Theoretical study of the negative ions of boron, aluminum, gallium, indium, and thallium

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The multiconfiguration Dirac-Fock method has been used to obtain the electron affinities of group-13 (IIIB) elements (B, Al, Ga, In, and Tl). Interactions among outer electrons (three for a neutral atom and four for an anion) in both ground and excited states were included in all calculations. Our calculated electron affinities for B, Al, Ga, In, and Tl are 0.260 eV, 0.433 eV, 0.305 eV, 0.393 eV, and 0.291 eV. We find that effects of exchange interaction and relativity on electron affinity are important in explaining the trend seen in the electron affinities of the elements of group 13. [S1050-2947(97)09602-9]

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I. INTRODUCTION

Many surprises are encountered in an attempt to describe the negative ions of the elements of a given column of the Periodic Table in a systematic manner. For example, among the negative ions of group-2 elements, Be$^-$ is a metastable ion [1,2], Mg$^-$ is unstable [3–7], and the ions such as Ca$^-$ and beyond are stable with progressively increasing binding energies [8]. Similarly, nitrogen, the lightest of the group-15 (VB) elements, does not form a stable negative ion but the subsequent group-15 elements do with increasing electron affinities [3,4].

To the best of the author's knowledge, a systematic study of the stability of the anions of the elements of group 13 (IIIB) (B, Al, Ga, In, and Tl) has not yet been published. But some calculations for electron affinities of the elements of group 13 have been reported. The electron affinity of boron has been calculated by a number of workers: 0.269 eV (Raghavachari [9]), 0.2732(2) eV (Froese-Fischer *et al.* [10]), 0.2668(30) eV (Sundholm and Olsen [11]); 0.273 eV (Noro *et al.* [12]), and 0.263 eV (Kendall *et al.* [13]). The perturbation [9], systematic multiconfiguration Hartree-Fock (MCHF) [10], large-scale Hartree-Fock (HF), and configuration-interaction (CI) [11] and multireference singly and doubly excited CI [12,13] approaches were used in these calculations. All the above calculations agree well with experiment (0.277±0.010 eV) [4]. Arnau, Motta, and Novoa [14], who used the CI method with pseudopotentials, obtained the electron affinities of 0.45 eV, 0.29 eV, 0.38 eV, and 0.27 eV for Al, Ga, In, and Tl, respectively. Their result for Al is in good agreement with experiment: 0.441±0.010 [4], and 0.44094$^{+0.00066}_{-0.00048}$ [15]. The accurate observed electron affinities for Ga, In, and Tl are not available [4]. Available experimental values [5] appear to be estimates with large error bars. Recently, Eliav *et al.* [16] used the multiconfiguration Dirac-Fock (MCDF) and relativistic coupled-cluster methods in their calculations for the electron affinity of Tl. Their result (0.40±0.05 eV) is much larger than the value obtained by Arnau, Motta, and Novoa [14] (0.27 eV). The

electron affinity obtained from the present calculations (0.291 eV) favors the latter value.

The purpose of the present work is to calculate the electron affinities of the elements of group 13 (B, Al, Ga, In, and Tl) and to attempt to understand the stability of their respective anions. Our study was carried out by comparing nonrelativistic HF, relativistic Dirac-Fock (DF), and multiconfiguration DF calculations. Multiconfiguration models account for most valence shell correlation effects; MCDF models also account for all of the dominant relativistic corrections to electronic structure.

A brief overview of the theory underlying our method is given in Sec. II. Some important details of our calculation are described in Sec. III. Our results are presented and compared with previous calculations and with measurements in Sec. IV. A summary and conclusions follow in Sec. V.

II. THEORY

A detailed presentation of the multiconfiguration Dirac-Fock theory may be found in Grant's review paper [17]. Our overview is intended only to establish notation and conventions. A relativistic many-body Hamiltonian H^R may be constructed from one-body Dirac operators $H^D(i)$ and two-body operators, here taken to be those due to the Coulomb interaction $H^C(ij)=e^2/|\mathbf{r}_i-\mathbf{r}_j|$, where e is the charge on the proton:

$$H^R=\sum_i H^D(i)+\sum_{i<j} H^C(ij). \tag{1}$$

The operator H^R commutes with the atomic total angular momentum operator $\mathbf{J}^2$, the z component of this operator J_z, and the atomic parity operator Π. Configuration state functions (CSFs) are eigenfunctions of these three operators with eigenvalues $J(J+1)$, M, and P, respectively (Hartree atomic units are used here and throughout unless specifically mentioned otherwise). CSFs are linear combinations of Slater determinants of relativistic orbitals,

$$\phi_{n\kappa}(\mathbf{r})=\frac{1}{r}\binom{P_{n\kappa}(r)\chi_{+\kappa m}(\hat{\mathbf{r}})}{iQ_{n\kappa}(r)\chi_{-\kappa m}(\hat{\mathbf{r}})}. \tag{2}$$

