J. Am. Chem. Soc. 1982, 104, 3801-3803

On the Geometric Mean Principle for Electronegativity Equalization

Robert G. Parr* and Libero J. Bartolotti†

Contribution from the Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514. Received November 12, 1981

Abstract: Conditions sufficient for the validity of the geometric mean principle for electronegativity equalization are shown to be in reasonable accord with facts. One needs valence-state atomic energies which decay exponentially with the number of electrons, with the decay parameter the same for each of the atoms being bound. An average value of 2.15 ± 0.59 is found for this parameter, which gives $A \sim 0.12I$ and $\chi \sim 0.28I$, where A, I, and χ are the electron affinity, ionization potential, and electronegativity, respectively. Also rationalized are various other properties of electronegativity, including how it comes about that with $\chi_A > \chi_B > \chi_C$ the electronegativities of A and B become equal in the species AB and yet when ABC is formed A acquires electrons from C in an amount determined by the original χ_A. The argument takes up from a density functional theory analysis given earlier (ref 1), which included a proof of the electronegativity equalization theorem.

I. Introduction

The electronegativity χ of an atom or molecule is the negative of the chemical potential μ of its electronic cloud:

$$\chi = -\mu = -(\partial E/\partial N)_{\rm v} \qquad (1)$$

This quantity has the same equalization property as does a macroscopic chemical potential: If free flow is allowed, electrons go from a region of high chemical potential to a region of low chemical potential, until both regions have the same chemical potential value.[1,2] This is a rigorous consequence of the density functional formulation[3] of ground-state quantum mechanics.

The equalization principle had been asserted long ago by Sanderson, reasoning rather differently.[4] Sanderson also postulated a geometric mean principle for the equalization: To a certain accuracy a molecule's final electronegativity is the geometric mean of the original atomic electronegativities.[5,6] The main purpose of the present paper is to exhibit a deduction of this postulate. Conditions sufficient for its validity will be found, and it will be shown to be a reasonable rule, generally though not universally valid, difficult to put to a definitive quantitative test. Various other aspects of electronegativity also will be considered.

On the basis of the analysis already given,[1] the case for the identification of the electronegativity as the chemical potential appears to be unassailable. The term chemical potential as it occurs in thermodynamics has long been accepted as a perspicuous description of the escaping tendency of a component from a phase. We have the very same properties here, at the molecular level, and we adopt the very same term. We shall employ both the words, "electronegativity" and "chemical potential", but we generally prefer the latter.

II. Two Difficulties: Valence States vs. Ground States, and the Elusiveness of Density Functional Theory

It is well to begin by frankly describing two difficulties which attend examination of this problem, which necessarily give our whole discussion a subjective and tentative nature.

First, while the density functional theory has already found a multitude of applications to diverse problems, in solid-state physics, surface physics, and chemistry, without exception these applications have involved approximations to the exact theory, and these approximations generally are crude on the standard of contemporary quantum chemistry. More important, the detailed form of the exact theory, and these approximations generally are crude on the standard of contemporary quantum chemistry. More important, the detailed form of the exact theory is not even known (although it is known to exist and is being sought). This means that detailed calculations to test accurately a formulation such as the one in the present paper are impossible at the present time.

Second, in a way somewhat reminiscent of the way the wave function approach to the same problem foundered on the difficulties and ambiguities associated with the atomic valence state,[7] the density functional description of atoms in molecules[1] entails a troublesome distinction between a valence state and a ground state [see below—it takes the valence state as the ground state of the atom in a perturbed environment]. If the electronegativity differences involved were very small, this would not produce major problems, but usually they are not very small. The consequence is that rather elaborate calculations and analysis are required before the proposed description can be put to full test. This problem is compounded by the fact that the calculations needed necessarily employ density functional methods, which are themselves subject to the first difficulty alluded to above.

Lest one despair, it may be noted that two papers have already appeared which would appear to constitute verification that the proposed description is quantitatively workable, one by Palke[8] and one by Guse.[9] Furthermore it will become clear that the loose argumentation which follows by its very nature can hardly be expected on refinement to lose its subjective implications.

