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On Atomic and Orbital Electronegativities and Hardnesses

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Abstract: Chemical concepts including global and orbital (or "divisional") electronegativity, hardness, softness, orbital hardness and softness kernel, and orbital Fukui index, for any given electronic system in a particular situation, are defined and relations among them are derived. Some results earlier obtained are used to illustrate uses of the formalism. Atomic parameters in various molecular circumstances are determined through semiempirical calculations as functions of corresponding atomic orbital population distributions. It is demonstrated how atomic energy changes such as ionization energy and electron affinity and transition energy can be calculated. Computed values agree well with experiment. The density-functional and L. C. Allen views of the electronegativity concept are reconciled.

I. Introduction

The density-functional theory of electronic structure is particularly appropriate for describing molecular electronic structure, because key quantities in density-functional theory are the familiar and useful concepts of electronegativity, atomic charge, hardness and softness, and frontier electrons.[1] The purpose of the present paper is to discuss atomic and atomic-orbital electronegativities and hardnesses in a manner appropriate when one is thinking of a molecule as a combination of atoms. Each atom in the molecule is an open system, in equilibrium with the other atoms with respect to interchange of electrons. The formulation we shall develop may, however, also be applied to the general case of a specific combination of functional groups and subgroups.

For an atom or molecule having N electrons moving in a field $v(\vec{r})$ due to nuclei, the ground-state energy $E[N,v]$ can be determined from a variational principle. The energy is a functional of the electron density,

$$E_v[\varrho] = \int \varrho(\vec{r})v(\vec{r})\,d\vec{r} + F[\varrho] \tag{1}$$

where $F[\varrho]$ is the sum of the electronic kinetic energy and the electron−electron repulsion energy and $E_v[\varrho]$ is a minimum for the true density provided that it is normalized to N. That is

$$\mu = v(\vec{r}) + \frac{\delta F}{\delta \varrho(\vec{r})} = \mu[N,v] = \text{constant} = \left(\frac{\partial E}{\partial N}\right)_v \tag{2}$$

The quantity μ, the Lagrange multiplier for the normalization constraint, is the chemical potential for the system. The last formula in eq 2 assumes that E is a continuous function of N. When E is not continuous, one should use a corresponding finite difference formula,[2]

$$\mu = -\frac{I + A}{2} = -\chi \tag{3}$$

where I and A are the ionization potential and electron affinity for the species and χ is the Mulliken electronegativity.[3] The chemical potential measures the escaping tendency of electrons from the species in its ground state. We call $-\mu$ or χ the absolute electronegativity.[4]

While the energy required to remove an electron is just I, equal weighting of I and A results in eq 3 because of the clear necessity to consider the *relative* tendencies of the two species to attract electrons. The energy required for $A + B \rightarrow A^+ + B^-$ is $I_A - A_B$; the energy required for $A + B \rightarrow A^- + B^+$ is $I_B - A_A$. These energies are equal if $I_A + A_A = I_B + A_B$. This was Mulliken's argument for eq 3.[3]

The sensitivity of μ to N is itself a positive quantity of much interest,

$$2\eta = \left(\frac{\partial \mu}{\partial N}\right)_v = \left(\frac{\partial^2 E}{\partial N^2}\right)_v \tag{4}$$

or in finite difference approximation

$$2\eta = I - A \tag{5}$$

This is the absolute hardness of the system.[5,6] Softness is the inverse of hardness,

$$S = \frac{1}{2\eta} = \left(\frac{\partial^2 N}{\partial E^2}\right)_v \tag{6}$$

Hardness measures resistance to the charge flow that a difference in electronegativities commands.

If in eqs 3 and 5 one uses isolated-atom ground-state I and A, there result first approximations to electronegativity and hardness of an atom in a molecule. The determination of electronegativity and hardness is not finished by these definitions. More accurate numerical values may be difficult to obtain in specific circumstances.

In the present paper, building on work already done by one of us on the electronegativities (chemical potentials) of individual orbitals in atoms,[7,8] we characterize and study the electronegativities and hardnesses of orbitals in atoms in various

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[⊗] Abstract published in *Advance ACS Abstracts*, March 1, 1995.

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states of ionization. Among other things, we shall demonstrate concordance with ideas of L. C. Allen.[9,10]

II. The Atom in a Molecule

The foregoing formulas hold for an open subsystem of a molecule provided that it is in equilibrium, and so we may apply them to an atom or functional group in a molecule. The atom (or functional group) in a molecule is not easily defined. There are always subjective factors for any definition, or strict partition of the molecule. What model one chooses is subject to one's particular needs.

For any given partitioning of the molecule into atomic fragments, we may take an atomic fragment to be a ground state of N electrons (not necessarily integral) in an external potential v, with v an "external" potential appropriate for the molecular environment of the fragment that in principle can be determined from an elaborate calculation.[4] Here and below where we use the term "atomic", the formal analysis usually applies as well to other partitionings.

Short of undertaking the determination of this atomic state, we may begin to discuss it, knowing that it is a perturbed ground state of the isolated atom, since an atom in different molecular environments still keeps its chemical identity but exhibits slightly different chemical behavior. We focus on atomic orbital quantities such as electronegativity and hardness and how they may be expected to be affected by the different molecular environments of the atom. We will not focus on how the effective external potential changes with environments. We rather concentrate on the atomic orbital population changes. In a series of important related studies, Nalewajski and co-workers have been developing the more global viewpoint.[11]

Consider, then, some particular equilibrium state of an atomic (or other) subsystem of a given molecular electronic system, the subsystem having energy $E(N,v)$. The subsystem may be itself regarded as an open electronic system in equilibrium with an electron heat bath that allows flows of electrons and energy between the system and bath. This system—the subsystem of the original molecule—may be studied by a finite-temperature grand canonical ensemble theory.[1] N and v determine everything, including the electron density $\varrho(\vec{r})$. The density may be distributed among component distinct little pieces,

$$\varrho(\vec{r}) = \sum_i \varrho_i(\vec{r}) \tag{7}$$

Integration gives

$$N = \sum_i n_i \tag{8}$$

where

$$n_i = \int \varrho_i(\vec{r})\, d\vec{r} \tag{9}$$

The n_i are orbital (or sub-subgroup) populations and in general are fractional numbers. The energy can be regarded as a functional $E[\{n_i\},v]$. A change in energy produced by a small change in N at constant v will be given by

$$dE = \sum_i (\partial E/\partial n_i)_{v,\{n_{j\neq i}\}}\, dn_i = \left[\sum_i \left(\frac{\partial E}{\partial n_i}\right)_{v,\{n_{j\neq i}\}} \left(\frac{dn_i}{dN}\right)_v\right] dN \tag{10}$$

Here $(\partial E/\partial N)_v$ is the subsystem chemical potential or negative electronegativity χ and $(\partial E/\partial n_i)_{v,j}$ defines the orbital chemical potential or negative orbital electronegativity,

$$\mu_i = \left(\frac{\partial E}{\partial n_i}\right)_{v,\{n_{j\neq i}\}} = -\chi_i \tag{11}$$

Note that in the derivative dn_i/dN, the other n_j are *not* held constant.

Now from eq 9 we find

$$(\partial n_i/\partial N)_v = \int [\partial \varrho_i(\vec{r})/\partial N]_v\, d\vec{r} = \int f_i(\vec{r})\, d\vec{r} \equiv f_i \tag{12}$$

while eq 7 gives a resolution of the Fukui function[12,13] for the subsystem,

$$(\partial \varrho(\vec{r})/\partial N)_v = f(\vec{r}) = \sum_i f_i(\vec{r}) \tag{13}$$

with

$$\sum_i f_i = 1 \tag{14}$$

Consequently we find

$$\mu = \sum_i \mu_i f_i \tag{15}$$

or

$$\chi = \sum_i \chi_i f_i \tag{16}$$

We recognize that the numbers f_i are fractions that reflect the reactivity of orbital (or subgroup) i in its molecular environment. When f_i is unity, and zero for other orbitals than i, the total subsystem Fukui function comes solely from orbital i; when f_i is other than unity, other orbitals participate in the Fukui function. Accurate determination of the functions $f_i(\vec{r})$ and indices f_i must rely on density-functional calculations.

