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Calculations with the quasirelativistic local-spin-density-functional theory for high-Z atoms

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The generalized-exchange local-spin-density-functional theory (LSD-GX) with relativistic corrections of the mass velocity and Darwin terms has been used to calculate statistical total energies for the neutral atoms, the positive ions, and the negative ions for high-Z elements. The effect of the correlation and relaxation correction on the statistical total energy is discussed. Comparing the calculated results for the ionization potentials and electron affinities for the atoms (atomic number Z from 37 to 56 and 72 to 80) with experiment, shows that for the atoms rubidium to barium both the LSD-GX and the quasirelativistic LSD-GX, with self-interaction correction, Gopinathan, Whitehead, and Bogdanovic's Fermi-hole parameters [Phys. Rev. A **14**, 1 (1976)], and Vosko, Wilk, and Nusair's correlation correction [Can. J. Phys. **58**, 1200 (1980)], are very good methods for calculating ionization potentials and electron affinities. For the atoms hafnium to mercury the relativistic effect has to be considered.

I. INTRODUCTION

The relativistic effect is very important for high-Z atoms, but the "full" relativistic calculation for these atoms is complicated, because the "large" and "small' components should be calculated simultaneously by solving the Dirac equation.[1] Cowan and Griffin[2] have described an approximate solution to the Dirac-Hartree-Fock (DHF) equations for atoms. Wood and Boring[3] and Selvaraj and Gopinathan[4] used this approach in the Dirac-Hartree-Fock-Slater (DHFS) and $\Xi\alpha$ methods. In this paper the approach of Cowan and Griffin is applied to the generalized-exchange local-spin-density-functional theory (LSD-GX) derived by Manoli and Whitehead[5] and Manoli.[6]

In previous papers[7,8] the ionization potentials and electron affinities for low-Z atoms, calculated using the LSD-GX theory with self-interaction correction[9] and Gopinathan, Whitehead, and Bogdanovic's (GWB) Fermi-hole parameters[10] (LSD-GX-SIC-GWB) were in excellent agreement with experiment. Therefore it would be expected that good results would also be obtained for high-Z atoms using the LSD-GX theory with self-interaction correction (LSD-GX-SIC) with the correlation correction, if the relativistic effect were included in calculating ionization potentials and electron affinities. The so-called quasirelativistic LSD-GX-SIC theory with GWB parameters (QR-LSD-GX-SIC-GWB) and Stoll, Pavlidou, and Preuss's[11] (SPP) and Vosko, Wilk, and Nusair's[12] (VWN) correlation corrections are used to calculate the statistical total energies for positive ions, neutral atoms, and some stable negative ions of high-Z elements. Finally, the ionization potentials and electron affinities for these atoms are obtained.

II. QUASIRELATIVISTIC LSD-GX-SIC THEORY

The equations for the Dirac central-field problem,[13,14] in Rydberg atomic units are

$$\begin{aligned}&\frac{dP_{nk}(r)}{dr}+\frac{k}{r}P_{nk}(r)-\left[\frac{2}{\alpha}+\frac{\alpha}{2}[V(r)-\varepsilon_{nk}]\right]Q_{nk}(r)=0\ ,\\&\frac{dQ_{nk}(r)}{dr}-\frac{k}{r}Q_{nk}(r)+\left[\frac{\alpha}{2}[V(r)-\varepsilon_{nk}]\right]P_{nk}(r)=0\ ,\end{aligned}\qquad(1)$$

where $V(r)$ is the central-field potential, ε_{nk} is the eigenvalue (minus the rest energy of the electron), and k is the relativistic quantum number,

$$k=\begin{cases}-(l+1) & \text{when } j=l+\frac{1}{2}\\ l & \text{when } j=l-\frac{1}{2}\ .\end{cases}$$

α is the fine-structure constant $\frac{1}{137.036}$. $P_{nk}(r)$ and $Q_{nk}(r)$ are the large and small components, respectively.

