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Application of the generalized-exchange local-spin-density-functional theory: Negative ions

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The generalized-exchange local-spin-density-functional theory with self-interaction correction has been used to calculate negative ions. The effect of the Fermi hole in the negative ions is discussed. The results are compared with experiment, Hartree-Fock, and other theoretical methods. It is shown that relaxation and correlation effects are very important for the negative ions.

I. INTRODUCTION

Local-spin-density-functional (LSD) theories are often used to calculate atoms, molecules, and solids, and these schemes have been successful in describing molecular bonding,[1,2] magnetism,[3–5] cohesion,[3–6] the surface electronic properties of metals[7,8] and semiconductors.[9–11] However, the calculation of accurate electron affinities, and the stability of negative ions has proved difficult:[12] most stable negative ions, such as H^-,[13] O^-, F^-,[14] and Cl (Ref. 15) are unstable in the $X\alpha$ (Ref. 16) and other LSD theories.[17] The correlation effect is often neglected in these theories and, consequently, the results are not in good agreement with experiment. Schwarz[14] compared the $X\alpha$ and Hartree-Fock (HF) exchange-correlation potentials for some stable negative ions, and showed that the stability of the negative ions is related to the one-electron energies in the two schemes. Sen[15] calculated the one-electron eigenvalues for the negative ions O^-, F^-, and Cl^- with the Hartree-Fock Gopinathan (HFG) method,[18] and suggested that the instability of the stable negative ions arises from a too crude treatment of the self-interaction potential.

In the present work the negative ions B^-, C^-, O^-, F^-, Na^-, Al^-, Si^-, S^-, and Cl^- have been calculated using the generalized-exchange local-spin-density-functional theory with self-interaction correction (LSD-GX-SIC) scheme of Manoli[19] and Manoli and Whitehead,[20] which is a generalization of the Hartree-Fock-Slater (HFS) scheme, with several Fermi holes. The results are compared with those from the HF,[21] other theoretical methods,[15,22] and experiment.[23,24]

II. THE LSD-GX-SIC THEORY

The equation of the one-electron spin orbital $u_i(\mathbf{r})$ in the Kohn and Sham scheme[16] in Rydberg atomic units is

$$[\hat{f}_1+V_C(\mathbf{r}_1)+V_{XC}(\mathbf{r}_1)]u_i(\mathbf{r}_1)=\epsilon_i u_i(\mathbf{r}_1)\ , \qquad (1)$$

where

$$\hat{f}_1=-\nabla_1^2-\frac{2Z}{r_1}\ .$$

V_C and V_{XC} are the Coulomb and exchange potentials, respectively. The Coulomb potential can be written

$$V_C(\mathbf{r}_1)=\int n(\mathbf{r}_2)(2/|\mathbf{r}_1-\mathbf{r}_2|)d^3r_2\ , \qquad (2)$$

where $n(\mathbf{r}_2)$ gives the electron density of the system at $\mathbf{r}_2$.

In the generalized-exchange local-spin-density-functional theory with self-interaction correction,[19,20] the orbital-dependence exchange potential is

$$\begin{aligned}V_{x_j}^{\text{GX-SIC}}(\mathbf{r})=-\frac{9c}{2}\alpha^{\text{lim}}\Bigg\{&\sum_i^s[n_s(\mathbf{r})+B_2n_i(\mathbf{r})]^{-2/3}n_i(\mathbf{r})-\tfrac{2}{3}\sum_i^s[n_s(\mathbf{r})+B_1n_i(\mathbf{r})][n_s(\mathbf{r})+B_2n_i(\mathbf{r})]^{-5/3}n_i(\mathbf{r})\\&+[n_s(\mathbf{r})+2B_1n_j(\mathbf{r})][n_s(\mathbf{r})+B_2n_j(\mathbf{r})]^{-2/3}\\&-\tfrac{2}{3}B_2[n_s(\mathbf{r})+B_1n_j(\mathbf{r})][n_s(\mathbf{r})+B_2n_j(\mathbf{r})]^{-5/3}n_j(\mathbf{r})\Bigg\}-f_j\langle u_j(\mathbf{r}')|\ |u_j(\mathbf{r}')\rangle+6c\alpha^{\text{SI}}n_j^{1/3}(\mathbf{r})\ .\end{aligned} \qquad (3)$$

The first term in Eq. (3) is the exchange potential with the self-interaction of electron j. The last two terms are the self-interaction correction. c is a constant equal to $(3/4\pi)^{1/3}$ and α^{SI} equals 0.866 173.