III. The Process of Molecule Formation

We summarize how one may describe the formation of a molecule AB in its ground state from atoms A and B in their ground states.[1] A and B have chemical potentials $\mu^0{}_{\rm A}$ and $\mu^0{}_{\rm B}$, electron densities $\rho^0{}_{\rm A}$ and $\rho^0{}_{\rm B}$, numbers of electrons $N^0{}_{\rm A}$ and $N^0{}_{\rm B}$, and nuclear potentials $v^0{}_{\rm A}$ and $v^0{}_{\rm B}$; AB has chemical potential $\mu_{\rm AB}$, electron density $\rho_{\rm AB}$, number of electrons $N_{\rm AB} = N^0{}_{\rm A} + N^0{}_{\rm B}$, and nuclear potential $v^0{}_{\rm A} + v^0{}_{\rm B}$. In the molecule *before charge transfer*, atoms A and B are in valence states A* and B*, having chemical potentials $\mu^*{}_{\rm A}$ and $\mu^*{}_{\rm B}$, electron densities $\rho^*{}_{\rm A}$ and $\rho^*{}_{\rm B}$, numbers of electrons $N^0{}_{\rm A}$ and $N^0{}_{\rm B}$, and nuclear potentials $v^*{}_{\rm A}$ and $v^*{}_{\rm B}$. In the molecule *after charge transfer*, atoms A and B are in states having chemical potentials $\mu_{\rm A}$ and $\mu_{\rm B}$ such that $\mu_{\rm A} = \mu_{\rm B} = \mu_{\rm AB}$, electron densities $\rho_{\rm A}$ and $\rho_{\rm B}$ such that $\rho_{\rm A} + \rho_{\rm B} = \rho_{\rm AB}$, and numbers of electrons $N_{\rm A}$ and $N_{\rm B}$ such that $N_{\rm A} + N_{\rm B} = N_{\rm AB} = N^0{}_{\rm A} + N^0{}_{\rm B}$. The valence states, characterized by the potentials $v^*{}_{\rm A}$ and $v^*{}_{\rm B}$, are defined by a minimum-promotion-energy criterion.[1] For simplicity, AB is assumed to have its equilibrium geometry.

The charge transfer $\Delta N = N_{\rm A} - N^0{}_{\rm A} = N^0{}_{\rm B} - N_{\rm B}$ is to first order proportional to electronegativity difference $\mu^*{}_{\rm A} - \mu^*{}_{\rm B}$, which will

---

† Aided by research grants to the University of North Carolina from the National Institutes of Health and the National Science Foundation.

(1) R. G. Parr, R. A. Donnelly, M. Levy, and W. E. Palke, *J. Chem. Phys.*, **68**, 3801 (1978).

(2) R. A. Donnelly and R. G. Parr, *J. Chem. Phys.*, **69**, 4431 (1978).

(3) P. Hohenberg and W. Kohn, *Phys. Rev. B: Solid State*, **136**, 864 (1964).

(4) R. T. Sanderson, *Science*, **114**, 670 (1951); **116**, 41 (1952); **121**, 207 (1955); *J. Chem. Educ.*, **29**, 539 (1952); **31**, 2, 238 (1954); "Chemical Bonds and Bond Energy", Academic Press, New York, 1976.

(5) R. T. Sanderson, *Science*, **114**, 670 (1951).

(6) For some preliminary calculations, see: N. K. Ray, L. Samuels, and R. G. Parr, *J. Chem. Phys.*, **70**, 3680 (1979).

(7) For example, W. Moffitt, *Rep. Prog. Phys.*, **17**, 173 (1954).

(8) W. E. Palke, *J. Chem. Phys.*, **72**, 2511 (1980).

(9) M. P. Guse, *J. Chem. Phys.*, **75**, 828 (1981).