The second-order differential equation used by Cowan and Griffin[2] is obtained by substituting $Q_{nk}(r)$ from the first equation of (1) into the second one to give

$$\frac{d^2}{dr^2}P_{nk}(r)=(g+f)P_{nk}(r)\ ,\qquad(2)$$

with

$$g=-\varepsilon_{nk}+\frac{l(l+1)}{r^2}+V(r)\qquad(3)$$

and

$$\begin{aligned}f&=-K[\varepsilon_{nk}-V(r)]^2-KB\frac{dV(r)}{dr}\left[\frac{d}{dr}-\frac{1}{r}\right]\\&\quad-KB\left[\frac{k+1}{r}\right]\frac{dV(r)}{dr}\\&=H_m(r)+H_D(r)+H_{\text{so}}(r)\ ,\end{aligned}\qquad(4)$$

where

$$K=\alpha^2/4,\quad B=[1+\tfrac{1}{4}\alpha^2(\varepsilon_{nk}-V)]^{-1}\ .$$

The operator f is the sum of the mass-velocity H_m, Darwin $H_D(r)$, and spin-orbital coupling $H_{so}(r)$ terms. For the present the spin-orbital term in the potential is neglected.

When $r \rightarrow 0$, the asymptotic form of the potential is

$$V(r) = -\frac{2Z}{r} \ . \tag{5}$$

Then the Darwin correction is positive for all orbitals with $l=0$, and zero for all others (i.e., $l \neq 0$). The equation used by Cowan and Griffin is

$$\left[-\frac{d^2}{dr^2} + \frac{l_i(l_i+1)}{r^2} + V_i(r) - \frac{\alpha^2}{4}[\varepsilon_i - V_i(r)]^2 - \delta_{l_i 0}\frac{\alpha^2}{4}\left[1 + \frac{\alpha^2}{4}[\varepsilon_i - V_i(r)]\right]^{-1} \frac{dV_i(r)}{dr}\left[\frac{dP_i/dr}{P_i} - \frac{1}{r}\right]\right] P_i(r) = \varepsilon_i P_i(r) \ . \tag{6}$$

In the LSD-GX-SIC theory,[5,6] the potential is

$$V_i(\mathbf{r}) = -\frac{2Z}{r} + V_{c_i}(\mathbf{r}) + V_{S_i}(\mathbf{r}) + V_{X_i}^{G}(\mathbf{r}) \ , \tag{7}$$

where $V_{c_i}(\mathbf{r})$ is the Coulomb potential without self-interaction given by

$$V_{c_i}(\mathbf{r}) = \sum_{j \neq i} f_j \langle u_j(\mathbf{r}') \| u_j(\mathbf{r}') \rangle \ , \tag{8}$$

$V_{S_i}(\mathbf{r})$ is the statistical self-interaction potential for the orbital i,[9]

$$V_{S_i}(\mathbf{r}) = 6c\alpha^{\mathrm{SI}} n_i^{1/3}(\mathbf{r}) \ , \tag{9}$$

while the generalized-exchange potential is

$$\begin{aligned} V_{X_i}^{G}(\mathbf{r}) = -\tfrac{9}{2}c\alpha^{\lim} \Bigg[& \sum_j^s [n_s(\mathbf{r}) + B_2 n_j(\mathbf{r})]^{-2/3} n_j(\mathbf{r}) - \tfrac{2}{3}\sum_j^s [n_s(\mathbf{r}) + B_1 n_j(\mathbf{r})][n_s(\mathbf{r}) + B_2 n_j(\mathbf{r})]^{-5/3} n_j(\mathbf{r}) \\ & + [n_s(\mathbf{r}) + 2B_1 n_i(\mathbf{r})][n_s(\mathbf{r}) + B_2 n_i(\mathbf{r})]^{-2/3} - \tfrac{2}{3}B_2[n_s(\mathbf{r}) + B_1 n_i(\mathbf{r})][n_s(\mathbf{r}) + B_2 n_i(\mathbf{r})]^{-5/3} n_i(\mathbf{r}) \Bigg] \ . \end{aligned} \tag{10}$$

Here c is a constant and equal to $(3/4\pi)^{1/3}$. $u_j(\mathbf{r})$, $n_j(\mathbf{r})$, and $n_s(\mathbf{r})$ are the one-electron eigenfunction, the electron densities for electron j and for all electrons with spin s, respectively, and α^{SI}, $\alpha^{\lim}$, B_1, and B_2 are parameters depending on the Fermi-hole shape. For the GWB Fermi hole, these parameters are in Ref. 9.

