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Electronegativities of the Elements from Simple Xα Theory

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Abstract: Electronegativities are calculated by a simple Xα method for the elements up to atomic number 54, employing a transition-state method devised for the purpose. Electron affinities also are determined.

I. Method

One might expect to find it in the literature, but we cannot: It is elementary to calculate electronegativities of the elements by the spin-independent Xα theory, and the values of electronegativities so obtained agree with values obtained by other means.

Electronegativity, χ, is, in the first instance, a quantitative property of an atom (or molecule), the negative of the slope of the ground-state electronic energy as a function of the number of electrons. This is the negative of the chemical potential, μ, of the density functional theory of Hohenberg and Kohn.[1,2]

$$\chi = -\mu = -(\partial E/\partial N)_v \tag{1}$$

Equivalently, it is the corresponding quantity in the first-order density-matrix functional theory that derives from Hohenberg-Kohn theory.[3]

From the point of view of conventional wave function theory, the determination of an electronegativity of a system of interest must be carried out by determination of the energy from the principle $\delta[\langle\psi|H|\psi\rangle - E\langle\psi|\psi\rangle] = 0$, for the system and two or more of its positive and/or negative ions. Numerical differentiation of the resultant E vs. N data then gives μ. In principle there is no objection to this procedure, but its computational difficulty and lack of physical perspicuity have meant that it has never been fully implemented.

Density functional theory provides a more attractive route to the electronegativity. The reason is twofold. First, the variational principle in the theory contains the electronegativity: $\delta[E[\rho] - \mu N[\rho]] = 0$. Secondly, the theory allows for the number of particles to be varied continuously, so that the differentiation in eq 1 can be carried out explicitly. While nonintegral numbers of electrons do not occur in nature, the concept of nonintegral populations of electrons on atoms in molecules long has been generally accepted as valid and useful in chemistry. It is natural in density functional theory.

In the present paper we present results of systematic calculations of electronegativities of atoms by a known density-functional technique: the spin nonpolarized Xα transition-state method.[4,5] This method entails the self-consistent solution of

$$\left[-\frac{1}{2}\nabla_1{}^2 + V_{\text{eff}}\right]\phi_i(1) = \epsilon_i\phi_i(1) \tag{2}$$

where

$$V_{\text{eff}} = -\frac{Z}{r_1} + \int \frac{\rho(2)}{r_{12}}\,\mathrm{d}\tau_2 - 3\alpha\left(\frac{3}{8\pi}\right)^{1/3}\rho^{1/3} \tag{3}$$

and

$$\rho(1) = \sum_i n_i|\phi_i(1)|^2 \tag{4}$$

The ground-state energy is then determined from

$$E[\rho] = \sum_i n_i\epsilon_i - J[\rho] + K_{X\alpha}[\rho] \tag{5}$$

Differentiation of eq 5 by the occupation number n_i yields[4,5]

$$(\partial E/\partial n_i)_{n_j} = \epsilon_i \tag{6}$$

This formula is the key formula for our application.

In the simple Xα model just outlined, for an ordinary atom or ion, orbitals contain integral numbers of electrons, and E

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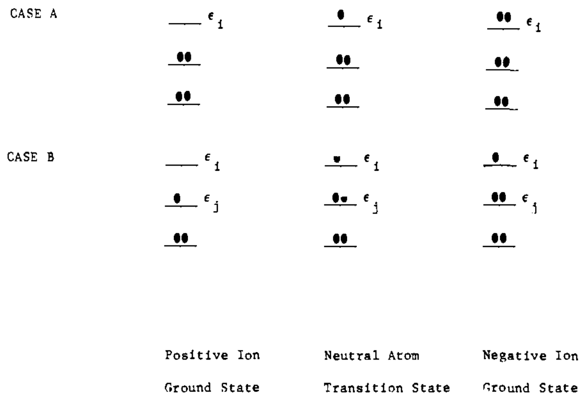

Figure 1. Transition states for determining electronegativities of atoms. Two main cases.

as a function of N is not differentiable; eq 1 cannot be used directly to get the electronegativity. Instead, the electronegativity of an atom may be determined from a knowledge of the ground-state configurations of the corresponding positive and negative ions, without use of any information about the ground state of the neutral species.

