

Exact exchange-optimized effective potential and self-compression of stabilized jellium clusters

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In this work, we have used the exchange-only optimized effective potential in the self-consistent calculations of the density functional Kohn-Sham equations for simple metal clusters in stabilized jellium model with self-compression. The results for the closed-shell clusters of Al, Na, and Cs with $N=2, 8, 18, 20, 34,$ and 40 show that the clusters are 3% more compressed here than in the local spin density approximation (LSDA). On the other hand, in the LSDA, neglecting the correlation results in a contraction by 1.4%.

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I. INTRODUCTION

The Kohn-Sham¹ (KS) density functional theory² (DFT) is one of the most powerful techniques in electronic structure calculations. However, the exact form of the exchange-correlation functional is still unknown and, in practice, one must use approximations. In spite of the success of the local spin density approximation¹ (LSDA) and the generalized gradient approximation³ (GGA), it is observed that, in some cases, these approximations fail to predict correct behaviors, even qualitatively. For example, in some $3d$ transition metal monoxides, which are Mott insulators, they predict metallic behaviors.⁴⁻⁷ On the other hand, appropriate self-interaction corrected versions of these approximations are observed to predict correct antiferromagnetic insulating behaviors for FeO and CoO.^{7,8} These observations motivates 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 (EEX) orbital dependent functional. Using the EEX functional leads to the correct asymptotic $1/r$ behavior of the KS potential for finite systems as well as to correct results for the high density limit in which the exchange energy is dominated.⁹ Although neglecting the correlation effects in orbital dependent functionals fails to reproduce the dispersion forces such as the van der Waals forces,^{10,11} the EEX in some respects is advantageous over the local and semilocal approximations.^{11,12} To obtain the local exchange potential from the orbital dependent functional, one should solve the optimized effective potential (OEP) integral equation. Recently, Kümmel and Perdew^{13,14} have invented an iterative method which allows one to solve the OEP integral equation accurately and efficiently even for three-dimensional systems. This method is used in this work.

To simplify the cluster problem, we have used the stabilized jellium model with self-compression^{15,16} (SJM-SC) employing spherical geometry for the jellium background. It has been shown that the application of the LSDA-SJM-SC to neutral metal clusters predicts smaller equilibrium r_s values than the bulk values for small clusters and converges to it for very large clusters.¹⁵ This trend is consistent with the results of *ab initio* calculations.^{17,18}

In this work, we have used the EEX-SJM-SC to obtain the equilibrium sizes and energies of closed-shell neutral N -electron clusters of Al, Na, and Cs for $N=2, 8, 18, 20, 34,$ and 40 (for Al, $N=18$ corresponds to Al_6 cluster and other

values do not correspond to a real Al_n). In order to have an estimate for the self-interaction effects, we have repeated the calculations for the exchange-only local spin density approximation (x-LSDA) in which the spin-polarized version of the Dirac form, $E_x = c_x \int d\mathbf{r} n^{4/3}$, is used. Comparison of the results shows that (except for $N=40$ in Al case) the relation $\bar{r}_s^{EEX} < \bar{r}_s^{x-LSDA} < \bar{r}_s^{LSDA}$. The organization of this paper is as follows. In Sec. II, we explain the calculational schemes. Section III is devoted to the results of our calculations and finally, we conclude this work in Sec. IV.

II. CALCULATIONAL SCHEMES

In this section, we first explain how to implement the exact exchange in the SJM and then will explain the procedure for the OEP calculations.

A. Exact-exchange stabilized jellium model

As in the original¹⁹ SJM, here the Ashcroft empty core pseudopotential²⁰ is used for the interaction of an electron with an ion of charge z . For a given bulk metal with Wigner-Seitz radius r_s^B , the core radius of the pseudopotential r_c is obtained by setting the pressure of the bulk system equal to zero [as in Eq. 7 of Ref. 21 but neglecting the correlation ϵ_c]

$$r_c(r_s^B) = \frac{(r_s^B)^{3/2}}{3} \{-2t_s(r_s) - \epsilon_x(r_s) - \epsilon_M(r_s)\}_{r_s=r_s^B}^{1/2}. \quad (1)$$