The statistical total energy of the atom, or ion, can be written as

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

where

$$\begin{aligned} U_{si}^{\mathrm{GX}}(\mathbf{r}) = & -9c\alpha^{\lim}[n_s(\mathbf{r}) + B_1 n_i(\mathbf{r})] \\ & \times [n_s(\mathbf{r}) + B_2 n_i(\mathbf{r})]^{-2/3} + 9c\alpha^{\mathrm{SI}} n_i^{1/3}(\mathbf{r}) \ . \end{aligned} \tag{12}$$

III. RESULTS AND DISCUSSION

Equation (6) is solved by means of the standard self-consistent-field (SCF) procedures;[15] outward numerical integration of each equation is started in the usual manner by means of a small-r series solution described in the Appendix. The relativistic-correction terms in Eq. (6) are treated as a part of the potential; that is, the radial function $P_i(r)$ and one-electron eigenvalue ε_i in the $(n-1)$th iteration are used to calculate the relativistic terms of the potential of Eq. (6) for the nth iteration, so the relativistic-correction terms in Eq. (6) are completely neglected in the first iteration.

Expression (11), the statistical total energy, has been used to calculate the positive ions and neutral atoms of elements rubidium to barium and hafnium to mercury, and the negative ions of some high-Z elements, by means of the wave functions in the QR-LSD-GX-SIC-GWB and LSD-GX-SIC-GWB theories. The wave functions in both QR-LSD-GX-SIC-GWB and LSD-GX-SIC-GWB theories are also used to calculate the SPP and VWN correlations with the self-interaction correlation correction[16] (SPP-SIC and VWN-SIC, respectively) for the corresponding neutral atoms, positive and negative ions.[8] Finally, the ionization potentials and electron affinities for these atoms are obtained in terms of the energy difference between the positive ion and neutral atom for the ionization potential, and between the neutral atom and negative ion for the electron affinity. The ionization potentials for these atoms in both QR-LSD-GX-SIC-GWB and LSD-GX-SIC-GWB theories are also calculated under the frozen-orbital approximation. All results are given in Tables I–IV.

Table I contains the ionization potentials for some high-Z atoms in the LSD-GX-SIC-GWB theory without and with the correlation correction (columns 3, 4, and 5, respectively). Column 6 gives the results without relaxation or correlation corrections. Columns 7 and 8 contain other work given by Savin *et al.*[17] using the Hartree-Fock[18] theory and experimental values.[19] The table shows that (i) the results are greatly improved by the correlation correction; (ii) the nonrelativistic results are in very good agreement with experiment for the atoms of the atomic number from 37 to 56. The percentage differences for these atoms are less than 5%, except for Zr. But the LSD-GX-SIC theory cannot accurately describe the

TABLE I. Ionization potentials (in Ry) for the high-Z atoms in the LSD-GX-SIC-GWB theory compared to other work and experiment. The values in the parentheses are the percentage differences equal to $[(I^{\text{expt}} - I^{\text{theor.}})/I^{\text{expt.}}]\times 100$.

