Self-consistent iterative solution of exchange-only optimized effective potential equations for

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Abstract
In this work, employing the exchange-only orbital-dependent functional, we have obtained an optimized effective potential using the simple iterative method proposed by Kümmel and Perdew (2003 *Phys. Rev. Lett.* **90** 43004). Using this method, we have solved the self-consistent Kohn–Sham equations for closed-shell simple metal clusters of Al, Li, Na, K, and Cs in the context of the jellium model. The results are in good agreement with those obtained by a different method by Engel and Vosko (1994 *Phys. Rev.* B **50** 10498).

1. Introduction

In spite of the success of the local density approximation (LDA) [1] and the generalized gradient approximations (GGA) [2, 3] for the exchange–correlation (XC) part of the total energy in the density functional theory (DFT) [4], it is observed that in some cases these approximations lead to qualitatively incorrect results. On the other hand, appropriate self-interaction corrected versions of these approximations are observed [5] to lead to correct behaviours. These observations motivate one to use functionals in which the self-interaction contribution is removed exactly. One of the functionals which satisfies this constraint is the exact exchange energy functional. Using the exact exchange functional leads to the correct asymptotic behaviour of the Kohn–Sham (KS) potential as well as to correct results for the high-density limit in which the exchange energy is dominant. Given an orbital-dependent exchange functional, one should solve the optimized effective potential (OEP) integral equation [6–8] to obtain the local exchange potential which is used in the KS equations. Application of this integral equation to three-dimensional systems [9–11] involves considerable technical

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difficulty and has some limitations. Recently, Kümmel and Perdew [12, 13] proposed an iterative method which allows one to solve the OEP integral equation accurately and efficiently.

In this work, using the exact exchange OEP method, we have obtained the ground state properties of simple neutral N-electron metal clusters of Al, Li, Na, K, and Cs with closed-shell configurations corresponding to $N = 2, 8, 18, 20, 34$, and 40 (for Al, only $N = 18$ corresponds to a real Al cluster, with six atoms). However, it is a well-known fact that the properties of alkali metals are dominantly determined by the delocalized valence electrons. In these metals, the Fermi wavelengths of the valence electrons are much larger than the metal lattice constants and the pseudopotentials of the ions do not significantly affect the electronic structure. This fact allows one to replace the discrete ionic structure by a homogeneous positive charge background; this is called the jellium model (JM). For closed-shell clusters, the spherical geometry is an appropriate assumption [14–16] and, therefore, we apply the JM to metal clusters by replacing the ions of an N-atom cluster with a sphere of uniform positive charge density and radius $R = (zN)^{1/3}r_s$, where z is the valence of the atom and r_s is the bulk value of the Wigner–Seitz (WS) radius for valence electrons. For Al, Li, Na, K, and Cs we take $r_s = 2.07, 3.28, 3.93, 4.96$, and 5.63, respectively.

The organization of this paper is as follows. In section 2 we explain the calculational schemes. Section 3 is devoted to the results of our calculations and, finally, we conclude this work in section 4.

2. Calculational schemes

In the JM, the total energy of a cluster with exact exchange is given by

$$E_{x-\text{JM}}[n_\uparrow, n_\downarrow, r_s] = T_s[n_\uparrow, n_\downarrow] + E_x[n_\uparrow, n_\downarrow] + \tfrac{1}{2} \int d\mathbf{r}\, \phi([n, n_+]; \mathbf{r})[n(\mathbf{r}) - n_+(\mathbf{r})], \tag{1}$$

in which

$$E_x = \sum_{\sigma=\uparrow,\downarrow} \sum_{i,j=1}^{N_\sigma} \int d\mathbf{r}\, d\mathbf{r}'\, \frac{\phi_{i\sigma}^*(\mathbf{r})\phi_{j\sigma}^*(\mathbf{r}')\phi_{j\sigma}(\mathbf{r})\phi_{i\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \tag{2}$$

and

$$\phi([n, n_+]; \mathbf{r}) = 2 \int d\mathbf{r}'\, \frac{[n(\mathbf{r}') - n_+(\mathbf{r}')]}{|\mathbf{r} - \mathbf{r}'|}. \tag{3}$$

