

Electronegativity and Hardness of Disjoint and Transferable Molecular Fragments

Ludwik Komorowski,^{*,†} Susan L. Boyd,[‡] and Russell J. Boyd[§]

Institute of Physical and Theoretical Chemistry, Technical University of Wrocław, Wyb. Wyspiańskiego 27, 50-370 Wrocław, Poland, Department of Chemistry, Mount Saint Vincent University, Halifax, Nova Scotia, Canada B3M 2J6, and Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3

Received: July 17, 1995; In Final Form: October 24, 1995[⊗]

Approximate Fukui indices have been derived from the atomic volumes of molecules as calculated within the framework of Bader's atoms-in-molecules theory. Parameters of the bond critical points $\{\nabla\rho(\mathbf{r}_c)\mathbf{n} = 0\}$ have been explored in calculating the hardness (η) and electronegativity (χ) of a selection of typical chemical groups, widely considered as transferable entities. Resulting η and χ indices demonstrate strong dependence on the nature of neighboring atoms and on the bond system vicinal to the group; however, they are not directly related to the group charges.

Introduction

The electron density in a molecule is of special interest since properties of the molecular system should find their ultimate explanation in a description of the system's electrons. Two remarkable approaches have been developed to quantify electron density. The first is due to Parr and co-workers, who applied density functional theory (DFT) to chemical systems and thereby offered a firm theoretical foundation for concepts such as electronegativity and hardness.^{1,2} The second approach, that of Bader *et al.*, is quantum topology; its major achievement is the general and fundamental definition of a quantum open system as "atom-in-molecule".^{3,4} There has been little overlap between these two mainstream efforts, even though they obviously offer complementary approaches: individual atoms are vital and distinguishable parts of a molecule, and a reasonable and theoretically sound description for the molecule and such properties as electronegativity and hardness is needed. The crucial point of the debate is the atom itself: DFT offers a picture of overlapping atoms within the molecule, whereas quantum topology divides the molecular space into fragments of nonoverlapping atomic basins.^{5,6} Combining the two perspectives obviously requires a theoretical approach. In this work we analyze properties of topological atoms, defined as quantum open systems according to Bader,⁷ while the properties in question are those derived by DFT, namely, electronegativity and chemical hardness.

The geometrical nature of atoms is defined by quantum topology.⁴ The dividing surface of an atom is given by the zero flux condition for electron density $\rho(\mathbf{r}_c)$:

$$\nabla\rho(\mathbf{r}_c)\cdot\mathbf{n} = 0 \quad (1)$$

This boundary condition leads to bonded atoms of a nonspherical shape, with their outermost surface defined by a near zero (typically 0.001 au) electron density surface. Consequently, volume (V) and charge (q) are readily determined for topological atoms. The resulting molecular volumes have been shown to parallel experimental data.⁸ Population analysis, involving integration of the electron density within the atom limits, gives results reasonably close to atomic charges from other population analyses.⁹ The overall energy of a molecule can be divided

into increments from the component open systems.³ Dividing the space into atomic regions involves cutting the bonds (bond paths) at specific points called bond critical points, where $\nabla\rho(\mathbf{r}_c)\mathbf{n} = 0$. This procedure defines a new kind of atomic radius. Properties of the bond critical point (namely, its position and electron density) reflect bond polarity and have been effectively used to produce an electronegativity scale for atoms and groups.^{10,11} The electron density at the bond critical point $\rho(\mathbf{r}_c)$ is also related to the bond length.^{12,13} Similar relationships between the electron density at the bond critical point and the bond energy have also been reported.¹⁴ The most appealing feature of topological atoms, often observed for groups, is their transferability: molecular fragments have been shown to retain their volume, charge, shape, and polarizability virtually unchanged in many molecules.⁸ This property strongly supports the concept of topological atoms, as it reflects the chemical identity of groups, a well-known and widely explored concept of chemists.

DFT has focused on local properties of the electron density within a molecule and on global ones for the entire system.¹⁵ The most significant result of this approach was the identification of Mulliken absolute electronegativity (χ) and chemical hardness (η) by Parr and Pearson:¹⁶

$$\chi = 1/2(I + A); \quad \eta = 1/2(I - A) \quad (2)$$

(I and A are the empirical ionization energy and electron affinity, respectively.) Rigorous DFT does not allow for distinguishing atoms in the system; however, a quantum chemical study based on a DFT formalism has been developed to describe the properties of bonded atoms without actually defining atoms in real space and is very much in the spirit of the Mulliken population analysis.¹⁷ Thus, if the population of an atom in the molecule M is given by N_A , then atomic electronegativity, hardness, and the Fukui index are, respectively,

$$\chi_A = -(\partial E/\partial N_A)_V \quad \eta_A = (\partial\chi_M/\partial N_A)_V \quad K_A = (\partial N_A/\partial N)_V \quad (3)$$

where V is the external potential.