In the LSD-GX theory, the parameters B_1, B_2, and α^{lim} obey the equations

$$\begin{aligned}\alpha^{\text{lim}}&=\frac{8}{9}\left[\frac{\pi^2}{12}\right]^{1/3}A_1A_2^{-2/3}\ ,\\B_1&=(\tfrac{1}{2}-A_1)/A_1\ ,\\B_2&=(\tfrac{1}{3}-A_2)/A_2\ ,\end{aligned} \qquad (4)$$

and

$$A_1=\int_0^1 h(u)u\,du,\quad u=r'/r_F\ ,$$

while

$$A_2=\int_0^1 h(u)u^2du\ ,$$

where $h(u)$ is the Fermi-hole function and r_F is the radius of the Fermi hole. If the Fermi-hole function is known it can be used to calculate the parameters for all atoms.

Slater[16] assumed the charge density to be uniform, i.e., homogeneous, hence

$$h^{H}(r')=1,\quad 0\le r'\le r_F\ . \tag{5}$$

Gopinathan, Whitehead, and Bogdanovic[25] (GWB) assumed

$$h^{\mathrm{GWB}}(r')=1-r'/r_F,\quad 0\le r'\le r_F\ . \tag{6}$$

Gázquez and Keller[26] modified an expression which had been derived by Wigner and Seitz,[27] and Wigner[28] to describe the correlation factor of electrons in a metal,

$$h^{W}(r')=[1+br'/r_F+b(r'/r_F)^2]\exp(-br'/r_F)\ . \tag{7}$$

Manoli and Whitehead[19] noted that α_s goes to $\frac{2}{3}$ when the number of electrons in the system goes to infinity, and obtained parameters which are independent of the shape of the Fermi hole and give the free-electron-limit Fermi hole (FEL). All these parameters have been given in Ref. 19.

III. ELECTRON AFFINITY

The electron affinity of an atom A is

$$\mathcal{E}(A)=E_{\mathrm{tot}}(A)-E_{\mathrm{tot}}(A^-)\ , \tag{8}$$

where $E_{\mathrm{tot}}(A)$ is the total energy of the ground state of the neutral atom A, and $E_{\mathrm{tot}}(A^-)$ is the total energy of the negative ion A^-.

In the LSD-GX-SIC scheme, the total energy of the ground state of A^- can be written

$$\begin{aligned}E_{\mathrm{tot}}^-=&\sum_{i\neq m} f_i\langle u_i(\mathbf{r})\,|\,f_r\,|\,u_i(\mathbf{r})\rangle+\tfrac{1}{2}\sum_{i,j\neq m} f_i f_j\langle u_i(\mathbf{r})u_j(\mathbf{r}')\,|\,|\,u_i(\mathbf{r})u_j(\mathbf{r}')\rangle\\&+\tfrac{1}{2}\sum_i^{s} f_i\langle u_i(\mathbf{r})\,|\,U_{si}^{\mathrm{GX}^-}(\mathbf{r})\,|\,u_i(\mathbf{r})\rangle+\tfrac{1}{2}\sum_i^{s'} f_i\langle u_i(\mathbf{r})\,|\,U_{s'i}^{\mathrm{GX}^-}(\mathbf{r})\,|\,u_i(\mathbf{r})\rangle+f_m\langle u_m(\mathbf{r})\,|\,f_r\,|\,u_m(\mathbf{r})\rangle\\&+\sum_{j\,(\neq m)} f_m f_j\langle u_m(\mathbf{r})u_j(\mathbf{r}')\,|\,|\,u_m(\mathbf{r})u_j(\mathbf{r}')\rangle+\tfrac{1}{2}f_m^2\langle u_m(\mathbf{r})u_m(\mathbf{r}')\,|\,|\,u_m(\mathbf{r})u_m(\mathbf{r}')\rangle\ ,\end{aligned} \tag{9}$$