Here, the background charge density is given by

$$n_+(\mathbf{r}) = n\theta(R - r); \qquad n = \frac{3}{4\pi r_s^3} \tag{4}$$

and $n(\mathbf{r})$ is calculated from

$$n(\mathbf{r}) = \sum_{\sigma=\uparrow,\downarrow} \sum_{i=1}^{N_\sigma} |\phi_{i\sigma}(\mathbf{r})|^2 \tag{5}$$

where $\phi_{i\sigma}(\mathbf{r})$ are the KS orbitals obtained from the self-consistent solutions of the set of equations

$$(\hat{h}_{\text{KS}\sigma} - \varepsilon_{i\sigma})\phi_{i\sigma}(\mathbf{r}) = 0. \tag{6}$$

In equation (6),

$$\hat{h}_{\text{KS}\sigma} = -\nabla^2 + v_{\text{eff}\sigma}(\mathbf{r}), \tag{7}$$

$$v_{\text{eff}\sigma}(\mathbf{r}) = v(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) + v_{x\sigma}(\mathbf{r}) \tag{8}$$

$$v_{\text{H}}(\mathbf{r}) = 2 \int d\mathbf{r}\, \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \tag{9}$$

All equations throughout this paper are expressed in Rydberg atomic units.

To solve the KS equations, one should first calculate the local exchange potential from the exchange energy functional. This is done via the solution of the OEP integral equation. Recently, Kümmel and Perdew [12, 13] have proved in a simple and elegant way that the OEP integral equation is equivalent to the equation

$$\sum_{i=1}^{N_\sigma} \psi_{i\sigma}^*(\mathbf{r})\phi_{i\sigma}(\mathbf{r}) + \text{c.c.} = 0, \tag{10}$$

in which $\phi_{i\sigma}$ are the self-consistent KS orbitals and $\psi_{i\sigma}$ are orbital shifts which are obtained from the solution of the following inhomogeneous KS equations:

$$(\hat{h}_{\text{KS}\sigma} - \varepsilon_{i\sigma})\psi_{i\sigma}^*(\mathbf{r}) = Q_{i\sigma}(\mathbf{r}), \tag{11}$$

with

$$Q_{i\sigma}(\mathbf{r}) = -[v_{x\sigma}(\mathbf{r}) - u_{xi\sigma}(\mathbf{r}) - (\bar{v}_{xi\sigma} - \bar{u}_{xi\sigma})]\phi_{i\sigma}^*(\mathbf{r}). \tag{12}$$

$\varepsilon_{i\sigma}$ are the KS eigenvalues which satisfy equation (6), and in the right-hand side of equation (12), $v_{x\sigma}(\mathbf{r})$ are the optimized effective potential and

$$u_{xi\sigma}(\mathbf{r}) = -\frac{2}{\phi_{i\sigma}^*(\mathbf{r})} \sum_{j=1}^{N_\sigma} \phi_{j\sigma}^*(\mathbf{r}) \int d\mathbf{r}' \frac{\phi_{i\sigma}^*(\mathbf{r}')\phi_{j\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \tag{13}$$

$$\bar{v}_{xi\sigma} = \int d\mathbf{r}\, \phi_{i\sigma}^*(\mathbf{r})v_{x\sigma}(\mathbf{r})\phi_{i\sigma}(\mathbf{r}), \tag{14}$$

$$\bar{u}_{xi\sigma} = \int d\mathbf{r}\, \phi_{i\sigma}^*(\mathbf{r})u_{xi\sigma}(\mathbf{r})\phi_{i\sigma}(\mathbf{r}). \tag{15}$$

At the starting point for solving the self-consistent OEP equations (11)–(15), the self-consistent KLI [17] orbitals and eigenvalues are used as input. Then we solve equation (11) to obtain the orbital shifts $\psi_{i\sigma}$. In the next step, we calculate the quantity

$$S_\sigma(\mathbf{r}) = \sum_{i=1}^{N_\sigma} \psi_{i\sigma}^*(\mathbf{r})\phi_{i\sigma}(\mathbf{r}) + \text{c.c.}, \tag{16}$$

the deviation of which from zero is a measure for the deviation from the self-consistency of the OEP KS orbitals. This quantity is used to construct a better exchange potential from

$$v_{x\sigma}^{\text{new}}(\mathbf{r}) = v_{x\sigma}^{\text{old}}(\mathbf{r}) + cS_\sigma(\mathbf{r}). \tag{17}$$

With this $v_{x\sigma}^{\text{new}}(\mathbf{r})$ and keeping the KS eigenvalues and orbitals fixed, we repeat the solution of equation (11). Repeating the 'cycle' (11), (16), (17) several times, the maximum value of $S_\sigma(\mathbf{r})$ will decrease to a desired small value (in our case down to 10^{-8} au). After completing cycles, the $v_{x\sigma}^{\text{new}}$ in conjunction with the KS orbitals are used to construct a new effective potential for 'iterating' the KS equations (6). The value of c in equation (17) is taken to be 30 as suggested in [13]. We have used ten cycles between two successive iterations. These procedures are repeated until the self-consistent OEP potentials are obtained.

