Table VI shows that the KLI approximation is as close to the exact OEP results when the LSDSICE energy functional is employed as it is to the OEP when the LSDSICA is used. With respect to the quality of energy functionals, the LSDSICE shows significant advantages and also minor disadvantages. Comparing with the LSDSICA, it offers a substantial improvement over the total energy as given by the OEP-HF results in Table I. While the LSDXSICE total energy is still too deep, it reduces the error by a factor of 5–10. However, even though its predictions for the highest-occupied orbital energy, for the removal energy and for the electron affinity are similar to those obtained by employing the LSDSICA, it appears all of them for all the systems considered tend slightly to go in the wrong direction rather than to be closer to the exact values.

Figure 4 shows a comparison between the OEP-LSDXSICE and the OEP-LSDSXSICA exchange potentials. The LSDSICE potentials retain the same fundamental structure as shown in the LSDSICA results. The nitrogen atom spin majority potential is slightly shallower than the LSDSICA counterpart. Comparison with Fig. 2 shows that the OEP-LSDXSICA potential is too deep, and that the LSDSICE improves the potential but only slightly. We see only one curve for the spin minority potential in Fig. 4. This is because for the nitrogen atom the two orbitals, $1s$ and $2s$, both are spherical symmetric, so the LSDSICA and LSDSICE results are extremely close. For the phosphorus

TABLE VI. Results of Kohn-Sham calculation with LSDSICE energy functional for some atomic systems with a spherical total eletron density. Atomic units are used.

Z	OEP-LSDSICE	KLI-LSDSICE	OEP-LSDSICE	KLI-LSDSICE
	Exchange-only E_t		Exchange-only $-\epsilon_m$	
7	−54.4259	−54.4247	0.5205	0.5212
10	−128.6158	−128.6148	0.7893	0.7902
11	−161.9306	−161.9297	0.1867	0.1869
12	−199.6987	−199.6975	0.2564	0.2565
15	−340.8002	−340.7979	0.3510	0.3511
18	−526.8925	−526.8890	0.5407	0.5410
19	−599.2417	−599.2378	0.1541	0.1542
20	−676.8476	−676.8434	0.2008	0.2009
	I (with correlation)		A (with correlation)	
11	0.1959	0.1958	0.0215	0.0215
12	0.2847	0.2847		
19	0.1653	0.1653	0.0204	0.0204
20	0.2284	0.2284		

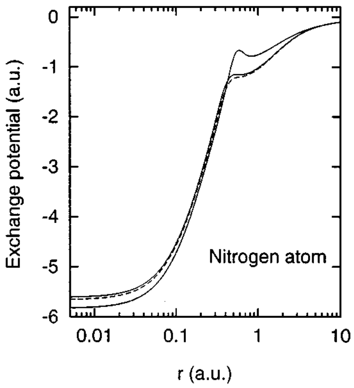

FIG. 4. Comparison of the exchange potential from the exchange-only OEP-LSDSICE calculation (solid lines) with the results from OEP-LSDSICA calculation (dashed lines). The curves with no ‘‘bump’’ are the spin-majority potentials. The spin-minority potentials in both approximations are nearly identical and the difference between them are not discernible in this figure.

atom, the improvement of the Kohn-Sham potentials is not discernible in the scale of Fig. 4, so its LSDSICE potentials are not presented.

VI. CONCLUSIONS

We have performed self-consistent Kohn-Sham atomic calculations with self-interaction-corrected LSD exchange and exchange-correlation energy functionals. One of our major goals is to investigate how the KLI works with the LSDSIC energy functional. The KLI-LSDSIC is shown to be a highly accurate approximation to OEP-LSDSIC, and in particular, both methods predict almost the exact same energy differences such as the ionization energies and the electron affinities for atoms $Z=1$–20. Since it has been previously shown that the KLI-HF results are very similar to those of the exact OEP-HF, the present results add further support to the belief that the KLI is generally an accurate approximation to the OEP method for any orbital-dependent energy functional. This suggests the application of the KLI-LSDSIC approach to more complex systems in performing optimized effective potential calculations for which the exact OEP integral equation cannot be solved.

Our objective is also to investigate how the LSDSIC energy functional works within a Kohn-Sham theory. This is done by comparing the OEP-LSDSICX and OEP-HF calculations. The LSDSIC is shown to be a much better approximation than the LSD alone in predicting most of the electronic properties. The LSDSIC predicts with a high accuracy the total energy and the highest-occupied orbital energy. Self-consistent calculations for negative ions become possible with the LSDSIC energy functional and the resulting electron affinities are in fair agreement with experiments, while the conventional LSD is not applicable to such systems. The application of the central-field approximation is an issue on how to implement the self-interaction correction. We show that the LSDSICE total energy is much better than that of LSDSICA, but other quantities such as the ionization potential and electron affinity are not improved if not made slightly worse.

