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Electron affinities for halogens calculated in the relativistic Hartree-Fock approach with atomic polarization

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Electron affinities are calculated with a procedure in which the change in the total correlation energy associated with the added electron is modeled by the interaction of the attached electron in a polarization potential of the atom. The single-configuration relativistic Hartree-Fock method, which by itself yields completely unsatisfactory affinities, is modified here by the addition of a single polarization potential with two parameters, the static dipole polarizability α and the size of the core r_0, which are determined independently of the affinity data. Results for halogen atoms are in excellent agreement with experimental data and with results of much more involved computations, where these have been successfully implemented.

INTRODUCTION

The elements with an almost closed p shell (halogens: F, Cl, Br, and I) are well known to possess positive and relatively large values of electron affinities.[1] It is also well known[1] that the restricted Hartree-Fock method yields completely unsatisfactory values of these electron affinities, at least for fluorine and chlorine, for which the results have been available. The explanation can be found in the more extended calculations[2–8] which, in contrast to the restricted Hartree-Fock method, include correlation effects. First, a large part of the energy stabilizing the negative ions (roughly 60% for F^- and 30% for Cl^-) comes from the change in correlation energy upon addition of the extra electron. Second, this change appears to be small for a p electron as long as empty orbitals are still available on the negative ion, but it is much larger when spins are being paired as in systems in which the added electron completes an np (Ref. 6) shell. This both accounts for the large electron affinities and explains the failure of the restricted Hartree-Fock approach. *Ab initio* calculations of electron affinities which include correlation contributions are rather complex and have mainly been restricted to light elements. In the case of the halogens, they have been mostly confined to the electron affinity of fluorine. No such calculations exist, to our knowledge, for bromine and iodine. Even the semiempirical results obtained with such methods as isoelectronic extrapolation and horizontal analysis refer almost exclusively to the first two periods of elements.[1]

The aim of this study is to calculate the electron affinities of the halogens fluorine through iodine. The approach employed is based on the classical picture in which the additional electron can be bound to a neutral atom because of the dipole and higher-order multipole moments induced in the neutral atoms by the electron, and the resulting attractive potential (polarization potential V_{pol}) has the asymptotic behavior $-\alpha/2r^4$ at large r, where α is the dipole polarizability of the atom. In this approach, the change in the total correlation energy upon the addition of an extra electron is replaced by the polarization interaction experienced by the attached electron. From the success of our previous calculations[9–11] with core polarization, we had reason to expect that this approach might yield values of electron affinities comparable to those obtained with extremely laborious and complex calculations which evaluate the change in the total correlation energy of the systems involved. A major advantage of the approach is that it retains the simple single-configuration character of the restricted Hartree-Fock method.

CALCULATIONS

The relativistic Hartree-Fock computer code of Desclaux,[12] modified by the authors to accommodate a polarization potential if desired, has been employed in this study. The polarization potential included in the one-electron Hamiltonian is of the form[9]

TABLE I. Parameters used in the calculations. Comparisons of electron affinities for halogens obtained in RHF + AP II computations employing two different sets of atomic dipole polarizabilities with experimental data. (Atomic units are used.)

				RHF+AP II		
Process	r_0	α^{HF} (Ref. 14)	$\alpha^{\mathrm{recommended}}$ (Ref. 13)	$\alpha=\alpha^{\mathrm{HF}}$	$\alpha=\alpha^{\mathrm{recommended}}$	Experiment (Ref. 1)
$\mathrm{F}(^2P_{3/2})\rightarrow\mathrm{F}^-(^1S_0)$	1.087	3.58	3.76	0.121 80	0.125 69	0.124 91±0.000 07
$\mathrm{Cl}(^2P_{3/2})\rightarrow\mathrm{Cl}^-(^1S_0)$	1.843	17.63	14.70	0.147 12	0.137 76	0.132 8 ±0.000 1
$\mathrm{Br}(^2P_{3/2})\rightarrow\mathrm{Br}^-(^1S_0)$	2.118	25.67	20.60	0.135 24	0.125 46	0.123 6 ±0.000 1
$\mathrm{I}(^2P_{3/2})\rightarrow\mathrm{I}^-(^1S_0)$	2.518	42.62	26.00	0.122 21	0.105 55	0.112 5 ±0.000 1

$$V_{\mathrm{pol}}=-\tfrac{1}{2}\alpha r^2(r^2+r_0^2)^{-3}\ . \qquad (1)$$

Values of static dipole polarizabilities α of neutral atoms recommended by Miller and Bederson[13] are used here, although in order to assess the sensitivity of the electron affinities to the choice of α, calculations are also performed with the set of α values computed by Fraga *et al.*[14] in a Hartree-Fock approximation. The cutoff radius r_0 is set to the mean radius of the outermost orbital (nlj) of the neutral atom. The values of parameters used are summarized in Table I.