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Here $P_{n\kappa}(r)$ and $Q_{n\kappa}(r)$ are, respectively, the large- and small-component radial wave functions; n is the principal quantum number κ is the relativistic angular quantum number: $\kappa = \pm(j + \frac{1}{2})$ for $l = j \pm \frac{1}{2}$; the spherical spinors $\chi_{\kappa m}(\hat{\mathbf{r}})$ are eigenfunctions of the one-electron angular momentum operators $\mathbf{j}^2$, $\mathbf{l}^2$, $\mathbf{s}^2$, and j_z, and of the parity operator π. Approximate atomic state functions (ASFs) may be constructed as linear combinations of CSFs with given J^P. The orbitals and the ASFs and their energies are calculated using the self-consistent-field (SCF) procedure appropriate to the variational extremum of the optimal level (OL) energy functional. We have used the GRASP92 package [18] in all calculations. GRASP92 is designed for MCDF calculations involving a large number of CSFs. The package is based on the Hamiltonian (1) and thus provides a nonperturbative treatment of relativistic effects.

III. METHOD

We performed separate OL and CI calculations to determine lowest total energies and wave functions of neutral B, Al, Ga, In, and Tl and their respective anions. We used differences of calculated total energies of the neutral atom and its anion to obtain the electron affinity.

A. SCF calculations

In our calculations for the neutral atoms, all the jj-coupled configuration state functions for $ns^2 np(^2P^o_{1/2})$ (where $n = 2$, 3, 4, 5, and 6 for B, Al, Ga, In, and Tl, respectively) arising from the distribution of three electrons among the orbitals shown in Tables II–VI were included. These distributions were limited to zero-, one-, and two-electron excitations to all the orbitals shown in Tables II–VI and three-electron excitations to only the orbitals shown in steps 1 and 2. All these excitations were from the above jj-coupled configurations.

In our calculations for the negative ions, all the jj-coupled CSFs for $ns^2 np^2(^3P^e_0)$ arising from the distribution of four electrons among the orbitals shown in Tables II–VI were included. These distributions were limited to zero-, one-, and two-electron excitations to all the orbitals shown in Tables II–VI and three- and four-electron excitations to only the orbitals shown in steps 1 and 2. All these excitations were from the above jj-coupled configurations.

Our SCF calculations were performed in steps. All orbitals shown in steps 1 and 2 were optimized separately. In steps 3 and 4, the orbitals obtained from the previous step were held fixed in a given step.

B. CI calculations

The following CI calculations were performed to estimate the effects of some three- and four-electron excitations, which were not included in the above SCF calculations, on the total energies. In step $3'$ shown in Tables II–VI, the orbitals included in step 3 were used to perform CI calculations to determine lowest total energies of the neutral atoms and their anions. In these calculations, all the jj-coupled CSFs for $ns^2 np(^2P^o_{1/2})$ (for the neutral atoms) and $ns^2 np^2(^3P^e_0)$ (for the anions) arising from the distribution of

TABLE I. Summary of Hartree-Fock (HF), Dirac-Fock (DF), and multiconfiguration Dirac-Fock (MCDF) electron affinities (EA) of B, Al, Ga, In, and Tl. Observed electron affinities of B and Al and the experimental estimates of electron affinities of Ga, In, and Tl, which were taken from Hotop and Lineberger [3,4], are also presented for comparison. The recent measurement [15] of the electron affinity of Al is also tabulated. All quantities are given in eV.

