ELECTRONEGATIVITIES AND HARDNESSES OF SEVERAL ATOMS AND IONS CALCULATED WITH THE Xα METHOD HAVING SELF-CONSISTENT PARAMETER α *

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The Xα method with self-consistent parameter α_{SCF} has been used to calculate electronegativities and hardnesses of several atoms and ions. Slater's transition state method has been applied, too. The Xα results are in agreement with the experimental data and other theoretical values.

1. Introduction

Recently, several chemical concepts have been rigorously established within the density functional theory [1-4]. The electronegativity is defined as the negative of the chemical potential of the density functional theory. The absolute hardness has been recently defined by Parr and Pearson [5] as the derivative of the chemical potential with respect to the number of electrons.

Atomic electronegativities have been calculated using several approximate energy functionals, especially the Xα method with the transition state concept [6] has been widely applied in the calculations [7-11]. Hardnesses of elements have also been determined with the Xα method [10, 11].

Here, electronegativities and hardnesses of several atoms and ions determined with the Xα method having a self-consistent parameter α are presented. (Recently, the ionization energies, electron affinities and chemical potentials of several elements have been calculated with this method [12].) Electronegativities and hardnesses of several singly, doubly and triply ionized positive ions have been calculated. The results are in good agreement with the experimental data.

2. Ab initio self-consistent parameter α in the Xα method

The way of calculating the self-consistent parameter α in the Xα method has been discussed in several earlier papers [13, 14]. Here, only an outline is presented. The starting point of the method is the free-electron gas model. The exchange potential acting on an electron with spin up is given by

*Dedicated to Academician D. Berényi on his 60th birthday

$$V_{X\uparrow}(\vec{r}) = -8F(\varsigma)\left(\frac{3}{4\pi}\rho_\uparrow(\vec{r})\right)^{1/3},\tag{1}$$

where

$$F(\varsigma) = \frac{1}{2} + \frac{1-\varsigma^2}{4\varsigma}\ln\left|\frac{1+\varsigma}{1-\varsigma}\right|\tag{2}$$

and

$$\varsigma = \frac{p}{p_F}\tag{3}$$

is the reduced momentum of the electron considered, p_F is the Fermi momentum and $\rho_\uparrow(\vec{r})$ is the total electron density of the electrons having spin up. The usual way of obtaining the Xα exchange potential is to introduce an averaging procedure in the Fermi sphere. If the average is done for the whole Fermi sphere the value proposed by Slater [15], $\alpha = 1$, is given. On the other hand, an average near the Fermi surface for a layer thickness of which goes to zero leads to $\alpha = 2/3$, the value suggested by Gáspár [16] and later Kohn and Sham [17]. A physically more plausible case between these extreme ones can be defined by an average for a layer with $\nu_{i\uparrow} = u_i^* u_i$ electrons in the unit volume near the Fermi surface. It leads to the exchange potential

$$V_{X\alpha\uparrow}^i\left(\vec{r}\right) = -6\alpha_\uparrow^i\left(\vec{r}\right)\left|\frac{3}{4\pi}\rho_\uparrow\left(\vec{r}\right)\right|^{1/3},\tag{4}$$

where

$$\alpha_\uparrow^i\left(\vec{r}\right) = \frac{\rho_\uparrow}{\nu_{i\uparrow}}\left[1 - \frac{1}{2}\varsigma_i^3 - \frac{1}{2}\varsigma_i + \frac{1}{4}(\varsigma_i^2 - 1)^2\ln\left|\frac{1+\varsigma_i}{1-\varsigma_i}\right|\right]\tag{5}$$

and

$$\varsigma_i = \left(1 - \frac{\nu_{i\uparrow}}{\rho_\uparrow}\right)^{1/3}.\tag{6}$$

The expression (6) gives different functions $\alpha_\uparrow^i\left(\vec{r}\right)$ for the different spin orbitals u_i. Recently, the r-dependence of the function $\alpha_\uparrow^i\left(\vec{r}\right)$ has been studied [18]. It is possible to introduce an average over the shells:

$$\alpha_\uparrow\left(\vec{r}\right) = \frac{\sum\limits_{i\uparrow} n_i\alpha_\uparrow^i\left(\vec{r}\right)}{\sum\limits_{i\uparrow} n_i},\tag{7}$$

where n_i is the occupation number of the shell i. It has been shown that $\alpha_\uparrow\left(\vec{r}\right)$ has only a slight r-dependence, it can be considered a constant value [14]. This constant value can be determined self-consistently and is generally referred to α_{SCF}. This way of calculating the exchange potential contains no fitting or adjustment, this method can be regarded an ab initio one.

3. Calculation of electronegativity and hardness in the $X\alpha$ method

The electronegativity χ has been defined [1, 19] as the negative of the chemical potential μ

$$\chi = -\mu = -\frac{\partial E}{\partial N}. \tag{8}$$

It has been shown [1, 7, 12] that the electronegativity can be approximated by the Mulliken formula [20]

$$\chi_M = \frac{1}{2}(I + A), \tag{9}$$

where I and A are the first ionization energy and the electron affinity, respectively. In the $X\alpha$ method, the electronegativity can be given by the highest occupied orbital energy in open shell systems [7, 12, 21] and with the transition-state method [6] in closed shell systems [7, 12].