		Present work					
		With relaxation					
			With correlation correction				
Z	Atom	Without correlation	SPP-SIC	VWN-SIC	Without relaxation or correlation	Other work	Expt.[a]
37	Rb	0.300 (2.2)	0.308 (−0.4)	0.311 (−1.3)	0.313 (−2.0)	0.275[b] (10.4) 0.284[c] (7.5) 0.283[d] (7.8)	0.307
38	Sr	0.371 (11.3)	0.410 (2.0)	0.419 (−0.1)	0.392 (6.3)		0.418
39	Y	0.452 (5.4)	0.484 (−1.3)	0.491 (−2.8)	0.437 (8.5)		0.478
40	Zr	0.408 (20.1)	0.464 (9.2)	0.476 (6.8)	0.464 (9.2)		0.511
41	Nb	0.495 (0.5)	0.494 (0.7)	0.494 (0.7)	0.512 (−2.9)		0.498
42	Mo	0.515 (1.3)	0.514 (1.5)	0.514 (1.5)	0.532 (−1.9)		0.522
43	Tc	0.432 (19.3)	0.500 (6.6)	0.514 (3.9)	0.517 (3.4)		0.535
44	Ru	0.520 (3.9)	0.530 (2.1)	0.534 (1.3)	0.532 (1.7)		0.541
45	Rh	0.521 (5.0)	0.535 (2.4)	0.539 (1.7)	0.532 (3.0)		0.548
47	Ag	0.521 (6.4)	0.541 (2.8)	0.546 (1.9)	0.530 (4.8)	0.434[b] (22.1) 0.459[c] (17.6) 0.456[d] (18.1)	0.557
48	Cd	0.589 (10.9)	0.633 (4.2)	0.641 (3.0)	0.607 (8.1)		0.661
49	In	0.380 (10.6)	0.400 (5.9)	0.406 (4.5)	0.393 (7.6)		0.425
50	Sn	0.506 (6.2)	0.521 (3.5)	0.526 (2.5)	0.526 (2.5)		0.540

TABLE I. *(Continued).*

		Present work					
		With relaxation			Without relaxation or correlation		
			With correlation correction				
Z	Atom	Without correlation	SPP-SIC	VWN-SIC		Other work	Expt.[a]
51	Sb	0.627	0.640	0.645	0.656		0.635
		(1.3)	(−0.8)	(−1.6)	(−3.3)		
52	Te	0.574	0.641	0.651	0.613		0.662
		(13.3)	(3.2)	(1.7)	(7.4)		
53	I	0.717	0.770	0.776	0.760		0.768
		(6.7)	(−0.2)	(−1.0)	(1.1)		
54	Xe	0.853	0.896	0.904	0.904		0.891
		(4.3)	(−0.5)	(−1.4)	(−1.4)		
55	Cs	0.272	0.278	0.281	0.284	0.246[b]	0.286
		(4.9)	(2.8)	(1.8)	(0.7)	(14.0)	
						0.255[c]	
						(10.8)	
						0.254[d]	
						(11.2)	
56	Ba	0.330	0.366	0.375	0.351		0.383
		(13.8)	(4.4)	(2.1)	(8.3)		
72	Hf	0.566	0.592	0.600	0.471		0.515
		(−10.0)	(−15.1)	(−16.6)	(8.5)		
73	Ta	0.420	0.484	0.498	0.490		0.579
		(27.5)	(16.4)	(14.0)	(15.4)		
74	W	0.426	0.494	0.510	0.519		0.586
		(27.4)	(15.8)	(13.0)	(11.5)		
75	Re	0.432	0.502	0.516	0.535		0.578
		(25.3)	(13.2)	(10.8)	(7.5)		
76	Os	0.475	0.533	0.545	0.541		0.640
		(25.7)	(16.7)	(14.8)	(15.4)		
77	Ir	0.508	0.563	0.574	0.560		0.661
		(23.2)	(14.9)	(13.2)	(15.3)		
78	Pt	0.527	0.543	0.551	0.538		0.661
		(20.3)	(17.9)	(16.7)	(18.7)		
79	Au	0.523	0.547	0.551	0.535	0.436[b]	0.678
		(22.8)	(19.3)	(18.7)	(21.1)	(35.7)	
						0.464[c]	
						(31.6)	
						0.460[d]	
						(32.2)	
80	Hg	0.586	0.629	0.637	0.604		0.767
		(23.6)	(17.9)	(16.9)	(21.2)		
	av%[e]	(12.6)	(7.2)	(6.3)	(7.8)		

[a] Reference 19.