Element	EA (HF)	EA (DF)	EA (MCDF)	EA (Experiment)
$_5$B	-0.267	-0.270	0.260	0.277 ± 0.010
$_{13}$Al	0.042	0.033	0.433	0.441 ± 0.010
				$0.44094^{+0.00066}_{-0.00048}$
$_{31}$Ga	-0.018	-0.075	0.305	$\approx 0.30 \pm 0.15$
$_{49}$In	0.162	0.030	0.393	$\approx 0.30 \pm 0.20$
$_{81}$Tl	0.210	-0.100	0.291	$\approx 0.20 \pm 0.20$

three (for the neutral atoms) and four (for the anions) electrons among the above orbitals were included. For the neutral atoms, these distributions were limited to zero, one-, two-, and three-electron excitations from the former configurations. For the anions, these distributions were limited to zero-, one-, two-, three-, and four-electron excitations from the latter configurations.

In step $4'$ shown in Tables II–VI, the orbitals included in step 4 were used to perform CI calculations. This step is similar to step $3'$ except that in these CI calculations, the distributions resulting from three- and four-electron excitations from the above configurations to the orbitals obtained from step 4 were not included. The contribution from these excitations to the total energies is relatively small.

IV. RESULTS AND DISCUSSIONS

A summary of Hartree-Fock, Dirac-Fock, and multiconfiguration Dirac-Fock electron affinities of B, Al, Ga, In, and Tl is presented in Table I. Observed electron affinities for B, Al, Ga, In, and Tl were taken from Hotop and Lineberger [3,4]. The recent measurement [15] of the electron affinity of aluminum is also presented. Calculated MCDF electron affinities of B and Al agree well with experiment. The MCDF electron affinities given in Table I do not increase gradually as the nuclear charge Z increases. We note that the calculated DF electron affinities given in Table I reproduce the above trend seen in MCDF electron affinities while generally underestimating the magnitudes. We also note that the HF electron affinities are larger than those of DF and the difference between the electron affinities obtained from these two approaches increases as Z increases. We discuss the trend seen in HF, DF, and MCDF electron affinities in the following subsections.

A. HF calculations

The observed electron affinity of aluminum is substantially higher than that of boron. As shown in Table I, the correlation contribution (i.e., the difference between the observed and HF electron affinities) (0.547 eV) needed to obtain the electron affinity of B is larger than that of Al (0.399 eV). This clearly indicates that an explanation of the

difference between the HF electron affinities of B and Al may also explain why the observed electron affinity of aluminum is substantially higher than that of boron.

The neutral aluminum atom has eight more electrons in addition to those in the neutral boron atom. Six of those occupy the $2p$ shell and the exchange interaction between them and the outer $3p$ electron helps to reduce the screening effect on the latter due to the inner electrons. This reduction in the screening effect enhances the HF electron affinity of neutral aluminum. This explanation is also valid for Si, P [19], S, and Cl, and can further be supported by investigating the contributions from the Coulomb and exchange interactions between $3p$ and $2p$ electrons to the HF energies of ground states of the neutral atom and its anion. This effective additional attraction (actually a reduction in Coulomb repulsion which results from the quantum statistics) of electrons in different orbits is well explained, for example, in Lindgren and Morrison [20].

According to the above explanation, when relativistic effects are neglected, the electron affinities of the elements shown in Table I should increase as the nuclear charge Z increases. As seen from the HF electron affinities tabulated in column 2 of Table I, the only exception to the above rule is Ga. Neutral Ga has a smaller HF (also MCDF) electron affinity than that of neutral Al. It is interesting to investigate this peculiar ''nonperiodic'' behavior of Ga.

The neutral gallium atom has eighteen more electrons in addition to those in the neutral aluminum atom. Ten of those occupy the $3d$ shell and another six occupy the $3p$ shell. The radial $3d$ orbital has no nodes and is more contracted than the radial $3p$ orbital. A contracted orbital screens the nucleus more effectively. As a result, as one goes from one element to another in column 1 of Table I, the relative increase in screening effect on the outer electron due to the additional inner electrons is larger for Ga than for Al. The exchange interaction between the outer $4p$ electron and the inner $3p$ and $3d$ electrons in Ga also helps to reduce the screening effect on the former due to the latter electrons. Though this reduction in screening enhances the HF electron affinity of gallium, the enhancement is not enough to provide a larger electron affinity for Ga than for Al.