The absolute hardness of an atom or a molecule has been defined by Parr and Pearson [5] as

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial^2 N}\right)_v = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_v, \tag{10}$$

where v is the external potential. It has been shown that the hardness can be approximated [5, 10, 11] as

$$\eta = \frac{1}{2}(I - A). \tag{11}$$

Table I
Hardnesses of several atoms (in eV)

Atom	η ($X\alpha_{SCF}$ method)	$\frac{1}{4}<r^{-1}>_i$	$\frac{1}{4}<r^{-1}>_i$ (α_{HF})	Other estimates for η A[10]	B[23]	C[5]
Li	2.08	2.33	2.42	4.03	3.06	2.38
B	2.82	4.17	4.14	4.33	4.39	6.01
C	5.57	5.37	5.32	5.50	5.49	5.00
O	7.39	7.65	7.61	6.14	6.42	6.08
F	8.25	8.77	8.73	7.37	7.52	7.01
Na	2.37	2,13	2.16	3.58	2.91	2.30
Al	2.96	2.62	2.64	2.83	2.94	2.77
Si	3.58	3.30	3.31	3.55	3.61	3.38
P	5.20	3.92	3.93	5.93	5.42	4.86
S	4.68	4.52	4.53	4.08	4.28	4.12
Ci	5.20	5.10	5.11	4.79	4.91	4.70
K	1.96	1.71	1.74	2.84	2.35	1.92
Br	4.60	4.27	4.28	4.28	4.40	4.24

Electronegativities of several atoms calculated with the $X\alpha$ method having self-consistent parameter α have already been presented [12]. Table I shows the hardnesses of several atoms determined with parameters α_{SCF}. The values in column

A have been obtained from a spin polarized $X\alpha$ calculation [10] with parameter α_{HF} [22]. The column B presents the results of a local-spin-density calculation [23]. The experimental data obtained from experimental ionization energies and electron affinities using the expression (11) [5] can be seen in the column C. The results of the $X\alpha$ method with parameter α_{SCF} are in agreement with the other estimates for the hardness. Gazquez and Ortiz [11] have shown that the hardness of an open shell atom can be approximated as the one-quarter of the expectation value r^{-1} of the highest occupied atomic orbital:

$$\eta = \frac{1}{4} < r^{-1} >_i .$$ (12)

Table I contains these expectation values determined with parameters α_{SCF} and α_{HF} [11]. They are really close to the other estimates for the hardness.

Parr and Pearson [5] have presented experimental hardnesses for several ions. Calculated values on hardness have not been published. Table II shows the results of the $X\alpha$ calculations with parameter α_{SCF}. We have obtained the Hartree–Fock results from [25] using Koopmans' theorem. Electronegativities of several positive ions have been calculated in the density functional theory [26]. Table II contains

Table II
Electronegativities, electron affinities and hardnesses of a few ions (in eV)

Ion	χ Calculated with ($X\alpha_{SCF}$ method)	A	η	χ Experimental values [5, 24]	A	η	χ Hartree–Fock results [25]	A	η
Al^+	11.85	5.14	6.71	12.4	6.0	6.4	11.75	5.7	6.05
Al^{2+}	23.18	18.56	4.62	23.6	18.8	4.8	22.95	17.8	5.15
Al^{3+}	75.26	27.80	47.46	74.2	28.4	45.8	75.05	28.1	46.95
Ca^+	8.45	5.81	2.71	9.0	6.1	2.9	8.3	5.3	3.0
Ca^{2+}	30.96	11.23	19.73	31.55	11.9	19.65	31.15	11.3	19.85
Ca^{3+}	59.34	50.69	8.65	59.25	51.2	8.05	59.5	51.0	8.5
Fe^+	11.71	8.00	3.72	12.05	7.9	4.15	13.04	7.0	6.04
Fe^{2+}	24.64	15.43	9.21	23.45	16.2	7.25	27.44	19.07	8.36
Fe^{3+}	43.37	33.85	9.52	42.75	30.7	12.05	46.1	35.8	10.3
Br^+	16.78	11.69	5.09	16.7	11.8	4.9	17.6	12.4	5.2
Br^{2+}	27.49	21.87	5.62	28.75	21.6	7.15	28.95	22.8	6.15
Br^{3+}	39.15	33.11	6.04	41.6	35.9	5.7	40.75	35.1	5.65

electronegativities and electron affinities of a few ions calculated with the $X\alpha$ method using the parameter α_{SCF} and Slater's transition state method [6, 12]. There is good agreement between the calculated and experimental data.

In conclusion, it can be stated that this ab initio way of calculating the exchange potential within the $X\alpha$ method is useful to determine the electronegativities and hardnesses of atoms and molecules. It is a parameter-free method, there is no fitting or adjustment in it.

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