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Effect of the correlation correction on the ionization potential and electron affinity in atoms

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The generalized-exchange local-spin-density-functional theory (LSD-GX) with self-interaction correction has been used to calculate the ionization potentials for the atoms (atomic number Z from 2 to 38) and the electron affinities for some selected atoms. The effects of the Coulomb correlation correction and relaxation on the ionization potential and electron affinity are discussed using the Stoll, Pavlidou, and Preuss [Theor. Chim. Acta **49**, 143 (1978)] correlation-energy expression, and the Vosko, Wilk, and Nusair (VWN) [Can. J. Phys. **58**, 1200 (1980)] expression. The theoretical results are compared to experiment. The LSD-GX theory with VWN correlation correction is the best method for calculating ionization potentials and electron affinities for atoms.

I. INTRODUCTION

Many calculations of the ionization potentials and the electron affinities of atoms have been made using the Hartree-Fock (HF) method and various local-spin-density-functional-approximation (LSDA) methods,[1–10] especially using the accurate multiconfiguration self-consistent field[11,12] (MC-SCF) and configuration interaction[13–15] (CI) methods. Most of these methods have been quite successful in describing ionization potentials for atoms, but the HF, $X\alpha$, *sp*-$X\alpha$, HHF, and LSD-GX methods cannot describe the negative ions exactly,[6,7,16,17] because the Coulomb correlation is neglected.

Much effort has focused on the Coulomb correlation[18–34] and its introduction into single-configuration calculations, such as the LSD theory, in order to get good results for atoms and molecules. Consequently, various expressions for introducing the Coulomb correlation correction have emerged. These expressions have been used to calculate the total energies,[26] ionization potentials,[23] and electron affinities[27] for atoms.

As discussed previously,[16,17] the Coulomb correlation correction is very important in calculating the electron affinities of atoms. The generalized exchange local-spin-density-functional theory with self-interaction correction[35,36] (LSD-GX-SIC) using the Gopinathan, Whitehead, and Bogdanovic[37] Fermi-hole parameters (LSD-GX-SIC–GWB) has been used to calculate the statistical total energies for several atoms, and positive and negative ions, together with the ionization potentials of elements helium to strontium and electron affinities for several typical atoms. The electron wave functions are used to calculate the correlation energy for the corresponding atom, positive and negative ions, and estimate the contribution of the correlation energy to the ionization potentials and electron affinities of atoms.

II. METHOD

A. Ionization potential and the electron affinity in the LSD-GX-SIC theory

The ionization potential and electron affinity of an atom, in Rydberg atomic units, are

$$E_{\mathrm{IP}}=E_{\mathrm{tot}}(A^{+})-E_{\mathrm{tot}}(A^{0})$$

and (1)

$$E_{\mathrm{EA}}=E_{\mathrm{tot}}(A^{0})-E_{\mathrm{tot}}(A^{-})\ ,$$

where $E_{\mathrm{tot}}(A^{+})$, $E_{\mathrm{tot}}(A^{0})$, and $E_{\mathrm{tot}}(A^{-})$ are the statistical total energies of the ground states of positive ion A^{+}, neutral atom A^{0}, and negative ion A^{-}, respectively.

In the LSD-GX-SIC theory,[35,36] the statistical total energy for the system is

$$E_{\mathrm{tot}}(A)=\sum_{i} f_i\langle u_i(\mathbf{r})|f_r|u_i(\mathbf{r})\rangle+\tfrac{1}{2}\sum_{i,j} f_i f_j\langle u_i(\mathbf{r})u_j(\mathbf{r}')\|u_i(\mathbf{r})u_j(\mathbf{r}')\rangle$$
$$+\tfrac{1}{2}\sum_{i}^{s} f_i\langle u_i(\mathbf{r})|U_{si}^{\mathrm{GX}}(\mathbf{r})|u_i(\mathbf{r})\rangle+\tfrac{1}{2}\sum_{i}^{s'} f_i\langle u_i(\mathbf{r})|U_{s'i}^{\mathrm{GX}}(\mathbf{r})|u_i(\mathbf{r})\rangle\ , \qquad (2)$$

where f_i ($i=1,2,\ldots,q$) are the occupation numbers of orbitals. The exchange energy density in the LSD-GX-SIC theory is

$$U_{si}^{\mathrm{GX}}(\mathbf{r})=-9C\alpha^{\mathrm{lim}}[n_s(\mathbf{r})+B_1 n_i(\mathbf{r})][n_s(\mathbf{r})+B_2 n_i(\mathbf{r})]^{-2/3}-f_i\langle u_i(\mathbf{r}')\|u_i(\mathbf{r}')\rangle+9C\alpha^{\mathrm{SI}}n_i^{1/3}(\mathbf{r})\ . \qquad (3)$$