If the above explanation is correct, a neutral atom that has a ground-state configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 4p \, ^2P^o_{1/2}$ (no $3d$ electrons) should have a larger HF electron affinity than of Al (0.042 eV). A neutral atom with such a ground state does not exist. But an excited level of neutral Sc provides such a state. If we calculate the HF electron affinity of the $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 4p^2 \, ^3P^e_0$ excited level of Sc$^-$ relative to the above level of neutral Sc, we obtain a value of 0.293 eV. This clearly supports the above explanation.

B. DF calculations and relativistic effects

The DF electron affinities shown in Table I are smaller than those of HF and the difference between the electron affinities obtained from these two approaches increases as Z increases. This shows clearly that the relativistic effects make important contributions to the electron affinities of these atoms. The contribution is most notable for Tl, which has a high atomic number.

To investigate the relativistic effects on the electron affinities of the atoms tabulated in Table I, we consider Tl and its anion. The approximate removal energy of an electron in a $6p_{1/2}$ valence orbital, I_{eff}, for neutral Tl is 0.193 hartree in HF approximation and 0.213 hartree in DF approximation. This shows that the relativistic $6p_{1/2}$ orbital in neutral Tl is more bound than its nonrelativistic counterpart. The I_{eff} for the negative ion of Tl is 0.221 hartree and 0.153 hartree in HF and DF approaches, respectively. In the anion the relativistic $6p_{1/2}$ orbital is less bound than its nonrelativistic counterpart, which is contrary to what happens in neutral Tl.

The fact that the relativistic effects influence the properties of valence orbitals is well known [21–23]. The interplay of many effects due to relativity decides the behavior of a valence orbital in a many-electron atom or ion. For example, an orbital of low angular momentum such as $s_{1/2}$ or $p_{1/2}$ traverses both the inner and outer regions of an atom and experiences a larger relativistic effect near the nucleus so that the electrons in such an orbital are attracted more strongly to the nucleus. This is a direct effect of relativity [21]. As a result of this effect, these orbitals contract in size and so screen the nucleus more effectively. This increase in screening of the nucleus reduces the binding energy of the electrons that occupy the inner orbitals of higher angular momentum such as $d_{3/2}$. The resulting expansion of the inner orbitals with higher angular momentum causes a decrease in shielding of the valence electrons and an increase of their binding energies. This is an indirect effect [21] due to relativity. The valence electrons can also experience the increase in screening of the nucleus due to the contraction of the inner orbitals of low angular momentum. This indirect effect due to relativity tends to lower the binding energies of the outer electrons. According to the previous comparison of the HF and DF removal energies of an electron in $6p_{1/2}$ valence orbital, the relativistic orbital is more bound than its nonrelativistic counterpart in neutral Tl and the inverse is true for the anion. This shows that it is difficult to predict which of the above effects dominates in a given many-electron atom or ion.

We conclude that relativity reduces the stability of the negative ion relative to the neutral Tl atom even though it increases the stability of both. As a result, the DF electron affinity of Tl is smaller than the HF counterpart. This is also true for B, Al, Ga, and In.

C. Multiconfiguration Dirac-Fock calculations

The results of our calculations are summarized in Tables II–VI. Our approach, described in Sec. II and III, accounts for the correlation energy among valence electrons in both ground and excited states; higher-order relativistic effects such as the transverse photon interaction, the self-interaction, and vacuum polarization, as well as other physical effects such as nuclear motion, are omitted.

As seen in Tables II–VI, both the SCF and CI calculations are converged. The electron affinity obtained from step $4'$ in Table II (0.260 eV) for B agree well with experiment (0.2779 ± 0.010 eV) [4]. This is also true for aluminum: 0.433 eV (calculated) and 0.441 ± 0.010 eV (experiment [4]). Our calculated electron affinities of Ga, In, and Tl are in qualitative agreement with available experimental values

TABLE II. Calculated total energies E of the $2s^2 2p^1(^2P^o_{1/2})$ ground state of the B atom and the $2s^2 2p^2(^3P^e_0)$ ground state of the B$^-$ anion. The electron affinity obtained from each step of the calculation appears in the last column. The observed electron affinity is 0.277 ± 0.010 eV [4]. In column 2, all the orbitals that have the same principle quantum number are implied by the spectroscopic label n.

