PHYSICAL REVIEW A VOLUME 40, NUMBER 1 JULY 1, 1989

Electron affinities of alkaline-earth and actinide elements calculated with the local-spin-density-functional theory

Yufei Guo* and M. A. Whitehead
Theoretical Chemistry Group, Department of Chemistry, McGill University, 801 Sherbrooke Street West, Montreal, Quebec, Canada H3A 2K6

(Received 22 March 1989)

The generalized exchange local-spin-density-functional theory with self-interaction correction and correction of the statistical exchange potential was used to calculate the electron affinities of alkaline-earth and actinide elements. The effect of relativistic correction by the mass velocity and Darwin terms and correlation correction on the electron affinities is discussed. The calculation of the negative ions shows that, although the correlation correction to the potential is very small, it is essential for obtaining converged values for most of the negative ions. The calculated results predict stable negative ions for the alkaline-earth elements Ca, Sr, Ba, and Ra, supporting the calculations of Vosko *et al.* [Phys. Rev. A **39**, 446 (1989)] and Fischer [Phys. Rev. Lett. **59**, 2263 (1987); Phys. Rev. A **39**, 963 (1989)]. Estimated electron affinities for the actinide elements are given.

I. INTRODUCTION

The existence of stable negative ions is well known.[1] Most neutral atoms in the periodic table bind an extra electron to form stable negative ions. Theoretical investigation of the structures is difficult because the contribution of the electron-correlation correction to the electron affinity of an atom is larger than the kinetic, Coulomb, and exchange energies.[2,3] Therefore the Hartree-Fock (HF) theory,[4] which is an accurate and simple procedure but does not include electron correlation, usually gives wrong electron affinities for atoms.[5]

The local-density-functional (LDF) theory,[6,7] while successful in describing atoms, molecules, and solids, has proved unreliable in calculating negative ions.[2] The stable negative ions, such as H^-,[8] Cl^-,[9] O^-, and F^-,[10] are predicted to be unstable by the $X\alpha$ theory[11] and other LDF theories. This is because of, firstly, the incomplete cancellation of the self-interaction in the Coulomb repulsion functional by that in the exchange functional,[10,12] and secondly, the neglect of electron correlation.

Since the papers which dealt with the self-interaction correction[13,14] (SIC) and electron-correlation correction[15,16] (ECC) in the local-spin-density-functional (LSD) theory, the self-interaction-corrected LSD theory with electron-correlation correction (SIC-LSD-ECC) has successfully predicted negative-ion structures.[3,17,18] The calculated electron affinities for most atoms are in excellent agreement with experiment.

A survey of the binding energies of atomic negative ions by Hotop and Lineberger[1] showed that most atomic negative ions are stable, except for the rare gases and alkaline-earth elements. The alkali-metal elements get a second electron in the outermost *s* orbital to form a stable negative ion, with a positive binding energy, whereas the alkaline-earth elements have the electron in another *p* or *d* orbital and therefore have negative values for the electron affinities, so that the negative ions of these elements do not exist.

Fischer *et al.*[19] reported a positive electron affinity for the alkaline-earth element Ca by the multiconfiguration Hartree-Fock (MCHF) method, with relativistic shift correction. The prediction was confirmed in an elegant experiment by Pegg *et al.*[20] Vosko *et al.*[21] found the negative ions for other alkaline-earth elements Sr^-, Ba^-, and Ra^- also stable by a HF calculation with relativistic shift and electron-correlation corrections, if the electron configurations are ns^2np ($n=4,5,6,7$) and not $(n-1)dns^2$. Fischer[22] studied the electron affinities of the alkaline-earth elements by MCHF theory, and also predicted positive affinities for the alkaline-earth elements Ca, Sr, and Ba in electron configuration ns^2np and not $(n-1)dns^2$.

The investigation of the negative ions of the alkaline-earth elements by the full LSD theory is interesting; it can be used to test the accuracy of the LSD theory which has been previously successful in calculating negative ions. If successful for the present systems, it is much easier and cheaper to use than other theories.

