Prediction of Electron Affinities from Fundamental Theorems Involving the Electron Density, $\langle r^{-1} \rangle$, and the Z^{-1} Perturbation Expansion

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ABSTRACT

The electron affinities of the elements H through F have been obtained within the framework of fundamental theorems involving the electron density, $\langle r^{-1} \rangle$, and the Z^{-1} perturbation expansion. The agreement between the predicted and observed values of electron affinities is very satisfactory.

SUMARIO

Se obtuvieron las afinidades electrónicas de los elementos H a F dentro del marco de los teoremas fundamentales que implican la densidad electrónica, $\langle r^{-1} \rangle$, y la expansión perturbacional Z^{-1}. La concordancia entre los valores de afinidades electrónicas predichos y observados es muy satisfactoria.

INTRODUCTION

Several approximate energy relationships have been given in recent years(1). A particularly important set of such formulas involve $\langle r^{-1} \rangle$ [2-5] and encouraging results have been reported for atoms and molecules [6-14]. Levy and Tal(15) have reported that results of surprising accuracy with semirigorous bounds, are obtained in a N-electron atom is visualized as having been formed by gradual increases in the nuclear charge with simultaneous additions of electrons.

Combining the Z^{-1} perturbation expansion(16)

$$E(Z, N) = \sum_{s=0}^{\infty} e_s(N) \, Z^{(2-s)} \tag{1}$$

and the Hellman-Feynman theorem (17-18)

$$-\left\langle r^{-1}\right\rangle_Z^N - (\partial E/\partial Z)_N = \sum_{s=0}^{\infty} (2-s)\, e_s\, (N)\, Z^{(1-s)} \quad (2)$$

Levy et al (19) obtained the formula

$$E_N = -\sum_{K=1}^{N} \left\{ K \left\langle r^{-1}\right\rangle_K + e_0\ (K)\ +\ A_{K-1} + Z_{K-1}\ (Z_K^{-2}-1)^{-1}\ e_3(K)\ - \right.$$
$$\left. Z_K^{-3}\ (Z_{K-1}-1)^2 \quad (2-3Z_K)\ e_4\ (K)\ +\ \cdots \right\} \quad (3)$$

where E_N denotes the exact nonrelativistic energy of a neutral atom with N electrons, A_{K-1} is the electron affinity of a neutral atom of K-1 electrons, e_0 (K) is the zeroorder perturbation coefficient for K electrons, and $\left\langle r^{-1}\right\rangle_K$ is given by

$$\left\langle r^{-1}\right\rangle_K = \int \frac{\rho\ (r,K)}{r}\ dr \quad (4)$$

where ρ (r, K) denotes the exact nonrelativistic density of a neutral atom with K electrons.

Levy et al (15) deduced a "trapezoid recursion relation" for the energy

$$E_N = -\sum_{K=1}^{N} \left\{ K\ \left\langle r^{-1}\right\rangle_K^{H-F} + e_0\ (K) \right\} \quad (5)$$

from Eq. (3) after assuming that: a) for neutral atoms, electron affinities are mostly positive, remain small in magnitude and vary periodically with increasing N, b) the contributions to Eq. (3), of terms involving e (K) (for s > 2) are expected to be small. Eq. (5) proved to be sufficient for accurate estimates of E_N (see third column of Table I in Ref. 15). $\left\langle r^{-1}\right\rangle_K^{H-F}$ denotes average values calculated from Hartree-Fock densities.

A direct calculation shows at once that assumption b) is wholly correct. However, assumption a) is not proper for the purpose of applying this kind of relationship to the calculation of total electronic energies, because electron affinities are not small in magnitude. Then, a convenient way to express the exact nonrelativistic energy of a neutral atom with N electrons is

$$E_N = -\sum_{K=1}^{N} \left\{ K\ \left\langle r^{-1}\right\rangle_K^{H-F} + e_0\ (K)\ +\ A_{K-1} \right\} \quad (6)$$

Owing to the non-existence of completely reliable experimental data for electron affinities, we deem appropriate to apply Eq. (6) to calculate such quantities. It must be taken into account that there exist highly accurate values for E_N (20), $\left\langle r^{-1}\right\rangle_K^{H-F}$ (21) and e (K) (22). The most actual and complete existing compilation of electron affinities is that of Chen and Wentworth (23).