To accomplish this, we employ a common technique in Xα theory, a transition-state method.[4] For determination of the electronegativity, we do calculations on the transition state for the process, the state with electron configuration halfway between the electron configurations of the positive and negative ions. For most (but not all) situations, this state is the ground state of the atom.

Figure 1 shows the two main cases, which cover the first 54 atoms in the periodic table. Either one or two orbitals are ordinarily involved in the transition from positive to negative ion; these are case A and case B in Figure 1. Degeneracies among orbitals often occur, but they do not affect the formal results.

Case A. One Orbital Involved. Here what happens as one goes from the positive ion to the negative ion is that a single orbital goes smoothly from zero to double occupancy. Call the orbital involved the ith. Then from eq 6 one has

$$\chi = -\epsilon_i^{\mathrm{t}} \qquad \text{(case A)} \tag{7}$$

The superscript t denotes the transition state, which may or may not be the same as the ground state. Usually it is.

Case B. Two Orbitals Involved. Here there is a change in the occupation numbers of two different orbitals in going from the positive to negative ion. These two orbitals undergo a change of one electron each. For atoms in this case, the transition state is never the ground state, but some excited state of the neutral atom. As the two electrons are added to the positive ion to give the negative ion, suppose they go into two different orbitals, the ith and the jth (see Figure 1). Then eq 6 gives

$$\chi = -\frac{1}{2}(\epsilon_i^{\mathrm{t}} + \epsilon_j^{\mathrm{t}}) \qquad \text{(case B)} \tag{8}$$

Of the 54 atoms here considered, 17 fall under this case.

Calculations of the first ionization potential I by the Xα transition state method may be found in the literature; the definitive work is that of Schwartz.[6] One defines the transition state as the state with the configuration halfway between that of the positive ion and that of the neutral atom, and applies eq 6.

We can proceed similarly for the electron affinities A, the transition states for which are readily defined. However, this scheme is nonconvergent for cases with negative electron affinities, and so we choose an alternative way to calculate electron affinities:

$$A = 2\chi - I \tag{9}$$

Positive and negative values of A can be calculated in this manner equally well.

Table I. Electronegativities and Electron Affinities of the Elements[a] (eV)

atom	transition state[b]	A[c]	χ[d]
H	$1s^1$	1.94 (2.63)	7.97
He	$1s^{1.5}2s^{0.5}$	−1.51	12.61
Li	$2s^1$	0.12 (0.43)	2.58
Be	$2s^{1.5}2p^{0.5}$	−1.57	3.80
B	$2p^1$	−1.12	3.40
C	$2p^2$	−0.37 (0.68)	5.13
N	$2p^3$	0.54 (1.61)	6.97
O	$2p^4$	1.60 (2.69)	8.92
F	$2p^5$	2.81 (3.91)	11.00
Ne	$2p^{5.5}3p^{0.5}$	−1.63	10.31
Na	$3s^1$	−0.05	2.32
Mg	$3s^{1.5}3p^{0.5}$	−1.37	3.04
Al	$3p^1$	−0.72	2.25
Si	$3p^2$	0.01 (0.56)	3.60
P	$3p^3$	0.86 (1.38)	5.01
S	$3p^4$	1.82 (2.32)	6.52
Cl	$3p^5$	2.90 (3.38)	8.11
Ar	$3p^{5.5}4s^{0.5}$	−1.29	7.11
K	$4s^1$	−0.05	1.92
Ca	$3d^{0.5}4s^{1.5}$	−2.08	1.86
Sc	$3d^{1.5}4s^{1.5}$	−1.32	2.52
Ti	$3d^{2.5}4s^{1.5}$	−0.70	3.05
V	$4s^1$	0.22	3.33
Cr	$4s^1$	0.58	3.45
Mn	$3d^{5.5}4s^{1.5}$	0.88 (1.45)	4.33
Fe	$3d^{6.5}4s^{1.5}$	1.35 (1.93)	4.71
Co	$4s^1$	2.09 (2.40)	3.76
Ni	$4s^1$	2.52 (2.85)	3.86
Cu	$4s^1$	0.52	3.95
Zn	$4s^{1.5}4p^{0.5}$	−1.79	3.66
Ga	$4p^1$	−0.91	2.11
Ge	$4p^2$	−0.10	3.37
As	$4p^3$	0.74	4.63
Se	$4p^4$	1.65	5.91
Br	$4p^5$	2.62	7.24
Kr	$4p^{5.5}5s^{1.5}$	−1.21	6.18
Rb	$5s^1$	−0.08 (0.18)	1.79
Sr	$4d^{0.5}5s^{1.5}$	−1.79	1.75
Y	$4d^1$	−1.42	2.25
Zr	$4d^{2.5}5s^{1.5}$	−0.37 (0.06)	3.01
Nb	$5s^1$	0.67 (0.93)	3.26
Mo	$5s^1$	0.62 (0.89)	3.34
Tc	$4d^{5.5}5s^{1.5}$	1.88 (2.31)	4.58
Ru	$5s^1$	0.53 (0.84)	3.45
Rh	$5s^1$	0.48 (0.82)	3.49
Pd	$5s^1$	−1.53	3.52
Ag	$5s^1$	0.40 (0.78)	3.55
Cd	$5s^{1.5}5p^{0.5}$	−1.52	3.35
In	$5p^1$	−0.67	2.09
Sn	$5p^2$	0.08 (0.51)	3.20
Sb	$5p^3$	0.85 (1.22)	4.27
Te	$5p^4$	1.65 (1.98)	5.35
I	$5p^5$	2.48 (2.79)	6.45
Xe	$5p^{5.5}6s^{0.5}$	−1.08	5.36