Three types of computation of the electron affinities have been performed. In the first (labeled "RHF" for relativistic Hartree-Fock) the electron affinity of X, $A^{\mathrm{RHF}}(X)$, is simply given by the difference between the total relativistic Hartree-Fock energies $E_{\mathrm{tot}}^{\mathrm{RHF}}$ of the ground states of parent atom X and its negative ion X^- (the Breit interaction is included in the total energies through a first-order perturbation treatment[12]):

$$A^{\mathrm{RHF}}(X)=E_{\mathrm{tot}}^{\mathrm{RHF}}(X)-E_{\mathrm{tot}}^{\mathrm{RHF}}(X^-)\ . \qquad (2)$$

A positive electron affinity means that a stable negative ion is predicted to exist. Because these calculations neglect correlation effects entirely, the values $A^{\mathrm{RHF}}(X)$ are expected to be much too low. They are presented only for reference and for assessing the influence of correlation.

In the second type of computation (RHF + AP I) the contribution arising from the dipole moment induced in the atomic core by the attached electron is included as a correction $\delta^{\mathrm{AP\,I}}$ to the RHF electron affinity A^{RHF} of Eq. (2):

$$A^{\mathrm{RHF+AP\,I}}(X)=A^{\mathrm{RHF}}(X)+\delta^{\mathrm{AP\,I}}\ . \qquad (3)$$

The atomic polarization (AP) correction $\delta^{\mathrm{AP\,I}}$ is evaluated from the difference between the *one-electron* energies of the extra $np_{3/2}$ electron in the negative ion computed without (ϵ) and with (ϵ^{AP}) the polarization potential (1), i.e.,

$$\delta^{\mathrm{AP\,I}}=\epsilon(np_{3/2})-\epsilon^{\mathrm{AP}}(np_{3/2})\ . \qquad (4)$$

As discussed further below, the error inherent in the one-electron approximation is largely canceled when the difference between atomic and ionic energies is calculated, and thus calculation of $A^{\mathrm{RHF+AP\,I}}$ may prove quite useful, particularly for heavier systems. The values of $\delta^{\mathrm{AP\,I}}$ are presented in Table II.

Finally, in the third type of computation (RHF + AP II), the electron affinity is again computed as the difference between total relativistic Hartree-Fock energies of the parent atom and its negative ion, but now the polarization potential (1) is included in both the atomic and ionic systems:

$$A^{\mathrm{RHF+AP\,II}}(X)=E_{\mathrm{tot}}^{\mathrm{RHF+AP}}(X)-E_{\mathrm{tot}}^{\mathrm{RHF+AP}}(X^-)\ . \qquad (5)$$

Here, the two contributions to the electron affinity which are simply added in Eq. (3), namely, the change in total relativistic Hartree-Fock energy of the system upon addition of the extra electron and the effect of the polarization of the atomic core by the additional electron, are simultaneously calculated. The inclusion in the parent atom of the same polarization potential as in the negative ion means, through the cancellation of other contributions, that the polarization interaction between the atom and the additional $np_{3/2}$ electron constitutes the entire correlation contribution to the electron affinity in the RHF + AP II computations. This correlation contribution $\delta^{\mathrm{AP\,II}}$ is simply the difference between electron affinities obtained in the RHF + AP II and RHF computations:

$$\delta^{\mathrm{AP\,II}}=A^{\mathrm{RHF+AP\,II}}(X)-A^{\mathrm{RHF}}(X)\ . \qquad (6)$$

We have found such a modeling of correlation effects by a polarization potential to be highly successful in related calculations.[9–11]

In a frozen-core calculation, in which the same atomic orbitals are used in both the atomic and ionic computations, the polarization contributions $\delta^{\mathrm{AP\,I}}$ and $\delta^{\mathrm{AP\,II}}$ would be identical. However, in our cal-

TABLE II. Comparison of experimental and calculated correlation energy contributions to the electron affinities of halogens with contribution of the polarization effect on the attached $np_{3/2}$ electron (in atomic units). For a detailed description see text.