These properties are related to the molecular electronegativity (χ_M) and hardness (η_M) by simple formulas:

$$\chi_M = \sum K_A \chi_A \quad \eta_M = \sum K_A \eta_A \quad (4)$$

(Electronegativity equalization is not implied, though it may be possible, depending on the actual calculation procedure.) The

[†] Technical University of Wrocław.

[‡] Mount Saint Vincent University.

[§] Dalhousie University.

[⊗] Abstract published in *Advance ACS Abstracts*, January 15, 1996.

analysis also includes the atomic softness indices (S_A) and their relationship to the global molecular softness ($S_M = 1/\eta_M$), as well as to atomic hardness:

$$S_A = K_A S_M \quad (5)$$

$$\sum S_A = S_M \quad \sum S_A \eta_A = 1 \quad (6)$$

The above formalism has been successfully applied to describe chemical groups and their substituent effects by means of atomic hardness and electronegativity parameters.¹⁸ Among numerous relationships, that between hardness (or softness) of the system and its geometry is particularly important. Gasquez and Ortiz proved¹⁹ that the global hardness parameter and the radius R for the free atom are inversely related:

$$1/S = \eta \propto 1/R \quad (7)$$

This has been confirmed by several other studies.^{1,20,21} Such findings provide grounds for analyzing atoms-in-molecules in a similar manner.

Geometrically Based Hardness Parameters

The topological nature of atoms defined by their boundaries makes it necessary to first consider the property of softness (inverse hardness) given by eq 7. Since atoms have nonspherical shapes, we assume for the softness of a bonded atom (S_A) of volume V_A that

$$S_A \propto (V_A)^{1/3} \quad (8)$$

Equations 5 and 6 then readily give

$$K_A = \frac{(V_A)^{1/3}}{\sum (V_A)^{1/3}} \quad (9)$$

This astonishingly simple relationship is valid as long as the topological atoms have well-defined volumes. Note that the atom would include the effect of any nonbonding electron pairs or π -electrons in the form of an increased contribution to its volume (or that of its group), which would result in a contribution to the atom's (or group's) soft character.

As discussed above, the global hardness of a given molecule is readily available through its relationship to ionization energy and electron affinity, eq 2. Decomposing global hardness η into contributions from atoms becomes crucial since only one equation (eq 4) is available. The very reasonable *fundamentum divisionis* is again suggested by the geometry. Topological atoms have well-defined critical points that divide each bond into distances from the bonded nuclei. The position of the bond critical point then yields a ratio of atomic radii for the given bonding situation. Thus, we assume, based on eq 7, that

$$\eta_A R_{A,c} = \eta_B R_{B,c} \quad (10)$$

where $R_{A,c}$ and $R_{B,c}$ denote the distance from atoms A and B, respectively, to the critical point (c). This is equivalent to assuming that the position of the critical point is determined by the inverse ratio of the hardness of the bonded atoms. Equation 10 may be written for every bond in the molecule, thus providing the set of additional equations necessary to solve eq 11 for individual atomic hardness parameters, η_A .

$$^{1/2}(I - A) = \sum K_A \eta_A \quad (11)$$

Geometrically Based Atomic Electronegativities

Atomic electronegativities within the topological model may be explored by another route. The bond charge model (BCM)

of the chemical bond, first proposed by Borkman and Parr,^{22,23} has recently been given a novel justification.²⁴ The model has also been shown to be consistent with the electronegativity and hardness concepts in DFT (see ref 1, p 233). Its focal point is the arbitrary assumption that the energy of a diatomic molecule may be expressed as a simple function of bond length R and bond charge q residing in the midpoint of the bond. While R is an independent variable, q is a parameter of the BCM model. Bader's concept of a molecule divided into disjoint atomic basins, and the available parameters of the resultant bond critical point [$R_{A,c}$, $\rho(\mathbf{r}_c)$] allow for extension of the BCM. The charge of the atom q_c and the corresponding distance of the nucleus from the critical point of the bond (R_c) denote the independent variables for an atomic basin in the diatomic molecule; then according to the BCM model we have $q_c = ^{1/2}\rho(\mathbf{r}_c)$. Since energies of disjoint atomic basins are additive,⁹ eq 3 and the BCM suggest that the electronegativity of atom A may be expressed as

$$\chi_A = -(\partial E/\partial N_A)_M = -(\partial E_A/\partial N_A)_{M,R_c} = (\partial E_A/\partial q_c)_{M,R_c} \quad (12)$$