| | Orbitals | B | | B$^-$ | | EA |
Step	included	n_{CSF}	E (hartree)	n_{CSF}	E (hartree)	(eV)
DF	$n=1,2$	1	-24.536616207	2	-24.526692987	-0.270
1	$n=1,2,3$	54	-24.604717706	144	-24.606434570	0.047
2	$n=1,2,3,4$	341	-24.608478064	1776	-24.616202341	0.210
3	$n=1,2,3,4,5$	573	-24.609423637	2170	-24.618272085	0.241
4	$n=1,2,3,4,5,6$	951	-24.609735374	2818	-24.618916311	0.250
3$'$	CI	1322	-24.609446253	12212	-24.618650857	0.250
4$'$	CI	1700	-24.609758188	12860	-24.619304648	0.260

[4,5] that appear to be rough estimates with large error bars. We find that inclusion of three- and four-electron excitations reduces the differences between the observed and calculated electron affinities of B and Al. A similar observation has been made by Raghavachari [9] and Froese-Fischer, Yunerman, and Gaigalas [10] in their calculations for the electron affinity of boron.

The electron affinities obtained from step 1 are smaller than those obtained from the DF calculations for all the elements except for B (see Tables II–VI). As an attempt to understand this ''unexpected'' effect, we compare the calculations of B and its anion with those of Al and its anion. As seen in Tables II and III, $n=1,2,3$ (where n is the principle quantum number) shells were included in these calculations. In B and its anion, all the $n=3$ orbitals are vacant. We notice that the interactions between the ground-state configuration of neutral B and the configurations that include $3p$ and $3d$ orbitals lower the ground-state energies, and the effect on the anion is larger than that on the neutral atom in this case. As a result, the interactions included in step 1 enhance the electron affinity of B. In Al and its anion, the $3s$ shell is occupied while the $3p$ shell is partially occupied and the $3d$ shell is vacant. We notice, in this case, that the interactions between the ground-state configuration of neutral Al and the configurations that include $3p$ and $3d$ orbitals lower the ground-state energies and the effect on the anion is smaller

than that on the neutral atom. As a result, the interactions included in step 1 diminish the electron affinity of Al. This is quite contrary to the effect on neutral B and its anion.

To seek an explanation for the above observations in B and Al, we have studied the wave functions obtained from step 1 for these atoms and their anions. We found that the interactions between the ground-state configurations and those arising from $3s3p^x3d$ (where $x=1$ for neutral Al and 2 for its anion) are quite important for both Al and its anion. These configurations result from exciting a single electron from the $3s$ closed shell. The $3s$ shell in Al and its anion can be regarded as a part of the core and the interactions of the above configurations with the ground-state configuration modify the core orbitals. This effect is sometimes referred to as a first-order *core polarization* [20]. The core polarization is expected to reduce the energy of the ground state. In accord with intuition, core-polarization effects are greater in the more compact neutral system than in the more loosely bound anion. This is the reason for the negative correlation contribution in step 1 for the electron affinity of Al. The core-polarization effects that result from exciting one electron from the $2s$ shell to the $3d$ shell in B and its anion are relatively small since the overlaps between the core and $3d$ orbitals are small. These effects are too weak to distort the effects of correlation on the electron affinities of B. We conclude that the unexpected effect seen in step 1 is due to a

TABLE III. Calculated total energies E of the $3s^2 3p^1(^2P^o_{1/2})$ ground state of the Al atom and the $3s^2 3p^2(^3P^e_0)$ ground state of the Al$^-$ anion. The electron affinity obtained from each step of the calculation appears in the last column. The observed electron affinity is 0.441 ± 0.010 eV [4], $0.44094^{+0.00066}_{-0.00048}$ [15]. In column 2, all the orbitals that have the same principle quantum number are implied by the spectroscopic label n.

| | Orbitals | Al | | Al$^-$ | | EA |
Step	included	n_{CSF}	E (hartree)	n_{CSF}	E (hartree)	(eV)
DF	$n=1,2$	1	-242.331118048	2	-242.332332950	0.033
1	$n=1,2,3$	13	-242.379515365	29	-242.373458530	-0.165
2	$n=1,2,3,4$	182	-242.388125648	838	-242.400579328	0.338
3	$n=1,2,3,4,5$	379	-242.389047072	1175	-242.403834579	0.402
4	$n=1,2,3,4,5,6$	722	-242.389303194	1766	-242.404586338	0.416
3$'$	CI	931	-242.389091399	8057	-242.404459586	0.418
4$'$	CI	1274	-242.389347641	8648	-242.405252744	0.433