0002-7863/82/1504-3801$01.25/0

be more or less the same as [though in fact different from] $\mu^0{}_A - \mu^0{}_B$. In the following we treat these electronegativity differences as the same, in order to examine in a roughly quantitative way the electronegativity behavior. In a more complete discussion the distinction would have to be preserved. The number of electrons on an atom is considered to be a continuous variable.[10]

IV. Geometric Mean Law for Electronegativity Neutralization

Given atom A with atomic number Z_A, number of electrons N_A, and energy $E_A(N_A)$ then chemical potential $\mu_A(N_A) = (\partial E_A/\partial N_A)_{Z_A}$ and similarly given atom B with Z_B, N_B, and $E_B(N_B)$ then $\mu_B(N_B) = (\partial E_B/\partial N_B)_{Z_B}$. Consider the process described above, involving transfer of ΔN electrons from B to A, producing a molecule AB with chemical potential $\mu_{AB} = \mu_A = \mu_B$. For this process we will have

$$\mu_{AB} = \mu_A = \mu_A(N^0{}_A + \Delta N) \tag{2}$$

and

$$\mu_{AB} = \mu_B = \mu_B(N^0{}_B - \Delta N) \tag{3}$$

Therefore

$$\mu^2{}_{AB} = \mu_A\mu_B = \mu_A(N^0{}_A + \Delta N)\mu_B(N^0{}_B - \Delta N) \tag{4}$$

From this it follows that a sufficient condition for the validity of

$$\mu^2{}_{AB} = \mu^0{}_A\mu^0{}_B \tag{5}$$

where $\mu^0{}_A$ and $\mu^0{}_B$ are the chemical potentials of neutral atoms A and B is that

$$\mu_A = \mu^0{}_A \exp[-\gamma(N_A - Z_A)] \tag{6}$$

and

$$\mu_B = \mu^0{}_B \exp[-\gamma(N_B - Z_B)] \tag{7}$$

That is, a simple geometric mean equalization principle holds if each chemical potential is exponential in the number of electrons and the fall-off parameter γ is the same in both.

For a molecule formed from three atoms A, B and C, the corresponding result is

$$\mu^3{}_{ABC} = \mu^0{}_A\mu^0{}_B\mu^0{}_C \tag{8}$$

provided that all chemical potentials behave in the same exponential way, again with the same fall-off parameter. For a species ABC... with N atoms,

$$\mu^N{}_{ABC...} = \mu^0{}_A\mu^0{}_B\mu^0{}_C... \tag{9}$$

If exponential fall-off parameters are not the same, there also would be a law of this general form, but with powers modified appropriately.

Another deduction is that the effective γ value for a molecule comprised of n atoms is $1/n$ times the γ value for the constituent atoms.

V. Test of the Geometric Mean Law. Theoretical Implications for $E(N)$ Curves

For an atomic system of atomic number Z,

$$\mu = (\partial E/\partial N)_Z \tag{10}$$

Therefore, for an atom, the hypothesis

$$\mu = \mu^0 \exp[-\gamma(N - Z)] \tag{11}$$

is equivalent to the hypothesis

$$E(N) = A \exp[-\gamma(N - Z)] + B \tag{12}$$

Either (11) or (12) will lead to a geometric mean electronegativity equalization principle, as has just been seen. The energy of an atom, near its neutral condition (a pervasively common one[11]), is an exponentially decreasing function of the number of electrons.

Table I. Ionization Potentials, Electron Affinities, Exponential Falloff Parameters, and Electronegativities for 34 Neutral Atoms[a]

