

Relativistic corrections to the atomic electron affinities

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The effect of relativistic corrections in the electron affinities (A_e) of the atoms (Li through I) has been determined. The relativistic contributions to the A_e are negative, except for Cu, Rh, and Ag atoms and are large for some transition-metal atoms. The values of the corrected A_e have been used in order to estimate the contribution of the correlation energies to the A_e .

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Atomic electron affinities (A_e 's) have attracted considerable attention because of their importance in astrophysical problems and low-temperature plasmas. The theoretical computation of atomic A_e 's is a difficult subject. Calculations for negative ions with a few electrons have now been perfected to such a degree that the available results are competitive with the experimental values, but for larger atomic systems the situation is quite different. The availability [1,2] of an excellent compilation of experimental values of A_e 's makes it possible to examine more completely the various contributions to the A_e 's.

The A_e of an atom A is defined as the difference between the total energies (E_T) of the ground states of A and A^- :

$$A_e = E_T(A) - E_T(A^-). \quad (1)$$

The total energy can be written as

$$E_T = E_{\text{HF}} + E_C + E_R, \quad (2)$$

where E_{HF} is the Hartree-Fock (HF) energy, E_C is the correlation energy, and E_R denotes the relativistic corrections. Therefore we can write [3,4] the A_e of an atom

$$A_e = A_{e\text{HF}} + A_{eC} + A_{eR}, \quad (3)$$

where the A_e is a sum of the three partial contributions (HF, correlation, and relativistic).

It is well known that the A_e 's calculated at the HF level are rather poor, the majority predicted as being smaller than zero. The correlation energy plays a fundamental role in the calculation of A_e 's and has been studied extensively for light atoms. However, the third contribution to the A_e , the relativistic term (A_{eR}), has not received a systematic treatment due to the lack of anion energies including relativistic corrections. Only the early work of Clementi [3] and the tabulation of Fraga, Karwowski, and Saxena [5] have reported values of A_e 's with relativistic corrections for light atoms. Bunge *et al.* [4] con-

cluded that relativistic contributions to the A_e 's are important in transition metals by estimating these contributions from numerical HF energies of neutral atoms [5] and from analytical HF energies of anions [6]. In the present paper, we have calculated systematically the relativistic contributions to A_e 's from the more recent accurate numerical HF wave functions for atoms [7] and anions [8,9] up to $Z = 54$.

Calculations of atomic and anion energies were carried out by a perturbative Dirac-Breit-Pauli-Hartree-Fock method using the RIAS program [10] and nonrelativistic wave functions obtained with the MCHF77 program [11], which reproduce the best numerical HF energies [7-9]. The experimentally determined configurations [12] of the atoms and anions were adopted, except for the anions of groups 2, 12, and 18, which are not stable [2]. The most abundant isotope was selected and the corresponding atomic masses taken from the compilation of Wapstra and Gove [12]. The relativistic effects included, as calculated by the RIAS program [10], are (i) mass variation, (ii) specific mass, (iii) one-electron Darwin correction, (iv) two-electron Darwin correction, (v) spin-spin contact, (vi) orbit-orbit, and (vii) relativistic mass correction. The spin-orbit energy for states with nonzero orbital angular momentum and atomic resonances [13] are not considered in this work, except as mentioned below.

The results for the relativistic corrections of A_e are

TABLE I. Relativistic corrections to the atomic electron affinities (in eV).

Atom	A_{eR}	Atom	A_{eR}	Atom	A_{eR}
Li	0.0000	Ti	-0.1475	Y	-0.0191
B	-0.0013	V	-0.1788	Zr	-0.3900
C	-0.0032	Cr	-0.0182	Nb	-0.0324
N	-0.0045	Mn	-0.2141	Mo	-0.0568
O	-0.0080	Fe	-0.2580	Tc	-0.5679
F	-0.0129	Co	-0.2995	Ru	-0.0060
Na	-0.0001	Ni	-0.3448	Rh	0.0171
Al	-0.0054	Cu	0.0197	Pd	-0.1140
Si	-0.0092	Ga	-0.0322	Ag	0.0598
P	-0.0109	Ge	-0.0442	In	-0.0792
S	-0.0147	As	-0.0493	Sn	-0.0917
Cl	-0.0192	Se	-0.0539	Sb	-0.0987
K	-0.0001	Br	-0.0585	Te	-0.0983
Sc	-0.0086	Rb	0.0000	I	-0.0978