In Eq. (3) the last two terms are the self-interaction correction. C is a constant and equal to $(3/4\pi)^{1/3}$. α^{lim}, B_1, and B_2 are the parameters depending on the Fermi-hole shape. For the GWB Fermi hole, these parameters have been given in Ref. 35.

B. Correlation correction to E_{IP} and E_{EA}

The Coulomb-hole concept is a fundamental idea developed by Wigner[38] for the electron correlation correction. The hole volume is directly related to the electron density.

In the LSD theory the correlation energy can be written[32,33]

$$E_c=\int [n_+(r)+n_-(\mathbf{r})]\varepsilon_c(n_+,n_-)d\tau \ . \tag{4}$$

The function $\varepsilon_c(n_+,n_-)$ is the correlation-energy density of the homogeneous electron gas with partial densities n_+ and n_- for the spin-up and spin-down electrons. In Eq. (4) the self-interaction correlation correction (SIC) is included. If the self-interaction correlation correction (SIC) is introduced into E_c by using the definition of Stoll, Pavlidou, and Preuss (SPP),[24] the correlation energy expression [Eq. (4)] becomes

$$\begin{aligned}E_c=&\int [n_+(\mathbf{r})+n_-(\mathbf{r})]\varepsilon_c(n_+,n_-)d\tau\\&-\int n_+(\mathbf{r})\varepsilon_c(n_+,0)d\tau-\int n_-(\mathbf{r})\varepsilon_c(0,n_-)d\tau \ .\end{aligned} \tag{5}$$

Here, two forms of $\varepsilon_c(n_+,n_-)$ are used:

First, the expression of Stoll-Pavlidou-Preuss (SPP) for ε_c (Ref. 24) is the following:

$$\varepsilon_c(n_+,n_-)=\varepsilon_P(r_s)+[\varepsilon_F(r_s)-\varepsilon_P(r_s)]f(\zeta) \ , \tag{6}$$

where

$$\varepsilon_i(r_s)=-C_i\left[(1+\chi_i^3)\ln\left[1+\frac{1}{\chi_i}\right]+\frac{1}{2}\chi_i-\chi_i^2-\frac{1}{3}\right] \quad (i=P,F)$$

and (7)

$$f(\zeta)=[(1+\zeta)^{4/3}+(1-\zeta)^{4/3}-2]/(2^{4/3}-2)$$

with

$$\chi_p=r_s/11.4, \quad r_F=r_s/15.9 \ ,$$

$$C_p=0.0666, \quad C_F=0.0406 \ ,$$

$$r_s=(4\pi n/3)^{-1/3}, \quad n=n_++n_-, \zeta=\frac{n_+-n_-}{n_++n_-} \ .$$

The superscripts P and F denote para- and ferromagnetic states, respectively, according to whether $\zeta=0$ or 1.

Second, through use of a Padé approximation interpolation, Vosko, Wilk, and Nusair (VWN)[34] derived representations for $\varepsilon_c^i(r_s)$, $i=P,F$ based on the calculation of Ceperley and Alder[39] of the ground-state energies for the polarized and unpolarized Fermi fluid. The representation of the correlation energy density can be written

$$\begin{aligned}\varepsilon_c^i(r_s)=A\Bigg[&\ln\frac{\chi^2}{X(\chi)}+\frac{2b}{Q}F(\chi)\\&-\frac{b\chi_0}{X(\chi_0)}\left[\ln\frac{(\chi-\chi_0)^2}{X(\chi)}+\frac{2(b+2\chi_0)}{Q}F(\chi)\right]\Bigg] \ ,\end{aligned} \tag{8}$$

where A, χ_0, b, and c are parameters determined separately for $i=P,F$ and

$$Q=(4c-b^2)^{1/2}, \quad X(\chi)=\chi^2+b\chi+c \ ,$$

and

$$F(\chi)=\tan^{-1}\frac{Q}{(2\chi+b)} \ .$$

Here $\chi=r_s^{1/2}=(4\pi n/3)^{-1/6}$. All these parameters have been given by Refs. 31 and 34.