3. Results and discussion

Taking spherical geometry for the jellium background, and the solution of the self-consistent KS equations, we have obtained the ground state properties of closed-shell 2, 8, 18, 20, 34, and 40-electron neutral clusters of Al, Li, Na, K, and Cs in the exact exchange jellium model and compared the results with those from the KLI and LSDA schemes.
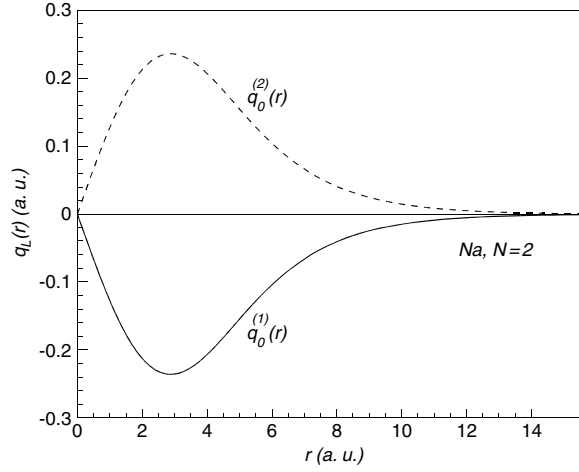
Figure 1. Source terms $q_{l=0,\sigma}^{(1)}$ and $q_{l=0,\sigma}^{(2)}$ in atomic units for Na$_2$. As is obvious, the two terms are equal and opposite in sign, so the orbital shift for $N = 2$ vanishes and the KLI and OEP results coincide.

To solve the KS and OEP equations for spherical geometry we take

$$\phi_{i\sigma}(\mathbf{r}) = \frac{\chi_{i\sigma}(r)}{r} Y_{l_i,m_i}(\Omega) \tag{18}$$

and

$$\psi_{i\sigma}(\mathbf{r}) = \frac{\xi_{i\sigma}(r)}{r} Y_{l_i,m_i}(\Omega). \tag{19}$$

Substituting equations (18) and (19) into (11), the inhomogeneous KS equation reduces to

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \varepsilon_{i\sigma} - v_{\mathrm{eff}\sigma}(r) - \frac{l_i(l_i + 1)}{r^2} \right] \xi_{i\sigma}(r) = q_{i\sigma}(r), \tag{20}$$

in which

$$q_{i\sigma}(r) = q_{i\sigma}^{(1)}(r) + q_{i\sigma}^{(2)}(r), \tag{21}$$

with

$$q_{i\sigma}^{(1)}(r) = \left[v_{xc\sigma}(r) - \bar{v}_{xi\sigma} + \bar{u}_{xi\sigma} \right] \chi_{i\sigma}(r), \tag{22}$$

and

$$q_{i\sigma}^{(2)}(r) = 2 \sum_{j=1}^{N_\sigma} \sum_{l=|l_i-l_j|}^{l_i+l_j} \frac{4\pi}{2l+1} \chi_{j\sigma}(r) B_\sigma(i, j, l; r) \overline{\left[I(l_j m_j, l_i m_i, lm_j - m_i) \right]^2}. \tag{23}$$

The quantities B and I in equation (23) are defined as

$$B_\sigma(i, j, l; r) = \int_{r'=0}^{r} \mathrm{d}r' \, \chi_{i\sigma}(r') \chi_{j\sigma}(r') \frac{r'^l}{r^{l+1}} + \int_{r'=r}^{\infty} \mathrm{d}r' \, \chi_{i\sigma}(r') \chi_{j\sigma}(r') \frac{r^l}{r'^{l+1}} \tag{24}$$