The subsystem hardness and softness can be resolved into orbital components in the same way. From eq 4, we obtain

$$2\eta = \frac{\partial}{\partial N}(\partial E/\partial N)_v = 2\sum_i f_i \eta_i = \sum_i \sum_j 2\eta_{ij} f_i f_j \tag{17}$$

where

$$\eta_i = \sum_j f_j \eta_{ij} \tag{18}$$

and

$$2\eta_{ij} = \partial^2 E/\partial n_i \partial n_j = 2\eta_{ji} = -\partial \chi_i/\partial n_j \tag{19}$$

is the orbital hardness kernel or matrix. To derive eq 17, extend eq 10 to include second-order terms.

Similarly, from eq 6, the softness is

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$$S = \frac{1}{2\eta} = \left(\frac{\partial^2 N}{\partial E^2}\right)_v = \sum_i s_i = \sum_i \sum_j s_{ij} \tag{20}$$

in which s_i is the orbital softness index

$$s_i = -\left(\frac{\partial n_i}{\partial \chi}\right)_v = f_i{\cdot}S = \sum_j s_{ij} \tag{21}$$

and s_{ij} is the orbital softness matrix, the inverse of the hardness matrix. Specifically,

$$2\sum_k s_{ik}{\cdot}\eta_{jk} = \delta_{ij} \tag{22}$$

from which

$$2\sum_k s_k{\cdot}\eta_k = 1 \tag{23}$$

follows. The hardness and softness thus are sums of orbital components (weighted differently), with each orbital component containing contributions from other orbitals.[14] Equations 20–22 can be used to determine Fukui indices if either the hardness or the softness matrix is known. It can be shown that, when the orbital (or regional) basis set is complete, the orbital or regional hardnesses defined in eq 18 are in fact equal to each other, and equal to the global hardness of the system.[14]

One special case of interest is the diagonalized hardness matrix. Then its inverse matrix, the softness matrix, is also in a diagonal form, and one has

$$s_{ii} = \frac{1}{2\eta_{ii}} \tag{24}$$

Nalewajski and co-workers have been modeling this situation effectively.[11]

If the change dN takes place only in the highest occupied or lowest unoccupied orbital (denoted by h), these formulas give

$$\chi = \chi_{\mathrm{h}} = -\mu \approx (I + A)/2 \tag{25}$$

and

$$\eta = \eta_{\mathrm{hh}} \approx (I - A)/2 \tag{26}$$

where μ is the chemical potential of the system. More generally, from eqs 10 and 17 χ and η will be determined whenever E is known as a unique functional of the n_i and v. For example, Slater's transition-state method[15,16] gives

$$I = E(n_i - 1) - E(n_i) \approx -\left(\frac{\partial E}{\partial n_i}\right)_{n_i - 1/2} = \chi_i(\mathrm{TS}) \tag{27}$$

where $\chi_i(\mathrm{TS})$ is the electronegativity of orbital i at the transition state $n_i - {}^1/_2$. Excited states can be similarly handled.

The principal formulas of this section may be compared with the exact formulas of density-functional theory[1,14]

$$\eta = \int f(\vec{r})\eta(\vec{r})\,\mathrm{d}\vec{r} = \frac{1}{2}\int\int \frac{\delta^2 F[\varrho]}{\delta\varrho(\vec{r})\delta\varrho(\vec{r}\,')} f(\vec{r})f(\vec{r}\,')\,\mathrm{d}\vec{r}\,\mathrm{d}\vec{r}\,' \tag{28}$$

$$2\eta(\vec{r},\vec{r}\,') = \frac{\delta^2 F[\varrho]}{\delta\varrho(\vec{r})\delta\varrho(\vec{r}\,')} \tag{29}$$

$$s(\vec{r}) = f(\vec{r})S = \int s(\vec{r},\vec{r}\,')\,\mathrm{d}\vec{r}\,' \tag{30}$$

$$\int f(\vec{r})\,\mathrm{d}\vec{r} = 1 \tag{31}$$

$$2\int\int s(\vec{r},\vec{r}\,')\eta(\vec{r}\,',\vec{r}\,'')\,\mathrm{d}\vec{r}\,' = \delta(\vec{r},\vec{r}\,'') \tag{32}$$

$$2\int s(\vec{r})\eta(\vec{r})\,\mathrm{d}\vec{r} = 1 \tag{33}$$

In eq 28, the local hardness $\eta(\vec{r})$ is naturally defined as[14]

$$\eta(\vec{r}) = \int \eta(\vec{r},\vec{r}\,')f(\vec{r}\,')\,\mathrm{d}\vec{r}\,' \tag{34}$$

and can be shown to be equal everywhere and equal to the global hardness η through eqs 30 and 32.

Note that there is ambiguity in the previous definition for the (ground state) local hardness as $[\delta\mu/\delta\varrho(\vec{r})]_v$,[14] since it is N and v that are two basic independent variables of an electronic system and ϱ depends on v, unless one thinks that the partial functional derivative with respect to ϱ for a ground state at a fixed v is equivalent to $[\partial(\cdot)/\partial N]_v$.

III. Method of Calculation

For our calculations we employ an extended Kohn–Sham scheme in a standard spin-restricted Xα approximation.[17] With the electron density written as

$$\varrho(\vec{r}) = \sum_i n_i \sum_s |\psi_i(\vec{x})|^2 \tag{35}$$

where the ψ_i are orthonormal spin orbitals and the sum over s is a sum over spins, the energy functional is

$$E[\varrho] = \sum_i -\frac{1}{2}n_i\int \psi_i^*\nabla^2\psi_i\,\mathrm{d}\vec{x} + \int v(\vec{r})\varrho(\vec{r})\,\mathrm{d}\vec{r} + J[\varrho] + E_{\mathrm{xc}}[\varrho] \tag{36}$$

For a fixed assignment of the n_i, minimization of eq 36 with respect to the orbitals gives

$$\left[-\frac{1}{2}n_i\nabla_i^2 + n_i v_{\mathrm{eff}}(\vec{r})\right]\psi_i = \epsilon_i{}'\psi_i \tag{37}$$

or, dividing by n_i

$$\left[-\frac{1}{2}\nabla^2 + v_{\mathrm{eff}}(\vec{r})\right]\psi_i = \epsilon_i\psi_i \tag{38}$$

where $\epsilon_i = \epsilon_i{}'/ni$ is an orbital energy. Further, from eq 36 follows, at the solution point,

$$(\partial E/\partial n_i)_{v,\{n_{j\neq i}\},\{\psi_i\}} = \epsilon_i = -\chi_i \tag{39}$$

This formula is due to Janak.[18] Because of the fixed orbital $\{\psi_i\}$ constraint in eq 39, Nalewajski has called the orbital quantities rigid orbital electronegativities.[11]

In earlier calculations,[7,8] these equations [eqs 35–39] were solved for a number of atoms and for various total charges and states of ionization. In the present paper, we extend the calculations to include hardnesses as well as electronegativities, using eqs 17–19 above. In most cases inner shells are taken

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Table 1. Valence Orbital Electronegativity Formulas for N, O, F, and for P, S, and Cl (eV). See Eq 40 of Text[a]

	N, O, F			P, S, Cl		
	2s	2p	3s	3s	3p	3d
B(0)	16.985	5.229	−2.958	102.046	132.574	22.840
B(*Z*)	−12.8525	−10.8706	−1.8976	−27.1067	−31.5368	−9.0377
B(s)	8.717	8.597	0.943	14.632	21.314	9.428
B(p)	7.585	9.217	1.994	23.037	24.280	11.143
B(d)	5.531	4.866	−0.353	12.558	37.056	3.617
B(*Z*,*Z*)	4.0108	3.7708	1.2660	1.7029	1.8126	0.7060
B(*Z*,s)	−5.6225	−5.7472	−2.0545	−2.1583	−2.6029	−1.8321
B(*Z*,p)	−5.3877	−5.7972	−2.3365	−2.6747	−2.7308	−1.6225
B(*Z*,d)	−2.6886	−2.6438	−1.4069	−1.9509	−3.3702	−1.0156
B(s,s)	1.612	1.976	0.788	0.957	1.053	2.163
B(s,p)	3.888	4.003	1.859	1.427	1.708	2.043
B(s,d)	2.635	2.313	1.536	3.377	2.348	1.436
B(p,p)	1.822	2.026	1.070	0.972	0.918	0.876
B(p,d)	1.941	2.058	1.211	2.086	2.476	1.778
B(d,d)	−1.322	−1.127	1.435	0.248	−1.393	0.310
std dev	0.32	0.29	0.24	0.42	0.35	0.14
corr coeff	1.000	1.000	0.999	0.999	0.999	1.000
no. of data fitted	36	34	19	32	32	22
av fitting error	1.1%	5.6%	11%	1.2%	6.1%	7.4%

[a] The ranges of atomic net charges for different electronic configurations used in Xα calculations are N (−1 to +1.5), P (−1.5 to +2); O, S (−1.5 to +1); F, Cl (−1 to +1).