Therefore, the contributions of the correlation energy with SIC to an ionization potential and electron affinity are

$$\Delta E_{\text{IP}}^{\text{corr}}=E_c^+-E_c^0$$

and (9)

$$\Delta E_{\text{EA}}^{\text{corr}}=E_c^0-E_c^- \ .$$

III. RESULTS AND DISCUSSION

The LSD-GX-SIC–GWB scheme has been used to calculate the statistical total energies of the neutral atoms and positive ions of elements helium to strontium, and the stable negative ions of elements hydrogen to potassium and copper to rubidium separately. The wave functions are used to calculate the corresponding SPP-SIC and VWN-SIC correlation energy for these atoms and positive and negative ions. The effect of the correlation potential[29] on the one-electron eigenvalue, ionization potential, and electron affinity has been considered. The results show that the correlation potential is too small to influence the one-electron eigenvalue ionization potential and electron affinity. This confirmed the observations of Refs. 29 and 40.

Table I gives the ionization potentials of the atoms helium to titanium, chromium to iron, and copper to strontium. In Table I column 3 gives the results included the relaxation without correlation correction, columns 2 and 3 show the values involved in the SPP-SIC and VWM-SIC correlation correction; other theoretical[5,14,41,42] values and experiments are listed in columns 6, 7, 8, and 9, respectively.

From Table I it may be seen that although the relaxation is involved in the calculation, the ionization potentials in the LSD-GX-SIC–GWB scheme (column 3) are still far away from the experiments, unless the correlation correction is included. The differences between these results and the experimental values are almost equal to

TABLE I. Ionization potentials (in rydbergs) for atoms in the LSD-GX-SIC–GWB scheme with correlation correction. The value in parentheses are equal to $(I^{\text{theor}} - I^{\text{expt}})/I^{\text{ext}}$.