$$I(l_j m_j, l_i m_i, lm) = \int \mathrm{d}\Omega \, Y_{l_j m_j}^*(\Omega) Y_{l_i m_i}(\Omega) Y_{lm}(\Omega), \tag{25}$$
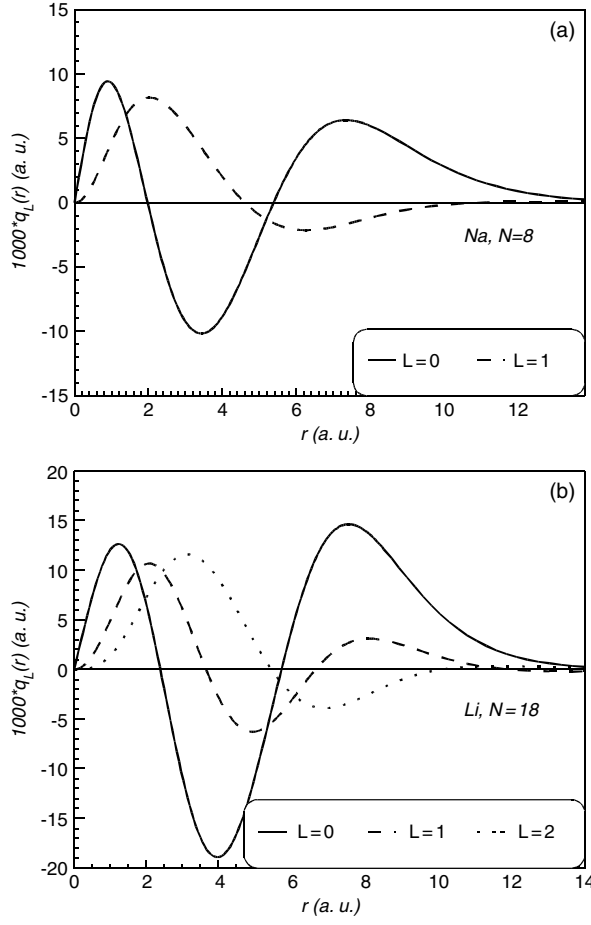
Figure 2. (a) Source terms $q_{l\sigma}$ in atomic units for Na_8 and (b) for Li_{18}. For Na_8, only $l = 0$ and $l = 1$ orbitals are occupied for each spin component, whereas for Li_{18}, the orbitals with $l = 0, 1, 2$ are occupied.

and the bar over I^2 implies averaging over m_i and m_j. Also, the expression for $\bar{u}_{xi\sigma}$ reduces to

$$\bar{u}_{xi\sigma} = -2 \sum_{j=1}^{N_\sigma} \sum_{l=|l_i-l_j|}^{l_i+l_j} \frac{4\pi}{2l+1} \overline{\left[I(l_j m_j, l_i m_i, l m_j - m_i)\right]^2} \int_0^\infty dr\, \chi_{i\sigma}(r)\chi_{j\sigma}(r) B_\sigma(i, j, l; r).$$

(26)

In figure 1, the source term components $q_{l=0,\sigma}^{(1)}$ and $q_{l=0,\sigma}^{(2)}$ are plotted as functions of the radial coordinate. As is seen, they are equal and opposite in sign, so they lead to zero orbital shift, i.e., $\xi_{l=0,\sigma}(r) = 0$. This result in turn leads to the coincidence of the KLI and OEP results.

In figures 2(a) and (b) the self-consistent source terms $q_{l\sigma}(r)$ of equation (22) are plotted as functions of the radial coordinate for Na_8 and Li_{18}, respectively. The corresponding orbital shifts $\xi_{l\sigma}$ are shown in figures 3(a) and (b). It should be noted that $q_{i\sigma}(r)$ and $\xi_{i\sigma}(r)$ must
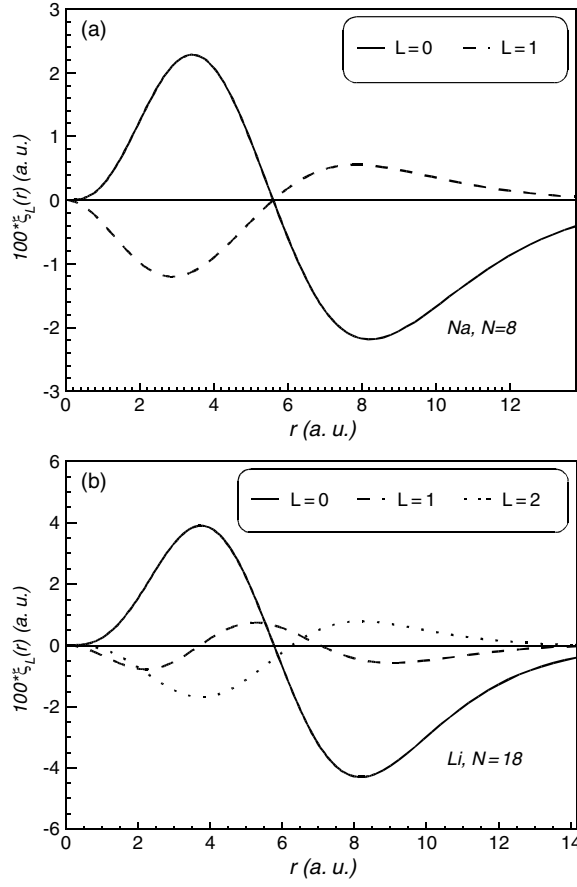
Figure 3. Orbital shifts $\xi_{l\sigma}$ in atomic units (a) for Na$_8$ and (b) for Li$_{18}$.