[b] These values were obtained by using the HF theory, Ref. 17.

[c] Obtained by using the HF theory with SPP-SIC under the frozen-orbital approximation, Ref. 17.

[d] The values were calculated by using the HF theory with SPP-SIC and relaxation correction, Ref. 17.

[e] $\text{av\%} = \left[\sum_{i=1}^{N} \left| (I_i^{\text{expt.}} - I_i^{\text{theor.}}) \right| / I_i^{\text{expt.}} \times 100 \right] \Big/ N.$

atoms for which the atomic numbers are bigger than 72 (the percentage differences exceed 10%); (iii) the LSD-GX-SIC results are much better than the Hartree-Fock (HF) results in describing ionization potentials for the high-Z atoms whether the correlation correction is included or not.

Table II gives the ionization potentials for some high-Z atoms obtained by using the QR-LSD-GX-SIC-GWB theory without and with correlation corrections (columns 3–6), other theoretical values given by Savin *et al.*[17] using the Dirac-Fock method[20] (DF), with and without correlation correction, and experiment.[19] From columns 4 and 5, it may be seen that the results in the QR-LSD-GX-SIC-GWB with SPP-SIC and VWN-SIC correlation correction are in excellent agreement with the experiment, particularly for atoms of atomic number from 72 to

TABLE II. Ionization potentials (in Ry) for high-Z atoms in the QR-LSD-GX-SIC-GWB theory compared to other work and experiment. The values in the parentheses are the percentage differences equal to $(I^{\text{expt}} - I^{\text{theor.}})/I^{\text{expt}} \times 100$.

		Present work					
		With relaxation			Without relaxation or correlation		
			With correlation correction				
Z	Atom	Without correlation	SPP-SIC	VWN-SIC		Other work	Expt.[a]
37	Rb	0.306 (0.3)	0.313 (−2.0)	0.315 (−2.6)	0.318 (−3.6)	0.279[b] (9.1) 0.289[c] (5.9) 0.288[d] (6.2)	0.307
38	Sr	0.377 (9.9)	0.416 (0.6)	0.425 (−1.6)	0.398 (4.9)		0.418
39	Y	0.423 (11.5)	0.455 (4.8)	0.462 (3.3)	0.448 (6.2)		0.478
40	Zr	0.418 (18.2)	0.477 (6.6)	0.489 (4.3)	0.477 (6.6)		0.511
41	Nb	0.519 (−4.3)	0.518 (−4.1)	0.518 (−4.1)	0.539 (−8.3)		0.498
42	Mo	0.543 (−4.0)	0.542 (−3.9)	0.542 (−3.9)	0.562 (−7.7)		0.522
43	Tc	0.446 (16.7)	0.518 (3.2)	0.532 (0.6)	0.538 (−0.5)		0.535
44	Ru	0.553 (−2.2)	0.563 (−4.0)	0.567 (−4.7)	0.567 (−4.7)		0.541
45	Rh	0.555 (−1.2)	0.570 (−4.0)	0.575 (−4.9)	0.568 (−3.6)		0.548
47	Ag	0.559 (−0.4)	0.580 (−4.2)	0.585 (−5.1)	0.570 (−2.4)	0.466[b] (16.3) 0.495[c] (11.1) 0.491[d] (11.8)	0.557
48	Cd	0.626 (5.3)	0.671 (−1.5)	0.678 (−2.6)	0.646 (2.2)		0.661
49	In	0.378 (11.1)	0.399 (6.2)	0.403 (5.2)	0.390 (8.3)		0.425
50	Sn	0.504 (6.6)	0.520 (3.7)	0.524 (2.9)	0.525 (2.7)		0.540

TABLE II. (*Continued*).