		Without	With correlation		Other work			
Z	Atom	correlation	SPP-SIC	VWM-SIC	*sp*-$X\alpha$[a]	HF[b]		Expt.[c]
2	He	1.722	1.823	1.8389	1.994	1.724		1.807
		(−4.7)	(0.9)	(1.8)	(10)	(−4.6)		
3	Li	0.390	0.392	0.393	0.416	0.393		0.396
		(−1.5)	(−1.0)	(−0.8)	(5.1)	(−0.8)		
4	Be	0.592	0.649	0.661	0.670	0.591		0.685
		(−13.6)	(−5.3)	(−3.5)	(−2.2)	(−13.7)		
5	B	0.564	0.591	0.598	0.615	0.584		0.610
		(−7.5)	(−3.1)	(−2.0)	(0.8)	(−4.3)		
6	C	0.801	0.820	0.827	0.868	0.794		0.828
		(−3.3)	(−1.0)	(−0.1)	(4.8)	(−4.1)		
7	N	1.045	1.059	1.066	1.117	1.022		1.069
		(−2.2)	(−0.9)	(−0.3)	(4.5)	(−4.4)		
8	O	0.867	0.964	0.971	1.285	0.875		1.001
		(−13.4)	(−3.7)	(−3.0)	(28.4)	(−12.6)		
9	F	1.190	1.265	1.271	1.435	1.154		1.280
		(−7.0)	(−1.2)	(−0.7)	(12.1)	(−9.8)		
10	Ne	1.510	1.571	1.579	1.638	1.463		1.585
		(−4.7)	(−0.9)	(−0.4)	(3.3)	(−7.7)		
11	Na	0.382	0.387	0.389	0.385	0.368		0.378
		(1.1)	(2.4)	(2.9)	(1.9)	(−2.6)		
12	Mg	0.506	0.555	0.566	0.554	0.485		0.562
		(−10.0)	(−1.2)	(0.7)	(−1.4)	(−13.7)		
13	Al	0.386	0.407	0.412	0.406	0.404		0.440
		(−12.3)	(−7.5)	(−6.4)	(−7.7)	(−8.2)		
14	Si	0.554	0.570	0.575	0.583	0.559		0.599
		(−7.5)	(−4.8)	(−4.0)	(−2.7)	(−6.7)		
15	P	0.793	0.805	0.810	0.757	0.742		0.808
		(−1.9)	(−0.4)	(0.2)	(−6.3)	(−8.2)		
16	S	0.661	0.739	0.748	0.878	0.662		0.761
		(−13.1)	(−2.9)	(−1.7)	(15.4)	(−13.0)		
17	Cl	0.874	0.935	0.942	0.993	0.867		0.956
		(−8.6)	(−2.2)	(−1.5)	(3.9)	(−9.3)		
18	Ar	1.805	1.136	1.143	1.141	1.088		1.158
		(−6.3)	(−1.9)	(−1.3)	(−1.5)	(−6.0)		
19	K	0.317	0.324	0.326	0.317	0.294		0.319
		(−0.6)	(1.6)	(2.2)	(−0.6)	(−7.8)		
20	Ca	0.401	0.443	0.452	0.432	0.375		0.449
		(−10.7)	(−1.3)	(0.7)	(−3.8)	(−16.5)		
21	Sc	0.420	0.470	0.480	0.476	0.390		0.482
		(−12.9)	(−2.5)	(−0.4)	(−1.2)	(−19.1)		
22	Ti	0.434	0.489	0.500	0.507	0.404		0.502
		(−13.5)	(−2.6)	(−0.4)	(1.0)	(−19.5)		
24	Cr	0.517	0.516	0.516	0.533	0.434		0.497
		(4.0)	(3.8)	(3.8)	(7.2)	(−12.7)		
25	Mn	0.467	0.532	0.545	0.579	0.434		0.546
		(−14.5)	(−2.6)	(−0.2)	(6.0)	(−20.5)		
26	Fe	0.512	0.569	0.579	0.603	0.463		0.581
		(−11.9)	(−2.1)	(−0.3)	(3.8)	(−20.3)		
29	Cu	0.561	0.578	0.583	0.576	0.470	0.541[d]	0.568
		(−1.2)	(1.8)	(2.6)	(1.4)	(−17.3)	(−4.8)	
							0.562[e]	
							(−1.0)	
30	Zn	0.640	0.688	0.696	0.677	0.559	0.673[d]	0.690
		(−7.2)	(−0.3)	(0.9)	(−1.9)	(−19.0)	(−2.5)	
							0.693[e]	
							(0.5)	
31	Ga	0.395	0.416	0.421	0.399	0.404		0.441
		(−10.4)	(−5.7)	(−4.5)	(−9.5)	(−8.4)		

TABLE I. (*Continued*).

		Without	With correlation		Other work		
Z	Atom	correlation	SPP-SIC	VWM-SIC	sp-$X\alpha$[a]	HF[b]	Expt.[c]
32	Ge	0.543	0.559	0.564	0.553	0.544	0.579
		(−6.2)	(−3.5)	(−2.6)	(−4.5)	(−6.0)	
33	As	0.689	0.701	0.706	0.699	0.698	0.721
		(−4.4)	(−2.8)	(−2.1)	(−3.1)	(−3.2)	
34	Se	0.627	0.701	0.710	0.795	0.610	0.717
		(−12.6)	(−2.2)	(−1.0)	(10.9)	(−14.9)	
35	Br	0.802	0.859	0.867	0.883	0.794	0.870
		(−7.8)	(−1.3)	(−0.3)	(1.5)	(−8.7)	
36	Kr	0.971	1.018	1.026	1.003	0.978	1.029
		(−5.6)	(−1.1)	(−0.3)	(−2.5)	(−5.0)	
37	Rb	0.301	0.309	0.311			0.307
		(−2.0)	(0.7)	(1.3)			
38	Sr	0.372	0.410	0.420			0.418
		(−11.0)	(−1.9)	(0.5)			
ave%[f]		(7.5)	(2.3)	(1.6)	(5.4)	(10.3)	

[a] Reference 5.

[b] Reference 41.

[c] Reference 43.

[d] Reference 14 with *ab initio* SCF-CI procedure.

[e] Reference 42 using HF method with correlation and relativistic correction.