behave such that

$$\int d\mathbf{r}\, Q_{i\sigma}(\mathbf{r})\phi_{i\sigma}(\mathbf{r}) = 0 \tag{27}$$

and

$$\int d\mathbf{r}\, \psi_{i\sigma}^*(\mathbf{r})\phi_{i\sigma}(\mathbf{r}) = 0 \tag{28}$$

are satisfied.

In order to solve the self-consistent OEP equations, we use the KLI self-consistent results as input. For the KLI calculations, we use (equation (23) of [13] with $\psi_{i\sigma}(\mathbf{r}) = 0$)

$$v_{x\sigma}^{\text{KLI}}(\mathbf{r}) = \frac{1}{2n_\sigma(\mathbf{r})} \sum_{i=1}^{N_\sigma} \{\phi_{i\sigma}(\mathbf{r})\phi_{i\sigma}^*(\mathbf{r})u_{xi\sigma}(\mathbf{r}) + |\phi_{i\sigma}(\mathbf{r})|^2(\bar{v}_{xi\sigma} - \bar{u}_{xi\sigma})\} + \text{c.c.} \tag{29}$$

The self-consistent exchange potentials of Li$_2$ and Al$_{18}$ are plotted in figures 4(a) and (b), respectively. For comparison, the LSDA exchange–correlation potentials are also included. One notes that in the Li$_2$ case, the KLI and OEP potentials are completely coincident, whereas in the Al case, the KLI and OEP potentials coincide only in the asymptotic region. On the other
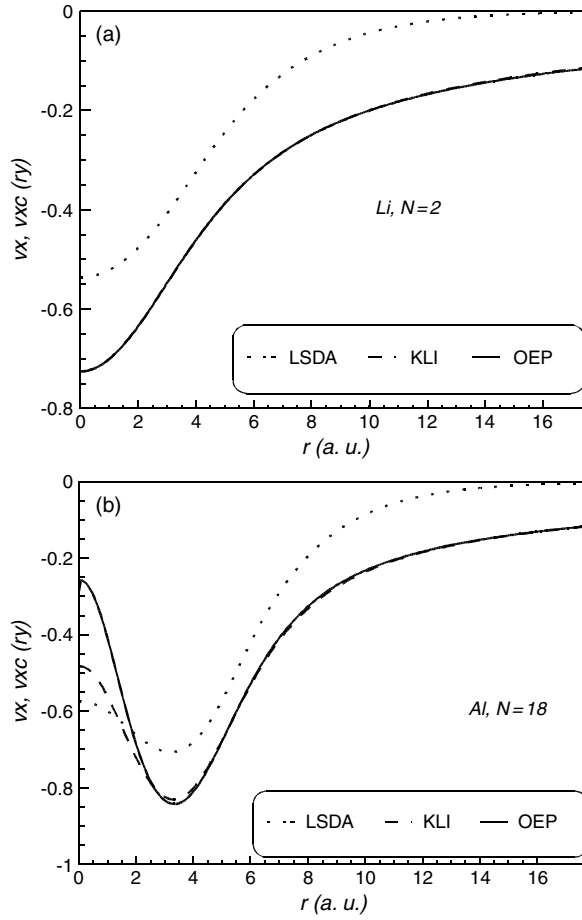
Figure 4. Exchange potentials in KLI and OEP schemes and exchange–correlation potentials in the LSDA, in rydbergs, for (a) Li_2 and (b) for Al_{18}. Here 18 refers to the number of electrons, which is equivalent to six Al atoms. For Li_2 the KLI and OEP results completely coincide, whereas for Al_{18} the coincidence occurs in the asymptotic region. The LSDA has incorrect exponential decay, whereas the KLI and OEP schemes give correct $1/r$ decays.

hand, the LSDA potential, because of having the wrong exponential asymptotic behaviour, decays faster than the KLI and OEP ones, which have correct asymptotic behaviours, going as $1/r$. In the Al case, $N = 18$ refers to the number of electrons, which corresponds to the number $n = 6$ of Al atoms.