Table 2. Valence Orbital Electronegativities for Fourth-Row Transition Elements (eV). See Eq 41 of Text[a]

	3d	4s	4p
B(0)	514.209	262.759	232.426
B(*Z*)	−63.7516	−33.3370	−30.1778
B(3d)	55.001	27.476	27.431
B(4s)	26.385	17.540	18.020
B(4p)	28.856	19.495	17.060
B(Z^2)	1.9411	1.0487	0.9546
B(Z,3d)	−3.3515	−1.7718	−1.7401
B(Z,4s)	−1.7103	−1.1803	−1.1931
B(Z,4p)	−1.7799	−1.2387	−1.0942
B($3d^2$)	1.3750	0.7231	0.7635
B(3d,4s)	1.395	0.928	1.023
B(3d,4p)	1.495	0.993	0.918
B($4s^2$)	0.361	0.132	0.216
B(4s,4p)	0.892	0.322	0.222
B($4p^2$)	0.519	0.190	0.000
std dev	0.37	0.27	0.29
corr coeff	1.000	1.000	1.000
no. of data fitted	108	108	101
av fitting error	10%	2.3%	13%

[a] The ranges of atomic net charges for different electronic configurations used in Xα calculations are Mn (−0.5 to +7) Fe (−0.5 to +3) Co (−0.5 to +4) Cu, Zn (−0.5 to +2.5).

to be full and their occupation numbers fixed, but the changes with electron configuration in valence shell orbitals are accounted for.

IV. Results

Principal results of the previous work[7,8] are master formulas for valence orbital electronegativities as functions of occupation numbers of the s, p, and d components (and 4f orbital for the lanthanoid elements). In Table 1 are given the formulas for N, O, F and P, S, Cl. In Table 2, the formula is given for the fourth-row transition elements. The results come from a large number of calculations by the methods described above.

Briefly to describe what was done, we consider for example, phosphor, sulfur, and chloride ions with various fractional charges q and valence states [Ne]$3s^a3p^b3d^c$. These were calculated by the spin-restricted Xα method using Schwarz atomic α values.[8,17] Here a, b, and c are fractional occupation numbers. For negative ions, valence orbitals, especially 3d orbitals, are diffuse. In order to make the calculations converge, a funnel-shaped potential with a depth of −2 au is added. The inner radius of the funnel potential is chosen to be as big as 10 au so as not to affect the shape and energy of valence orbitals too much (the outer cutoff radius is taken to be 50 au). The negative value of the orbital energy is the orbital electronegativity [eq 39] of the corresponding valence state. This is a function of the original assumed orbital occupation numbers. Approximate formulas are then obtained by fitting the electronegativity of each kind of valence atomic orbital, using a second-order polynomial in the valence orbital occupation numbers a, b, and c and atomic number values Z. The results are listed in Table 1.

In refs 7 and 8, orthonormal Slater-type orbital functions were used to fit the numerical atomic orbitals obtained by the Xα procedure to get Slater orbital exponents. Valence orbitals were found to change considerably between different valence ionic states. Their Slater orbital exponents were fitted separately as linear functions of valence orbital occupation numbers and atomic numbers. The previous purpose was to provide parameters for semiempirical SCF calculations since those parameters take care of the changing molecular environment to a certain degree. However, the purpose of the present paper is to use these approximate data as special examples and applications of the general formalism derived above and to examine the corresponding hardness parameters.

For N, O, F and P, S, Cl, the formula is

$$\chi_i = B(0) + B(Z)Z + B(s)n_s + B(p)n_p + B(d)n_d + B(Z^2)Z^2 + B(Z,s)Z{\cdot}n_s + B(Z,p)Z{\cdot}n_p + B(Z,d)Z{\cdot}n_d + B(s^2)n_{s^2} + B(s,p)n_s{\cdot}n_p + B(s,d)n_s{\cdot}n_d + B(p^2)n_{p^2} + B(p,d)n_pn_d + B(d^2)n_{d^2} \quad (40)$$

(i = s, p, d = 2s, 2p, 3s for N, O, F; 3s, 3p, 3d for P, S, Cl, respectively). Here χ_i is the electronegativity of valence orbital, $\{n_i\}$ is the population of valence orbitals, Z is the atomic number, and $B(i,j)$ is the corresponding coefficient before the term $(n_i{\cdot}n_j)$ (i, j = Z, 2s, 2p, 3s for N, O, F; Z, 3s, 3p, 3d for P, S, Cl). Values of coefficients are given in Table 1, taken from ref 8 and reorganized here. Thus for any particular atom or ion of N, O, F or P, S, Cl, with a given valence state, valence orbital electronegativities may be calculated by substitution of valence orbital occupation numbers into eq 40.

For the fourth-row transition elements, the formula is

$$\chi_i = B(0) + B(Z)Z + B(3\text{d})n_{3\text{d}} + B(4\text{s})n_{4\text{s}} + B(4\text{p})n_{4\text{p}} + B(Z^2)Z^2 + B(Z,3\text{d})Z{\cdot}n_{3\text{d}} + B(Z,4\text{s})Z{\cdot}n_{4\text{s}} + B(Z,4\text{p})Z{\cdot}n_{4\text{p}} + B(3\text{d}^2)n_{3\text{d}^2} + B(3\text{d},4\text{s})n_{3\text{d}}{\cdot}n_{4\text{s}} + B(3\text{d},4\text{p})n_{3\text{d}}{\cdot}n_{4\text{p}} + B(4\text{s}^2)n_{4\text{s}^2} + B(4\text{s},4\text{p})n_{4\text{s}}{\cdot}n_{4\text{p}} + B(4\text{p}^2)n_{4\text{p}^2} \quad (41)$$

$$(i = 3\text{d}, 4\text{s}, 4\text{p})$$

in which χ_i is the electronegativity of valence orbital i with the population of n_i, Z is the atomic number, and $B(i,j)$ is the corresponding coefficient before the term $(n_i{\cdot}n_j)$ $(n_i, n_j = Z, n_{3\text{d}}, n_{4\text{s}}, n_{4\text{p}})$. Values of coefficients are given in Table 2. These were fitted to calculated results for Mn, Fe, Co, Cu, and Zn. See ref 7 and 8, where results can be found also for Se, Br, Mo, and the lanthanoid elements.