[f] $\text{ave\%}=[\sum_{i=1}^{N}|(I_i^{\text{theor}}-I_i^{\text{expt.}})|/I_i^{\text{expt}}\times 100]/N$.

those in the HF scheme in which the relaxation effect is also included. Comparing the results in columns 3, 6, 7, and 9 shows that the ionization potentials did not improve much, even though the relaxation effect in the process of ionization is considered. This means that the relaxation effect is not a major one.

The results in columns 4 and 5 show that once the correlation correction is introduced into the calculation of ionization potentials, the results are improved and are in excellent agreement with experiment. Columns 4, 5, and 9 show that the results with the VWM-SIC correlation correction are closer to experiment than those with the SPP-SIC correction. The differences between the results in the LSD-GX-SIC–GWB with VWM-SIC and the experiments are less than 5% for all atoms except for Al. The average difference is equal to 1.6% in the LSD-GX-

TABLE II. Ionization potentials (in rydbergs) for vanadium, cobalt, and nickel calculated using the LSD-GX-SIC–GWB scheme with correlation correction.

		Electron configuration		Without	With correlation		Other work	
Z	Atom	Atom	Ion	correlation	SPP-SIC	VWN-SIC	sp-$X\alpha$[b]	Expt.[a]
23	V	$3d^3 4s^2$	$3d^2 4s^2$	0.867	0.894	0.901		
23	V	$3d^3 4s^2$	$3d^4$	0.369	0.411	0.418	0.512	0.495
				(−25.5)	(−17.1)	(−15.6)	(3.3)	
23	V	$3d^3 4s^2$	$3d^3 4s^1$	0.446	0.505	0.517		0.519
				(−14.1)	(−2.7)	(−0.4)		
27	Co	$3d^7 4s^2$	$3d^6 4s^2$	0.910	0.983	0.989		0.949
				(−4.1)	(−3.6)	(4.2)		
27	Co	$3d^7 4s^2$	$3d^8$	0.531	0.530	0.537	0.558	0.578
				(−8.1)	(−8.2)	(−7.1)	(−3.4)	
27	Co	$3d^7 4s^2$	$3d^7 4s^1$	0.550	0.603	0.612		0.609
				(−9.7)	(−1.0)	(0.5)		
28	Ni	$3d^8 4s^2$	$3d^7 4s^2$	1.041	1.107	1.114		
28	Ni	$3d^8 4s^2$	$3d^9$	0.468	0.475	0.481	0.565	0.561
				(−16.6)	(−15.4)	(−14.3)	(0.8)	
28	Ni	$3d^8 4s^2$	$3d^8 4s^1$	0.583	0.633	0.642		0.638
				(−8.6)	(−0.8)	(0.7)		

[a] Reference 43.

[b] Reference 5.

TABLE III. Electron affinities (in rydbergs) for atoms in the LSD-GX-SIC–GWB scheme with correlation correction.