TABLE IV. Calculated total energies E of the $4s^2 4p^1 (^2P^o_{1/2})$ ground state of the Ga atom and the $4s^2 4p^2 (^3P^e_0)$ ground state of the Ga$^-$ anion. The electron affinity obtained from each step of the calculation appears in the last column. The experimental estimate of the electron affinity is $\approx 0.30 \pm 0.15$ eV [3,4]. In column 2, both spin-orbit components are implied by omitting the angular momentum quantum number suffix from the spectroscopic label: e.g., $5f = (5f_{5/2}, 5f_{7/2})$.

| | | Ga | | Ga$^-$ | | EA |
| | Orbitals | | | | | |
Step	varied	n_{CSF}	E (hartree)	n_{CSF}	E (hartree)	(eV)
DF	$1s, \ldots, 4s, 4p$	1	-1942.566206179	2	-1942.563458589	-0.075
1	$1s, \ldots, 4f$	35	-1942.610015220	117	-1942.600425625	-0.261
2	$5s, \ldots, 5g$	422	-1942.617817186	3053	-1942.625364695	0.205
3	$6s, \ldots, 6h$	699	-1942.618550754	3534	-1942.628741712	0.277
4	$7s, \ldots, 7g$	1071	-1942.618655140	4169	-1942.629318289	0.290
3$'$	CI	1950	-1942.618584113	25645	-1942.629330848	0.292
4$'$	CI	2322	-1942.618688983	26280	-1942.629908436	0.305

first-order core-polarization effect. A similar effect is also seen in Ga, In, and Tl.

D. Comparison with previous calculations

1. Boron

Many calculations for the electron affinity of boron were published. Only a brief review of these calculations is given here and a detailed presentation may be found in a recent paper by Froese-Fischer, Ynnerman, and Gaigalas [10]. Raghavachari [9] used the Møller-Plesset perturbation approach [24] to obtain an electron affinity of 0.269 eV for boron. Sundholm and Olsen [11] obtained the electron affinity of boron by large-scale HF and CI calculations. Their value is 0.2668(30) eV. The multireference singly and doubly excited CI was the method used by Noro *et al.* [12]. Their calculated electron affinity is 0.273 eV. A similar method was used by Kendall, Dunning, and Harrison [13] to obtain an electron affinity of 0.263 eV for boron. All the above calculations agree well with experiment $(0.277 \pm 0.010$ eV) [4].

Froese-Fischer, Ynnerman, and Gaigalas [10] used a systematic MCHF procedure to obtain a value of 0.2732(2) for the electron affinity which is in excellent agreement with experiment $(0.277 \pm 0.010$ eV) [4]. In some respects, the

present calculations are the relativistic generalization of their calculations. The purpose of the present calculations is to study the electron affinities of all the elements of group 13 (B, Al, Ga, In, and Tl). In order to use, for all the elements, similar models that are not too large for the computational facilities available but are accurate enough to obtain electron affinities that are in reasonable agreement with experiment, we decided to use a model for boron that is smaller than that used by Froese-Fischer, Ynnerman, and Gaigalas [10]. Froese-Fischer *et al.* claimed that the reduction in the electron affinity of boron due to the relativistic effect is about 1.1 meV. We also find that the relativistic reduction is quite small for boron and the major reason for the difference between our calculated electron affinity (0.260 eV) and their result [0.2732(2)] is the size of the basis set used in each of these two calculations.

2. Aluminum, gallium, and indium

Arnau, Motta, and Novoa [14] used the multireference singly and doubly excited CI method to calculate the electron affinities of Al, Ga, and In. In their calculations, the pseudopotentials of Durand and Barthelat [25] were used to describe the core electrons in the above atoms and their anions. They claimed that the effects of relativity on the inner electrons were partially included in their calculations, while

TABLE V. Calculated total energies E of the $5s^2 5p^1 (^2P^o_{1/2})$ ground state of the In atom and the $5s^2 5p^2 (^3P^e_0)$ ground state of the In$^-$ anion. The electron affinity obtained from each step of the calculation appears in the last column. The experimental estimate of the electron affinity is $\approx 0.30 \pm 0.20$ eV [3,4]. In column 2, both spin-orbit components are implied by omitting the angular momentum quantum number suffix from the spectroscopic label: e.g., $5f = (5f_{5/2}, 5f_{7/2})$.