[a] See text for detailed description of methods of calculation. A is the electron affinity of the atom in its ground state; χ is the electronegativity. [b] The configuration of the transition state shows whether case A or case B of Figure 2 is involved. When two orbitals are needed to describe the configuration, it is case B. [c] Calculated from eq 9 of text except for values in parentheses, which are calculated by transition-state method. [d] Calculated from eq 7 or 8 of text.

II. Results

Table I gives electronegativities χ and electron affinities A of the first 54 atoms in the periodic table, calculated by the method described.[7] The electronegativity values are plotted in Figure 2.

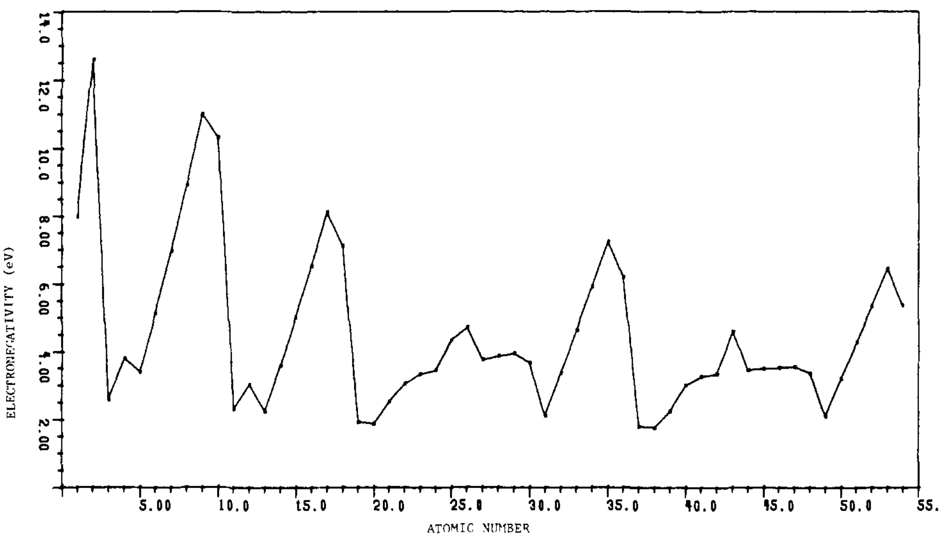

Figure 2. Electronegativities of the elements, calculated from the Xα method. For numerical values, see Table I.