Here, M represents the collection of all possible variables within the molecule, including the position of interatomic surfaces given by eq 1 and, specifically, the positions of the bond critical points around the atom in question. Such a definition is consistent with the concept of an atom as a well-defined, and possibly transferable, part of space. (The derivative given by eq 12 may not, however, be identical to the DFT value from eq 3, $(\partial E/\partial N_A)_{\nu}$ since an additional constraint is present; i.e., the atomic basin does not change: therefore, χ_A in eq 12 represents the electronegativity of a rigid topological atom and is not necessarily subject to electronegativity equalization.) From the energy form of the BCM we now get an expression for electronegativity in a system at equilibrium.¹ The molecule is divided into atomic basins only, while the bond charge q_c at critical point c is split into equal contributions from vicinal atoms. The BCM energy form, $W_A(R_c, q_c)$, may be written for each atomic basin separately. Thus,

$$W_A(R_c, q_c) = E_A(q_c) - Cq_c^2/R_c + Dq_c/R_c^2 \quad (13)$$

where $E_A(q_c)$ contains all internal energy variables of a basin, while the remaining two terms represent contributions from the bond charge of a chosen bond. Since W_A must be at a minimum with respect to q_c , we obtain for a system in equilibrium

$$\chi_A = -D/R_c^2 + 2q_c C/R_c \quad (14)$$

where D and C are constants. Electronegativity of an atom may also be expressed in the more general traditional functional form:¹

$$\chi_A = \chi_A^\circ + 2\eta_A q_c \quad (15)$$

where χ_A° is the electronegativity at zero charge, i.e., for a free atom. From eqs 14 and 15 we therefore obtain for the atoms-in-molecules model

$$\chi_{A(M)}^\circ = -D/R_c^2 \quad (16)$$

$$\eta_{A(M)} = C/R_c \quad (17)$$

The subscript (M) emphasizes that in general χ_A , χ_A° , and η_A are functions of R_c and of other variables within the molecule. The expression for hardness, eq 17, has already been implied by eq 10 and explored in relating the hardness parameters of vicinal atomic basins. Equation 16 allows for a similar procedure to be applied to the electronegativities of vicinal

atoms. The D/R^2 term in the BCM has been recognized as a kinetic energy contribution.^{1,24} Within the Thomas-Fermi model parameter D has a universal value; however, Ghosh and Parr obtained variable parameters D for a selection of homonuclear diatomic molecules, with parameter D being associated with the bond.²⁴ It seems reasonable here to assume that D has the same value for both of the atomic basins which meet at a specific bond critical point c ; hence, the following relationship between electronegativities of vicinal atoms is obtained from eqs 14–16:

$$[\chi_A - 2\eta_A q_c]R_{A,c}^2 = [\chi_B - 2\eta_B q_c]R_{B,c}^2 \quad (18)$$

Equations of this type may be written for each nonequivalent bond providing the set of additional equations necessary to solve eq 19 for individual atomic electronegativity parameters, χ_A and χ_B :

$$^{1/2}(I + A) = \sum K_A \chi_A \quad (19)$$

The resulting electronegativities (in general $\chi_A \neq \chi_B$) represent indices derived for rigid, disjoint atoms-in-molecules separated by bond critical points and satisfy the definition given in eq 12.

Group and Molecular Properties

Parameters for any chosen group of atoms may also be obtained¹⁸

$$\chi_G = \frac{\sum_{A \in G} K_A \chi_A}{\sum_{A \in G} K_A} \quad (20)$$

$$\eta_G = \frac{\sum_{A \in G} K_A \eta_A}{\sum_{A \in G} K_A} \quad (21)$$

The Fukui index for a group is simply $K_G = \sum_{A \in G} K_A$.