where

$$U_{si}^{\mathrm{GX}^-}(\mathbf{r})=-9c\alpha^{\mathrm{lim}}[n_s(\mathbf{r})+B_1n_i(\mathbf{r})][n_s(\mathbf{r})+B_2n_i(\mathbf{r})]^{-2/3}-f_i\langle u_i(\mathbf{r}')\,|\,|\,u_i(\mathbf{r}')\rangle+9c\alpha^{\mathrm{SI}}n_i^{1/3}(\mathbf{r}) \tag{10}$$

and

$$\begin{aligned}E_{\mathrm{tot}}=&\sum_{i\neq m} f_i\langle u_i(\mathbf{r})\,|\,f_r\,|\,u_i(\mathbf{r})\rangle+\tfrac{1}{2}\sum_{i,j\neq m} f_i f_j\langle u_i(\mathbf{r})u_j(\mathbf{r}')\,|\,|\,u_i(\mathbf{r})u_j(\mathbf{r}')\rangle\\&+\tfrac{1}{2}\sum_{i\neq m}^{s} f_i\langle u_i(\mathbf{r})\,|\,U_{si}^{\mathrm{GX}^0}(\mathbf{r})\,|\,u_i(\mathbf{r})\rangle+\tfrac{1}{2}\sum_i^{s'} f_i\langle u_i(\mathbf{r})\,|\,U_{s'i}^{\mathrm{GX}^0}(\mathbf{r})\,|\,u_i(\mathbf{r})\rangle\ .\end{aligned} \tag{11}$$

In the frozen orbital approximation, substituting Eqs. (9) and (11) into (8) gives

$$\begin{aligned}\mathcal{E}_m=&-f_m\langle u_m(\mathbf{r})\,|\,f_r\,|\,u_m(\mathbf{r})\rangle-\sum_{j\,(\neq m)} f_m f_j\langle u_m(\mathbf{r})u_j(\mathbf{r}')\,|\,|\,u_m(\mathbf{r})u_j(\mathbf{r}')\rangle\\&-\tfrac{1}{2}f_m^2\langle u_m(\mathbf{r})u_m(\mathbf{r}')\,|\,|\,u_m(\mathbf{r})u_m(\mathbf{r}')\rangle-\tfrac{1}{2}\sum_{i\,(=m)}^{s} f_i\langle u_i(\mathbf{r})\,|\,U_{si}^{\mathrm{GX}^-}(\mathbf{r}')\,|\,u_i(\mathbf{r})\rangle+\tfrac{1}{2}\sum_{i\,(\neq m)}^{s} f_i\langle u_i(\mathbf{r})\,|\,U_{si}^{\mathrm{GX}^0}(\mathbf{r})\,|\,u_i(\mathbf{r})\rangle\\\approx&-\epsilon_m+\frac{3c}{2}\alpha^{\mathrm{SI}}\langle u_m(\mathbf{r})\,|\,n_m^{1/3}(\mathbf{r})\,|\,u_m(\mathbf{r})\rangle-\frac{9c}{2}\alpha^{\mathrm{lim}}(1+B_1)\langle u_m^2(\mathbf{r})\,|\,[n_s^{(-)}(\mathbf{r})+B_2n_m(\mathbf{r})]^{-2/3}\,|\,u_m^2(\mathbf{r})\rangle\\&+\frac{9c}{2}\alpha^{\mathrm{lim}}\tfrac{2}{3}(1+B_2)\langle u_m^2(\mathbf{r})\,|\,[n_s^{(-)}(\mathbf{r})+B_2n_m(\mathbf{r})]^{-5/3}[n_s^{(-)}(\mathbf{r})+B_1n_m(\mathbf{r})]\,|\,u_m^2(\mathbf{r})\rangle\\&+\frac{9c}{2}\alpha^{\mathrm{lim}}\frac{2}{3}\left\langle u_m^2(\mathbf{r})\,\middle|\,\sum_{i\neq m}^{s}[n_s^{(-)}(\mathbf{r})+B_2n_i(\mathbf{r})]^{-5/3}n_i(\mathbf{r})\,\middle|\,u_m^2(\mathbf{r})\right\rangle\\&-\frac{9c}{2}\alpha^{\mathrm{lim}}\frac{5}{9}\left\langle u_m^2(\mathbf{r})\,\middle|\,\sum_{i\neq m}^{s}[n_s^{(-)}(\mathbf{r})+B_2n_i(\mathbf{r})]^{-8/3}[n_s^{(-)}(\mathbf{r})+B_1n_i(\mathbf{r})]n_i(\mathbf{r})\,\middle|\,u_m^2(\mathbf{r})\right\rangle\ ,\end{aligned} \tag{12}$$