| | | In | | In$^-$ | | EA |
| | Orbitals | | | | | |
Step	varied	n_{CSF}	E (hartree)	n_{CSF}	E (hartree)	(eV)
DF	$1s, \ldots, 5s, 5p$	1	-5880.437669573	2	-5880.438769377	0.030
1	$1s, \ldots, 5s, 5p, 5d, 4f$	35	-5880.476517841	117	-5880.474707045	-0.049
2	$6s, 6p, 6d, 5f, 5g$	422	-5880.483119569	3053	-5880.494909075	0.321
3	$7s, 7p, 7d, 6f, 6g, 6h$	699	-5880.483775615	3534	-5880.497509796	0.374
4	$8s, 8p, 8d, 7f$	996	-5880.483847518	4034	-5880.497898233	0.382
3$'$	CI	1950	-5880.483803329	25645	-5880.497931166	0.384
4$'$	CI	2247	-5880.483875579	26145	-5880.498320010	0.393

TABLE VI. Calculated total energies E of the $6s^2 6p^1 (^2P^o_{1/2})$ ground state of the Tl atom and the $6s^2 6p^2 (^3P^e_0)$ ground state of the Tl$^-$ anion. The electron affinity obtained from each step of the calculation appears in the last column. The experimental estimate of the electron affinity is $\approx 0.20 \pm 0.20$ eV [3,4]. In column 2, both spin-orbit components are implied by omitting the angular momentum quantum number suffix from the spectroscopic label: e.g., $5f = (5f_{5/2}, 5f_{7/2})$.

Step	Orbitals varied	Tl		Tl$^-$		EA (eV)
		n_{CSF}	E (hartree)	n_{CSF}	E (hartree)	
DF	$1s, \ldots, 6s, 6p$	1	-20274.831047838	2	-20274.827382810	-0.100
1	$1s, \ldots, 6s, 6p, 6d, 5f$	35	-20274.861639351	117	-20274.857720904	-0.107
2	$7s, 7p, 7d, 6f, 5g$	422	-20274.868473374	3053	-20274.876624423	0.222
3	$8s, 8p, 8d, 7f, 6g, 6h$	699	-20274.869220046	3534	-20274.879219904	0.272
4	$9s, 9p, 9d, 8f$	996	-20274.869327347	4034	-20274.879701380	0.282
3$'$	CI	1950	-20274.869244403	25645	-20274.879574696	0.281
4$'$	CI	2247	-20274.869351812	26145	-20274.880056281	0.291

these effects for the outer electrons were ignored. Unfortunately, it is difficult to present a detailed analysis of the above effects included in the pseudopotentials. The electron affinities obtained from these calculations for Al, Ga, and In are 0.45, 0.29, and 0.38 eV, respectively. These values are in good agreement with our results shown in Tables III–V.

3. Thallium

Arnau, Motta, and Novoa [14] obtained an electron affinity of 0.27 eV for Tl. As already mentioned above, some effects of relativity on the inner electrons were included in their calculations. Recently, Eliav et al. [16] used the MCDF and relativistic coupled-cluster methods in their calculations for the electron affinity of Tl. The coupled-cluster method that they used is an extension of the nonrelativistic open-shell approach [20]. The 35 ''external electrons'' of Tl were correlated in their calculations by the above relativistic coupled-cluster method with single and double excitations. Their first set of calculations with Tl$^-$ orbitals predicts an electron affinity of 0.42 eV. The second set of calculations with Tl$^+$ orbitals predicts a value of 0.33 eV. They claimed the former result is more accurate than the latter and their final estimate of the electron affinity for Tl is 0.40 ± 0.05 eV.