Orbital hardnesses may now be obtained from eqs 17–19, by appropriate differentiation of eqs 40 and 41. From Table 1, for N, O, and F, we find (q is atomic net charge)

$$\eta_{2\text{p},2\text{p}} = 1.189 + 0.897n_{2\text{s}} + 0.872n_{2\text{p}} + 1.870n_{3\text{s}} + 2.899q = -4.609 - 2.002n_{2\text{s}} - 2.027n_{2\text{p}} - 1.030n_{3\text{s}} + 2.899Z \quad (42)$$

$$\eta_{2\text{p},2\text{s}} = 1.449 + 0.897n_{2\text{s}} + 0.872n_{2\text{p}} + 1.717n_{3\text{s}} + 2.874q \quad (43)$$

$$\eta_{2\text{s},2\text{p}} = 1.596 + 0.750n_{2\text{s}} + 0.872n_{2\text{p}} + 1.723n_{3\text{s}} + 2.694q \quad (44)$$

$$\eta_{2\text{s},2\text{s}} = 1.264 + 1.200n_{2\text{s}} + 0.867n_{2\text{p}} + 1.494n_{3\text{s}} + 2.812q \quad (45)$$

For P, S, Cl, etc., we find

$$\eta_{3\text{p},3\text{p}} = 1.514 + 0.511n_{3\text{s}} + 0.447n_{3\text{p}} + 0.128n_{3\text{d}} + 1.366q \quad (46)$$

$$\eta_{3\text{s},3\text{s}} = -7.316 - 0.957n_{3\text{s}} - 0.714n_{3\text{p}} - 1.688n_{3\text{d}} + 1.079Z \quad (47)$$

Similarly, for the fourth-row transition elements we obtain from Table 2

$$\eta_{3\text{d},3\text{d}} = 2.663 + 0.300n_{3\text{d}} + 0.978n_{4\text{s}} + 0.928n_{4\text{p}} + 1.676q = -27.500 - 1.375n_{3\text{d}} - 0.697n_{4\text{s}} - 0.748n_{4\text{p}} + 1.67575Z \quad (48)$$

$$\eta_{4\text{s},4\text{s}} = 1.853 + 0.126n_{3\text{d}} + 0.458n_{4\text{s}} + 0.430n_{4\text{p}} + 0.590q = -8.770 - 0.464n_{3\text{d}} - 0.132n_{4\text{s}} - 0.161n_{4\text{p}} + 0.59015Z \quad (49)$$

These formulas are all "first-order" formulas, whereas eqs 40 and 41 are "second-order". It is doubtful whether representation of the hardnesses to second order often would be necessary.[19]

Whenever only one valence orbital, the highest occupied orbital for subtracting electrons or lowest unoccupied orbital for adding electrons, is involved, one has eqs 25 and 26. For example, in this paper (and also in most common cases), for the fourth-row transition elements, we only consider the orbital 3d or 4s; 2p only for N, O, and F; 3p for P, S, and Cl. The Fukui indices f_i for these orbitals would be taken as 1, for other orbitals zero. Various results are listed in Tables 3–5; correlations of values derived from Tables 1 and 2 with experimental data[5] are shown in Figures 1–6. Agreement with experiment is generally good.

Table 3. Electronegativities and Hardnesses of B, C, N, O, and F (eV)

	B ($2s^2\,2p^1$)	C ($2s^2\,2p^2$)	N ($2s^2\,2p^3$)	O ($2s^2\,2p^4$)	F ($2s^2\,sp^5$)
$\chi_{2\text{p}}$ (eq 40 of text)	3.04	4.88	6.71	8.54	10.38
$\chi_{2\text{s}}$ (eq 40)	10.80	13.94	17.96	22.88	28.68
χ (eq 16)[a]	8.21	9.41	11.21	13.32	15.61
χ (eq 16)[b]	4.27	5.83	7.57	9.38	11.22
$(I + A)/2$ (TS) (eq 27)	3.70	5.38	7.21	9.05	10.88
χ_{exptl} (ref 5)	4.29	6.27	7.30	7.54	10.41
$\eta_{2\text{p},2\text{p}}$ (eq 42)	3.86	4.73	5.60	6.47	7.34
$\eta_{2\text{p},2\text{s}}$ (eq 43)	4.12	4.99	5.86	6.73	7.60
$\eta_{2\text{s},2\text{p}}$ (eq 44)	3.97	4.84	5.71	6.58	7.46
$\eta_{2\text{s},2\text{s}}$ (eq 45)	4.53	5.40	6.26	7.13	8.00
η (eq 17)[a]	4.24	4.99	5.79	6.63	7.55
η (eq 17)[b]	3.93	4.77	5.63	6.49	7.36
$(I - A)/2$ (TS) (eq 27)	3.86	4.73	5.60	6.47	7.34
η_{exptl} (ref 5)	4.01	5.0	7.23	6.08	7.01

[a] The weighting factor f_i taken to be normalized valence electron occupation number $n_i/\sum n_i$. [b] Using normalized $(n_i g_i/\chi_i)$ as Fukui index. Here n_i is the occupation number, g_i is the orbital degeneracy, and is the χ_i orbital electronegativity.

Several approximations have been made in these examples, and so there are various sources of errors: first, the spin-restricted Xα method has been used, which corresponds only to an average of valence states. A spin-polarized approach would improve the accuracy in open shell cases, e.g., for B($2s^2$-$2p^1$), C($2s^2 2p^2$), and O($2s^2 2p^4$) in Table 3 and Figure 1, P^+($3s^2$-$3p^2$), S^+($3s^2 3p^3$) in Table 4 and Figure 3, and Fe^{3+}($3d^5$) etc., in Table 5 and Figure 6, where errors are among the biggest. For instance, the spin-restricted Xα method (Schwarz α_{HF} value in ref 17 is used) gives for B $\chi_{2\text{p}} = 3.41$ eV (better than 3.04 eV in Table 3 when compared with experimental $\chi = 4.29$ eV), while the spin-unrestricted Xα method gives for B $\chi_{2\text{p}} = 4.08$ eV. For C, $\chi_{2\text{p}}$ of spin-restricted Xα method is 5.14 eV (again better than the corresponding value of 4.88 eV in Table 3), but the result by the unrestricted approach is 6.40 eV. The experimental value is 6.27 eV. For Fe^{3+}($3d^5$), the experimental value of hardness is 12.08 eV,[5] the value from eq 48 is 9.19 eV. From direct spin-restricted Xα calculations, $(I - A)/2$ is 9.38 eV if I and A are calculated by the energy differences of Fe^{4+}($3d^4$), Fe^{3+}($3d^5$), and Fe^{2+}($3d^6$) ions; it is 9.52 eV if I and A are calculated by transition states $Fe^{3.5+}$($3d^{4.5}$) and $Fe^{2.5+}$($3d^{5.5}$) [eq 27]. However, according to spin-unrestricted Xα calculations, $(I - A)/2$ is 12.50 eV if I and A are obtained from taking energy differences of Fe^{4+}($3d^{\alpha4\beta0}$) and Fe^{3+}-($3d^{\alpha5\beta0}$), Fe^{3+}($3d^{\alpha5\beta0}$) and Fe^{2+}($3d^{\alpha5\beta1}$); it is 12.51 eV if I and A are taken respectively to be the negative orbital energy of the transition state $\chi_{3\text{d}\alpha}$ for $Fe^{3.5+}$($3d^{\alpha4.5\beta0}$) and $\chi_{3\text{d}\beta}$ for $Fe^{2.5+}$-($3d^{\alpha5\beta0.5}$). In addition, energy density functional methods including correlation functionals should further improve the results.

A second error is introduced by the use of the empirical fitting formulas in Tables 1 and 2. The second-order polynomial including cross terms of valence orbital occupation numbers and atomic numbers was chosen to fit the valence orbital electronegativities of various atomic states. This produces

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(19) Fuentealba, P.; Parr, R. G. *J. Chem. Phys.* **1991**, *94*, 5559.