		Present work					
		With relaxation			Without relaxation or correlation		
			With correlation correction				
Z	Atom	Without correlation	SPP-SIC	VWN-SIC		Other work	Expt.[a]
51	Sb	0.627 (1.3)	0.640 (−0.8)	0.644 (−1.4)	0.655 (−3.1)		0.635
52	Te	0.573 (13.5)	0.641 (3.2)	0.651 (1.7)	0.612 (7.6)		0.662
53	I	0.716 (6.8)	0.770 (−0.2)	0.776 (−1.0)	0.761 (1.0)		0.768
54	Xe	0.853 (4.3)	0.896 (−0.5)	0.905 (−1.5)	0.905 (−1.5)		0.891
55	Cs	0.282 (1.4)	0.290 (−1.4)	0.293 (−2.4)	0.294 (−2.8)	0.256[b] (10.5) 0.266[c] (7.0) 0.265[d] (7.3)	0.286
56	Ba	0.343 (10.4)	0.379 (1.0)	0.388 (−1.3)	0.362 (5.5)		0.383
72	Hf	0.475 (7.7)	0.502 (2.4)	0.508 (1.3)	0.525 (−2.0)		0.515
73	Ta	0.477 (17.6)	0.545 (5.9)	0.561 (3.1)	0.556 (4.0)		0.579
74	W	0.484 (17.5)	0.561 (4.3)	0.576 (1.8)	0.600 (−2.3)		0.586
75	Re	0.488 (15.6)	0.574 (0.8)	0.590 (−2.0)	0.623 (−7.7)		0.578
76	Os	0.551 (13.8)	0.617 (3.5)	0.629 (1.6)	0.634 (0.9)		0.640
77	Ir	0.602 (9.0)	0.660 (0.2)	0.668 (−1.0)	0.666 (−0.7)		0.661
78	Pt	0.656 (0.8)	0.680 (−2.8)	0.684 (−3.4)	0.676 (−2.2)		0.661
79	Au	0.664 (2.0)	0.691 (−2.0)	0.691 (−2.0)	0.678 (0.0)	0.565[b] (16.7) 0.604[c] (10.9) 0.597[d] (11.9)	0.678
80	Hg	0.719 (6.2)	0.762 (0.6)	0.770 (−0.4)	0.741 (3.3)		0.767
	av%[e]	(7.8)	(2.8)	(2.6)	(3.8)		

[a] Reference 19.

[b] These values were obtained by using the DF theory, Ref. 17.

[c] Obtained by using the DF theory with SPP-SIC under the frozen-orbital approximation, Ref. 17.

[d] The values were calculated by using the DF theory with SPP-SIC and relaxation correction, Ref. 17.

[e] $\mathrm{av}\% = \left[\sum_{i=1}^{N} |(I_i^{\mathrm{expt.}} - I_i^{\mathrm{theor.}})| / I_i^{\mathrm{expt.}} \times 100 \right] \Big/ N.$

80: the percentage differences in the LSD-GX-SIC-GWB theory are greater than 10%, but they are less than 3.5% in the QR-LSD-GX-SIC-GWB theory. Generally speaking, the results without relaxation and correlation corrections are better than those with relaxation and without correlation correction. The results with correlation and relaxation corrections, as expected, are much better than those with relaxation but without correlation corrections or with correlation but without relaxation correction. This is because in the process of ionization, the effect of relaxation adjusts the ion structure in the lowest-energy state, the relaxation decreases the ionization potential of an atom, but the correlation effect increases the ionization potential. However, the decrease in the relaxation and increase in the correlation are not equal. Comparing the present work in columns 3–6 and other work in column 7 with the experiments in column 8 shows that the QR-LSD-GX-SIC-GWB theory is much better than the DF method in calculating ionization potentials for the high-Z atoms. It is worth pointing out the QR-LSD-

TABLE III. Electron affinities (in Ry) for high-Z atoms in the QR-LSD-GX-SIC-GWB theory compared to the experimental values. The values in the parentheses are the percentage differences equal to $(\mathrm{EA}^{\mathrm{expt.}}-\mathrm{EA}^{\mathrm{theor.}})/\mathrm{EA}^{\mathrm{expt.}}\times 100$.