atom	I[b]	A[c]	γ	$-\mu$
H	13.595	0.7542	2.89	2.31
Li	5.390	0.620	2.16	1.51
B	8.296	0.278[d]	3.40	0.98
C	11.256	1.268	2.18	3.12
O	13.614	1.462	2.23	3.65
F	17.42	3.399	1.63	6.90
Na	5.138	0.546	2.24	1.37
Al	5.984	0.442[d]	2.61	1.24
Si	8.149	1.385	1.77	2.96
P	10.484	0.7464	2.64	2.12
S	10.357	2.0772	1.61	4.16
Cl	13.01	3.615	1.28	6.41
K	4.339	0.5012	2.16	1.22
V	6.74	0.526[e]	2.55	1.46
Cr	6.763	0.667[e]	2.32	1.71
Fe	7.90	0.164[f]	3.87	0.65
Co	7.86	0.662[g]	2.47	1.79
Ni	7.633	1.157[g]	1.89	2.57
Cu	7.724	1.226	1.84	2.68
Se	9.75	2.0206	1.57	4.01
Br	11.84	3.364	1.26	5.91
Rb	4.176	0.4860	2.15	1.18
Zr	6.84	0.427[e]	2.77	1.26
Nb	6.88	0.894[e]	2.04	2.10
Mo	7.10	0.747[e]	2.25	1.88
Rh	7.46	1.138[e]	1.88	2.52
Pd	8.33	0.558[e]	2.70	1.62
Ag	7.574	1.303	1.76	2.77
Sn	7.342	1.25	1.77	2.67
Sb	8.639	1.05	2.11	2.52
Te	9.01	1.9708	1.52	3.83
I	10.454	3.061	1.24	5.31
			av value of γ is	2.51

[a] I, A, and μ values in eV. γ defined by eq 12 of text. [b] All values from C. E. Moore, "Atomic Energy Levels". *Natl. Bur. Stand. (U.S.) Circ.*, No. 467 (Vol. I 1949); (Vol. II 1952); (Vol III 1958). [c] Except where indicated otherwise, these values are from H. Hotop and W. C. Lineberger, *J. Phys. Chem. Ref. Data*, 4, 539 (1975). [d] C. S. Feigerle, R. R. Corderman, and W. C. Lineberger, *J. Chem. Phys.*, 74, 1513 (1981). [e] C. S. Feigerle, R. R. Corderman, S. V. Bobashev and W. C. Lineberger, *J. Chem. Phys.*, 74, 1580 (1981). [f] P. C. Engelking and W. C. Lineberger, *Phys. Rev. A*, 19, 149 (1979). [g] R. R. Corderman, P. C. Engelking, and W. C. Lineberger, *J. Chem. Phys.*, 70, 4474 (1979).

Is this reasonable? Certainly yes. Indeed, from what we now know it appears clear that the standard situation in fact is that a neutral atom (or molecule) will have a first ionization potential much bigger than its electron affinity and much smaller than its second ionization potential. The first electron affinity will be small and positive or zero, the second electron affinity will be smaller still and positive or zero, etc.[12] That is, the standard situation surely is as pictured in Figure 1. The standard situation is well described by an exponential. This argument does not depend on actual data as such but rather on general principles. The exponential form of eq 11 and 12 is therefore reasonable. Whether γ is to some extent universal will be our next concern.

VI. Determination of Parameters γ from Experimental Data

Continuing to suppose that we can test our ideas by using ground-state data only, we have calculated γ values for various species by using actual ionization potential and electron affinity

---

(10) On this point, see: M. S. Gopinathan and M. A. Whitehead, *Isr. J. Chem.*, 19, 209 (1980); J. Katriel, R. G. Parr, and M. R. Nyden, *J. Chem. Phys.*, 74, 2397 (1981).

(11) On p 273 of L. Pauling, "Nature of the Chemical Bond", 3rd ed., Cornell University Press, Ithaca, NY, 1960, read "In general the electronic structure of substances is such as to cause each atom to have essentially zero resultant electric charge." Pauling attributes the original statement of this principle to Langmuir.

(12) A negative electron affinity is impossible for an isolated system, because always more stable than A^- in such a case will be A plus a free electron. A negative atom *in a molecule* could behave differently.