Hotop and Lineberger[1] listed the electron affinities of the elements up to $Z=86$, with some missing. There are few of reliable results for electron affinities of elements ($Z\geq 87$). Bratsch and Lagowski[23] obtained electron affinities for the actinides in 1984 by considering the energy variations associated with changes in the $5f$ orbital population, while Sen *et al.*[24] calculated electron affinities by using the SIC-LSD (Ref. 25) and LSD-GX-SIC theories with the relativistic and correlation corrections. Bratsch and Lagowski[23] predicted the ground-state electron affinities of the actinides within the range $+1.0$ to -0.3 eV, with an estimated uncertainty of ± 0.3 eV for the elements whose electron affinities are $+0.3$ to -0.3 eV and ± 1 eV for Fm and Md (the electron affinities are 1.0 eV for Fm and -0.1 eV for Md). Sen *et al.*[24] predicted the electron affinities for the actinides more accurately than Bratsch and Lagowski, but got converged values for only half the actinides. It is essential to attempt to get more reasonable electron affinities for these elements by calculation.

The generalized-exchange local-spin-density-functional (LSD-GX) theory derived by Manoli and Whitehead[26,27] with the self-interaction correction[28] (LSD-GX-SIC) and with the correction of the statistical exchange potential[29] (LSD-GX-CSEP) is used to calculate the electron affinities for the alkaline-earth and actinide elements from the differences of the statistical total energies for the corresponding negative ions and the neutral atoms. The effects of the relativistic correction of mass velocity and Darwin terms,[30–32] and of the electron-correlation correction[15,16] on the electron affinities are considered. The present results are in very good agreement with the HF calculation, and strongly support the predictions by Fischer *et al.*[19] and Vosko *et al.*[21] Estimated values of the electron affinities for the actinides are calculated, which are within the estimated uncertainty of Bratsch and Lagowski.[23]

II. THEORY

The LSD-GX-SIC and LSD-GX-CSEP [LSD-GX-SIC (CSEP)] theories can be found in the literature.[3,28,29,33] Only a brief description follows. The one-electron Schrödinger equation, in Rydberg atomic units, is

$$[\hat{f}+V_{C_j}(\mathbf{r})+V_{X_j}^{\mathrm{GX}}(\mathbf{r})+V_j^{\mathrm{SIC\,(CSEP)}}(\mathbf{r})]u_j(\mathbf{r})=\epsilon_j u_j(\mathbf{r}) , \tag{1}$$

where

$$\hat{f}=-\nabla^2-\frac{2Z}{r} . \tag{2}$$

$V_{C_j}(\mathbf{r})$ is the pure Coulomb potential excluding the Coulomb self-interaction, and $V_{X_j}^{\mathrm{GX}}(\mathbf{r})$ is the generalized statistical exchange potential; they can be explicitly written as

$$V_{C_j}(\mathbf{r})=\int n(\mathbf{r}')(2/|\mathbf{r}-\mathbf{r}'|)d\mathbf{r}'-\int n_j(\mathbf{r}')(2/|\mathbf{r}-\mathbf{r}'|)d\mathbf{r}' \tag{3}$$

and

$$V_{X_j}^{\mathrm{GX}}(\mathbf{r})=-\tfrac{9}{2}c\alpha^{\mathrm{lim}}\left[\sum_i^s n_i(\mathbf{r})g_i^{-2/3}(\mathbf{r})-\tfrac{2}{3}\sum_i^s n_i(\mathbf{r})f_i(\mathbf{r})g_i^{-5/3}(\mathbf{r})+[f_j(\mathbf{r})+B_1n_j(\mathbf{r})]g_j^{-2/3}(\mathbf{r})-\tfrac{2}{3}B_2n_j(\mathbf{r})f_j(\mathbf{r})g_j^{-5/3}(\mathbf{r})\right] . \tag{4}$$