TABLE I. The negative of the eigenvalues in Ry of the ground states of several negative ions calculated using the LSD-GX-SIC theory with FEL, Wigner, GWB, and H Fermi holes, compared to other theoretical results.

			Present work					
Z	Ion	$(nl)_s$	FEL	Wigner	GWB	H	HFG[a]	HF[b]
5	B^-	$1s_\uparrow$	14.9855	14.9406	14.8982	14.6855		
		$1s_\downarrow$	14.9675	14.9197	14.8741	14.6372		
		$1s_{av}$	14.9765	14.9302	14.8861	14.6614		14.8494
		$2s_\uparrow$	0.5536	0.5416	0.5321	0.5250		
		$2s_\downarrow$	0.4575	0.4289	0.4021	0.2777		
		$2s_{av}$	0.5055	0.4853	0.4671	0.4014		0.4847
		$2p_\uparrow$	0.0186	0.0228	0.0276	0.0700		0.0526
6	C^-	$1s_\uparrow$	22.0403	21.9910	21.9447	21.7125		
		$1s_\downarrow$	21.9856	21.9292	21.8757	21.5947		
		$1s_{av}$	22.0129	21.9601	21.9102	21.6536		21.9122
		$2s_\uparrow$	0.7392	0.7425	0.7475	0.8096		
		$2s_\downarrow$	0.5304	0.5032	0.4781	0.3605		
		$2s_{av}$	0.6348	0.6228	0.6128	0.5850		0.7454
		$2p\uparrow$	0.0792	0.0906	0.1025	0.1815		0.1538
8	O^-	$1s_\uparrow$	40.5383	40.4786	40.4209	40.1102		
		$1s_\downarrow$	40.4919	40.4271	40.3646	40.0257		
		$1s_{av}$	40.5151	40.4528	40.3928	40.0679	39.417	40.3963
		$2s_\uparrow$	1.3457	1.3595	1.3731	1.4619		
		$2s_\downarrow$	1.2304	1.2302	1.2309	1.2592		
		$2s_{av}$	1.2881	1.2948	1.3020	1.3605	1.574	1.6265
		$2p_\uparrow$	0.2651	0.2813	0.2970	0.3862		
		$2p_\downarrow$	0.0795	0.0875	0.0961	0.1573		
		$2p_{av}$	0.1908	0.2038	0.2167	0.2946	0.479	0.2585
9	F^-	$1s_{\uparrow\downarrow}$	51.7489	51.6768	51.6080	51.2429	50.529	51.6590
		$2s_{\uparrow\downarrow}$	1.6171	1.6306	1.6445	1.7417	2.009	2.1489
		$2p_{\uparrow\downarrow}$	0.2504	0.2675	0.2846	0.3860	0.628	0.3617
11	Na^-	$1s_{\uparrow\downarrow}$	80.5681	80.5084	80.4511	80.1506		80.6628
		$2s_{\uparrow\downarrow}$	4.3615	4.4027	4.4429	4.6777		5.2995
		$2p_{\uparrow\downarrow}$	2.4311	2.4697	2.5077	2.7253		2.7418
		$3s_{\uparrow\downarrow}$	0.0273	0.0277	0.0280	0.0295		0.0249
13	Al^-	$1s_\uparrow$	116.4973	116.4254	116.3568	116.0076		
		$1s_\downarrow$	116.4945	116.4223	116.3533	116.0014		
		$1s_{av}$	116.4959	116.4238	116.3550	116.0045		116.6161
		$2s_\uparrow$	8.2902	8.3316	8.3724	8.6207		
		$2s_\downarrow$	8.2858	8.3267	8.3669	8.6123		
		$2s_{av}$	8.2880	8.3291	8.3697	8.6165		9.4323
		$2p_\uparrow$	5.7088	5.7474	5.7858	6.0172		
		$2p_\downarrow$	5.7035	5.7414	5.7791	6.0068		
		$2p_{av}$	5.7062	5.7444	5.7824	6.0120		6.0503
		$3s_\uparrow$	0.4878	0.4801	0.4735	0.4611		
		$3s_\downarrow$	0.4374	0.4209	0.4052	0.3281		
		$3s_{av}$	0.4626	0.4505	0.4394	0.3946		0.4176
		$3p_\uparrow$	0.0163	0.0191	0.0222	0.0479		0.0397
14	Si^-	$1s_\uparrow$	136.9239	136.8526	136.7849	136.4491		
		$1s_\downarrow$	136.9138	136.8414	136.7728	136.4302		
		$1s_{av}$	136.9188	136.8470	136.7789	136.4396		137.1058
		$2s_\uparrow$	10.5079	10.5561	10.6041	10.8968		
		$2s_\downarrow$	10.4926	10.5395	10.5862	10.8724		
		$2s_{av}$	10.5002	10.5478	10.5951	10.8846		11.7933
		$2p_\uparrow$	7.5867	7.6326	7.6785	7.9565		
		$2p_\downarrow$	7.5684	7.6126	7.6569	7.9267		