Z	Atom	Without correlation	With correlation		Other work				Expt.[c]
			SPP-SIC	VWM-SIC	Unrelaxed[a]	Relaxed[b]	EA		
1	H	−0.0240	0.0389	0.0521					0.0577
		(−141.6)	(−32.6)	(−9.7)					
3	Li	−0.0055	0.0296	0.0397					0.0456
		(−112.1)	(−35.1)	(−12.9)					
5	B	0.0042	0.0128	0.0160	0.0050	−0.0071	0.0162[d]	0.0110[e]	0.0204
		(−79.4)	(−37.3)	(−21.6)	(−75.5)	(−134.8)	(−20.7)	(−46.1)	
6	C	0.0745	0.0833	0.0876	0.0521	0.0433	0.0897[d]	0.0816[e]	0.0932
		(−20.1)	(−10.6)	(−6.0)	(−44.1)	(−53.5)	(−3.8)	(−12.5)	
							0.0794[f]	0.0838[g]	
							(−14.8)	(−10.1)	
8	O	0.0180	0.0753	0.0815	0.0892	−0.0179	0.1000[d]	0.0831[e]	0.1075
		(−83.3)	(−30.0)	(−24.2)	(−17.0)	(−166.7)	(−7.0)	(−22.7)	
								0.0801[f]	
								(−25.5)	
9	F	0.1742	0.2231	0.2301	0.1838	0.0966	0.2462[d]	0.2293[e]	0.2498
		(−30.3)	(−10.7)	(−7.9)	(−26.4)	(−61.3)	(−1.4)	(−8.2)	
							0.2337[f]	0.2535[h]	
							(−6.4)	(−1.5)	
11	Na	−0.0009	0.0319	0.0413					0.0401
		(−102.2)	(−20.4)	(3.0)					
13	Al	0.0163	0.0211	0.0230	0.0390	0.0257			0.0325
		(−49.8)	(−35.1)	(−29.2)	(20.0)	(−20.9)			
14	Si	0.0802	0.0864	0.0890	0.0979	0.0848			0.1018
		(−21.2)	(−15.1)	(−12.6)	(−3.8)	(−16.7)			
16	S	0.0925	0.1419	0.1487	0.1577	0.0934			0.1527
		(−39.4)	(−7.1)	(−2.6)	(3.3)	(−38.8)			
17	Cl	0.2107	0.2521	0.2591	0.2431	0.1866			0.2657
		(−20.7)	(−5.1)	(−2.5)	(−8.5)	(−29.8)			
19	K	0.0019	0.0300	0.0384					0.0368
		(−94.8)	(−18.5)	(4.3)					
29	Cu	0.0453	0.0807	0.0883			0.0856[i]	0.0713[j]	0.0903
		(−49.8)	(−10.6)	(−2.2)			(−5.0)	(−21.0)	
31	Ga	0.0148	0.0192	0.0208	0.0406	0.0291			0.0222
		(−33.3)	(−13.5)	(−6.3)	(82.9)	(31.1)			
32	Ge	0.0796	0.0854	0.0877	0.1349	0.1266			0.0897
		(−11.3)	(−4.8)	(−2.2)	(50.4)	(41.1)			
34	Se	0.0989	0.1460	0.1531	0.1622	0.1139			0.1485
		(−33.4)	(−1.7)	(3.1)	(9.2)	(−23.3)			
35	Br	0.2042	0.2437	0.2506	0.2420	0.2032			0.2470
		(−17.3)	(−1.3)	(1.5)	(−2.0)	(−17.7)			
37	Rb	0.0035	0.0302	0.0384					0.0357
		(−90.2)	(−15.4)	(7.6)					
ave%[k]		(57.2)	(16.9)	(8.9)					

[a] The values were calculated by using the LSD-GX–FEL with KG's (Ref. 28) correlation correction under frozen-orbital approximation (Ref. 17).

[b] The values were obtained by using the simple relaxation model derived by Gazquez and Ortiz (Ref. 6) in the LSD-GX–FEL theory (Ref. 17).

[c] Expt. (Refs. 45 and 46).

[d] Reference 27.

[e] Reference 13.

[f] Reference 12.

[g] Reference 15.

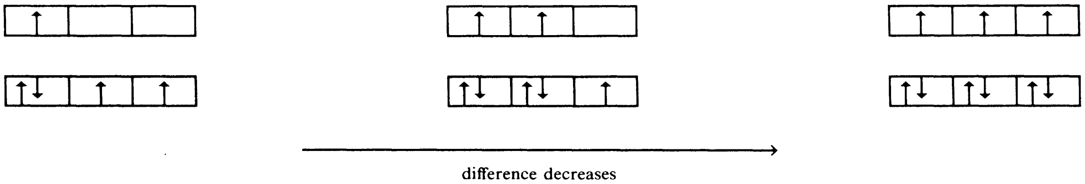
[h] Reference 44.

[k] $\text{ave\%}=[\sum_{i=1}^{N}|(I_i^{\text{theor}}-I_i^{\text{expt}})|/I_i^{\text{expt}}\times 100]/N$.

SIC–GWB scheme with VWM-SIC correlation correction less than 2.3% with SPP-SIC, 5.4% in the *sp-Xα* scheme, 7.5% in the LSD-GX-SIC–GWB without correlation correction, and 10% in the HF scheme.

In Table I column 8 gives several other results for Cu and Zn given by Sunil and Jordan[14] using an *ab initio* SCF-CI procedure and by Jankowski and Polasik[42] using the HF method with correlation and relativistic correction. The differences between the theoretical results for these three schemes with the experiments are almost the same. But it is worth pointing out that the LSD-GX-SIC scheme is the simplest and cheapest one in these schemes and has been applied to a wide range of atoms successfully.