$V_j^{\mathrm{SIC\,(CSEP)}}(\mathbf{r})$ in Eq. (1) is the exchange SIC potential in the LSD-GX-SIC theory or the CSEP in the LSD-GX-CSEP theory. It is

$$V_j^{\mathrm{SIC}}(\mathbf{r})=6c\alpha^{\mathrm{SI}}n_j^{1/3}(\mathbf{r}) \tag{5}$$

in the LSD-GX-SIC theory or

$$V_j^{\mathrm{CSEP}}(\mathbf{r})=27c\alpha^{\mathrm{lim}}n_j(\mathbf{r})\left[(1+B_1)g_j^{-2/3}(\mathbf{r})-\tfrac{2}{3}[(1+B_2)f_j(\mathbf{r})+(B_1+B_2+B_1B_2)n_j(\mathbf{r})]g_j^{-5/3}(\mathbf{r})+\tfrac{5}{9}B_2(2+B_2)n_j(\mathbf{r})f_j(\mathbf{r})g_j^{-5/3}(\mathbf{r})-\tfrac{2}{3}\sum_i^s n_i(\mathbf{r})g_i^{-5/3}(\mathbf{r})+\tfrac{5}{9}\sum_i^s n_i(\mathbf{r})f_i(\mathbf{r})g_i^{-8/3}(\mathbf{r})\right] \tag{6}$$

in the LSD-GX-CSEP theory. In Eqs. (4) and (6),

$$f_i(\mathbf{r})=n_s(\mathbf{r})+B_1n_i(\mathbf{r}) \tag{7}$$

and

$$g_i(\mathbf{r})=n_s(\mathbf{r})+B_2n_i(\mathbf{r}) . \tag{8}$$

In all the equations, $n(\mathbf{r})$, $n_s(\mathbf{r})$, and $n_i(\mathbf{r})$ are the total electron density, the density of the electron with spin s, and the ith electron density, respectively. c is a constant and equal to $(3/4\pi)^{1/3}$. The parameters B_1, B_2, α^{lim}, and α^{SI} are constants depending on the Fermi-hole shape. A few Fermi shapes have been proposed;[26,34–36] the corresponding parameter values B_1, B_2, α^{lim}, and α^{SI} were reported by Manoli and Whitehead.[26,37]

For the high-Z atoms, the relativistic effect has to be considered. The equations for the Dirac central field problem[38,39] consist of two coupled integro-differential equations for the so-called "large" and "small" components of the wave function. Cowan and Griffin[30] have described an approximate solution to the Dirac-Hartree-Fock (DHF) equations for atoms. Following their approximation, the one-electron Schrödinger equation is

$$\left[-\frac{d^2}{dr^2}+\frac{l_j(l_j+1)}{r^2}+V_j(r)-\frac{\alpha^2}{4}[\epsilon_j-V_j(r)]^2-\delta_{l_j0}\frac{\alpha^2}{4}\left[1+\frac{\alpha^2}{4}[\epsilon_j-V_j(r)]\right]^{-1}\frac{dV_j(r)}{dr}\times\left[\frac{dP_j/dr}{P_j}-\frac{1}{r}\right]\right]P_j(r)=\epsilon_jP_j(r) , \tag{9}$$

where $P_j(r)$ is radial wave function, i.e., the large component in the DHF theory, and α is the fine-structure constant, 1/137.036. The potential is

$$V_j(\mathbf{r})=-\frac{2Z}{r}+V_{C_j}(\mathbf{r})+V_{X_j}^{\mathrm{GX}}(\mathbf{r})+V_j^{\mathrm{SIC\,(CSEP)}}(\mathbf{r}) . \tag{10}$$

The wave functions and one-electron eigenvalues in Eq. (1) in the LSD-GX-SIC (CSEP) theory and in Eq. (9) in the LSD-GX-SIC (CSEP) theory, with the relativistic correction of mass velocity and Darwin terms, henceforth called the quasirelativistic LSD-GX-SIC or CSEP (QR-

LSD-GX-SIC or CSEP) theory, are solved numerically by means of standard self-consistent field (SCF) procedures.