The α parameters are those given by Schwartz[8] for ground-state atoms such that the virial ratio is satisfied if Xα orbitals are inserted into the Hartree–Fock expressions for the energy components. (Agreement was found with Schwartz on the numerical values of the ionization potentials of the first 36 atoms, except that we obtain 19.19 eV for F, while he has 19.21 eV.)

For cases A and B, the values of χ were determined from eq 7 and 8, respectively. Ionization potentials were calculated by the transition-state method following Schwartz.[6]

The electron affinities were determined from eq 9 in all cases and by the transition-state method in some cases (values in parentheses). We expect the values obtained from eq 9 to be generally lower than the others, because the orbitals used for χ and I both are too contracted for the description of the relaxation effects associated with the simple removal of an electron from a negative ion.

Third-order effects on computed ionization potentials are known to be very small.[4,9] We have computed the third-order effects on electronegativities and find them to be small also: 0.41 eV for the hydrogen atom but at least an order of magnitude less for all other cases.

III. Discussion

Our results perhaps provide the first systematic and comprehensive tabulation of electronegativities and electron affinities of the elements by a single coherent theoretical method.[10]

We do not wish to emphasize comparison of our values with "experimental values", because the model is only a first step: systematic improvements of it are possible and are bound to give improved results. Also, the use of a spin-independent model means that averages over all multiplets arising from the ground-state configuration are what we are dealing with, not pure ground states.

Nevertheless, it is clear that the numerical results are very satisfactory. The electronegativities in Table I and Figure 2 exhibit most known trends, and the numerical values agree semiquantitatively with other scales. The electron affinities are probably less accurate. Comparison with what is known about them, from, for example, the recent tabulation of Hotop and Lineberger,[11] shows that our values are uncertain by about 1 eV. Trends appear to be reasonable.

Concerning the electronegativities, their direct calculation as the slope, with respect to change of N, of the ground-state energy of the atom, evaluated for the neutral atom, can be considered as a possible alternative to our transition-state method. For the typical open-shell case, this works well, and gives identically the same answer as the transition-state method, eq 7. But for other cases, including the typical closed-shell case, this method runs into difficulties owing to the fact that the orbital vacated in ionization differs from the orbital filled in the adding of an electron; the E vs. N curve has a discontinuous derivative at the neutral atom. One can arbitrarily average the left and right derivatives, but even this often fails because of the need to determine a virtual orbital energy for the ground state. For example, we could not implement this method for either He or Ne but we could for Be. For Be, we find $\chi = 3.52$ eV, somewhat smaller than the value 3.80 eV given in the table.

Our preferred method for determining the electronegativity, namely, treating by the transition-state method the two-electron change all the way from positive to negative ion, has an interesting connection with Mulliken's definition of electronegativity, $\chi_M = 1/2(I + A)$. Namely, if the energy curve through the transition state were parabolic, its slope by the transition-state method would reproduce the correct χ_M provided that the energy functional used is accurate.

Interesting possibilities exist for relating electronegativities to excitation energies due to the fact that transition states for computing electronegativities, Figure 1, are related to states of the neutral atom. Consider case B, for example. We see from Figure 1 that the transition state in question is identically the transition state for the lowest electronic excitation process. The corresponding excitation energy is

$$\Delta E = \epsilon_i^{\,t} - \epsilon_j^{\,t} \tag{10}$$

so that we have, from eq 8,

$$\chi = \frac{1}{2}\Delta E - \epsilon_i^{\,t} \approx \frac{1}{2}\Delta E \tag{11}$$

where to obtain the final simplification we have used the fact that for this case $\epsilon_i^{\,t}$ usually is on the order of 1 eV or less. A correlation of the form of eq 11 was discovered in this laboratory in 1976 by Professor William Palke.[12]

It may be pointed out that eq 7 and 8 are not restricted to Xα theory. Thus, employing a spherically symmetric ensemble average within Hartree–Fock theory, Linderberg and Ohrn[13] have equated (for open-shell systems only) the valence orbital Lagrangian multiplier with the electronegativity of the atom. As in Xα theory, the orbital Lagrangian multipliers of this ensemble average are not ionization potentials in the sense of Koopmans' theorem, but they are given by eq 6. Equations 7 and 8 also hold in exact theory, in which all the quantities $(\partial E/\partial n_i)_{n_j}$ are equal to the electronegativity.[2,3,14]

Systematic extension of this whole line of analysis to the spin-polarized Xα method[4] is recommended. Applications to molecules are easy to carry through with presently available Xα technology.