Z	Atom	Without correlation	With correlation SPP-SIC	 VWN-SIC	Expt.[a]
37	Rb	0.0039 (89.1)	0.0308 (13.8)	0.0391 (−9.4)	0.0357
40	Zr	0.0469 (−49.8)	0.0337 (−7.6)	0.0342 (−9.2)	0.0313
44	Ru	0.0313 (59.6)	0.0674 (12.8)	0.0752 (2.7)	0.0773
45	Rh	0.0440 (47.4)	0.0801 (4.2)	0.0879 (−5.1)	0.0836
47	Ag	0.0645 (32.7)	0.0996 (−4.0)	0.1064 (−11.1)	0.0958
49	In	0.0205 (12.7)	0.0254 (−8.0)	0.0273 (−16.4)	0.0235
50	Sn	0.0840 (6.4)	0.898 (−0.2)	0.0908 (−1.2)	0.0897
51	Sb	0.0107 (86.4)	0.0645 (18.4)	0.0752 (4.8)	0.0790
52	Te	0.1035 (28.5)	0.1475 (−1.8)	0.1543 (−6.6)	0.1448
53	I	0.1934 (14.0)	0.2314 (−2.9)	0.2383 (−5.9)	0.2249
55	Cs	0.0049 (85.9)	0.0303 (12.8)	0.0371 (−6.9)	0.0347
72	Hf	−0.0117	−0.0039	0.0020	≈0
74	W	0.0098 (83.7)	0.0566 (5.6)	0.0684 (−13.9)	0.0600
76	Os	0.0273 (66.8)	0.0820 (0.3)	0.0859 (−4.4)	0.0823
78	Pt	0.1133 (27.6)	0.1484 (5.1)	0.1563 (0.1)	0.1564
79	Au	0.1250 (26.3)	0.1602 (5.6)	0.1719 (−1.3)	0.1697
av%[b]		(47.8)	(6.9)	(6.6)	

[a] References 21 and 22.

[b] $\mathrm{av}\% = \left[\sum_{i=1}^{N} |\,\mathrm{EA}_i^{\mathrm{expt.}}-\mathrm{EA}_i^{\mathrm{theor.}})\,|\,/\mathrm{EA}_i^{\mathrm{expt.}}\times 100\right]\Big/N.$

TABLE IV. Ionization potentials and electron affinity (in Ry) for atom palladium in different electron configurations in the QR-LSD- and LSD-GX-SIC-GWB theories with correlation correction. The values in the parentheses are the percentage differences equal to $(I^{\text{expt.}} - I^{\text{theor.}})/I^{\text{expt.}} \times 100$.

Z	Atom	Elec. config. Atom	Ion	Without correlation	With correlation SPP-SIC	VWN-SIC	Expt.[a]
			Relativistic ionization potentials				
46	Pd	$4d^{10}$	$4d^9$	0.6182 (−1.0)	0.6631 (−8.3)	0.6709 (−9.6)	0.6122
46	Pd	$4d^9 5s^1$	$4d^9$	0.5566 (−0.6)	0.5762 (−4.1)	0.5811 (−5.0)	0.5533
			Nonrelativistic ionization potentials				
46	Pd	$4d^{10}$	$4d^9$	0.6289 (−2.7)	0.6738 (−10.1)	0.6816 (−11.3)	0.6122
46	Pd	$4d^9 5s^1$	$4d^9$	0.5205 (5.9)	0.5381 (2.7)	0.5430 (1.9)	0.5533
			Relativistic electron affinities				
46	Pd	$4d^{10}$	$4d^9 5s^2$	−0.0068 (122.1)	0.0029 (90.5)	0.0078 (74.8)	0.0310

[a] References 19, 21, and 22.

GX-SIC theory is much easier and cheaper to use than the DF theory.