III. RESULTS AND DISCUSSION

The one-electron Schrödinger equations (1) in the LSD-GX-SIC or CSEP theory and (9) in the QR-LSD-GX-SIC or CSEP theory with Gopinathan, Whitehead, and Bogdanovic Fermi-hole (GWB) parameters[35] have been used and attempts made to get converged values for the negative ions of the alkaline-earth and actinide elements. It failed to converge for all the negative ions of the alkaline-earth elements including both electron configurations ns^2np and $(n-1)dns^2$ and for most negative ions of the actinide elements; the SCF procedure was divergent. In the previous calculations of the negative ions,[3,18] which are stable in Hotop and Lineberger's paper,[1] Eqs. (1) and (9) can be converged to the SCF values except for some excited configurations of the negative ions.

The elements can be classified into two categories: (i) elements which involve one orbital in going from the neutral atom to the negative ion and (ii) elements involving two orbitals going from the neutral atom to the negative ion. In Hotop and Lineberger's paper[1] all the negative ions involving one orbital are stable, whereas almost all the negative ions involving two orbitals are unstable except for the transition-metal elements Sc, Y, and Pd. Previous calculations of the electron affinities of atoms[3,18] also showed that Eqs. (1) and (9) worked very well in predicting the electron affinities for the first category elements and failed for the second category. In the Roothaan-Hartree-Fock theory, Clementi and Roetti[40] reported the calculation of the negative ions for the elements $Z<54$ except for the alkaline-earth elements and the rare gases (they either did not calculate or found divergence). Recently, Vosko *et al.*[21] reported the results of the negative ions for the alkaline-earth elements by the HF theory with the density-functional correlation-correction potential. The electron-correlation–correction energy and potential which are[41]

$$E_C=\int n(\mathbf{r})\epsilon_C(\mathbf{r}_S,\zeta)d\tau \tag{11}$$

and

$$\mu_c^{\pm}(\mathbf{r})=\frac{\partial}{\partial n_{\pm}(\mathbf{r})}[n(\mathbf{r})\epsilon_C(r_S,\zeta)]\ , \tag{12}$$

respectively, proposed by Vosko, Wilk, and Nusair[16] (VWN), have been included in their calculation. In Eqs. (11) and (12), $n_+(\mathbf{r})$ and $n_-(\mathbf{r})$ are the densities of up and down spin electrons, where

$$n(\mathbf{r})=n_+(\mathbf{r})+n_-(\mathbf{r})\ , \tag{13}$$

$\xi_C(r_S,\zeta)$ is the correlation-energy density and depends on the electron gas parameter r_S, which is defined by

$$r_S=\left[\frac{3}{4\pi n(\mathbf{r})}\right]^{1/3}\ , \tag{14}$$

and the fractional spin polarization

$$\zeta=\frac{n_+(\mathbf{r})-n_-(\mathbf{r})}{n(\mathbf{r})}\ . \tag{15}$$

The superscripts ± on $\mu_C(\mathbf{r})$ in Eq. (12) stand for the spin up and spin down.

Equations (1) and (9) combined with Eq. (12), the VWN correlation-correction potential, have been tested on the alkaline-earth and actinide elements. The calculations showed that the LSD-GX-SIC theory with GWB parameters and VWN correlation-correction potential works very well for all the negative ions of the alkaline-earth elements whose electron configurations are ns^2np, but not for configurations $(n-1)dns^2$, and very well for most of the negative ions of the actinides. The LSD-GX-CSEP theory with GWB parameters and VWN correlation-correction potential works very well for *both* the electron configurations ns^2np and $(n-1)dns^2$ of alkaline-earth negative ions.

The reason why the LSD-GX-CSEP theory with GWB parameter and VWN correlation-correction potential works for both the electron configurations ns^2np and $(n-1)dns^2$ of the alkaline-earth negative ions is that the CSEP theory is derived by making the one-electron eigenvalue in the LSD theory equal to that in the HF theory, and includes both the SIC and the correction of the statistical exchange approximation.