	$F(^2P)\rightarrow F^-(^1S)$	$Cl(^2P)\rightarrow Cl^-(^1S)$	$Br(^2P)\rightarrow Br^-(^1S)$	$I(^2P)\rightarrow I^-(^1S)$
Experimental correlation contribution [nonrelativistic approach, Eq. (10)]	0.075 46	0.0395		
Calculated correlation contribution (nonrelativistic approach); authors and methods:				
Staemmler and Jungen (Ref. 2) (independent electron pair correlation, IEPA)	0.083 8			
Sasaki and Yoshimine (Ref. 3) (including single through quadrupole excitations)	0.064 5			
Weiss (Ref. 4) (symmetry-adapted pair correlation, SAP)	0.078			
Moser and Nesbet (Refs. 5 and 6) (Bethe-Goldstone method including three-particle terms)	0.073 7	0.0445		
Clementi and McLean (Ref. 7), Clementi *et al.* (Ref. 8) (extrapolated semiempirical correlation correction)	0.074	0.0359		
	$F(^2P_{3/2})\rightarrow F^-(^1S_0)$	$CL(^2P_{3/2})\rightarrow Cl^-(^1S_0)$	$Br(^2P_{3/2})\rightarrow Br^-(^1S_0)$	$I(^2P_{3/2})\rightarrow I^-(^1S_0)$
Experimental correlation contribution [relativistic approach, Eq. (11)]	0.075 90	0.040 06	0.036 3	0.032 2
Contribution of polarization effect on the attached $np_{3/2}$ electron:				
Calculated from one-electron energies of the $np_{3/2}$ electron (δ^{API} in RHF + API)	0.067 66	0.041 41	0.035 47	0.023 69 (0.033 11)[a]
Calculated from the RHF + AP II and RHF electron affinities (δ^{APII})	0.076 68	0.044 97	0.038 16	0.025 24 (0.035 20)[a]
Contribution of polarization effect to the relaxation energy of the negative ion's core: $\Delta_r - \Delta_r^p$. This contribution is responsible for difference between δ^{API} and δ^{APII}: $\Delta_r - \Delta_r^p = \delta^{\mathrm{APII}} - \delta^{\mathrm{AOI}}$.	0.009 01	0.003 56	0.002 69	0.001 55 (0.002 09)[a]

[a] See footnote a to Table III.

culations the orbitals are allowed to "relax" as the additional electron is removed, and the difference between $\delta^{\mathrm{AP\,II}}$ and $\delta^{\mathrm{AP\,I}}$ arises only from the *change* in relaxation energy when polarization is included:

$$\delta^{\mathrm{AP\,II}}=\delta^{\mathrm{AP\,I}}+(\Delta_r-\Delta_r^p)\ , \tag{7}$$

where

$$\begin{aligned}\Delta_r&=-\epsilon(np_{3/2})-[E_{\mathrm{tot}}^{\mathrm{RHF}}(X)-E_{\mathrm{tot}}^{\mathrm{RHF}}(X^-)]\\&=-\epsilon(np_{3/2})-A^{\mathrm{RHF}}\end{aligned} \tag{8}$$

and

$$\begin{aligned}\Delta_r^p=&-\epsilon^{\mathrm{AP}}(np_{3/2})\\&-[E_{\mathrm{tot}}^{\mathrm{RHF+AP\,II}}(X)-E_{\mathrm{tot}}^{\mathrm{RHF+AP\,II}}(X^-)]\\=&-\epsilon^{\mathrm{AP}}(np_{3/2})-A^{\mathrm{RHF+AP\,II}}\end{aligned} \tag{9}$$