Table 4. Electronegativities and Hardnesses of P, S, and Cl (eV)

	P ($3s^2\ 3p^3$)	S ($3s^2\ 3p^4$)	Cl ($3s^2\ 3p^5$)	P^+ ($3s^2\ ep^2$)	S^+ ($3s^2\ 3p^3$)	Cl^+ ($3s^2\ 3p^4$)
χ_{3p}	4.58	6.27	7.95	13.25	15.84	18.42
χ_{exptl}	5.62	6.22	8.30	15.09	16.88	18.39
$\eta_{3p,3p}$	3.88	4.32	4.77	4.80	5.24	5.68
η_{exptl}	4.88	4.14	4.68	4.61	6.52	5.42
I [eq 10 of text]	8.77	10.90	13.03	18.36	21.38	24.41
I_{exptl}	10.48	10.38	13.01	19.70	23.40	23.80
A [eq 10 of text]	1.01	2.25	3.49	8.77	10.90	13.03
A_{exptl}	0.75	2.08	3.62	10.48	10.36	13.01
$(I + A)/2$ (TS [eq 27 of text]	4.81	6.50	8.18	13.48	16.06	18.64
$(I + A)/2$ [eq 10 of text]	4.87	6.57	8.26	13.56	16.14	18.72
$(I - A)/2$ [eq 10 or 27 of text]	3.88	4.32	4.77	4.80	5.24	5.69

Table 5. Electronegativities and Hardnesses of the Fourth-Row Elements[a] (eV)

									Cu		
d^ns^2	(Sc)	(Ti)	(V)	(Cr)	Mn	Fe	Co	(Ni)	$d^{10}s^1$	d^9s^2	Zn
χ_{4s}	4.04	4.18	4.33	3.55	4.62	4.77	4.91	5.06	3.91	5.21	5.35
χ_{expl}	3.34	3.45	3.6	3.72	3.72	4.06	4.3	4.40	4.48		4.45
η_{4s4s}	2.90	3.03	3.15	2.94	3.40	3.52	3.65	3.78	3.57	3.90	4.03
η_{expl}	3.20	3.37	3.1	3.06	3.72	3.81	3.6	3.25	3.25		4.94

$3d^n$	(Sc^{2+})	(Ti^{2+})	(V^{2+})	(Cr^{2+})	Mn^{2+}	Fe^{2+}	Co^{2+}	(Ni^{2+})	Cu^{2+}	Zn^{2+}
χ_{3d}	17.45	19.20	20.89	22.51	24.1	25.5	26.9	28.1	29.5	30.7
χ_{expl}	18.78	20.5	22.0	23.7	24.6	23.4	25.3	26.7	28.6	28.8
η_{3d3d}	6.3	6.6	6.9	7.22	7.5	7.8	8.12	8.42	8.7	9.0
η_{expl}	5.98	6.9	7.3	7.23	9.0	7.2	8.22	8.50	8.3	10.9

$3d^n$	(Ti^{3+})	(V^{3+})	(Cr^{3+})	Mn^{3+}	Fe^{3+}	Co^{3+}	(Ni^{3+})	Co^+ d^7s^1		Cu^+ d^{10}
χ_{3d}	33.81	36.10	38.32	40.46	42.54	44.54	46.48	12.36	(χ_{4s})	13.46
χ_{expl}	35.38	38.01	40.0	42.4	42.73	42.4	45.0	12.46		14.01
η_{3d3d}	7.99	8.29	8.59	8.89	9.19	9.49	9.79	3.79	(η_{ss})	7.34
η_{expl}	7.89	8.70	9.1	8.8	12.08	8.9	9.9	4.60		6.28

[a] Elements in parentheses not included when fitting formulas of electronegativities. Experimental values are from ref 5.

additional fitting errors, e.g., for the cases of B and C mentioned above, of which no data were used to obtain the fitting formulas. Another example is N. Its experimental electronegativity value is 7.3 eV (Table 3), the calculated value from the fitting formula (the third column in Table 1 for χ_{2p}) is 6.71 eV. Nevertheless, the direct spin-restricted Xα method calculation gives the result of 6.98 eV for the electronegativity of atomic nitrogen 2p orbitals. It can be seen in Figures 1–6 and Tables 3–5 that erorrs for hardness are seemingly larger than for electronegativity. This is because hardness formulas [eqs 42–49] are linear functions of valence orbital occupation numbers and atomic number or atomic charge. Errors are caused by taking partial derivatives of approximate analytical functions [eqs 40 and 41]. Furthermore, when determining eqs 40 and 41, certain atoms were not included, for example, B and C and those elements in parentheses in Table 5. When one interpolates or extrapolates the data, errors are unavoidable.

Another error is associated with the choices of Fukui orbital indices f_i in eqs 16–18. In the calculations here reported, we simply assume one frontier orbital is involved—the HOMO atomic orbital. It would be a reasonable alternative approximation to use $f_{HOMO} = {}^1/_2$ and $f_{LUMO} = {}^1/_2$. In many cases, the results will still be the same. For example, B $2s^22p^1$, 2p orbital is the HOMO but also the LUMO. However, for fully filled subshell cases, the results of these two choices of Fukui indices are different. Consider another example, the boron ion B^+ with ionic configuration of $2s^22p^0$. Calculated according to eq 40 and Table 1, its $\chi_{2s} = 20.56$ eV, $\chi_{2p} = 12.77$ eV. Hence by eq 16, the atomic electronegativity is ${}^1/_2\,\chi_{2s} + {}^1/_2\,\chi_{2p} = 16.66$ eV. The corresponding experimental value of $(I + A)/2$ is 16.73 eV.[20] Differences between the two choices are more common for transition elements. There are also other reasonable choices of Fukui indices. Table 3 gives out two other choices for Fukui orbital indices, one of which, a, may lead to Allen's definition for electronegativity,[9,10] f_i proportional to occupation numbers for valence orbitals, 0 for inner shell orbitals. We do not elaborate here. The arguments in ref 2 are relevant in this connection.

From Tables 3 to 5, it can be seen that the valence orbital χ and η change considerably as the electronic configuration changes, especially when the total charge of an atom changes. To calculate the actual total χ and η of the atom, the key problem is to determine the orbitals which have great population changes and the values of their population changes relative to the change of total number of electrons in the atom; namely, the Fukui reactivity indices f_i for orbitals, $\Delta n_i/\Delta N$ in eqs 16 and 17. These are in general different for adding and subtracting electrons. Usually only a few valence orbitals need to be considered. If only one orbital is involved, the last approximate equality in eq 26 would be "exact" since the empirical fitting formulas for orbital hardnesses are first order in orbital population no matter whether "I" and "A" are calculated from the exact eq 10 or from the approximate eq 27 of the transition state theory. One may find that $\eta_{ij} \approx \eta_{ji}$ [not the exact identity of eq 19] since the formulas used here for hardnesses are not exact.

In ending this section, we show a way of calculating Fukui indices, using eqs 20–22 and the diagonalized valence orbital hardness matrix of the nitrogen atom. According to Table 3 [or eqs 42–45], the hardness matrix for N($2s^2\ 2p^3$) is,

$$\begin{pmatrix} \eta_{2p,2p} & \eta_{2p,2s} \\ \eta_{2s,2p} & \eta_{2s,2s} \end{pmatrix} = \begin{pmatrix} 5.60 & 5.86 \\ 5.71 & 6.26 \end{pmatrix}$$

After a unitary transformation, the above matrix becomes,

$$[\eta^{D}_{ij}] = \begin{pmatrix} 0.061 & 0 \\ 0 & 11.80 \end{pmatrix}$$

which has the following inverse matrix,

$$[s^{D}_{ij}] = \begin{pmatrix} 8.24 & 0 \\ 0 & 0.042 \end{pmatrix}$$

by the use of eq 22. The Fukui indices may thus be obtained by eqs 20 and 21 as $f_{2p} = 0.995$ and $f_{2s} = 0.005$. This supports the argument of choosing the highest occupied orbital only. Calculations on other atoms in Table 3 give similar results.

V. Discussion

We here have demonstrated how for a given set of orbital populations in a system, which may be fractional, one can obtain orbital electronegativities and hardnesses. Different sets of

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(20) Lide, D. R., *et al.*, Eds. *Handbook of Chemistry and Physics*, 73rd ed.; CRC Press Inc.; Ann Arbor, 1992–1993.