Therefore Eqs. (1) and (9) with GWB parameters and

TABLE I. Electron affinities for Mg, Ca, Sr, Ba, and Ra calculated by the LSD-GX-SIC theory with VWN correlation, compared with other nonrelativistic calculations and experiment (Ry).

		Configuration			This work		HF[a]		
Z	Element	Atom	Ion	No correlation	SPP	VWN	(VWN)	MCHF[b]	Expt.[c]
12	Mg	$3s^2$	$3s^23p^1$	−0.0059	0.0079	0.0056			
20	Ca	$4s^2$	$4s^24p^1$	−0.0112	0.0150	0.0105	0.0102	0.140	0.086±0.014
38	Sr	$5s^2$	$5s^25p^1$	−0.0113	0.0163	0.0117	0.0142	0.256	
56	Ba	$6s^2$	$6s^26p^1$	−0.0117	0.0209	0.0156	0.0194	0.554	
88	Ra	$7s^2$	$7s^27p^1$	−0.0112	0.0220	0.0168	0.0206		

[a] Reference 21.
[b] Reference 22.
[c] Reference 20.

TABLE II. Electron affinities for Mg, Ca, Sr, Ba, and Ra calculated by the QR-LSD-GX-SIC theory with VWN correlation, compared with other calculations and experiment (Ry).

		Configuration			This work		HF[a]		
Z	Element	Atom	Ion	No correlation	SPP	VWN	(VWN)	MCHF[b]	Expt.[c]
12	Mg	$3s^2$	$3s^2 3p^1$	−0.0058	0.0078	0.0056			
20	Ca	$4s^2$	$4s^2 4p^1$	−0.0110	0.0146	0.0102	0.0096	0.124	0.086±0.014
38	Sr	$5s^2$	$5s^2 5p^1$	−0.0106	0.0146	0.0104	0.0118	0.212	
56	Ba	$6s^2$	$6s^2 6p^1$	−0.0105	0.0175	0.0129	0.0146	0.296	
88	Ra	$7s^2$	$7s^2 7p^1$	−0.0090	0.0121	0.0085	0.0092		

[a] Reference 21.
[b] Reference 22.
[c] Reference 20.

TABLE III. Electron affinities for Mg, Ca, Sr, Ba, and Ra calculated by the LSD-GX-CSEP theory with VWN correlation, compared with HF and experiment (Ry).

		Configuration			This work		HF[a]	
Z	Element	Atom	Ion	No correlation	SPP	VWN	(VWN)	Expt.[b]
12	Mg	$3s^2$	$3s^2 3p^1$	−0.0454	−0.0019	−0.0099		
20	Ca	$4s^2$	$4s^2 4p^1$	−0.0341	0.0115	0.0035	0.0102	0.086±0.014
		$4s^2$	$3d^1 4s^2$	−0.1608	−0.0723	−0.0885		
38	Sr	$5s^2$	$5s^2 5p^1$	−0.0296	0.0136	0.0061	0.0142	
		$5s^2$	$4d^1 5s^2$	−0.1176	−0.0427	−0.0560		
56	Ba	$6s^2$	$6s^2 6p^1$	−0.0232	0.0198	0.0127	0.0194	
		$6s^2$	$5d^1 6s^2$	−0.0349	0.0398	0.0264	0.0154	
88	Ra	$7s^2$	$7s^2 7p^1$	−0.0211	0.0210	0.0141	0.0206	
		$7s^2$	$6d^1 7s^2$	−0.0192	0.0530	0.0401	0.0332	

[a] Reference 21.
[b] Reference 20.

TABLE IV. Electron affinities for Mg, Ca, Sr, Ba, and Ra calculated by the QR-LSD-GX-CSEP theory with VWN correlation, compared with HF (with relativistic and VWN correlation corrections) and experiment (Ry).

