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Relativistic and Correlation Corrections to Electron Affinities of Alkali and Halogen Atoms*

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Electron affinities (EAs) of alkali and halogen atoms have been calculated using Hartree–Fock and Dirac–Hartree–Fock methods. Comparing the results with the experimental values, relativistic and correlation corrections to EAs have been estimated. In the case of alkalines correlation correction constitute110%–120% of the experimental EA values. In the case of halogens the corresponding numbers are 30%–60%. Relativistic effects are negligibly small for alkalines but significant for halogens (40% of the experimental value for At).

Key words: Electron affinities – relativistic corrections – correlation corrections.

1. Introduction

Theoretical prediction of atomic electron affinities (EAs) remains one of the most elusive problems [1, 2]. It is well known that both Hartree–Fock (HF) and standard Hartree–Fock–Slater (HFS) methods fail to interpret experimental values of EAs. For example, halogen atom negative ions, experimentally known as the most stable, are predicted to be unstable within HFS theory [3–6]. Alkali ions remain unstable also in HF theory [7–9]. The crucial contribution to EA, deciding whether a given species is stable or not, is the correlation energy. A number of authors calculated EAs for atoms of the first two rows of the periodic

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table with a relatively high accuracy using configuration interaction and many-body perturbation techniques. Rather complete reports on the results of these advanced calculations are given in recent reviews by Hotop and Lineberger [2], Moiseiwitsch [10] and Massey [11], where also references to the specific papers may be found.

Very little is known about influence of relativistic effects on the EA values. Bunge and Bunge [1] have briefly discussed relativistic corrections ΔE_{rel} to EAs of a number of atoms basing on perturbative Dirac–Breit–Pauli–Hartree–Fock calculations by Fraga et al. [7–9]. They noted, that the corrections are not very significant (do not exceed 0.04 eV) up to K^- and that their values may be both negative and positive. A table of heavy atom EA values calculated using the relativistic HFS method has recently been published by Sen et al. [12]. In a very recent paper Cole and Perdew [14] calculated electron affinities of the elements with $Z < 86$ using the local spin density approximation and including a part of relativistic corrections (Darwin and mass-velocity). The aim of the present paper is to estimate relativistic and correlation corrections to EAs of halogen and alkali atoms. The corrections are obtained from comparison of Hartree–Fock (HF), Dirac–Hartree–Fock (DHF) and experimental EA values.

2. Results and Discussion

Calculations were performed using the relativistic DHF program by Desclaux [13]. In order to avoid an interference of purely numerical effects, we have used the same program in the nonrelativistic calculations, setting the fine structure constant to be equal 10^{-11}. An electron affinity value may be decomposed in the following way

$$\mathrm{EA} = \mathrm{EA}_K + \Delta E_R + \Delta E_c + \Delta E_{\mathrm{rel}}$$

where

EA_K = the nonrelativistic Koopmans' EA (appropriate negative ion orbital energy)
ΔE_R = electron relaxation energy resulting from self-consistent adjustment of the neutral atom orbitals
ΔE_c = correlation energy change on going from a negative ion to the neutral atom
ΔE_{rel} = relativistic correction.

We disregard here smaller contributions as cross-term corrections (e.g. change in the relativistic correction due to the orbital relaxation or due to the electron correlation), quantum electrodynamic effects, specific mass effect, etc.

Nonrelativistic Koopmans' electron affinities EA_K, together with estimates of all the corrections, are collected in Table 1. The values of EA_K are equal to the orbital energies (taken with the opposite sign) of the highest occupied HF orbitals

Table 1. Nonrelativistic Koopmans' electron affinities, corrections and experimental values. All quantities in eV

Z	Atom	EA_K	ΔE_R	ΔE_c	ΔE_{rel}	ΔE_{SO}[a]	Experiment[b]
3	Li	0.395	−0.517	0.742	0.000		0.620
11	Na	0.363	−0.466	0.648	0.001		0.546
19	K	0.281	−0.360	0.579	0.001		0.501
37	Rb	0.259	−0.341	0.562	0.006		0.486
55	Cs	0.227	−0.230	0.463	0.012		0.472
9	F	4.921	−3.560	2.074	−0.036	−0.026	3.399
17	Cl	4.087	−1.509	1.100	−0.063	−0.047	3.615
35	Br	3.788	−1.192	0.993	−0.225	−0.185	3.364
53	I	3.512	−0.927	0.901	−0.425	−0.372	3.061
85	At	3.366	−0.917	1.4	−1.064	−1.0	2.8

[a] Relativistic splitting of the highest occupied HF orbital energy
[b] Recommended by Hotop and Lineberger [2]

of the negative ions. Electron relaxation correction ΔE_R has been obtained as a difference between HF value of EA (calculated from the total HF energies of the neutral atom and the negative ion) and EA_K. Relativistic correction ΔE_{rel} is equal to a difference between relativistic and nonrelativistic highest occupied orbital energies of the negative ion. The difference between the experimental value of EA and $\mathrm{EA}_K + \Delta E_R + \Delta E_{\mathrm{rel}}$ is assumed to be equal to ΔE_c. The value of ΔE_R is always negative since the neutral atom ground state energy decreases in the SCF procedure. On the other hand, ΔE_c is expected to be positive, since the absolute value of the (negative) correlation correction is likely to be lesser in the case of a neutral atom. As it is seen in Table 1 ΔE_R and ΔE_c compensate each other to some extent. This compensation is not entirely fortuitous – the stronger coupling of the extra electron in the outer shell, the bigger are the absolute values of both ΔE_R and ΔE_c. Therefore $\mathrm{EA}_K + \Delta E_{\mathrm{rel}}$ give much better estimates of the experimental EAs than the corresonding HF or DHF values. In particular, the alkali ions are predicted to be stable if both ΔE_R and ΔE_c are neglected in a calculation.

The ground states of the halogen atoms and of their negative ions are, respectively, $^2\mathrm{P}_{3/2}$ and $^1\mathrm{S}_0$. A part of ΔE_{rel} is due to a difference between the relativistic shifts of $^1S_0$ and of the gravity center of $^2\mathrm{P}$. Another part, ΔE_{SO}, is due to $^2\mathrm{P}_{1/2} - {}^2\mathrm{P}_{3/2}$ splitting. The values of ΔE_{SO} constitute a major part of ΔE_{rel} and are listed in the last column of Table 1. It seems that, except for very accurate calculations, it is sufficient to include the spin-orbit part of the relativistic correction in estimates of EAs.

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Note added in proof. Relativistic and correlation corrections to EAs for halogens have recently been studied by J. Migdalek and W. E. Baylis: Phys. Rev. **A26**, 1839 (1982)