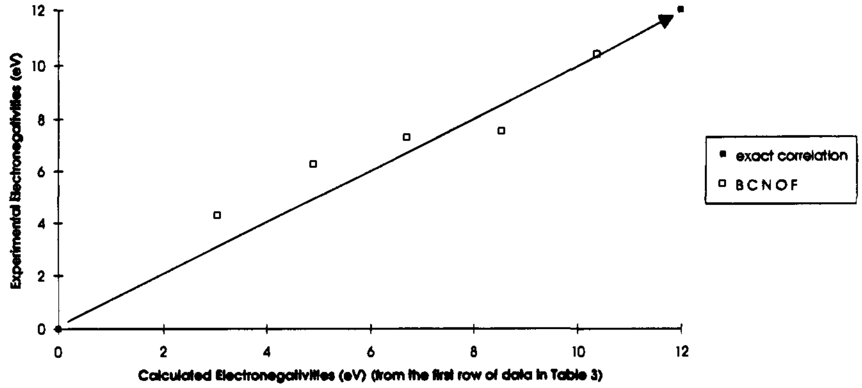

Figure 1. Calculated and experimental electronegativities for B, C, N, O, F.

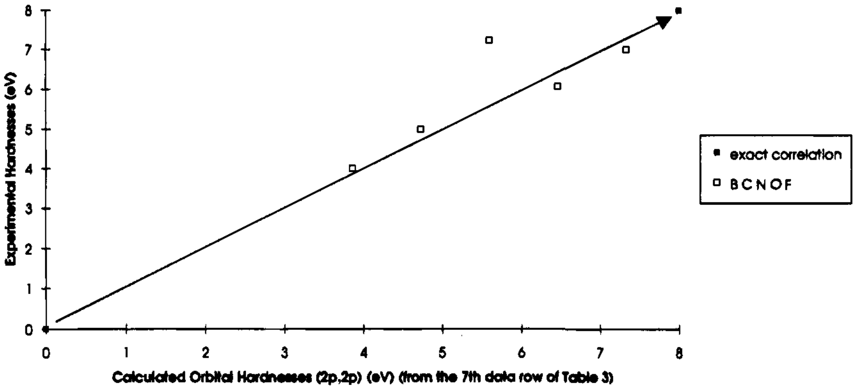

Figure 2. Calculated and experimental hardnesses for B, C, N, O, F.

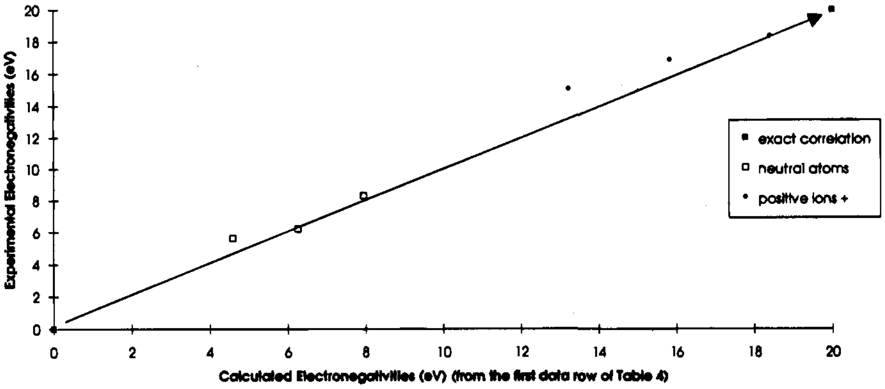

Figure 3. Calculated and experimental electronegativities for P, S, Cl.

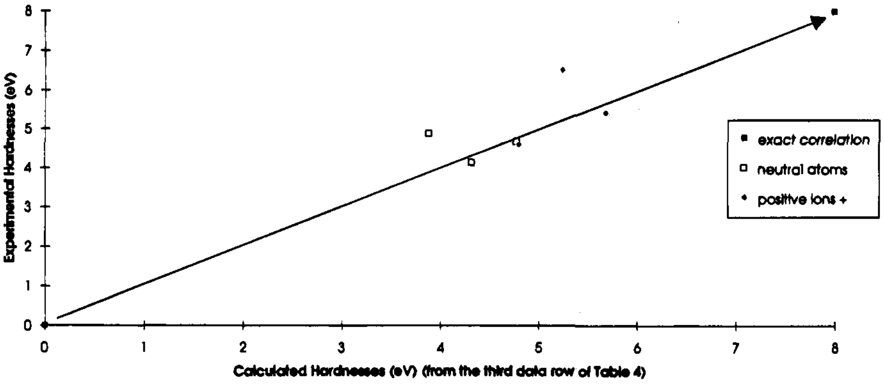

Figure 4. Calculated and experimental hardnesses for P, S, Cl.

occupation numbers reflect the different effects on the system of different environments.

Our results could be further improved by using higher order fitting polynomials for $\{\chi_i\}$. Hardness values of higher accuracy would thus be achieved since hardness is the second derivative of energy. Still further, spin-unrestricted calculations may give more accurate results,[16] especially for atoms like nitrogen and oxygen, having open shells. One should go beyond the Xα method to get better results. For heavy atoms like the lanthanoids, relativistic calculations are needed for high ac-

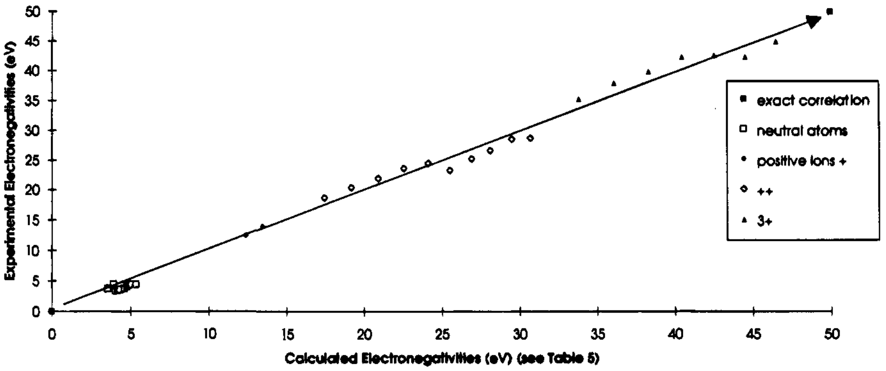

Figure 5. Calculated and experimental electronegativities for Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn.

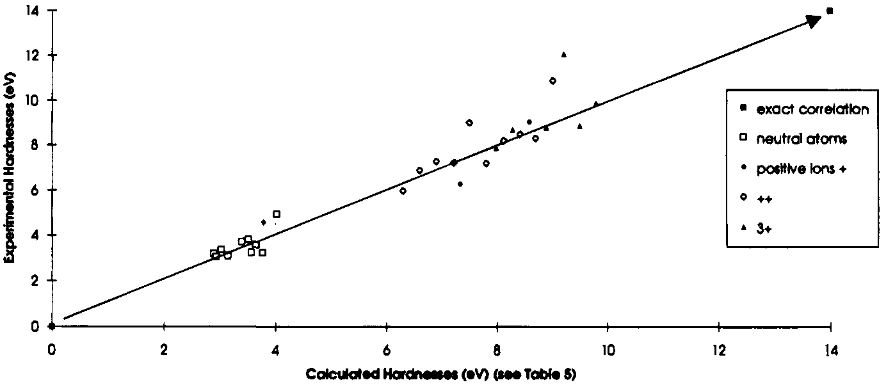

Figure 6. Calculated and experimental hardnesses for Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn.

curacy. Each of these further measures will increase the amount of computational work.