		Configuration			This work		HF[a]	
Z	Element	Atom	Ion	No correlation	SPP	VWN	(VWN)	Expt.[b]
12	Mg	$3s^2$	$3s^2 3p^1$	−0.0452	−0.0019	−0.0100		
20	Ca	$4s^2$	$4s^2 4p^1$	−0.0342	0.0109	0.0030	0.0096	0.086±0.014
		$4s^2$	$3d^1 4s^2$	−0.1665	−0.0785	−0.0946		
38	Sr	$5s^2$	$5s^2 5p^1$	−0.0302	0.0117	0.0043	0.0118	
		$5s^2$	$4d^1 5s^2$	−0.1273	−0.0546	−0.0673		
56	Ba	$6s^2$	$6s^2 6p^1$	−0.0257	0.0150	0.0081	0.0146	
		$6s^2$	$5d^1 6s^2$	−0.0681	0.0046	−0.0082	−0.0236	
88	Ra	$7s^2$	$7s^2 7p^1$	−0.0229	0.0121	0.0059	0.0092	
		$7s^2$	$6d^1 7s^2$	−0.0869	−0.0216	−0.0325	−0.0562	

[a] Reference 21.
[b] Reference 20.

TABLE V. Electron affinities for actinides calculated by using QR-LSD-GX-SIC theory with VWN correlation compared with other calculations (Ry). The asterisk denotes no convergence obtained.

				QR-LSD-GX-SIC-GWB				
		Configuration		No correlation	With correlation			Energy variation extrapolated[b]
Z	Element	Neutral	Negative		SPP	VWN	SIC-LSD[a]	
89	Ac	$6d^17s^2$	$6d^27s^2$	-0.0156	0.0437	0.0322	0.0206	0.022
90	Th	$6d^27s^2$	$6d^37s^2$	0.0361	0.1005	0.0863	0.0706	0.037
91	Pa	$5f^26d^17s^2$	$5f^26d^27s^2$	-0.0071	0.0530	0.0406	0.0243	0.022
92	U	$5f^36d^17s^2$	$5f^36d^27s^2$	-0.0086	0.0516	0.0390	0.0213	0.022
93	Np	$5f^46d^17s^2$	$5f^46d^27s^2$	-0.0123	0.0477	0.0351	0.0176	0.022
94	Pu	$5f^67s^2$	$5f^77s^2$	-0.0986	-0.0203	-0.0370		
95	Am	$5f^77s^2$	$5f^77s^27p^1$	-0.0068	0.0104	0.0076		
96	Cm	$5f^16d^17s^2$	$5f^76d^27s^2$	-0.0255	0.0330	0.0208	0.0022	0.022
97	Bk	$5f^97s^2$	$5f^{10}7s^2$	-0.2215	-0.1096	-0.1265		
98	Cf	$5f^{10}7s^2$	$5f^{11}7s^2$	-0.1687	-0.0571	-0.0745		
99	Es	$5f^{11}7s^2$	$5f^{12}7s^2$	-0.1146	-0.0042	-0.0219		
100	Fm	$5f^{12}7s^2$	$5f^{13}7s^2$	-0.0651	0.0439	0.0260	*	-0.007
101	Md	$5f^{13}7s^2$	$5f^{14}7s^2$	-0.0175	0.0900	0.0719	*	0.074
102	No	$5f^{14}7s^2$	$5f^{14}7s^27p^1$	-0.1803	-0.1692	-0.1709		
103	Lr	$5f^{14}6d^17s^2$	$5f^{14}6d^27s^2$	-0.0503	-0.0156	-0.0230	*	0.022

[a] Reference 24.

[b] Reference 23.

VWN correlation-correction potential have been used to calculate the wave functions and eigenvalues of the neutral atoms and the negative ions for the alkaline-earth and the actinide elements. The calculated wave functions were then used to calculate the statistical total energies and the VWN correlation-correction energies for the corresponding atoms and negative ions using the LSD-GX-SIC or CSEP and QR-LSD-GX-SIC or CSEP theories. To compare the VWN correlation correction with that proposed by Stoll, Pavlidou, and Preuss[15] (SPP), the wave functions in Eqs. (1) and (9) with GWB parameters and VWN correlation correction were used to evaluate the SPP correlation-correction energies. Finally, the electron affinities of the alkaline-earth and the actinide elements were obtained by means of the difference of the statistical total energies with and without correlation-correction energies between the neutral atom and negative ion. All these results are listed in Tables I–V.