are the relaxation energies of the negative-ion core relative to the neutral atom in its ground state without and with polarization included, respectively. In the "frozen-core" approximation $\Delta_r=\Delta_r^p=0$ and consequently $\delta^{\mathrm{AP\,II}}=\delta^{\mathrm{AP\,I}}$. Of course, the "frozen-core" approximation is in our case entirely unrealistic since both Δ_r and Δ_r^p are by no means negligible in comparison with both ϵ and ΔE_{tot}. The values of Δ_r and Δ_r^p are 0.130 64 and 0.121 63, 0.055 20 and 0.051 65, 0.043 73 and 0.041 04, and 0.033 22 and 0.031 68 for F, Cl, Rb, and I, respectively, and they are of the same order of magnitude as ϵ and ΔE_{tot}. However, the *difference* $\Delta_r-\Delta_r^p$ is one order-of-magnitude smaller than Δ_r or Δ_r^p and, except for fluorine, also one order-of-magnitude smaller than the difference in the one-electron energies of the attached $np_{3/2}$ electron, $\epsilon(np_{3/2})-\epsilon^{\mathrm{AP}}(np_{3/2})=\delta^{\mathrm{AP\,I}}$. Therefore, the difference usually may be neglected; this leads to the RHF + AP I computations which do not include the change in the relaxation energy of the negative-ion core in the presence of the polarization potential V_{pol}.

DISCUSSION

Table I demonstrates the dependence of the results obtained in the RHF + AP II approach on the dipole polarizabilities. It may be seen that computations with the "recommended"[13] values of static dipole polarizabilities of neutral atoms are in better agreement with experiment than those with the Hartree-Fock (HF) values of Fraga *et al.*[14] The values recommended by Miller and Bederson[13] for F, Cl, and Br have been computed by Werner and Meyer[15] and Reinsch and Meyer[16,17] who applied the method of finite perturbation of Cohen and Roothaan,[18] with wave functions obtained from the pseudo-natural-orbital configuration interaction (PNO-CI) and the coupled-electron-pair approximation (PNO-CEPA) of Meyer.[19] The accuracy of these data is estimated at +2% by the authors. The value of polarizability for I is scaled from self-consistent-field Hartree-Fock calculations of Thorhallsson *et al.*[20] by forcing agreement with better values where available, and the accuracy of the resulting polarizability is estimated to be 50%. The values of polarizabilities computed in the Hartree-Fock approximation by Fraga *et al.*[14] are slightly (5%) lower than the recommended value for F, 20−25% higher for Cl and Br and as much as 64% larger for I. However, even the 64% change in the dipole polarizability used for I causes only a 16% change in the computed electron affinity.

In Table III we have compared the calculated and measured electron affinities for halogens. The results $A^{\mathrm{RHF+AP\,I}}$ and $A^{\mathrm{RHF+AP\,II}}$ agree remarkably well with the experimental data. The largest discrepancy (for iodine) does not exceed 8% and is very probably due to the rather inaccurate value of dipole polarizability discussed above, since for remaining systems, where much more accurate polarizabilities are available, the agreement is consistently better. Indeed, when the polarizability $\alpha=36$ a.u. determined by the empirical method of Atoji[21] is used, with the r_0 of Table I, the calculated affinity for iodine lies within 3% of experiment. The overall agreement with experiment is slightly better for values obtained in RHF + AP II computations, but the difference between results of the two approaches decreases with increasing number of electrons in the system. We shall return to this point later.

Electron affinities of F and Cl obtained from other calculations which include correlation effects are also presented. Since these calculations are all nonrelativistic and thus give electron affinities with respect to the term center of gravity of the parent atoms, the original values are given in parentheses and values corrected for the experimental energy difference between the ground $^2P_{3/2}$ state and the term center of gravity are presented as the first entries. It can be seen that our electron affinities are well within the range of theoretical values from the different approaches which include correlation.

In the first part of Table II the correlation contribution to the electron affinities of halogens as calculated by different authors in nonrelativistic approaches are compared with the so-called "experimental"[1] correlation contribution $A_{\mathrm{corr}}^{\mathrm{nonrel}}$ computed from the nonrelativistic Hartree-Fock electron af-

TABLE III. Comparison of calculated and measured electron affinities for F, Cl, Br, and I (in atomic units).