The LSDSIC Kohn-Sham potential is deeper than that of the OEP-HF and the LSD one is shallower. However, the LSDSIC potential is much closer to the exact one, and in particular, it has the correct $-1/r$ long-range behavior so that the highest-occupied orbital energy is accurately approximated. One of the unfortunate respects is that the ‘‘bump (or bumps)’’ in the exact potentials is (or are) often missed in the results of the LSDSIC. Numerical evidence shows that the LSDSIC potential of a spin channel has a ‘‘bump’’ only for a few lightest atoms. The LSDSICE improves LSDSICA Kohn-Sham potentials only slightly, and the fundamental features remain the same.

ACKNOWLEDGMENTS

One of the authors (J.B.K.) is grateful for a grant from the U.S. Army Research Office in support of this work. The calculations of this work were performed on SUN workstations in the Brooklyn College Atrium Computer Laboratory.

---

[1] See, for example, R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, New York, 1989).
[2] See, for example, J. B. Krieger, Jiqiang Chen, Y. Li, and G. J. Iafrate, Int. J. Quantum Chem. Symp. **29**, 79 (1995), and references therein.
[3] A. D. Becke, Phys. Rev. A **38**, 3098 (1988).
[4] J. Perdew, Phys. Rev. Lett. **55**, 1665 (1985); J. Perdew and Y. Wang, Phys. Rev. B **33**, 8800 (1986).
[5] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
[6] M. R. Pederson and C. C. Lin, J. Chem. Phys. **88**, 1807 (1988), and references therein.
[7] M. R. Pederson, R. A. Heaton, and C. C. Lin, J. Chem. Phys. **80**, 1972 (1984); **82**, 2688 (1985).
[8] Benny G. Johnson, Carlos A. Gonzales, Peter M. W. Gill, and John A. Pople, Chem. Phys. Lett. **221**, 100 (1994).
[9] E. S. Fois, J. I. Penman, and P. A. Madden, J. Chem. Phys. **98**, 6352 (1993); **98**, 6361 (1993).
[10] J. D. Talman and W. F. Shadwick, Phys. Rev. A **14**, 36 (1976).
[11] J. B. Krieger, Y. Li, and G. J. Iafrate, in *Density Functional Theory*, Vol. 337 of *NATO Advanced Study Institute, Series B: Physics*, edited by E. K. U. Gross and R. M. Dreizler (Plenum, New York, 1995), and references therein.
[12] J. B. Krieger, Jiqiang Chen, and G. J. Iafrate, Bull. Am. Phys. Soc. **41**, 748 (1996).
[13] Jiqiang Chen, J. B. Krieger, and G. J. Iafrate, Bull. Am. Phys. Soc. **41**, 748 (1996).
[14] Y. Li, J. B. Krieger, M. R. Norman, and G. J. Iafrate, Phys. Rev. B **44**, 437 (1991).
[15] M. R. Norman and D. D. Koelling, Phys. Rev. B **30**, 5530 (1984).
[16] V. Sahni, J. Gruenebaum, and J. Perdew, Phys. Rev. B **26**, 4371 (1982).
[17] J. G. Harrison, J. Chem. Phys. **78**, 4562 (1983).
[18] Jiqiang Chen, R. O. Esquivel, and M. J. Stott, Philos. Mag. B **69**, 1001 (1994).

[19] Jiqiang Chen, J. B. Krieger, R. O. Esquivel, M. J. Stott, and G. J. Iafrate, Phys. Rev. A **54**, 1910 (1996).

[20] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13 244 (1992); J. P. Perdew, in *Electronic Structure of Solids '91*, edited by P. Ziesche and H. Eschrig (Akademie-Verlag, Berlin, 1991); J. P. Perdew and Y. Wang (unpublished).

[21] E. R. Davidson, S. A. Hagstrom, S. J. Chakravorty, V. M. Umar, and C. F. Fischer, Phys. Rev. A **44**, 7071 (1991).

[22] L. A. Curtiss, K. Raghavachari, G. W. Trucks, and J. A. Pople, J. Chem. Phys. **94**, 7221 (1991).

[23] P. M. W. Gill, B. G. Johnson, J. A. Pople, and M. J. Frisch, Int. J. Quantum Chem. Symp. **26**, 319 (1992).

[24] R. G. Pearson, Inorg. Chem. **27**, 734 (1988).