A. Alkaline-earth elements

Tables I–IV summarize the electron affinities for the alkaline-earth elements in the LSD-GX-SIC or CSEP and QR-LSD-GX-SIC or CSEP theories with GWB parameters and without and with SPP and VWN energy-correlation correction and compared with other theoretical calculations[21,22] and experiment.[20] Tables I and II show that (i) the contributions of the kinetic, Coulomb, and exchange energies to the electron affinities are negative, and almost are equal except in Mg; (ii) the electron affinities become positive once the energy-correlation correction is added; the electron correlation makes the negative ions stable; and (iii) the relativistic contribution to the electron affinities is negative, which is the opposite to the relativistic contribution to the ionization potential of atoms which is usually positive. These features parallel HF theory.[21]

Comparing the present results with HF (Ref. 21) and MCHF (Ref. 22) calculations shows that the QR-LSD-GX-SIC theory results with VWN energy-correlation correction are in excellent agreement with HF, whereas the QR-LSD-GX-SIC theory with SPP energy-correlation correction overestimates the electron affinities. The MCHF theory obviously overestimates the electron affinities compared to HF, the present work, and experiment.

It is interesting that the predicted values for the electron affinity of Mg in both LSD-GX-SIC and QR-LSD-GX-SIC theories with SPP or VWN energy-correlation correction are positive. Therefore the negative ion Mg^- is stable. Subtracting the overestimated value for Mg, in contrast with Ca, the electorn affinity for Mg is probably around zero.

Tables III and IV list the calculated electron affinities of the alkaline-earth elements in both the electron configurations ns^2np and $(n-1)dns^2$ using the LSD-GX-CSEP and QR-LSD-GX-CSEP theories with GWB parameters and SPP and VWN energy-correlation correction. The contributions of the kinetic, Coulomb, and exchange energies to the electron affinities are more negative in the LSD-GX-CSEP theory than in the LSD-GX-SIC theory for the configuration ns^2np, increasing with atomic number Z. Comparing with HF and experiment shows that the values for these elements in the configuration ns^2np in the QR-LSD-GX-SIC theory with SPP energy-correlation correction are very close to HF; the values with the VWN correction are underestimated.

The negative ions in configurations $(n-1)dns^2$ converged in the LSD-GX-CSEP and QR-LSD-GX-CSEP theories with the VWN correlation-correction potential, but not in the LSD-GX-SIC and QR-LSD-GX-SIC theories. Some also do not converge in the HF theory with the density-functional correlation-correction potential.[21] The present results for Ba and Ra are slightly larger than HF.

B. Actinides

The electron affinities of the actinides with and without SPP and VWN energy-correlation correction in the QR-LSD-GX-SIC theory with GWB parameters are listed in Table V and compared with the SIC-LSD calculations[24] and the values estimated by using the energy variation extrapolation.[23] The present results in LSD-GX-SIC theory with the SPP or VWN energy-correlation correction are larger than those in the SIC-LSD theory and also larger than the extrapolated values, except for Cm, Md, and Lr. However, the results in the LSD-GX-SIC theory with VWN energy-correlation correction are within the estimated uncertainty of the extrapolated results, except for Th and Lr.

As mentioned before, the electron affinities are usually positive for elements involving a single orbital, according to the previous calculations[3,18] and Hotop and Lineberger's paper[1] for the elements $Z<87$. Therefore the negative ions are usually stable for the first category elements. The few exceptions in the actinide elements are shown in Table V, where Pu, Bk, Cf, and Es, while first-category elements, have negative electron affinities and are unstable. Therefore the extra electrons in these elements must go into orbitals other than $5f$, if they are stable.

Am belongs to the second category element using two orbitals, but its negative ion is stable according to the present calculation. Other electron configurations of negative ions, like $5f^7 6f^1 7s^2$ and $5f^8 7s^2$, have been tried, but no converged results have been obtained. The extra electron of Am$^-$ goes to the $5p$ orbital instead of $5f$ and $6d$. From Table V, one may see that Th$^-$ and Md$^-$ are the most stable negative ions according to the present calculation, in agreement with Bratsch and Lagowski's estimation.