(i) Reconciliation With the Electronegativity Equalization Principle. Consider an electronic system in a ground state with a certain number of electrons N_0. The chemical potential μ of the system is

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{v,N=N_0} = \left[\frac{\delta E}{\delta \rho}\right]_v \qquad (50)$$

This is a global constant through the system. At the ground state, the energy functional derivative with respect to the electron density should be equal everywhere in the system. Electronegativity has been equalized. Let the system be divided arbitrarily into many subsystems $\{i\}$, each subsystem i with the number of electrons n_i. For fixed external potential v, the differential energy change of the total system associated with infinitesimal change of N is

$$\mathrm{d}E = \mu\,\mathrm{d}N = \mu\sum_i \mathrm{d}n_i = \sum_i \mu\,\mathrm{d}n_i = \sum_i (\partial E/\partial n_i)_j\,\mathrm{d}n_i \qquad (51)$$

where

$$\mu_i = \partial E/\partial n_i = \mu \text{ (for all } i) \qquad (52)$$

This result does not conflict with other discussions in this paper, for here the system is confined to the ground state, and the total number of electrons is a constant. Thus, due to a small perturbation of the number of electrons in any subsystem, there will be a charge relocation among all the subsystems in order for the system to remain in the ground state. The $\{n_i\}$ are dependent on each other.[21] In such a case there is in general an ambiguity for the partial derivative $(\partial E/\partial n_i)_v$. Suppose $E(N)$ (for fixed $v(\vec{r})$) is a well-defined function, which may be explicitly written down as $E(\{n_i\})$. Then by the use of a simple approach described elsewhere,[14] we have eq 51 and also a sum condition for the $\{n_i\}$, namely,

$$\sum_i n_i - N_0 = f(n_i) = 0 \qquad (53)$$

Indeed, often there are other relations among the $\{n_i\}$,

$$h(\{n_i\}) = 0 \qquad (54)$$

Therefore, one has

$$\mathrm{d}f = \sum_i (\partial f/\partial n_i)_j\,\mathrm{d}n_i = 0 \qquad (55)$$

and

$$\mathrm{d}h = \sum_i (\partial h/\partial n_i)_j\,\mathrm{d}n_i = 0 \qquad (56)$$

Multiplying df and dh by arbitrary functions $g(\{n_i\})$ and $c(\{n_i\})$, respectively, and adding to eq 51, we find

$$\mathrm{d}E = \sum\nolimits_i[(\partial E/\partial n_i)_j^0 + g(\{n_i\})(\partial f/\partial n_i)_j + c(\{n_i\})(\partial h/\partial n_i)_j]\,\mathrm{d}n_i \qquad (57)$$

where $(\partial E/\partial n_i)_j^0$ is the analytic partial derivative calculated from the function $E(\{n_i\})$. Thus

$$(\partial E/\partial n_i)_j = (\partial E/\partial n_i)_j^0 + g(\{n_i\})(\partial f/\partial n_i)_j + c(\{n_i\})(\partial h/\partial n_i)_j = (\partial E/\partial n_i)_j^0 + g(\{n_i\}) + c(\{n_i\})(\partial h/\partial n_i)_j \qquad (58)$$

where the arbitrary multipliers g and c depend on the model one may choose. For instance, one can always select c so that all $(\partial E/\partial n_i)_j$ are equal to a same constant μ as in eq 52.

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(21) See also: Politzer, P.; Weinstein, H. *J. Chem. Phys.* **1979**, *71*, 4218.

This situation may be compared with a multicomponent thermodynamic system in equilibrium having particle-permeable "walls" between different phases. Another important example is the set of natural spin orbitals for a ground-state system with constant total number of electrons,[4] where one finds

$$\left(\frac{\partial E}{\partial n_i}\right)_{\varphi_i, n_j} = \mu \text{ [for all orbitals } i \ (0 < n_i < 1)] \qquad (59)$$

The above result, eq 59, is obtained from the total energy minimization through constrained variations of both orbital set $\{\varphi_i\}$ and occupation number $\{n_i\}$.

In this paper, we have considered Kohn–Sham orbitals where the occupation numbers of the various orbitals are independent; N is a variable and not a constant N_0. Kohn–Sham orbitals result from the variation of total energy with respect to the set of orbitals $\{\psi_i\}$ only.

(ii) Simple Illustrative Applications. The Maximum Hardness Principle. (1) For illustrative purpose, consider a simple diatomic molecule NO under fixed external potential as a part of a reaction system from an electronically dynamic point of view. Its experimental electronegativity from gas phase $(I + A)/2$ is 4.645 eV.[20] It is calculated at the experimental bond length of 1.1506 Å[20] by the spin-unrestricted Xα method, using $\alpha = 0.7$ and the numerical atomic SCF minimal basis. Its HOMO is half-filled degenerate α orbitals 2e with orbital energy of −4.92 eV, which is also the LUMO. Hence the 2e orbital electronegativity is 4.92 eV. By setting $f_{\text{HOMO}} = {}^1/_2$ and $f_{\text{LUMO}} = {}^1/_2$, we get the molecular electronegativity $\chi = 4.92$ eV, i.e., $(\chi_{\text{HOMO}} + \chi_{\text{LUMO}})/2$, the negative of the Fermi energy. [In comparison, for Hartree–Fock orbitals, one has $\chi \approx -(\epsilon_{\text{HOMO}} + \epsilon_{\text{LUMO}})/2$ and $\eta \approx (\epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}})/2$, since $I \approx -\epsilon_{\text{HOMO}}$, $A \approx -\epsilon_{\text{LUMO}}$]. The atomic composition of HOMO (LUMO) orbital 2e(α) of NO is 62.4% N 2p and 37.6% O 2p. This hints $f_{\text{N2p}} \approx 0.624$ and $f_{\text{O2p}} \approx 0.376$. To verify this, we have done Xα calculations with the same external potential to fractionally charged molecules $\text{NO}^{+0.1}$ and $\text{NO}^{-0.1}$. We find when going from a neutral NO molecule to a slightly positively charged molecule $\text{NO}^{+0.1}$, $f_{\text{N2p}} = (\mathrm{d}n_{\text{N2p}}/\mathrm{d}N)_v = 0.650$ and $f_{\text{O2p}} = (\mathrm{d}n_{\text{O2p}}/\mathrm{d}N)_v = 0.465$ [$f_{\text{N}} = (\mathrm{d}n_{\text{N}}/\mathrm{d}N)_v = 0.591$ and $f_{\text{O}} = (\mathrm{d}n_{\text{O}}/\mathrm{d}N)_v = 0.409$] by Milliken population analysis; when going in a different direction from neutral NO molecule to slightly negatively charged molecule $\text{NO}^{-0.1}$, $f_{\text{N2p}} = (\mathrm{d}n_{\text{N2p}}/\mathrm{d}N)_v = 0.649$ and $f_{\text{O2p}} = (\mathrm{d}n_{\text{O2p}}/\mathrm{d}N)_v = 0.464$ [$f_{\text{N}} = (\mathrm{d}n_{\text{N}}/\mathrm{d}N)_v = 0.591$ and $f_{\text{O}} = (\mathrm{d}n_{\text{O}}/\mathrm{d}N)_v = 0.409$], almost the same! That should be the case and understandable. Then can we construct molecular χ or η from previously obtained data for free spherical ions? When a nitrogen atom and an oxygen atom come close to each other to form a NO molecule, the external potential to each original free atom is changed. The original spherically symmetric field is broken, which causes great changes in atomic orbitals. For instance, 2p atomic orbitals of N and O are split, distributed among several frontier molecular orbitals of NO. By the fixed external potential atomic orbital data discussed above in this paper, only a rough average value is obtainable, which is not accurate and useless. Without considering the effect of the change of external potential, one cannot satisfactorily answer the above question. More work needs to be done. At the moment, the quantitative solution is still to be given through MO calculations. The atomic electronegativity—*frontier* atomic orbital electronegativity—*in a molecule* may be considered to have been equalized to give the molecular electronegativity—the *frontier* molecular orbital electronegativity.