TABLE I. (*Continued*).

			Present work					
Z	Ion	$(nl)_s$	FEL	Wigner	GWB	H	HFG[a]	HF[b]
		$2p_{\mathrm{av}}$	7.5776	7.6226	7.6677	7.9416		7.9957
		$3s_\uparrow$	0.6223	0.6233	0.6255	0.6602		
		$3s_\downarrow$	0.5069	0.4906	0.4756	0.4050		
		$3s_{\mathrm{av}}$	0.5646	0.5570	0.5505	0.5326		0.6030
		$3p_\uparrow$	0.0619	0.0697	0.0778	0.1297		0.1230
16	S^-	$1s_\uparrow$	183.0350	182.9661	182.9006	182.5783		
		$1s_\downarrow$	183.0265	182.9568	182.8907	182.5637		
		$1s_{\mathrm{av}}$	183.0308	182.9615	182.8956	182.5710		183.3519
		$2s_\uparrow$	15.7820	15.8446	15.9062	16.2721		
		$2s_\downarrow$	15.7703	15.8320	15.8927	16.2547		
		$2s_{\mathrm{av}}$	15.7762	15.8383	15.8995	16.2634		17.3503
		$2p_\uparrow$	12.1556	12.2168	12.2774	12.6335		
		$2p_\downarrow$	12.1414	12.2014	12.2610	12.6123		
		$2p_{\mathrm{av}}$	12.1485	12.2091	12.2692	12.6229		12.7099
		$3s_\uparrow$	0.9662	0.9746	0.9833	1.0451		
		$3s_\downarrow$	0.9088	0.9099	0.9118	0.9395		
		$3s_{\mathrm{av}}$	0.9375	0.9423	0.9476	0.9923		1.1586
		$3p_\uparrow$	0.1671	0.1794	0.1916	0.2615		
		$3p_\downarrow$	0.1004	0.1069	0.1138	0.1608		
		$3p_{\mathrm{av}}$	0.1404	0.1504	0.1604	0.2213		0.2148
17	Cl^-	$1s_{\uparrow\downarrow}$	208.6252	208.5544	208.4875	208.1638	207.647	209.0103
		$2s_{\uparrow\downarrow}$	18.7515	18.8182	18.8842	19.2790	20.203	20.4578
		$2p_{\uparrow\downarrow}$	14.7599	14.8258	14.8912	15.2790	16.165	15.3907
		$3s_{\uparrow\downarrow}$	1.1256	1.1347	1.1442	1.2123	1.386	1.4659
		$3p_{\uparrow\downarrow}$	0.2008	0.2139	0.2267	0.3031	0.468	0.2998

[a] Reference 15.
[b] Reference 21.

where $n_s^{(-)}$ is the total electron density of the negative ion. In Eq. (12), the higher-order terms which are smaller than

$$[n_m(\mathbf{r})/n_s^{(-)}(\mathbf{r})]^3$$

are neglected.