Here, t_s and ϵ_x are the kinetic and exchange energy per particle for an electron gas system, respectively, and ϵ_M is the average Madelung energy.¹⁹ Using Eq. (1) for a given metal shows that the core radius assumes smaller values compared to the case when the correlation is present. In the EEX-SJM-SC, the total energy of a cluster is given by

$$\begin{aligned} E_{EEX-SJM}[n_\uparrow, n_\downarrow, r_s, r_s^B] &= E_{EEX-JM}[n_\uparrow, n_\downarrow, r_s] \\ &+ (\epsilon_M + \bar{w}_R) \int d\mathbf{r} n_+(\mathbf{r}) + \langle \delta v \rangle_{WS} \\ &\times \int d\mathbf{r} \Theta(\mathbf{r}) [n(\mathbf{r}) - n_+(\mathbf{r})], \quad (2) \end{aligned}$$

where, E_{EEX-JM} is the total energy in the exact-exchange jellium model with the exchange energy given by

$$E_x = \sum_{\sigma=\uparrow,\downarrow} \sum_{i,j=1}^{N_\sigma} \int d\mathbf{r} d\mathbf{r}' \frac{\phi_{i\sigma}^*(\mathbf{r}) \phi_{j\sigma}^*(\mathbf{r}') \phi_{j\sigma}(\mathbf{r}) \phi_{i\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (3)$$

All equations throughout this paper are expressed in Rydberg atomic units. Here, n_σ with $\sigma = \uparrow, \downarrow$ are the electron spin densities and r_s is the Wigner-Seitz (WS) radius for the jellium sphere of the cluster. \bar{w}_R is the average value of the repulsive part of the pseudopotential, $n(\mathbf{r})$ and $n_+(\mathbf{r})$ are the total electron density and the jellium background density, respectively. $\Theta(\mathbf{r})$ is the step function with unit value inside the jellium and zero for the outside. $\langle \delta v \rangle_{WS}$ is the average of the difference potential over the WS cell and the difference potential δv is defined as the difference between the pseudopotential of a lattice of ions and the electrostatic potential of the jellium positive background. As in the original¹⁹ SJM (but in the absence of the correlation energy component), at equilibrium density we have

$$\langle \delta v \rangle_{WS} = -\frac{1}{3} [2t_s(n^B) + \varepsilon_x(n^B)]. \quad (4)$$

To obtain the equilibrium size and energy of a N -atom cluster in EEX-SJM-SC, we solve the equation

$$\left. \frac{\partial}{\partial r_s} E(N, r_s, r_c) \right|_{r_s = \bar{r}_s(N)} = 0, \quad (5)$$

where N and r_c are kept constant and E is given by Eq. (2). The procedure for the x-LSDA is the same as above except for that the Dirac exchange energy must be used.

B. The OEP equations

Kümmel and Perdew¹⁴ have proved, in a simple way, that the OEP integral equation is equivalent to

$$\sum_{i=1}^{N_\sigma} \psi_{i\sigma}^*(\mathbf{r}) \phi_{i\sigma}(\mathbf{r}) + \text{c.c.} = 0. \quad (6)$$

$\phi_{i\sigma}$ are the self-consistent KS orbitals and $\psi_{i\sigma}$ are orbital shifts. The self-consistent orbital shifts and the local exchange potentials are obtained from the iterative solutions of inhomogeneous KS equations. Taking spherical geometry for the jellium background and inserting

$$\phi_{i\sigma}(\mathbf{r}) = \frac{\chi_{i\sigma}(r)}{r} Y_{l_i, m_i}(\Omega), \quad (7)$$

and

$$\psi_{i\sigma}(\mathbf{r}) = \frac{\xi_{i\sigma}(r)}{r} Y_{l_i, m_i}(\Omega), \quad (8)$$

in to the inhomogeneous KS equation [Eq. 21 of Ref. 14], one obtains²²

$$\left[\frac{d^2}{dr^2} + \varepsilon_{i\sigma} - v_{eff\sigma}(r) - \frac{l_i(l_i + 1)}{r^2} \right] \xi_{i\sigma}(r) = q_{i\sigma}(r). \quad (9)$$