In figures 5(a) and (b), we have shown the self-consistent densities for Li_2 and Al_{18}, respectively. As in the potential case, for Li_2 the KLI and OEP densities completely coincide, whereas for Al_{18} the coincidence is only in the asymptotic region.

In table 1, we have listed the self-consistent calculated ground state properties of the closed-shell clusters of Al, Li, Na, K, Cs for $N = 2, 8, 18, 20, 34$, and 40. For comparison of our OEP results with those obtained by Engel and Vosko (EV) [18], we have also included the results for Al, Na, and Cs. The EV results are based on gradient expansion which, in principle, is valid only for slow variations of density as in a bulk solid. However, for finite systems such as clusters or surfaces, the EV results may differ from the exact OEP results. Comparison
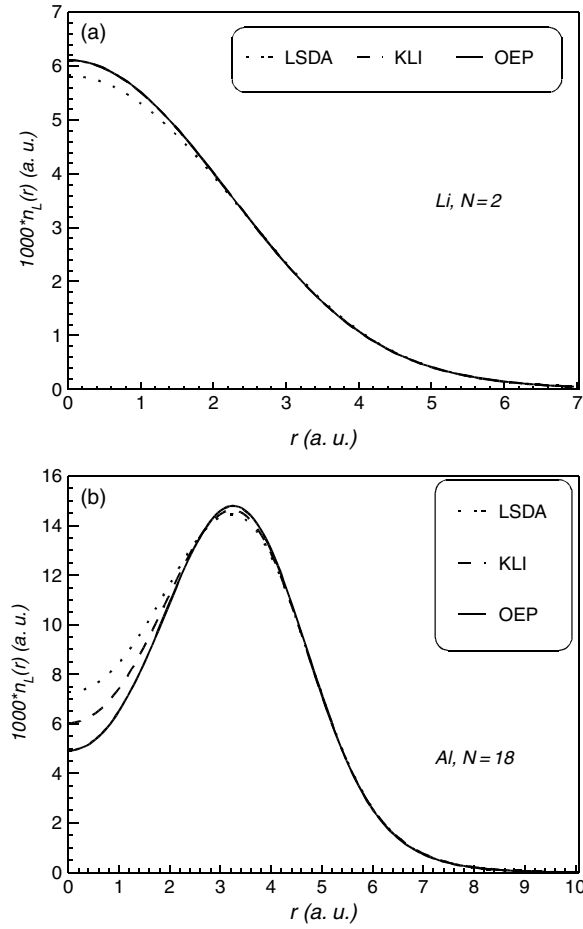
Figure 5. Densities in atomic units (a) for Li_2 and (b) for Al_{18}. Here, as for the potentials, we have full coincidence for Li_2 and asymptotic coincidence for Al_{18}.

of our OEP total energies with those of EV for Na clusters shows a difference of 0.002% on average. On the other hand, the EV exchange energies differ, on average, by 0.001% and the average difference in ε_H is 0.08%. From the computational cost point of view, these quite small differences make the EV method advantageous for calculations within above-mentioned accuracies.

Now we compare the total energies and the exchange energies in the KLI, OEP, and LSDA schemes. Comparison of the total energies shows that the OEP energies, on average, are 1.2% less than those of the KLI scheme. We do not compare the total energies of OEP and LSDA schemes because in the LSDA there is a correlation contribution. On the other hand, comparison of the exchange energies shows that on average, the exchange energies from the OEP scheme are 0.33% more negative than those from the KLI scheme, whereas they are 9% more negative than those from the LSDA scheme.

Another feature in the OEP scheme which should be noted is the contraction of the KS eigenvalue bands relative to those of the KLI scheme. The results in table 1 show that for all N, the relation $\Delta^{OEP} < \Delta^{KLI}$ holds. Here, $\Delta = \varepsilon_H - \varepsilon_L$ is the difference between the

Table 1. Absolute values of total and exchange energies as well as highest occupied and lowest occupied Kohn–Sham eigenvalues in rydbergs. The LSDA total energies include the correlation energies as well.