From column 5 it may be seen that for the transition-metal atoms, the ionization potentials are a little bigger than the experiments for the atoms which involved two orbitals in going from the neutral atom to the positive ion, i.e., Cr, and a little smaller for the atoms which involved one orbital in going from the neutral atom to the positive ion, i.e., Sc, Ti, Mn, and Fe. For other atoms, the ionization potentials are a little bigger than experiment for these atoms in which the outermost electrons are *s* electrons, except for Li and Be, and are a little smaller than experiment for others. It also may be seen that differences between the present results with the experiments decrease as the occupation number of the p_s subshell increases, that is,



This is because the fuller the subshell, the more accurate the spherical approximation in the LSD-GX scheme.

Table II shows the ionization potentials for the transition-metal atoms vanadium, cobalt, and nickel from the neutral atoms to three differential final states. In the process of ionization, if one 4*s* electron is removed to infinity and another one is relaxed to a 4*d* electron, the ionization potentials in the LSD-GX-SIC–GWB with or without correlation correction for these atoms are smaller than experiment, and if only one 4*s* electron is removed and another one still stays in a 4*s* subshell, the ionization potentials are bigger than experiment except for V. However, the average value of these two situations almost equals experiment. This shows that the two final states interact strongly, and thus the Slater transition-state theory gives good results.

The electron affinities for several atoms calculated by using the LSD-GX-SIC–GWB theory with and without correlation correction are listed in Table III. Column 6 gives the results obtained by means of the LSD-GX–FEL (free-electron limit Fermi-hole parameters) with the correlation correction[28] under the frozen-orbital approximation.[17] Column 7 shows the results calculated using the simple relaxation model derived by Gazquez and Ortiz[6] in the LSD-GX–FEL scheme. Columns 8 and 9 list other theoretical values evaluated using the HF method with Møller-Plesset perturbation theory through complete fourth order using several large basis sets,[27] CI,[13–15] MCSCF,[12] the fixed-node quantum Monte Carlo method,[44] and HF with correlation and relativistic correction.[42] The experiments[45,46] are listed in the last column.

Comparing the results in column 3 (include the relaxation without correlation correction) and column 7 (simple relaxation model without correlation correction) with the experiments shows that although the relaxation effect is perfectly calculated the electron affinities for these atoms are not much improved. But once the correlation correction is included, the results are in very good agreement with experiment.

From columns 4 and 5, one can see that the results with the VWM-SIC correlation correction are better than these with the SPP-SIC correction. The average difference in percentage in the LSD-GX-SIC–GWB scheme for these atoms is 8.9% with VWM-SIC, 16.9% with SPP-SIC, and 57.2% without correlation correction. Comparing the present results with VWM-SIC correlation correction and other theoretical values in columns 8 and 9 with the experiments shows that, although the LSD-GX-SIC theory is simple relative to the other *ab initio* methods listed, the electron affinities in this scheme for these atoms are equal to those in any other complicated methods.

IV. CONCLUSION

The LSD-GX-SIC–GWB theory with VWN-SIC correlation correction is a powerful method for calculating ionization potentials and electron affinities. The results from this theory are so close to experiment that it can be used to predict the ionization potential of any atom which is unknown experimentally. The agreement of the present results with experiment increases with atomic number for these atoms. Therefore it is possible to get good results for the high-*Z* atoms by using the LSD-GX-SIC theory with the correlation correction, if the relativistic effect is considered in the calculation of ionization potential and electron affinity.

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[1] M. S. Gopinathan, J. Phys. B **12**, 521 (1979).

[2] B. Rooney, T. J. Tseng, and M. A. Whitehead, Phys. Rev. A **22**, 1375 (1980).

[3] K. Schwarz, J. Phys. B **8**, 1339 (1978).

[4] N. H. F. Beebe, Chem. Phys. Lett. **19**, 290 (1973).

[5] S. Manoli and M. A. Whitehead, J. Chem. Phys. **81**, 841 (1984).

[6] J. L. Gazquez and E. Ortiz, J. Chem. Phys. **81**, 2741 (1984).

[7] L. J. Bartolotti, S. R. Gadre, and R. G. Parr, J. Am. Chem. Soc. **102**, 2945 (1980).