Here, $\varepsilon_{i\sigma}$ and $v_{eff\sigma}$ are the KS eigenvalues and effective potentials, respectively. The right hand side of Eq. (9) can be written as

$$q_{i\sigma}(r) = q_{i\sigma}^{(1)}(r) + q_{i\sigma}^{(2)}(r), \quad (10)$$

with

$$q_{i\sigma}^{(1)}(r) = [v_{x\sigma}(r) - \bar{v}_{xi\sigma} + \bar{u}_{xi\sigma}] \chi_{i\sigma}(r), \quad (11)$$

in which,

$$\bar{v}_{xi\sigma} = \int_0^\infty dr \chi_{i\sigma}(r) v_{x\sigma}(r) \chi_{i\sigma}(r) \quad (12)$$

and

$$\begin{aligned} \bar{u}_{xi\sigma} = & -2 \sum_{j=1}^{N_\sigma} \sum_{l=|l_i-l_j|}^{l_i+l_j} \frac{4\pi}{2l+1} \overline{[I(l_j m_j, l_i m_i, l m_j - m_i)]^2} \\ & \times \int_0^\infty dr \chi_{i\sigma}(r) \chi_{j\sigma}(r) B_\sigma(i, j, l; r). \end{aligned} \quad (13)$$

Here,

$$I(l_j m_j, l_i m_i, l m) = \int d\Omega Y_{l_j m_j}^*(\Omega) Y_{l_i m_i}(\Omega) Y_{l m}(\Omega), \quad (14)$$

and

$$\begin{aligned} B_\sigma(i, j, l; r) = & \int_{r'=0}^r dr' \chi_{i\sigma}(r') \chi_{j\sigma}(r') \frac{r'^l}{r^{l+1}} \\ & + \int_{r'=r}^\infty dr' \chi_{i\sigma}(r') \chi_{j\sigma}(r') \frac{r'^l}{r'^{l+1}}. \end{aligned} \quad (15)$$

The bar over I^2 implies average over m_i and m_j . On the other hand, the quantity $q_{i\sigma}^{(2)}$ reduces to

$$\begin{aligned} q_{i\sigma}^{(2)}(r) = & 2 \sum_{j=1}^{N_\sigma} \sum_{l=|l_i-l_j|}^{l_i+l_j} \frac{4\pi}{2l+1} \chi_{j\sigma}(r) B_\sigma(i, j, l; r) \\ & \times \overline{[I(l_j m_j, l_i m_i, l m_j - m_i)]^2}. \end{aligned} \quad (16)$$

The procedure for the self-consistent iterative solutions of the OEP equations is explained in Refs. 14 and 22.

III. RESULTS AND DISCUSSION

We have used the EEX-SJM-SC to obtain the equilibrium sizes and energies of closed-shell 2, 8, 18, 20, 34, and 40 electron neutral clusters of Al, Na, and Cs.

In Table I, we have listed the equilibrium r_s values, total energies and exchange energies. As is seen, the equilibrium r_s values of the clusters are almost the same up to three decimals for²³ the KLI and OEP schemes whereas, there are significant differences between the OEP, x-LSDA, and LSDA values. The almost identity of the KLI and OEP r_s values is because these schemes are asymptotically identical. On the other hand, the average 1.5% larger \bar{r}_s values in the x-LSDA than in the OEP can be explained by the fact that in

TABLE I. Equilibrium sizes \bar{r}_s in bohrs, the absolute values of total and exchange energies in Rydbergs are compared for KLI, OEP, x-LSDA, and LSDA schemes. In the LSDA, the total energies include the correlation energies as well.