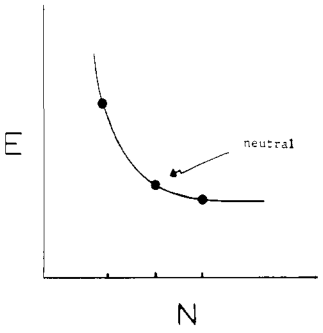

Figure 1.

values. Results are given in Table I. While γ certainly is not a universal constant, its values fall in a fairly narrow range. We find, with the standard deviation indicated

$$\gamma = 2.15 \pm 0.59 \tag{13}$$

which gives for the relations among ionization potential, electron affinity, and chemical potential

$$A = e^{-\gamma} I = (0.12 \pm 0.07)I \tag{14}$$

$$\mu = \gamma(e^{\gamma} - 1)^{-1} I = -(0.28 \pm 0.11)I \tag{15}$$

The electron affinity is about one-eighth of the ionization potential; the chemical potential is about three-tenths of it. We also have

$$\mu = [IA/(I - A)] \ln (I/A) \tag{16}$$

VII. Atomic Electronegativity Memory Effects in the Formation of a Polyatomic Molecule from Its Constituent Groups

Suppose for example that $\mu^0{}_A < \mu^0{}_B < \mu^0{}_C$, where A, B, and C are atoms, and consider the molecules AB and ABC. In AB, $\mu_A = \mu_B = \mu_{AB} = (\mu^0{}_A \mu^0{}_B)^{1/2}$; A and B electronegativities have been equalized. Nevertheless, as one adds C to give ABC, with $\mu_A = \mu_B = \mu_C = \mu_{ABC} = (\mu^0{}_A \mu^0{}_B \mu^0{}_C)^{1/3}$, there is a transfer of more electrons to A than there would have been if A had not been originally more electronegative than B.

A numerical illustration makes this effect clear. Take $\mu^0{}_A = 2$, $\mu^0{}_B = 3$, $\mu^0{}_C = 4$, and $\gamma = 2$ and say $N^0{}_A = N^0{}_B = N^0{}_C = 1$. Then in AB, $\mu_{AB} = 2.45$, $N_A = 1.10$, and $N_B = 0.90$, and in ABC, $\mu_{ABC} = 2.88$, $N_A = 1.18$, $N_B = 0.98$, and $N_C = 0.84$. The last figures may be compared with the distribution in a species DDC made from an atom D with $\mu^0{}_D = 2.45$, for which one obtains $\mu_{DDC} = 2.88$, $N_D = 1.08$, and $N_C = 0.84$. Note that N_A in ABC is more than N_D in DDC, as well as more than N_A in AB.

VIII. Charge Transfer, Electronegativity Difference, and Energy Effect of Charge Transfer

From eq 2, 3, 6, and 7, one obtains

$$\Delta N = \frac{1}{2\gamma} \ln \frac{\mu^0{}_B}{\mu^0{}_A} \approx 0.23 \ln \frac{\mu^0{}_B}{\mu^0{}_C} \tag{17}$$

which is the formula giving the number of electrons which flow from B to A on AB formation. The corresponding energy change in the molecule will be

$$\Delta E = \int_{N^0{}_A}^{N^0{}_A + \Delta N} \mu_A \, dN_A + \int_{N^0{}_B}^{N^0{}_B - \Delta N} \mu_B \, dN_B = \mu^0{}_A \frac{1}{\gamma}[1 - \exp(-\gamma \Delta N)] + \mu^0{}_B \frac{1}{\gamma}[1 - \exp(+\gamma \Delta N)] \tag{18}$$

For small ΔN, this reduces to

$$\Delta E = (\mu^0{}_A - \mu^0{}_B)\Delta N \tag{19}$$

and the energy stabilization is proportional to the electronegativity difference and the number of electrons transferred. To second order in ΔN, the formula is

$$\Delta E = (\mu^0{}_A - \mu^0{}_B)\Delta N - \tfrac{1}{2}(\mu^0{}_A + \mu^0{}_B)\gamma(\Delta N)^2 \approx (\mu^0{}_A - \mu^0{}_B)\Delta N - 1.08(\mu^0{}_A + \mu^0{}_B)(\Delta N)^2 \tag{20}$$

These formulas are in general accord with what is known about such quantities. The values of electronegativities in Table I lead to values of ΔN and ΔE which seem reasonable for these quantities as here defined, although smaller than the "partial ionic character" and "extra ionic energy" of Pauling.[13] Use of modified electronegativities[14] permits reproduction of those Pauling quantities. In any case the general shape of our ΔE vs. ΔN curve appears to be more or less correct.