As explained previously, our approach accounts for the correlation energy among valence electrons in both ground and excited states of Tl and its anion. All possible one- and two-electron excitations and some three- and four-electron excitations from the relevant ground states of Tl

$(6s^2 6p\ ^2P^o_{1/2})$ and Tl$^-$ $(6s^2 6p^2\ ^3P^e_0)$ to the excited orbitals shown in Table VI were included in our calculations. All dominant relativistic effects were also included; higher-order relativistic effects such as the transverse photon interaction, the self-interaction, and vacuum polarization were omitted. Our result, shown in Table VI (0.291 eV), is in good agreement with that of Arnau, Motta, and Novoa (0.27 eV). Calculated electron affinity of Eliav et al. [16] (0.40 ± 0.05 eV) is much larger than either of the above results. Their result is also larger than the observed electron affinity of Pb (0.364 ± 0.008 eV [4]), which lies next to Tl in the Periodic Table.

A comparison of the available observed electron affinities of some elements of group 13 (B and Al) with those of the neighboring elements of group 14 (C and Si) in the Periodic Table is given in Table VII. As seen from Table VII, the observed electron affinities of C and Si are larger than those of B and Al. The ground-state configurations of the anions of groups 13 and 14 are $ns^2 np^2$ and $ns^2 np^3$ (half-full np shell), respectively. The ground state of a given anion of group 14 elements contains a half-full np shell and its greater stability might be expected from elementary arguments based on the Pauli exclusion principle [26,19] by ignoring the relativistic effects.

The relativistic effects can be ignored for lighter elements but make important contributions to the electron affinity of a heavier element such as Pb, which has a high atomic number. The observed electron affinity of Pb is only 364 meV,

TABLE VII. Comparison of available observed electron affinities of some elements of groups 13 and 14. Observed electron affinities are taken from Hotop and Lineberger [3,4]. The recent measurement [15] of the electron affinity of Al is also shown. Calculated DF electron affinities are tabulated in columns 2 and 5.

Element (group 13)	EA (eV)		Element (group 14)	EA (eV)	
	DF	Experiment		DF	Experiment
$_5$B	-0.270	0.277 ± 0.010	$_6$C	0.542	1.2629 ± 0.0003
$_{13}$Al	0.033	0.441 ± 0.010 $0.44094^{+0.00066}_{-0.00048}$	$_{14}$Si	0.930	1.385 ± 0.005
$_{81}$Tl	-0.100		$_{82}$Pb	-0.185	0.364 ± 0.008

which is much lower than that of the other elements of group 14. This is another example of an effect of relativity as seen from the DF electron affinity given in Table VII. As explained in Sec. III B, relativity also reduces the stability of the negative ion of Tl relative to the neutral atom. It is interesting to note that the DF electron affinity of Pb (-0.185 eV) is lower than that of Tl (-0.100 eV). Hence, if the Pb^- ion is more stable than the Tl^- ion, then the electron-correlation contribution to the electron affinity of Pb must be larger than that for Tl. Our calculations, which yield an electron affinity of 0.291 eV for Tl that is smaller than the observed electron affinity of Pb, support the above conjecture. But the calculations of Eliav et al. [16] support the contrary. A more accurate observed electron affinity of Tl is needed to evaluate the above two different calculations.

V. CONCLUSIONS

The multiconfiguration Dirac-Fock method has been used to obtain the electron affinities of group-13 elements (B, Al, Ga, In, and Tl). The MCDF-OL functional was used in the calculations of energies for the lowest-lying state for a neutral atom and its anion. Electron affinities are obtained as the difference between an estimate of the lowest-lying state of a negative ion and the corresponding neutral atom. The MCDF calculations have been enlarged in a systematic manner so as to obtain some insight into their convergence with the size of the configuration state function basis. Interactions among outer electrons (three for a neutral atom and four for an anion) in both ground and excited states were included in all calculations.

Our calculated electron affinities for B, Al, Ga, In, and Tl are 0.260 eV, 0.433 eV, 0.305 eV, 0.393 eV, and 0.291 eV. The calculated electron affinities of B and Al agree well with experiment [4]. Our calculated electron affinities of Ga, In, and Tl are in qualitative agreement with available experimental values [4]. The electron affinity of Tl obtained from the present calculations is smaller than the value reported by Eliav et al. [16] (0.40 ± 0.05 eV).

We find that effects of exchange interaction and relativity on electron affinity are important in explaining the trend seen in the MCDF electron affinities of the elements of group 13. For example, relativity reduces the stability of a negative ion of these elements relative to the respective neutral atom even though it increases the stability of both. As a result, the DF electron affinity of a given element of group 13 is smaller than the HF counterpart. This effect is most notable for Tl, which has a high atomic number.

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