Results and Discussion

Fukui indices K_G were calculated according to eq 9 using two different sets of data for atomic volumes: (i) those as determined directly by the Bader method with 0.001 envelope, using the modified PROAIM package (see ref 11 and references cited therein), and (ii) those obtained by standard method from atomic refractions R_D reported in the literature²⁵ or calculated from the available physical constants, i.e., n_D^{20} and d^{20} (refractive indices and densities, respectively; see ref 20 for the data source). The resulting K_G indices for a selection of groups are collected in Table 1. There is a surprisingly good match between the two sets of Fukui indices for groups, the deviation being significant only for small polar molecules such as H_2O and HCN . (It is known that refractions may vary substantially between molecules for groups bonded by a polarized bond, and thus standard values of refractions used throughout the calculations do not reproduce volumes of atoms in such molecules.) However, the reasonably accurate Fukui indices obtained from atomic refractions for a majority of the organic molecules studied suggested that the method may be safely used instead of *ab initio* calculation of the atomic volumes; this approach may be of particular value with large molecules, where the atomic volumes based on the *ab initio* techniques may not be available.

TABLE 1: Calculated Fukui Indices K_G for Groups (G) Bonded to a Hydrogen Atom and Experimental Data for Electronegativity (χ_{HG}) and Hardness (η_{HG}) of the Respective Molecules

molecule HG	K_G		electronegativity χ_{HG}^b (V)	hardness η_{HG}^b (V/e)
	from atomic refractions ^a	from atomic vol		
HF		0.692 ^c	5.0	11.0
HCl		0.648	4.7	8.0
HCN	0.635	0.749	5.7	8.0
HOH	0.698	0.749 ^c	3.1	9.5
HSH	0.757	0.726	4.2	6.2
HNH ₂	0.777	0.783 ^c	2.6	8.2
HPH ₂	0.802	0.765	4.1	6.0
HCH ₃	0.813	0.806 ^c	2.5	10.3
HCH ₂ F	0.811	0.813	3.2	9.4
HCH ₂ Cl	0.837	0.829	3.8	7.5
HCH ₂ CN	0.859	0.854	4.7	7.5
HCH ₂ NO ₂	0.878	0.875	5.79	5.34
HCH ₂ COOH	0.890	0.887	4.6	6.4
HCOH	0.786	0.776	4.7	6.2
HCOCH ₃	0.876	0.867	4.5	5.7
HCONH ₂	0.855	0.841	4.2	6.2
HCH ₂ OCH ₃	0.899	0.893	2.0	8.0
HOCOCH ₃	0.899	0.915	4.6	6.4
HCHCH ₂	0.857	0.846 ^c	4.4	6.2
HCCH	0.807	0.795 ^c	4.4	7.0
HC ₆ H ₅	0.935	0.924 ^c	4.1	5.3

^a Atomic refractions based on ref 25 and references therein. ^b From ref 26. ^c Atomic volumes from ref 4.

TABLE 2: Calculated Bond Critical Point Parameters (au) for Bonds within Selected Molecules Listed in Table 1^a

molecule	bond A–X	$R_{A,c}$	$R_{X,c}$	$R_{X,c}/R_{A,c}$	$\rho(\mathbf{r}_c)$
HCN	C≡N	0.724	1.416	1.956	0.490
CH ₃ F	C–F	0.815	1.763	2.163	0.236
CH ₃ Cl	C–Cl	1.388	1.984	1.429	0.184
CH ₃ CN	C–C	1.177	1.597	1.357	0.268
	C≡N	0.727	1.417	1.949	0.490
CH ₃ NO ₂	C–N	0.901	1.893	2.101	0.258
	N–O(1)	1.088	1.165	1.071	0.550
	N–O(2)	1.083	1.167	1.078	0.552
CH ₃ COOH	C–C	1.307	1.530	1.171	0.276
	C=O	0.733	1.510	2.060	0.440
	C–O(H)	0.800	1.718	2.147	0.310
HCHO	C=O	0.729	1.509	2.070	0.430
CH ₃ CHO	C–C	1.370	1.472	1.074	0.273
	C=O	0.730	1.514	2.074	0.430
NH ₂ CHO	C–N	0.833	1.715	2.059	0.331
	C=O	0.737	1.517	2.058	0.433
CH ₃ OCH ₃	C–O	0.835	1.795	2.147	0.268

^a $R_{A,c}$ and $R_{X,c}$ are the distances from the bond critical point to the respective atom; $\rho(\mathbf{r}_c)$ is the electron density at the bond critical point.