Atom	r_s	N	LSDA				KLI			
			$-E$	$-E_x$	$-\varepsilon_L$	$-\varepsilon_H$	$-E$	$-E_x$	$-\varepsilon_L$	$-\varepsilon_H$
Al[b]	2.07	2	0.0944	0.5936	0.3821	0.3821	0.0557	0.7016	0.5973	0.5973
		8	0.3087	2.7822	0.6957	0.3806	−0.0660	3.0178	0.8552	0.5418
		18	0.4519	6.6899	0.8606	0.3411	−0.6023	7.0693	0.9710	0.4618
		20	0.6444	7.4183	0.8556	0.3215	−0.5493	7.7898	0.9662	0.4333
		34	0.7603	13.1379	0.9522	0.3103	−1.4409	13.7043	1.0356	0.4066
		40	1.0806	15.3585	0.9497	0.3082	−1.6022	15.8635	1.0369	0.3996
Li	3.28	2	0.2327	0.4324	0.2736	0.2736	0.1866	0.5074	0.4203	0.4203
		8	1.0141	1.9015	0.4074	0.2752	0.6708	2.0538	0.5097	0.3779
		18	2.3050	4.4733	0.4714	0.2598	1.3930	4.7233	0.5404	0.3338
		20	2.6056	4.9417	0.4681	0.2303	1.5677	5.1710	0.5316	0.2992
		34	4.4619	8.6619	0.5065	0.2494	2.5990	9.0347	0.5570	0.3061
		40	5.2635	10.1016	0.5014	0.2267	2.9843	10.3981	0.5491	0.2794
Na	3.93	2	0.2462	0.3787	0.2381	0.2381	0.1988	0.4428	0.3627	0.3627
		8	1.0737	1.6290	0.3333	0.2402	0.7465	1.7551	0.4177	0.3249
		18	2.4664	3.8049	0.3777	0.2297	1.6128	4.0135	0.4338	0.2896
		20	2.7664	4.1991	0.3748	0.2018	1.7944	4.3852	0.4250	0.2577
		34	4.7746	7.3347	0.4022	0.2232	3.0446	7.6461	0.4424	0.2679
		40	5.6075	8.5495	0.3976	0.2002	3.4899	8.7840	0.4337	0.2412
K	4.96	2	0.2448	0.3174	0.1981	0.1981	0.1970	0.3693	0.2979	0.2979
		8	1.0596	1.3306	0.2594	0.2006	0.7553	1.4280	0.3245	0.2658
		18	2.4442	3.0822	0.2874	0.1943	1.6667	3.2447	0.3294	0.2389
		20	2.7275	3.3986	0.2851	0.1700	1.8420	3.5380	0.3214	0.2120
		34	4.7230	5.9117	0.3030	0.1908	3.1617	6.1552	0.3320	0.2229
		40	5.5338	6.8879	0.2995	0.1701	3.6226	7.0565	0.3234	0.1988
Cs	5.63	2	0.2382	0.2875	0.1789	0.1789	0.1907	0.3335	0.2669	0.2669
		8	1.0252	1.1904	0.2271	0.1816	0.7341	1.2742	0.2833	0.2376
		18	2.3652	2.7459	0.2490	0.1768	1.6290	2.8866	0.2846	0.2144
		20	2.6351	3.0268	0.2471	0.1548	1.7969	3.1446	0.2772	0.1904
		34	4.5646	5.2538	0.2613	0.1743	3.0932	5.4652	0.2851	0.2007
		40	5.3452	6.1206	0.2584	0.1554	3.5445	6.2591	0.2770	0.1787