IX. Conclusions

For the reasons already stated in section II, the formulas given in this paper may not have quantitative predictive value; at the very least much further study is needed to test the extent that they do. Nevertheless, it is clear that the geometric mean electronegativity equalization principle is a reasonable postulate for the chemistry of neutral atoms.

When an atom is nearly neutral it seems that the proposal that its energy is an exponentially decaying function of the number of electrons is more reasonable than the classical supposition that the energy is a quadratic function of the number of electrons.[15] The latter hypothesis leads, as by now is well known, to the Mulliken formula for electronegativity.[16]

$$\mu = -\chi = (I + A)/2 \tag{21}$$

Our proposed formula leads instead to eq 14, 15, and 16, and our analysis (of data) leads further to the approximate constancy of the A to I and μ to I ratios. Quadratic fitting is generally superior for predicting second ionization potentials, but that is not the present concern.

The approximate constancy of γ is a result that implies that in some approximate sense the process $A^+ \rightarrow A \rightarrow A^-$ is the same for all atoms. If we think of this process as the addition of first one and then a second electron to a positive core, that there be an underlying approximate energetic similarity among all cases is reasonable. This idea can be made more quantitative (though still crude) if it is supposed that the 0-to-2 electrons are described by a density $\rho = N(\zeta^3/\pi)\exp(-2\zeta r)$ and an energy functional $E = T + V_{ne} + V_{ee}$, with $T = N(\zeta^2/2)$, $V_{ne} = -N\zeta$, and $V_{ee} = [1 - (1/N)](1/2)N^2(5/8)\zeta = (N^2 - N)(5/16)\zeta$. Minimizing E with respect to ζ gives $\zeta = (21 - 5N)/16$, which gives $\mu(N = 1) = -(3/16) = -5.1$ eV [a reasonable sort of "universal" electronegativity value] and $[(\partial^2 E/\partial N^2)/(\partial E/\partial N)] = -2.8$ at $N = 1$, whereas our empirical value of $-\gamma$ is about -2.2.

It is important to note that the geometric mean law, to the extent that it is valid, constitutes a prediction on how molecular electronegativities are related to atomic electronegativities and does not trivially extend to a prediction of molecular electronegativities from functional group electronegativities. This is because the primary sites for electron attraction in a molecule are nuclei (atoms). Thus μ_{ABC} is not $(\mu_A \mu_{BC})^{1/2}$ but $(\mu^0{}_A \mu^0{}_B \mu^0{}_C)^{1/3}$, etc. Note however that electronegativities of polyatomic species are predicted to obey specific combining rules [eq 9]. For example, two isomers are predicted to have the same electronegativity.

Many further studies are called for by this analysis. Experimental I, A, and μ values are much needed for molecules as well as atoms. Theoretical studies extending the pioneering works of Palke[8] and Guse[9] will be valuable, and the distinctions between ground and valence states of atoms must be examined in detail in the density functional formalism.

Acknowledgment. R.G.P. thanks Professor J. D. H. Donnay of McGill University both for a letter which catalyzed this research and for providing an inspiring personal example some years ago. A referee is responsible for the remark at the end of section IV.

---

(13) L. Pauling, "Nature of the Chemical Bond", 3rd ed., Cornell University Press, Ithaca, NY, 1960.

(14) For example, L. J. Bartolotti, S. R. Gadre, and R. G. Parr, *J. Am. Chem. Soc.*, **102**, 2945 (1980).

(15) H. O. Pritchard and F. H. Sumner, *Proc. R. Soc. London, Ser. A*, **235**, 136 (1956); R. P. Iczkowski and J. L. Margrave, *J. Am. Chem. Soc.*, **83**, 3547 (1961).

(16) R. S. Mulliken, *J. Chem. Phys.*, **2**, 782 (1934); **3**, 573 (1935).