Process	RHF	RHF + AP I	RHF + AP II	Other theory	Experiment
$F(^2P_{3/2})\rightarrow F^-(^1S_0)$	0.049 01	0.116 68	0.125 69	0.1324(0.1331) (Ref. 2)	0.124 91±0.000 07 (Refs. 1,25)
				0.114(0.115) (Ref. 3)	0.124 95±0.000 07 (Ref. 26)
				0.127(0.128) (Ref. 4)	0.127 9 (Ref. 27)
				0.123(0.124) (Ref. 5)	0.133 (Ref. 28)
				0.1263(0.1269) (Ref. 22)	0.127 5 (Ref. 29)
				0.118(0.119) (Ref. 23)	
				0.123(0.124) (Ref. 7)	
				0.105(0.105) (Ref. 24)	
$Cl(^2P_{3/2})\rightarrow Cl^-(^1S_0)$	0.092 79	0.134 20	0.137 76	0.138(0.139) (Ref. 6)	0.132 8±0.000 1 (Ref. 1)
				0.1293(0.1306) (Ref. 8)	
$Br(^2P_{3/2})\rightarrow Br^-(^1S_0)$	0.087 30	0.122 77	0.125 46		0.123 6±0.000 1 (Ref. 1)
$I(^2P_{3/2})\rightarrow I^-(^1S_0)$	0.080 30	0.104 00 (0.113 41)[a]	0.105 55 (0.115 50)[a]		0.112 5±0.000 1 (Ref. 1)

[a] Values resulting when the static dipole polarizability of iodine as given by Atoji (Ref. 21), namely $\alpha=36$ a.u., is used together with the r_0 given in Table I.

finities and the experimental values of the energy difference between term centers of gravity:

$$A_{\mathrm{corr}}^{\mathrm{nonrel}}=A^{\mathrm{expt}}[X(^2P)\rightarrow X^-(^1S)] -A^{\mathrm{HF}}[X(^2P)\rightarrow X^-(^1S)]\ . \tag{10}$$

In the second part of Table II the corresponding experimental correlation contribution evaluated in the relativistic approach,

$$A_{\mathrm{corr}}^{\mathrm{rel}}=A^{\mathrm{expt}}[X(^2P_{3/2})\rightarrow X^-(^1S_0)] -A^{\mathrm{RHF}}[X(^2P_{3/2})\rightarrow X^-(^1S_0)]\ , \tag{11}$$

is compared with the contribution of the polarization effect on the attached $np_{3/2}$ electron as calculated in the present paper from one-electron energies ($\delta^{\mathrm{AP\,I}}$) and from the RHF-AP II and RHF electron affinities ($\delta^{\mathrm{AP\,II}}$). Since, as judged from the comparison of relativistic and nonrelativistic experimental correlation contributions, the relativistic effects are small, the calculated polarization contributions can be compared directly to the correlation contributions found by other authors. Both $\delta^{\mathrm{AP\,I}}$ and $\delta^{\mathrm{AP\,II}}$ contributions agree to within 13% with experimental correlation contributions except for iodine where the relative difference reaches 26%. They also agree very well with calculated correlation contributions available for fluorine and chlorine. The considerable discrepancy for iodine is reduced to 10% when Atoji's value of α is used.

As mentioned in the previous section, the difference $\delta^{\mathrm{AP\,II}}-\delta^{\mathrm{AP\,I}}$ corresponds to the *change* $\Delta_r-\Delta_r^p$ in the relaxation energy of the negative-ion core in the presence of the polarization potential V_{pol}. It is seen from Table II that the influence of polarization on relaxation energy decreases with an increasing number of electrons present in the system, and this brings the results of both RHF + AP I and II computations together. From the values of Δ_r and Δ_r^p given in the previous section, not only the change in relaxation energy due to the polarization, but also the relaxation energy itself decreases with increasing number of electrons in the system and tends to zero for systems with an infinite number of electrons, where the difference between the frozen- and relaxed-core approximations disappears. Therefore, it might be tempting to use the frozen-core approximation and Koopmans' theorem to evaluate the electron affinities[30] for heavier systems. However, the resulting neglect of the total relaxation energy Δ_r is much more severe an approximation than a neglect of the *difference* $\Delta_r-\Delta_r^p$. Evidently, the very good agreement obtained for the electron affinity of iodine in the frozen-core approximation by

Synek and Grossgut[30] is rather fortuitous, because if the relaxation energy of the core is taken into account, the result is roughly 30% lower than the experimental value.

We conclude that the approach presented in this study, in which the correlation contribution to the electron affinity is replaced by the additional polarization interaction seen by the extra electron, yields electron affinities in very good agreement with both experiment and the most sophisticated theoretical calculations. Virtually no additional computational effort is required beyond that for the restricted relativistic Hartree-Fock computations, even though the latter by itself yields completely unsatisfactory results. The present approach does require a knowledge of static dipole polarizability α of the parent atom, but as may be seen for the case of iodine for which we are lead to suggest that Atoji's value[21] may be an improvement on the value recommended by Miller and Bederson,[13] the accuracy requirements for α are rather low.

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