Atom	r_s	N	OEP				EV[a]		
			$-E$	$-E_x$	$-\varepsilon_L$	$-\varepsilon_H$	$-E$	$-E_x$	$-\varepsilon_H$
Al[b]	2.07	2	0.0557	0.7016	0.5973	0.5973	0.0557	0.7016	0.5973
		8	−0.0653	3.0248	0.8507	0.5416	−0.0653	3.0248	0.5417
		18	−0.5998	7.0987	0.9608	0.4600	−0.5998	7.0987	0.4600
		20	−0.5480	7.8071	0.9618	0.4326	−0.5480	7.8071	0.4316
		34	−1.4354	13.7536	1.0298	0.4027	−1.4354	13.7535	0.4027
		40	−1.6000	15.8913	1.0307	0.3956	−1.6001	15.8913	0.3955
Li	3.28	2	0.1866	0.5074	0.4203	0.4203	—	—	—
		8	0.6714	2.0591	0.5076	0.3781	—	—	—
		18	1.3952	4.7474	0.5352	0.3328	—	—	—
		20	1.5689	5.1842	0.5295	0.3000	—	—	—
		34	2.6040	9.0778	0.5533	0.3037	—	—	—
		40	2.9865	10.4195	0.5464	0.2783	—	—	—

Table 1. (Continued.)

Atom	r_s	N	OEP				EV[a]		
			$-E$	$-E_x$	$-\varepsilon_L$	$-\varepsilon_H$	$-E$	$-E_x$	$-\varepsilon_H$
Na	3.93	2	0.1988	0.4428	0.3627	0.3627	0.1988	0.4428	0.3626
		8	0.7470	1.7598	0.4162	0.3251	0.7470	1.7598	0.3252
		18	1.6148	4.0354	0.4298	0.2888	1.6148	4.0354	0.2888
		20	1.7956	4.3974	0.4237	0.2588	1.7956	4.3974	0.2600
		34	3.0493	7.6870	0.4392	0.2659	3.0494	7.6870	0.2662
		40	3.4920	8.8038	0.4320	0.2410	3.4920	8.8036	0.2414
K	4.96	2	0.1970	0.3693	0.2979	0.2979	—	—	—
		8	0.7557	1.4319	0.3235	0.2660	—	—	—
		18	1.6685	3.2639	0.3266	0.2383	—	—	—
		20	1.8431	3.5490	0.3211	0.2134	—	—	—
		34	3.1662	6.1934	0.3295	0.2214	—	—	—
		40	3.6247	7.0744	0.3230	0.1994	—	—	—
Cs	5.63	2	0.1907	0.3335	0.2669	0.2669	0.1907	0.3335	0.2669
		8	0.7345	1.2778	0.2826	0.2378	0.7345	1.2777	0.2378
		18	1.6307	2.9044	0.2823	0.2139	1.6307	2.9043	0.2132
		20	1.7980	3.1553	0.2773	0.1920	1.7980	3.1553	0.1925
		34	3.0974	5.5020	0.2830	0.1994	3.0974	5.5020	0.1974
		40	3.5462	6.2788	0.2766	0.1791	3.5465	6.2763	0.1795

[a] Data from [18].
[b] Here, $N = 18$ corresponds to the Al_6 cluster and the other values of N do not correspond to real Al clusters.

maximum occupied and minimum occupied KS eigenvalues. For $N = 2$, we have $\Delta = 0$. The results show that the maximum relative contraction, $|\Delta^{OEP} - \Delta^{KLI}|/\Delta^{KLI}$, is 2.6%, which corresponds to Cs_{18}.

4. Summary and conclusion

In this work, we have considered the exchange-only jellium model in which we have used the exact orbital-dependent exchange functional. This model is applied to the closed-shell simple metal clusters of Al, Li, Na, K, and Cs. For the local exchange potential in the KS equation, we have solved the OEP integral equation by the iterative method proposed recently by Kümmel and Perdew [13]. By solving the self-consistent KS equations, we have obtained the ground state energies of the closed-shell clusters ($N = 2, 8, 18, 20, 34, 40$) for the LSDA, KLI, and OEP schemes. The KLI and OEP results are the same for neutral two-electron clusters. However, for $N \neq 2$, the densities and potentials in the KLI and OEP schemes coincide for large r values. The OEP exchange and effective potentials show correct $1/r$ behaviour in contrast to the incorrect exponential behaviour shown by the LSDA. The total energies in the OEP scheme are more negative than those from the KLI scheme by 1.2% on average. On the other hand, the exchange energies from the OEP scheme are about 0.33% more negative than those from the KLI scheme, whereas they are about 9% more negative than those from the LSDA. The widths of the occupied bands, $\varepsilon_H - \varepsilon_L$, in the OEP scheme are contracted relative to those in the KLI scheme by at most 2.6%, which corresponds to Cs_{18}. In spite of the validity of the gradient expansion method for slow variations in density, comparison of our OEP results with those of EV shows excellent agreement.

Acknowledgments

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