IV. RESULTS AND DISCUSSION

The negative ions B^-, C^-, O^-, F^-, Na^-, Al^-, Si^-, S^-, and Cl^- and the corresponding neutral atoms were calculated using the LSD-GX-SIC scheme with the FEL, Wigner, GWB, and homogeneous Fermi-hole parameters (henceforth called the GX-FEL, GX-W, GX-GWB, and GX-H, respectively).

A. Eigenvalues

Table I gives the one-electron eigenvalues and average eigenvalues of each subshell; the average eigenvalue equals

$$(\epsilon_{nl\uparrow}N_{nl\uparrow}+\epsilon_{nl\downarrow}N_{nl\downarrow})/(N_{nl\uparrow}+N_{nl\downarrow}) .$$

They are compared to the HFG eigenvalues of Sen[15] and the HF eigenvalues of Clementi and Roetti.[21]

The GX-FEL, GX-W, GX-GWB, and GX-H eigenvalues of the 1s electrons for all the negative ions are in very good agreement with those of HF. Almost all the eigenvalues of the 2s subshell are a little higher than those of HF as are the eigenvalues of the 2p electron which are not in the outermost subshell. The GX-H eigenvalues of the 2p electrons are very close to the HF eigenvalues. They are better than those calculated with the HFG method. For the outermost electrons, the GX-FEL, GX-W, and GX-GWB eigenvalues are greater than those of HF, while the GX-H eigenvalues are closer to those of HF except for Na^-. All of the GX eigenvalues are closer to those of HF than the HFG eigenvalues.

According to Koopmans's approximation,[29] the one-electron eigenvalues in the HF method are equal to the binding energies of the electrons. Although the frozen orbital approximation is an approximation, Table I shows that the LSD-GX-SIC scheme is the best in describing the electron binding energy of negative ions.

In both the LSD-GX-SIC and HFG schemes, the self-interaction correction of the electron has been removed; therefore, the one-electron eigenvalue in both schemes should be equal to the corresponding one-electron value (i.e., the orbital energy) in the HF scheme. However, this is not true for the negative ions. The accuracy of the self-interaction correction is measured by comparing the one-electron eigenvalues. From Table I, the one-electron eigenvalues for the 1*s* and *np* electrons are in much better agreement with those of the HF than those in the HFG method. For the 2*s* and 3*s* electron, the HFG scheme is a little better than the LSD-GX-SIC scheme. Table I shows that the self-interaction corrections in both LSD-GX-SIC and HFG schemes are *not perfect* for the negative ions. Nevertheless, the self-interaction correction in the LSD-GX-SIC scheme is more accurate than that in the HFG method.

B. Electron affinity

Table II gives the negative values of the statistical total energies of the ground state for several atoms and negative ions and the HF energies given by Ref. 21. The total energies of the atoms and the corresponding negative ions are calculated separately using the LSD-GX-SIC scheme. The electron affinities for these atoms calculated using Eq. (8) and those obtained using experimental methods given by Refs. 22 and 23 are also in Table II.

It can be seen that the GX-GWB and GX-H results are closer to the experimental values than those of the GX-FEL and GX-W. But the GX-GWB electron affinities are smaller and GX-H electron affinities larger than the corresponding experiment; they are better than the HF and $X\alpha$ results. It is difficult to estimate the electron affinity of an atom by using the HF and $X\alpha$ schemes, since they are unreliable; for example, the electron affinity for B^- is negative in the HF and $X\alpha$ schemes, and therefore B^- is unstable; but experimentally B^- is stable.