Atom	r_s^B	N	KLI			OEP			x-LSDA			LSDA		
			\bar{r}_s	$-\bar{E}$	$-E_x$	\bar{r}_s	$-\bar{E}$	$-E_x$	\bar{r}_s	$-\bar{E}$	$-E_x$	\bar{r}_s	$-\bar{E}$	$-E_x$
Al ^a	2.07	2	1.430	1.5700	0.9253	1.430	1.5700	0.9253	1.468	1.4364	0.7574	1.506	1.5585	0.7541
		8	1.744	5.8640	3.6018	1.744	5.8647	3.6089	1.775	5.5768	3.2430	1.793	6.1204	3.2361
		18	1.876	12.7709	7.9467	1.876	12.7734	7.9760	1.898	12.3315	7.3889	1.909	13.5947	7.3850
		20	1.846	14.3309	8.8532	1.847	14.3319	8.8706	1.869	13.8729	8.2870	1.881	15.2718	8.2738
		34	1.928	23.9914	14.9857	1.928	23.9968	15.0339	1.944	23.3442	14.1758	1.950	25.7679	14.1829
		40	1.901	28.2841	17.5064	1.901	28.2863	17.5348	1.893	27.6468	16.9255	1.926	30.4900	16.7211
Na	3.99	2	3.403	0.8409	0.4785	3.403	0.8409	0.4785	3.475	0.7721	0.3918	3.538	0.8646	0.3964
		8	3.664	3.2841	1.8579	3.663	3.2846	1.8632	3.719	3.1343	1.6774	3.745	3.5261	1.6856
		18	3.784	7.3064	4.1549	3.784	7.3084	4.1772	3.821	7.0700	3.8619	3.838	7.9710	3.8769
		20	3.758	8.1240	4.5669	3.758	8.1251	4.5794	3.800	7.8873	4.2867	3.816	8.8856	4.2995
		34	3.834	13.7980	7.8340	3.833	13.8028	7.8751	3.862	13.4458	7.4017	3.875	15.1665	7.4223
		40	3.813	16.1410	9.0432	3.813	16.1431	9.0632	3.843	15.8198	8.6726	3.855	17.8365	8.6906
Cs	5.63	2	5.006	0.6123	0.3494	5.006	0.6123	0.3494	5.109	0.5624	0.2856	5.213	0.6395	0.2910
		8	5.261	2.3990	1.3322	5.261	2.3994	1.3363	5.342	2.2918	1.2039	5.383	2.6135	1.2133
		18	5.390	5.3547	2.9775	5.389	5.3564	2.9963	5.443	5.1842	2.7658	5.472	5.9215	2.7821
		20	5.366	5.9403	3.2589	5.366	5.9414	3.2701	5.425	5.7729	3.0640	5.451	6.5894	3.0784
		34	5.445	10.1156	5.6044	5.445	10.1200	5.6423	5.488	9.8599	5.2875	5.508	11.2652	5.3122
		40	5.428	11.8123	6.4416	5.428	11.8144	6.4598	5.472	11.5881	6.1873	5.493	13.2347	6.2061

^aHere, $N=18$ corresponds to Al₆ cluster and other N 's do not correspond to a real Al clusters.

the x-LSDA, the self-interaction contribution of an electron tends to expand its wave function, and therefore, in the x-LSDA, the equilibrium is achieved at larger r_s values. To illustrate the trend in the \bar{r}_s values, we calculate the difference ($\bar{r}_s^{LSD} - \bar{r}_s^{KLI}$) for all species. The result shows that the difference is about 3% on average. We therefore conclude that the EEX-SJM-SC predicts smaller bond lengths compared to the LSDA-SJM-SC. Comparison of the \bar{r}_s values for the LSDA and x-LSDA shows that bond lengths in the LSDA is about 1.4% larger on average. This difference should be attributed to the correlation effects.

Comparison of the equilibrium total energies of the OEP and KLI shows that OEP energies are on average 0.02% more negative. This result should be compared to the simple JM results,^{22,24} which is 1.2%. On the other hand, comparison of the exchange energies shows that on the average, the exchange energies in OEP is 0.34% more negative than those in the KLI. The same comparisons between OEP and x-LSDA shows that $E_x^{OEP} < E_x^{x-LSDA}$ by 5.2% on average, and $E_x^{OEP} < E_x^{LSDA}$ by 11% on average.

Finally, we compare the results of LSDA and x-LSDA, which will show the correlation effects. As is seen in Table I, the total energies are close to each other for the high-density cases. That is, in the high-density limit the exchange dominates the correlation. However, the total energies in the LSDA are more negative by 10% on average which is due to the correlation effects. On the other hand, the difference in the exchange energies is about 0.96% on average, which is quite a small fraction. In the high-density limit, the inequality $E_x^{x-LSD} < E_x^{LSDA}$ holds, whereas, in the low-density limit, the inequality changes sign.

In Table II, we have listed the lowest and highest occupied KS eigenvalues for different schemes. As in the simple²² JM, the OEP KS eigenvalue bands are contracted relative to those of the KLI. That is, for all N , the relation $\Delta^{OEP} < \Delta^{KLI}$ holds. Here, $\Delta = \epsilon_H - \epsilon_L$ is the difference between the maximum occupied and minimum occupied KS eigenvalues. For the same external potential, the OEP and KLI results coincide for two-electron systems and $\Delta=0$. The results in Table II show that the maximum relative contraction, $|\Delta^{OEP} - \Delta^{KLI}| / \Delta^{KLI}$, is 2.7% which corresponds to Cs₁₈.