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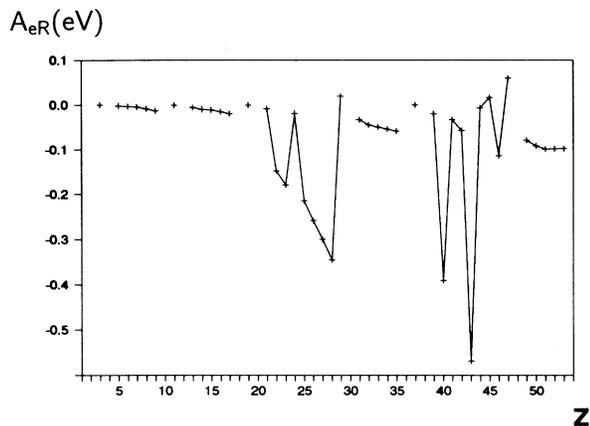


FIG. 1. Relativistic contribution to the electron affinity (A_{eR}) vs the atomic number (in eV).

summarized in Table I. A_{eR} has been calculated as the corrected A_e minus A_{eHF} , so that a positive value of A_{eR} indicates that the corrected A_e is greater than A_{eHF} .

The main conclusions to be drawn from Table I are as follows. The relativistic corrections increase with Z (except for the alkaline metals). The elements of groups 13–17 show a regular behavior, with increasing Z and from left to right in the Periodic Table. The transition metals are affected by the greatest changes, but these changes are not periodic, because of the different configurations. It is interesting to note that only three values in Table I are positive; they correspond to Cu, Rh, and Ag, for which consideration of the relativistic correction improves the theoretical prediction.

In order to see the periodic behavior the results of the relativistic contribution to the electron affinity A_{eR} are displayed in Fig. 1. We can observe parallel behavior for atoms in groups 1 and 13–17, and see that relativistic effects in the A_e 's of transition metals are more important. A_{eR} increases with Z in the first row of transition metals, except for Sc, Cr, and Cu and that their ground states correspond to configurations with exceptions to the aufbau principle of the Periodic Table in neutral atoms or in anions. In Sc^- its configuration is $(\dots 3d^1 4s^2 4p^1)$, in Cr it is $(\dots 3d^5 4s^1)$, and in Cu it is $(\dots 3d^{10} 4s^1)$; the rest of atoms and anions show a normal behavior [7,8].

The second row of transition metals presents many exceptions among the neutral atoms and anions [7,8]. Only Zr and Tc elements show ground states in neutral atoms with a $4d^n 5s^2$ configuration and in anions with a $4d^{n+1} 5s^2$ configuration. Both Zr and Tc give values of A_{eR} corresponding to parallel behavior of the first row of transition metals. Figure 1 shows the relationship between values of A_{eR} and the atom and anion configurations.

Although the E_R values are greater than the E_C values

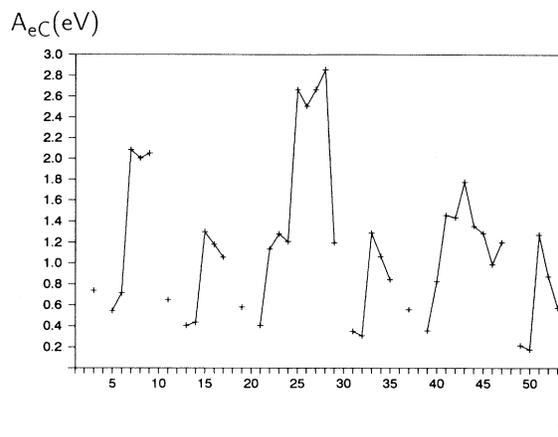


FIG. 2. Correlation contribution to the electron affinity (A_{eC}) vs the atomic number (in eV).