The differences between the theoretical and experimental values in Table II occur for two reasons. Firstly, the

TABLE II. The negative of statistical total energies of the ground state for several atoms and negative ions, calculated using the LSD-GX-SIC theory with the FEL, Wigner, GWB, and H Fermi hole, and the electron affinities $\mathcal{E}$, compared to the results obtained using HF, $X\alpha$, and experiment (Ry).

		Present work						
Z	Ion and atom	FEL	Wigner	GWB	H	HF[a]	$X\alpha$[b]	Expt[c]
5	B^-	48.9294	48.9759	49.0222	49.3103	49.0384		
	B	48.9506	48.9841	49.0180	49.2292	49.0581		
	$\mathcal{E}$	−0.0212	−0.0082	0.0042	0.0811	−0.0197	−0.054	0.0204
6	C^-	75.1910	75.2944	75.3954	75.9832	75.4176		
	C	75.1615	75.2417	75.3209	75.7914	75.3772		
	$\mathcal{E}$	0.0295	0.0527	0.0745	0.1918	0.0404	−0.013	0.0932
8	O^-	149.0626	149.2973	149.5257	150.8395	149.5790		
	O	149.0859	149.2999	149.5083	150.7101	149.6187		
	$\mathcal{E}$	−0.0233	−0.0026	0.0174	0.1294	−0.0397	0.098	0.1075
9	F^-	198.1983	198.5355	198.8624	200.7074	198.9187		
	F	198.0899	198.3934	198.6884	200.3743	198.8186		
	$\mathcal{E}$	0.1084	0.1421	0.1740	0.3331	0.1001	0.168	0.2498
11	Na^-	322.5245	323.0327	323.5237	326.2713	323.7093		
	Na	322.5269	323.0341	323.5246	326.2697	323.7178		
	$\mathcal{E}$	−0.0025	−0.0014	−0.0009	0.0016	−0.0085	0.012	0.0401
13	Al^-	482.0873	482.7921	483.4724	487.2719	483.7556		
	Al	482.0869	482.7835	483.4561	487.2063	483.7534		
	$\mathcal{E}$	0.0004	0.0086	0.0163	0.0656	0.0022	−0.028	0.0325
14	Si^-	575.8010	576.6279	577.4252	581.8577	577.7789		
	Si	575.7500	576.5619	577.3450	581.7002	577.7086		
	$\mathcal{E}$	0.0510	0.0660	0.0802	0.1575	0.0703	0.022	0.1018
16	S^-	792.4631	793.5459	794.5879	800.3543	795.0764		
	S	792.3992	793.4676	794.4957	800.1825	795.0097		
	$\mathcal{E}$	0.0639	0.0783	0.0922	0.1718	0.0667	0.147	0.1527
17	Cl^-	916.1712	917.4046	918.5906	925.1231	919.1534		
	Cl	916.0045	917.2156	918.3801	924.8032	918.9637		
	$\mathcal{E}$	0.1667	0.1890	0.2105	0.3199	0.1897	0.221	0.2657

[a] Reference 21.

[b] Reference 22.

[c] References 23 and 24.

electron affinity is expressed as a small difference between two large quantities in Eq. (8) and is therefore subject to numerical errors. Secondly, the correlation effects between electrons of different spin directions are neglected. Raghavachari[12] has used Møller-Plessert perturbation theory to calculate the electron affinities of first-row atoms and discussed the electron-correlation effects on the electron affinities.

The electron affinities of Eq. (12) for these atoms are also calculated using the LSD-GX-SIC theory with the FEL, Wigner, GWB, and H Fermi hole under the frozen orbital approximation (the results are not listed). The results show, as expected, that the frozen orbital approximation is poor for calculating the electron affinity of an atom, because the outmost electron is very loosely bound. Consequently, the relaxation effect of the system going from negative ions to neutral atom is very important, especially in calculating the electron affinity, but less so in calculating the ionization potential.

V. CONCLUSION

It is necessary to consider the self-interaction correlation when the LSD theory is used to calculate negative ions. Thus the observation made in Refs. 14 and 15 is confirmed. To obtain good results, it is necessary to consider relaxation and correlation effects.

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