The electron affinities for some high-Z atoms obtained using the QR-LSD-GX-SIC-GWB theory without and with SPP-SIC and VWN-SIC are given in Table III. Corresponding to the elements in Table II, some atoms are missing in Table III, because for these atoms some of the negative ions are not stable experimentally[21] and some are not convergent for the experimental electron configurations (e.g., excited-electron configuration of negative ions) in the QR-LSD-GX-SIC-GWB theory. From Table III, it can be seen that the results without correlation correction are very far from experiment,[21,22] i.e., the theoretical values are much smaller than experiment, except for Zr. Once the correlation correction is added, the electron affinities for those atoms are improved. Especially for the atoms Sb and W, the contribution of the correlation energy to the electron affinity is much bigger than that of the kinetic energy, Coulomb and exchange interaction energies of the electrons. Comparing columns 4 and 5 with experiment, column 6, it is clear that the results with the SPP-SIC and VWN-SIC are in very good agreement with experiment: the results with VWN-SIC are a little better than those with SPP-SIC for those atoms, on the average—difference percentages are 6.6% for the former, 6.9% for the latter, and 47.8% for those without correlation correction.

Table III gives the ionization potentials of the ground and first excited-electron configurations of the atom palladium and the electron affinity in the QR-LSD-GX-SIC-GWB theory. The results show that both SPP-SIC and VWN-SIC overestimate the Coulomb correlation of the electron configuration $4d^{10}$ for the neutral atom palladium. The multiconfiguration interaction has to be used in order to describe the correlation correction accurately.

IV. CONCLUSION

The LSD-GX-SIC-GWB theory with VWN-SIC correlation correction can describe the ionization potential accurately for the atoms for which the atomic number Z is less than 56, but the relativistic effect has to be considered for the atoms of atomic number $Z > 72$. The ionization potentials and electron affinities for the high-Z atoms in the QR-LSD-GX-SIC-GWB theory are in very good agreement with experiment, so that this theory can be used to predict the ionization potentials of any high-Z atoms which are unknown experimentally.

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APPENDIX

To derive the series solution to Eq. (6) at small r for the two initial values it was necessary to start the outward integration using the Numerov method, assuming that the potential is

$$V_i(r) = -\frac{2Z}{r} + A + Br \tag{A1}$$

and that the radial wave functions have the form

$$P_{nl}(r) = r^{\gamma}(a_0 + a_1 r + a_2 r^2 + a_3 r^3 + a_4 r^4) \tag{A2}$$

when $l \neq 0$.

Substituting Eqs. (A1) and (A2) into Eq. (6),

$$\gamma = \tfrac{1}{2}[1 + (1 + 4l(l+1) - 4\alpha^2 Z^2)^{1/2}] \, . \tag{A3}$$

The other coefficients are exactly the same as in the Hartree-Fock-Slater (HFS) theory[15] when $l = 0$.

Substituting Eqs. (A1) and (A2) into Eq. (6), and collecting like powers of r and equating like powers of r,

$$\gamma = (1 - \alpha^2 Z^2)^{1/2} \, , \tag{A4}$$

$$\begin{aligned}
a_1 &= \frac{-2Z}{(\gamma+1)^2+\delta}a_0 \, , \\
a_2 &= \frac{-2Za_1}{(\gamma+2)^2+\delta}+\frac{c\gamma-d}{(\gamma+2)^2+\delta}a_0 \, , \\
a_3 &= \frac{-2Za_2}{(\gamma+3)^2+\delta}+\frac{c(\gamma+1)-d}{(\gamma+3)^2+\delta}a_1+\frac{-Ba_0}{(\gamma+3)^2+\delta} \, , \\
a_4 &= \frac{-2Za_0}{(\gamma+4)^2+\delta}+\frac{c(\gamma+2)-d}{(\gamma+4)^2+\delta}a_2+\frac{-Ba_1}{(\gamma+4)^2+\delta} \, ,
\end{aligned} \tag{A5}$$

where

$$\begin{aligned}
\delta &= \alpha^2 Z^2 - 1 \, , \\
c &= \frac{B}{2Z} \, , \\
d &= A+\varepsilon_i+\frac{B}{2Z}+\frac{\alpha^2}{4}\varepsilon_i^2 \, .
\end{aligned} \tag{A6}$$

The treatment of parameters A and B is the same as that in the HFS theory.

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