On account of the foregoing discussion, the purpose of this communication is to report the results obtained, within the framework of Eq. (6), for the electron affinities of the elements H through F.

RESULTS AND DISCUSSION

All the necessary data to apply Eq. (6) is displayed in Table I. In Table II, we list the values of electron affinities calculated from Eq. (6) together with experimental data and the results of recent reports by different authors for comparison purposes. There is no doubt that the overall agreement with available experimental data is rather satisfactory, indicating that the present method is appropriate for the prediction of electron affinities. Comparing with the works of Edlen(24), Fraga(25), Lai et al (26), and Kregar et al (27), it is seen that the present method of determinig the electron affinities is quite different because it uses highly accurate data, and consequently it is very restrictive and does not allow any ambiguity (as in those cases where adjustable parameters are introduced). The results of our calculation of electron affinities tend to support the semiempirical predictions of Kregar et al (27), and Fraga (25), and the calculations of Lai et al(26) which are based on sum rules plus relativistic corrections. It may be convenient to discuss those cases for which no true experimental values are available, taking into consideration previous predictions.

The most important points to be inferred from an inspection of the values in Table II are:

a) The most manifest observation concerns the value for Be. We consider that, beyond any doubt, the experimental data must be in error and that the true value should be closer to those of the present work ($\sim$0.5 eV), in very good agreement with Lai and Fraga's results.

b) From the different theoretical results for He, it seems plausible that one would estimate an electron affinity of about -0.4 eV, i.e. about twice the estimated experimental value.

c) Although there is not complete agreement in numerical values, the electron affinity for N is most probably negative.

To summarize, we have proposed, in this paper, a very simple scheme for calculating the electron affinities of the elements H through F on the basis of fundamental theorems involving the electron density, $\langle r^{-1} \rangle$, and the $1/Z$ perturbation expansion theory. We have found that the accordance between our prediction of electron affinities and those of other methods is very satisfactory. It, in his turn, allowed us to derive several conclusions regarding available and estimated experimental data.

TABLE I

PERTURBATION COEFFICIENTS $e_0(N)$, AVERAGE VALUES $\langle r^{-1} \rangle_N$, AND

EXACT ATOMIC BINDING ENERGIES E_N FOR $N = 1 - 9$ (ATOMIC UNITS).

N	$-e_0(N)$ [a]	$\langle r^{-1} \rangle_N$ [b]	$-E_N$ [c]
1	0.500	1.0000	0.50000
2	1.000	1.6873	2.9037
3	1.125	1.9052	7.4781
4	1.250	2.1022	14.6670
5	1.375	2.2759	24.6531
6	1.500	2.4482	37.8440
7	1.625	2.6194	54.5870
8	1.750	2.7824	75.0630
9	1.875	2.9465	99.7250

(a) Ref. 22
(b) Ref. 21
(c) Ref. 20

TABLE II

ELECTRON AFFINITIES (eV)

Atom	This work	Lal et al [a]	Lal et al [b]	Fraga [c]	Kregar et al [d]	Experim. [e]
H	0.792	0.798	0.609	0.57	-	0.754
He	-0.440	-0.296	-0.357	-0.54	-	(-0.22)
Li	0.819	0.550	0.468	0.55	1.26	0.620
Be	-0.501	-0.593	-0.591	-0.45	-1.35	(-2.5)
B	0.046	0.046	0.044	0.27	-0.15	0.24
C	0.876	1.074	1.027	1.53	1.70	1.270
N	-0.903	-0.495	-0.591	-0.23	-0.53	0.0±0.2
O	0.503	0.872	0.895	1.65	2.06	1.465
F	2.454	3.065	3.104	3.20	5.47	3.339

(a) Ref. 26, Eq. (4)
(b) Ref. 26, Eq. (6)
(c) Ref. 25
(d) Ref. 27
(e) Ref. 23. The values given in parentheses have not been determined experimentally.

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