Acknowledgment. This work was aided by research grants to the University of North Carolina from the National Institutes of Health and the National Science Foundation.

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Theoretical Study of Halobenzenium Ions

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Abstract: Electronic structures in the ab initio LCAO-SCF approximation are determined for benzene, fluorobenzene, and chlorobenzene and for benzenium and *o*, *m*, and *p*-fluoro- and chlorobenzenium ions. The reliability of the calculations, done in a double ζ contracted Gaussian basis, is affirmed by the agreement between predicted and observed proton affinities and ionization energies. Evidence is presented which supports the concept that the transition state for most electrophilic substitution reactions of monosubstituted benzenes is a σ complex, similar in structure to the Wheland intermediate and very different in its properties from the reactant molecules. Excellent correlation is found between positional selectivity of electrophilic substitution and the electronic properties of the model halobenzenium ions, whereas no correlation is found between selectivity and the properties of the parent monohalobenzene molecules.

Two types of intermediates are thought to occur in electrophilic aromatic substitution reactions, a π complex[1-3] (benzonium ion or encounter complex) and a σ complex[4] (benzenium ion or Wheland intermediate). The π complex is a loose association of an electrophile with an aromatic ring π-electron system. In the σ complex the electrophile is covalently bound to a ring carbon atom.

Wheland[4] proposed the σ complex as a model of the transition state for electrophilic aromatic substitution. Theoretical calculations,[5,6] low-temperature NMR spectra,[7,8] and the crystal structure of a salt of heptamethylbenzenium[9] have since shown the existence of stable σ complexes.

In this work protodeprotonation of halobenzenes is studied theoretically as a prototype electrophilic aromatic substitution reaction. Emphasis is on position selection in electrophilic substitution reactions of fluorobenzene and chlorobenzene. Ab initio single determinant LCAO-SCF calculations are performed in a flexible "double-ζ" basis on benzene, fluorobenzene, and chlorobenzene, as well as *o*-, *m*-, and *p*-fluorobenzenium and *o*-, *m*-, and *p*-chlorobenzenium ions. Orbital energies and σ, π, total, and frontier orbital[10] charge densities of the reactants and transition state models are assessed as reactivity indexes.[11] Because chemical shifts from nuclear magnetic resonance may give useful information about electron distributions in molecules, correlations between charge densities and proton and ^{13}C chemical shifts are also examined.

This is the first detailed theoretical study of electrophilic substitution in monosubstituted benzenes in which all three of the benzenium ion isomers are included. Previous work has either been limited to one or two isomers[5,6,12] or has reported only proton affinities.[13]

Results and Discussion

Computational. The C, F, and H bases were the [9s,5p/4s] set of Huzinaga[14] contracted (4s,2p/2s) by Dunning.[15] The Cl set was Veillard's[16] [12s,9p] contracted (6s,4p) by Dunning.[17] The hydrogen set and part of the carbon were scaled to optimize the energy in a set of calculations on the ethylene molecule. The hydrogen scale factor was 1.3; the factor for the in-the-molecular-plane carbon p functions was 1.03 and that for the out-of-plane 0.98.

Electron-repulsion integrals over atomic functions were generated in a molecular fragment scheme. The principal fragments were a C_6H_5 benzene fragment (Figure 1) and a C_6H_4 benzenium ion fragment (Figure 2). To generate the integral file for one of the substituted benzenes, for example, a halogen atom was placed at the vacant position in the benzene fragment and integrals involving the functions centered at this atom were added to the files of integrals already evaluated for the main fragment and the substituent atom. Calculations were done with the POLYATOM system of programs[18] modified to incorporate an integral pretest and the machinery for assembling molecular fragments. The integral pretest is used to efficiently eliminate integrals with negligibly small values.

The geometric configurations of the species are shown in Figures 1 and 2. No geometry optimization was done. The structure of the benzene fragment is the experimentally determined[19] benzene structure less one hydrogen atom; that of

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