[5], the A_{eR} values are smaller than A_{eC} . In Fig. 2, we have plotted the difference between the experimental A_e and the corrected A_e (HF and relativistic contributions), which gives a measurement of A_{eC} , as seen from Eq. (3).

The experimental values of A_e have been taken from Ref. [2], except for N and Mn, for which we have used the estimated values (-0.07 and -1.28 , respectively) from Ref. [1]. Inspection of Fig. 2 shows that Mn, Fe, Co, and Ni have higher values of A_{eC} ; In and Sn have the lowest values of A_{eC} , but even those values are higher (0.22 and 0.18 , respectively) than the corresponding A_{eR} of Table I.

The behavior of alkaline metals (separated crosses in Fig. 2) is similar along the Periodic Table, with values of about 0.6 eV. The variation of A_{eC} for the elements of groups 13–17 is very similar, with the maximum value for the elements of group 15 corresponding to the p^3 configuration; i.e., the A_e of the nitrogen group elements will be changed considerably when the correlation energy is included. The differences between the two series of transition metals are due to the changes in the configurations of the ground states.

As a further test, we have carried out calculations including the spin-orbit interaction, which is important in the heavier elements. The most unfavorable atom considered is I, where the original A_{eC} value 0.5722 eV would change to 0.9373 eV when including the spin-orbit interaction. Otherwise the shape of Fig. 2 is only modified for elements from $Z=49$ – 53 by a slight displacement.

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

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

[3] E. Clementi and A. D. McLean, *Phys. Rev.* **133A**, 419 (1964); E. Clementi, A. D. McLean, D. L. Raimondi, and M. Yoshimine, *ibid.* **133A**, 1274 (1964); E. Clementi, *ibid.* **135A**, 980 (1964); *J. Chem. Phys.* **42**, 2783 (1965).

- [4] C. F. Bunge and A. V. Bunge, *Int. J. Quantum Chem.* **12S**, 345 (1978); C. F. Bunge, M. Galán, R. Jáuregui, and A. V. Bunge, *Nucl. Instrum. Methods* **202**, 299 (1982).
- [5] S. Fraga, J. Karwowski, and K. M. S. Saxena, *Handbook of Atomic Data* (Elsevier, Amsterdam, 1976).
- [6] S. Fraga, K. M. S. Saxena, and B. W. N. Lo, *At. Data* **3**, 323 (1972); S. Fraga and K. M. S. Saxena, *ibid.* **4**, 255 (1972); S. Fraga and K. M. S. Saxena, *ibid.* **4**, 269 (1972).
- [7] C. F. Bunge, J. A. Barrientos, A. V. Bunge, and J. A. Cogordan, *Phys. Rev. A* **46**, 3691 (1992); C. F. Bunge, J. A. Barrientos, and A. V. Bunge, *At. Data Nucl. Data Tables* **53**, 113 (1993).
- [8] T. Koga, H. Tatewaki, and A. J. Thakkar, *J. Chem. Phys.* **100**, 8140 (1994).
- [9] J. M. García de la Vega, *J. Phys. B* **27**, L447 (1994).
- [10] S. Fraga, M. Klobukowski, J. Muszynska, K. M. S. Saxena, and J. A. Sordo, *Phys. Rev. A* **34**, 23 (1986); S. Fraga, M. Klobukowski, J. Muszynska, K. M. S. Saxena, J. A. Sordo, and J. D. Climenhaga, *Comput. Phys. Commun.* **47**, 159 (1987); S. Fraga, M. Klobukowski, J. Muszynska, E. San Fabián, K. M. S. Saxena, J. A. Sordo, and T. L. Sordo, *Research in Atomic Structure* (Springer-Verlag, Berlin, 1993).
- [11] C. Froese Fischer, *Comput. Phys. Commun.* **14**, 145 (1978).
- [12] A. H. Wapstra and N. B. Gove, *Nucl. Data Tables A* **9**, 265 (1971).
- [13] S. J. Buckman and C. W. Clark, *Rev. Mod. Phys.* **66**, 539 (1994).