(2) Here we describe a rough model for illustrating potential applications of the formulas and data given in this paper, neglecting changes of external potentials, to study the formation of chemical bonds between heteroatoms. We consider iron and sulfur atoms to first-order approximation located infinitely far away from each other, nevertheless undergoing electron interchange leading to chemical potential equalization. We suppose that only one frontier orbital (possibly degenerate) for each atom is involved, i.e., 3p orbital for S, and for Fe, 3d for addition of electrons, 4s for subtraction. Through electronegativity equalization—equating χ_{4s} (Fe $3d^6\,4s^{2-q}$) to χ_{3p} (S $3s^2\,3p^{4+q}$), we get charge distribution of the FeS moleule, $\text{Fe}^{+0.095}\text{S}^{-0.095}$ ($q = 0.095$), from Tables 1 and 2. Furthermore, we find at this charge equilibrated state, the hardness of this molecule is larger than the hardness for all other nonequilibrium charge distributions! (See Table 6). General maximum hardness principles will be discussed elsewhere.[22]

Table 6. Molecular Hardnesses of FeS for Different Charge Distributions (eV)

	$\text{Fe}^{-0.1}\text{S}^{+0.1}$	Fe^0S^0	$\text{Fe}^{.095}\text{S}^{-.095}$ (equil)	$\text{Fe}^{+0.1}\text{S}^{-0.1}$	$\text{Fe}^{+0.2}\text{S}^{-0.2}$	Fe^+S^-
η	2.24	3.05	3.37	3.36	2.95	~0

When calculating molecular hardnesses here, we use the finite-difference approximation of eq 26 and make a simplification,

$$\eta = \frac{I_{\min} - A_{\max}}{2} \qquad (60)$$

where $I_{\min}$ is the minimum value of the ionization potentials of the atoms in the molecule and $A_{\max}$ the maximum electron affinity of those atoms. That is, we choose the reaction with the lowest possible energy increase or maximum energy lowering without considering the relaxation of ionized molecules. More completely, the positive and negative molecular ion states could also be subject to charge equilibration, and then their energy relative to the neutral molecule could be calculated by integration of eq 10.

For example, we calculate the ionization energy of iron atom *in the molecule* $\text{Fe}^{+0.095}\text{S}^{-0.095}$ by integration of eq 10 and the use of Table 2:

$$I_{\text{Fe}} = \int_{0.095}^{1.905} \chi_{4s}(\text{Fe}[3d^6 4s^{n_{4s}}])\,\mathrm{d}n_{4s} = 9.03 \text{ eV} \qquad (61)$$

or via transition state theory [eq 27],

$$I_{\text{Fe}} = \chi_{4s}(\text{TS}) = \chi_{4s}(\text{Fe}[3d^6 4s^{1.405}]) = 9.02 \text{ eV} \qquad (62)$$

In the same way, we find the ionization potential of the sulfur atom in the molecule:

$$I_{\text{s}} = \int_{3.095}^{4.095} \chi_{3p}(\text{S}[3s^2 3p^{n_{3p}}])\,\mathrm{d}n_{3p} = 9.99 \text{ eV} \qquad (63)$$

or by eq 27,

$$I_{\text{s}} = \chi_{3p}(\text{TS}) = \chi_{3p}(\text{S}[3s^2 3p^{3.595}]) = 9.91 \text{ eV} \qquad (64)$$

We then find, approximately, $I_{\text{Fe}} = 9.03$ eV as the ionization potential of the molecule. Similarly the electron affinity of the atom iron in the molecule is

$$A_{\text{Fe}} = \int_6^7 \chi_{3d}(\text{Fe}[3d^{n_{3d}} 4s^{1.905}])\,\mathrm{d}n_{3d} = 2.30 \text{ eV} \qquad (65)$$

or by the transition state formula [eq 27],

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(22) Liu, G. H.; Parr, R. G. In preparation.

$$A_{\mathrm{Fe}} = \chi_{3\mathrm{d}}(\mathrm{TS}) = \chi_{3\mathrm{d}}(\mathrm{Fe}[3\mathrm{d}^{6.5}4\mathrm{s}^{1.905}]) = 2.18\ \mathrm{eV} \quad (66)$$

The electron affinity of *S* in the molecule is

$$A_{\mathrm{s}} = \int_{4.095}^{5.095} \chi_{3\mathrm{p}}(\mathrm{S}[3\mathrm{s}^2 3\mathrm{p}^{n_{3\mathrm{p}}}])\,\mathrm{d}n_{3\mathrm{p}} = 1.51\ \mathrm{eV} \quad (67)$$

or by eq 27,

$$A_{\mathrm{s}} = \chi_{3\mathrm{p}}(\mathrm{TS}) = \chi_{3\mathrm{p}}(\mathrm{S}[3\mathrm{s}^2 3\mathrm{p}^{4.595}]) = 1.43\ \mathrm{eV} \quad (68)$$

Taking $A_{\mathrm{Fe}} = 2.30$ eV to be the electron affinity of the molecule, the hardness of the molecule is 3.37 eV.

Similarly, we acquire hardness values of the molecule for several other charge distributions and find the equilibrium one resulting from electronegativity equalization to have a maximum hardness value. See Table 6.

Following this simple scheme, we may also study other molecules, e.g., achieving equilibrium charge distributions $\mathrm{Fe}^{+0.192}\mathrm{O}^{-0.192}$, $\mathrm{Fe}^{+0.269}\mathrm{Cl}_2{}^{-0.134}$, $\mathrm{Fe}^{+0.309}\mathrm{Cl}_3{}^{-0.103}$, etc. The molecular hardness values are 3.34, 4.00, and 2.40 eV, respectively. The hardness differences between composite atoms are 2.53, 1.09, and 1.11 eV, and 0.70 eV for $\mathrm{Fe}^{+0.095}\mathrm{S}^{-0.095}$. The chemical bond between two atoms with greater difference of hardnesses as between oxygen and iron should have less covalent nature.

The charges obtained by the foregoing method are smaller than intuitively expected. This is probably because of neglect of changes of external potential. By considering this factor, that is, by bringing atoms closer, into the actual range of chemical bond interactions, we may obtain new molecular charge distributions through electronegativity equalization, using Slater-type orbitals to calculate interaction potential energy[23,24] (or by simple bond charge model[1]) for a particular geometry. The Slater orbital exponents themselves are also functions of orbital populations;[7,8] this then is a self-consistent process. The relative energies for different geometries are calculable; hence the equilibrium geometry may be predicted in principle by a simple semiempirical method.

(iii) Reconciliation With the Electronegativity Ideas of L. C. Allen. Allen has introduced as an electronegativity measure the average valence-electron ionization potential, the quantity[9,10]

$$\chi_{\mathrm{spect}} = -\frac{\sum\limits_{\mathrm{valence}} n_i \epsilon_i}{\sum n_i} \quad (69)$$

This is a useful index, as Allen has shown.

Note that eq 69 is a special case of our eq 16, the case for which the change d*N* is equally partitioned among all valence electrons. Accordingly, Allen's formula is correct in an average sense. Different situations correspond to uneven partitioning, however, which is the essence of the old valence-state ideas of Pauling,[25] Mulliken,[3] and Moffitt.[26] One should only view eq 69 as an average electronegativity measure.

Allen furthermore does not accept the principle of electronegativity equalization.[10] This he cannot do for the reason that he does not like the idea that an atom in a molecule can bear a nonintegral number of electrons. We do accept that idea. Chemical potential (electronegativity) equalization follows.

In ref 10, Allen gives five arguments against electronegativity equalization. Replies are as follows: (1) That μ changes as it equalizes does not obliterate the identity of atoms. It only means that the atom is changed from the free atom, in its charge, in the external potential in which its electrons move, and in that it has become an open system. (2) We do not believe that there is any "untenably narrow" element in our discussion. It is quite the reverse! (3) We have never said or meant to imply that "only the charge" characterizes the atom in the molecule. Emphatically not! This does not preclude examining the effects of change in charge (as in the present paper). Works of Nalewajski are particularly relevant in this connection.[11] (4) It is no surprise that Allen's index does not display full equalization characteristics. It should not. (5) The "intrinsic force" toward equalization is, of course, total energy minimization[27] or, equivalently, chemical potential equalization. For an early discussion of how Mulliken electronegativity differences indeed are zeroed on molecular formation, see the 1958 paper by Parks and Parr.[27] The variational principle does it.

It is not easy to quantify the electronegativity of an atom in a molecule. Hopefully it differs to second order from isolated atomic values, more or less, and optimism to this effect appears to be justified from the successful long-time use of properties of "the atom" in discussing molecular properties. Difficulties in this aspect of the subject are real, but they should not be permitted to obscure the validity of the fundamental concepts involved.

Finally, we call attention to the original beautiful argument of Mulliken,[3] given in the text above following eq 3. Charge transfer is driven by *relative* electron attracting powers. Equation 69 does not define the right index when the ϵ_i are ionization potentials. Equation 16, in contrast, does.

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