[8] Y. Zhao, Z. Zhang, and Y. Guo, J. At. Mol. Phys. (China) **2**, 62 (1985).

[9] K. Schwarz, Chem. Phys. Lett. **57**, 605 (1978).

[10] K. D. Sen, Chem. Phys. Lett. **74**, 201 (1980).

[11] C. F. Fisher, J. B. Lagowski, and S. H. Vosko, Phys. Rev. Lett. **59**, 2263 (1987).

[12] B. H. Botch and T. H. Dunning, Jr., J. Chem. Phys. **76**, 6046 (1982).

[13] F. Sasaki and M. Yoshimine, Phys. Rev. A **9**, 17, 26 (1974).

[14] K. K. Sunil and K. D. Jordan, J. Chem. Phys. **82**, 873 (1985).

[15] J. Kalcher and R. Janoscher, Chem. Phys. **104**, 251 (1986).

[16] Y. Guo, S. Manoli, and M. A. Whitehead, Phys. Rev. A **38**, 1120 (1988).

[17] Y. Guo and M. A. Whitehead, Phys. Rev. A (to be published).

[18] P. Gombas, *Pseudopotentials* (Springer, New York, 1967).

[19] G. C. Lie and E. Clementi, J. Chem. Phys. **60**, 1275, 1288 (1974).

[20] W. J. Carr, Jr., Phys. Rev. **122**, 1437 (1961).

[21] W. J. Carr, Jr. and A. A. Maradudin, Phys. Rev. A **133**, 371 (1964).

[22] R. G. Gordon and Y. S. Kim, J. Chem. Phys. **56**, 3122 (1972); **60**, 1842 (1974).

[23] S. Ma and K. A. Brueckner, Phys. Rev. **165**, 18 (1968).

[24] H. Stoll, C. M. Pavlidou, and H. Preuss, Theor. Chim. Acta **49**, 143 (1978).

[25] O. Gunnarson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).

[26] E. San-Fabián and F. Moscardó, J. Chem. Phys. **81**, 4008 (1984).

[27] K. Raghavachari, J. Chem. Phys. **82**, 4142 (1985).

[28] J. Keller and J. L. Gázquez, Phys. Rev. A **20**, 1289 (1979).

[29] S. Manoli and M. A. Whitehead, Phys. Rev. A **23**, 2150 (1981).

[30] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[31] G. S. Painter, Phys. Rev. B **24**, 4264 (1981).

[32] H. Stoll, E. Golka, and H. Preuss, Theor. Chim, Acta **55**, 29 (1980).

[33] A. Savin, P. Schwerdtfeger, H. Preuss, H. Silberbach, and H. Stoll, Chem. Phys. Lett. **98**, 226 (1983).

[34] S. H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1980).

[35] S. Manoli and M. A. Whitehead, Phys. Rev. A **34**, 4629 (1986).

[36] S. Manoli, Ph.D. thesis, McGill University, 1986 (unpublished).

[37] M. S. Gopinathan, M. A. Whitehead, and R. Bogdanovic, Phys. Rev. A **14**, 1 (1976).

[38] E. P. Wigner, Phys. Rev. **46**, 1002 (1934).

[39] D. M. Ceperly and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[40] S. Manoli and M. A. Whitehead, in *Local Density Approximations in Quantum Chemistry and Solid State Physics,* edited by J. P. Dahl and J. Avery (Plenum, New York, 1984).

[41] E. Clementi and C. Roetti, At. Data Nucl. Data Tables **14**, 177 (1974).

[42] K. Jankowski and M. Polasik, J. Phys. B **18**, 2133 (1985).

[43] C. E. Moore, *Atomic Energy Levels,* Natl. Bur. Stand. (U.S.) Circ. No. 467 (U.S. GPO, Washington, D.C., 1949), Vol. I; *ibid.,* Vol. II (1952); *ibid.,* Vol. III (1955).

[44] R. N. Barnett, P. J. Reynolds, and W. A. Lester, Jr., J. Chem. Phys. **84**, 4992 (1986).

[45] R. G. Parr and L. J. Bartolotti, J. Am. Chem. Soc. **104**, 3801 (1982).

[46] H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data **14**, 731 (1985).