IV. CONCLUSION

Although the electron-correlation-correction potential is very small compared to the Coulomb, exchange, and SIC potentials, it is very important in the present calculations. This correction determines whether the negative ions for the alkaline-earth and most of the actinide elements converge.

The QR-LSD-GX-SIC or CSEP theory with correlation-correction potential can be used to predict the electron affinities of the alkaline-earth and actinide elements. The electron affinities are as good as the HF theory with density-functional correlation-correction potential, and are much easier and cheaper to use. The present results of the alkaline-earth elements strongly support the prediction of the stable negative ions Ca$^-$, Sr$^-$, Ba$^-$, and Ra$^-$ made by Fischer *et al.*[19] and Vosko *et al.*,[21] if their electron configurations are ns^2np.

ACKNOWLEDGMENTS

This research was supported by the Natural Science and Engineering Research Council of Canada.

---

[*] Permanent address: Department of Applied Physics, National University of Defense Technology, Changsha, Hunan, People's Republic of China.

[1] H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data **4**, 539 (1975); **14**, 731 (1985).

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

[3] Y. Guo and M. A. Whitehead, Phys. Rev. A **39**, 28 (1989).

[4] C. F. Fischer, *The Hartree-Fock Method for Atoms* (Wiley, New York, 1977).

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

[6] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[7] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[8] H. B. Shore, J. H. Rose, and E. Zaremba, Phys. Rev. B **15**, 2858 (1977).

[9] K. Schwarz, J. Phys. B **11**, 1339 (1978).

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

[11] J. C. Slater, Phys. Rev. **81**, 385 (1951).

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

[13] M. S. Gopinathan, Phys. Rev. A **15**, 2135 (1977).

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

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

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

[17] J. G. Harrison, J. Chem. Phys. **86**, 2849 (1987).

[18] Y. Guo and M. A. Whitehead, Phys. Rev. A **38**, 3166 (1988).

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

[20] D. J. Pegg, J. S. Thompson, R. N. Compton, and G. D. Alton, Phys. Rev. Lett. **59**, 2267 (1987).

[21] S. H. Vosko, J. B. Lagowski, and I. L. Mayer, Phys. Rev. A **39**, 446 (1989).

[22] C. F. Fischer, Phys. Rev. A **39**, 963 (1989).

[23] S. G. Bratsch and J. J. Lagowski, Chem. Phys. Lett. **107**, 136 (1984).

[24] K. D. Sen, P. Politzer, Y. Guo, and M. A. Whitehead (unpublished).

[25] L. A. Cole and J. P. Perdew, Phys. Rev. A **25**, 1265 (1982).

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

[27] S. Manoli, Ph.D. thesis, McGill University, 1986.

[28] S. Manoli and M. A. Whitehead, Phys. Rev. A **38**, 630 (1988).

[29] Y. Guo and M. A. Whitehead (unpublished).

[30] R. D. Cowan and D. C. Griffin, J. Opt. Soc. Am. **66**, 1010 (1976).

[31] J. H. Wood and A. M. Boring, Phys. Rev. B **18**, 2701 (1978).

[32] V. Selvaraj and M. S. Gopinathan, Phys. Rev. A **29**, 3007 (1984).

[33] Y. Guo and M. A. Whitehead (unpublished).

[34] J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill, New York, 1974), Vol. 4.

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

[36] J. L. Gàzquez and J. Keller, Phys. Rev. A **16**, 1358 (1977).

[37] S. Manoli and M. A. Whitehead, Collect. Czech. Chem. Commun. **53**, 2279 (1988).

[38] L. I. Shiff, *Quantum Mechanics*, 3rd ed. (McGraw-Hill, New York, 1968).

[39] I. P. Grant, Proc. R. Soc. London, Ser. A **262**, 555 (1961).

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

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