Table 1 lists experimental data for electronegativity (χ) and hardness (η) of the molecules under study; only the experimental data preselected by Pearson²⁶ have been used, since electronegativity and hardness for bonded atoms and groups are crucially dependent on the data source of the molecular χ and η . The lack of reliable experimental measurements for electron affinities for molecules has been the main limiting factor in the selection of molecules.

Calculations of the group electronegativity (χ_G) and group hardness (η_G) were performed by two methods.

Method 1. Atomic Resolution. The calculated bond critical point parameters R_c and $\rho(\mathbf{r}_c)$ were used as reported by ref 11 for the H–G bonds. For other bonds the parameters were calculated by the modified PROAIM package and are listed in Table 2. The electronic structure was determined by the GAUSSIAN 90 program using the HF/6-31G(d) basis set and the program-optimized geometry (see ref 11 and references cited

TABLE 3: Average Bond-Critical-Point Parameters (Neutral Molecules Only; au)^a

bond H-X	$R_{H,c}$	R_{HX}	$R_{X,c}/R_{H,c}$	$\rho(\mathbf{r}_c)$	no. of points
H-CH ₂	0.746 ± 0.014	2.047 ± 0.006	1.744 ± 0.013	0.283 ± 0.004	31
H-CH<	0.726 ± 0.019	2.037 ± 0.008	1.806 ± 0.018	0.290 ± 0.007	14
H-C-	0.682 ± 0.026	2.028 ± 0.20	1.974 ± 0.027	0.300 ± 0.008	16
H-O	0.341 ± 0.004	1.797 ± 0.005	4.270 ± 0.004	0.363 ± 0.008	13
H-S	0.877 ± 0.55	2.508 ± 0.003	1.860 ± 0.034	0.210 ± 0.011	5
H-N	0.458 ± 0.024	1.895 ± 0.014	3.138 ± 0.020	0.346 ± 0.007	18
H-P	1.366 ± 0.006	2.626 ± 0.016	0.922 ± 0.018	0.177 ± 0.008	4
H-Si	1.441 ± 0.025	2.795 ± 0.044	0.940 ± 0.053	0.123 ± 0.006	10

^a $R_{H,c}$ and $R_{X,c}$ are distances from the bond-critical-point to hydrogen and to the partner atom, respectively. R_{HX} is the bond length; $\rho(\mathbf{r}_c)$ is the electron density at the bond critical point. The number of points indicates the bond distances which have been averaged to arrive at the given data.¹¹

therein). The hardness of each atom η_A was calculated first according to eqs 10 and 11; then the group hardness was found using eq 21. Electronegativities for individual atoms, as well as for the group, were obtained in a similar manner using eqs 18–20. Only Fukui indices calculated from atomic volumes were used in this approach.

Method 2. One-Bond Resolution. The Fukui indices from atomic refractions were used here. The molecule was split into two parts: the hydrogen atom (H) and the respective group (G). The set of average bond-critical-point parameters in a series of molecules was used for the H-X bond (Table 3) rather than actual bond parameters. Average parameters were calculated using data from ref 11, where the weak sensitivity of the bond-critical-point parameters to the molecular environment beyond the nearest neighbors has already been pointed out. The relative position of the bond critical point given by the ratio of R_c within a bond is even less sensitive to changes at atoms farther than one bond away. Method 2 contains the implicit assumption that eqs 10 and 18 hold not only for atoms, but for molecular fragments as well. The purpose of using the approximate method 2 was to reveal to what extent the resulting group parameters are modified by the approximations applied on the input.

Adapting the BCM equations to the electronegativity of atomic basins is crucial for both methods. Application of the model to disjoint atomic basins separated by critical points reflects all known properties of the electron density in the bond region. The dissociation limit is of particular interest: when $\rho(\mathbf{r}_c) = 0$ (i.e., no bond), the electronegativity becomes identical to χ° (i.e., that of the free atom). From eq 16, $\chi^\circ \propto 1/R_c^2$, which implies a finite atomic radius R_c , for an atom. This well-known relationship has a rich literature, recently collected in ref 1. For homonuclear diatomic molecules the electronegativity and hardness of the atoms are identical to those for the molecule, irrespective of $\rho(\mathbf{r}_c)$; however, for an unsymmetrical homonuclear fragment, atoms will have different χ and η parameters only if the position of the bond critical point is away from the bond center.