IV. SUMMARY AND CONCLUSION

In this work, we have considered the EEX-SJM-SC, in which we have used the exact orbital-dependent exchange functional. This model is applied for the simple metal clusters of Al, Na, and Cs. For the local exchange potential in the KS equation, we have solved the OEP integral equation by the iterative method. By finding the minimum energy of an N -atom cluster as a function of r_s , we have obtained the equilibrium sizes and energies of the closed-shell clusters ($N=2, 8, 18, 20, 34, 40$) for the four schemes of LSDA, KLI, OEP, and x-LSDA. The results show that in the EEX-SJM, the clusters are more contracted relative to the x-LSDA-SJM. The reason is that the self-interaction energy of an electron decreases as the wave function of that electron expands. On the other hand, the KLI and OEP results show equal values (up to three decimals) for the equilibrium r_s values. This has origins in the identity of the OEP and KLI schemes in the asymptotic regions. The equilibrium sizes in the LSDA and

TABLE II. The absolute values at equilibrium state of the highest occupied and lowest occupied Kohn-Sham eigenvalues in Rydbergs are compared for KLI, OEP, x-LSDA, and LSDA schemes.

Atom	N	KLI		OEP		x-LSDA		LSDA	
		$-\varepsilon_L$	$-\varepsilon_H$	$-\varepsilon_L$	$-\varepsilon_H$	$-\varepsilon_L$	$-\varepsilon_H$	$-\varepsilon_L$	$-\varepsilon_H$
Al	2	0.8152	0.8152	0.8152	0.8152	0.4367	0.4367	0.5012	0.5012
	8	1.1142	0.6714	1.1088	0.6713	0.8201	0.3919	0.8821	0.4605
	18	1.1727	0.5507	1.1619	0.5492	0.9497	0.3310	1.0129	0.4009
	20	1.1856	0.5000	1.1804	0.4993	0.9665	0.2964	1.0282	0.3622
	34	1.2055	0.4826	1.1998	0.4789	1.0192	0.2939	1.0853	0.3649
	40	1.2202	0.4490	1.2136	0.4450	1.0541	0.2761	1.0965	0.3401
Na	2	0.3883	0.3883	0.3883	0.3883	0.1951	0.1951	0.2437	0.2437
	8	0.4467	0.3406	0.4451	0.3408	0.2963	0.1936	0.3453	0.2434
	18	0.4544	0.2989	0.4502	0.2981	0.3373	0.1805	0.3859	0.2308
	20	0.4485	0.2672	0.4470	0.2682	0.3361	0.1565	0.3851	0.2042
	34	0.4583	0.2750	0.4551	0.2730	0.3588	0.1728	0.4078	0.2236
	40	0.4520	0.2480	0.4502	0.2477	0.3564	0.1534	0.4055	0.2017
Cs	2	0.2723	0.2723	0.2723	0.2723	0.1324	0.1324	0.1724	0.1724
	8	0.2923	0.2405	0.2913	0.2406	0.1843	0.1343	0.2247	0.1752
	18	0.2907	0.2141	0.2880	0.2134	0.2061	0.1285	0.2461	0.1696
	20	0.2850	0.1921	0.2847	0.1935	0.2048	0.1118	0.2454	0.1509
	34	0.2897	0.1992	0.2873	0.1977	0.2176	0.1252	0.2580	0.1668
	40	0.2835	0.1797	0.2831	0.1801	0.2157	0.1115	0.2564	0.1512

the x-LSDA differ by 1.4% on average. In the LSDA and KLI, the difference is 3% on average. The total energies in the OEP are more negative than the KLI by 0.02% on the average. It should be mentioned that in the simple JM, the KLI and OEP total energies for Al were positive (except for $N=2$). On the other hand, the exchange energy in the OEP is

about 0.34% more negative than that in the KLI. Comparison of the OEP and x-LSDA shows a difference of 5.2% in the total energies and 11% in the exchange. The difference in the exchange energies of LSDA and x-LSDA is small (about 0.96%), whereas the total energy in the LSDA is about 10% more negative which is due to the correlation effects.

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