The results of calculations performed by the two methods are compared in Table 4 for groups bonded to a hydrogen atom. For the 20 molecules studied, the one-bond resolution method generally yields lower values for both χ and η , on average by -0.43 ± 0.58 V and -0.61 ± 0.87 V/e, respectively, which is a relative error of about -14% and -10% . Thus, despite its simplicity, method 2 may be considered a reasonable approach. Table 4 also contains the results for groups with multiple bonds. The general trend displayed by these data is that hardness and group electronegativity systematically decrease with increasing number of open bonds at the group central atom. The series CH₃, CH₂, CH, and C provides a very clear example of such a trend.

All calculated parameters are collected in Table 5 for the bonded hydrogen atom and in Table 6 for other groups. The

TABLE 4: Electronegativity (V) and Hardness (V/e) Indices for Selected Groups Bonded to the Hydrogen Atom^a

group	atomic resolution		one-bond resolution	
	χ_G	η_G	χ_G	η_G
-CN	3.42	5.84	3.37	5.90
-OH	2.48	7.53	1.68	4.78
>O	1.27	3.57		
-SH	3.42	5.44	2.89	5.13
>S	1.69	3.76		
-NH ₂	2.38	7.55	1.84	5.55
>NH	2.04	5.56		
>N-	1.27	3.84		
-PH ₂	4.14	6.03	4.20	6.09
>PH	4.21	6.09		
>P-	4.41	6.25		
-CH ₃	2.44	10.04	2.25	9.04
>CH ₂	2.36	9.64		
>CH-	2.19	8.88		
>C<	1.73	6.78		
-CH ₂ F	2.91	8.62	2.72	8.24
>CHF	2.44	7.39		
≥CF	1.57	5.10		
-CH ₂ Cl	3.41	6.94	3.15	6.69
>CHCl	2.83	6.08		
≥CCl	1.84	4.62		
-CH ₂ CN	4.11	6.80	3.92	6.79
>CHCN	3.27	5.82		
≥CCN	2.13	4.32		
-CH ₂ NO ₂	4.87	4.76	4.81	4.90
-CH ₂ COOH	4.00	5.81	3.95	5.92
-CH ₂ CHO	4.25	5.31	2.59	4.75
-CH ₂ OCH ₃	1.94	7.77	1.49	5.69
-CHO	3.08	5.29	3.30	5.29
-COCH ₃	3.94	5.91	3.58	5.08
-CONH ₂	3.45	5.46	3.28	5.43
-OCOCH ₃	4.80	6.56	2.58	4.81
-CH=CH ₂	4.17	5.98	3.58	5.56
-CH=CH-	3.84	5.66		
>C=C<	2.38	4.25		
-C≡CH	3.70	6.24	3.25	5.89
-C≡C-	2.52	4.98		
-C ₆ H ₅	3.64	4.79	3.52	5.04
C ₆ (benzene)	2.48	3.97		

^a The data have been calculated by two methods as described in the text.

volume of the bonded hydrogen atom increases with a decrease in its charge, at least when the neighboring atoms belong to the same period; an example of this is in the series HF, HOH, HNH₂, and HCH₃. This results because the position of the bond critical point, equivalent to the atomic radius for hydrogen, is sensitive to substitution on the closest vicinal atom, as indicated in Table 3; for instance the $R_{H,c}$ in CH, CH₂, and CH₃ groups is 0.682, 0.726, and 0.746 au, respectively. The same effect is observed for the R_c for other bonds (see Table 2), as illustrated by the R_c for the carbon atom in CH₃ being strongly dependent on the nature of its neighbor. The volume of the CH₃ in CH₃-G, however, is insensitive to G (207 ± 9 au, Table 6), even when the charge of G changes dramatically. The same is

TABLE 5: Parameters Calculated for Bonded Hydrogen Atoms, Including Fukui Index (K_H) Calculated from Atomic Volumes, Atomic Volumes (V_H) and Atomic Charges (q_H) Calculated by Integration over Atomic Basins, and Electronegativity (χ_H) and Hardness (η_H) Calculated by the Atomic Resolution Method

hydrogen atom in molecule H-G	K_H	V_H (au)	q_H	χ_H (V)	η_H (V/e)
H-F	0.308	11.49 ^a	0.779	12.34	25.83
H-Cl	0.352	37.60	0.027	5.57	8.93
H-CN	0.251	35.88	0.242	12.32	14.44
H-OH	0.251	18.97 ^a	0.628	4.91	15.43
H-SH	0.274	50.83	0.005	6.27	8.21
H-NH ₂	0.217	32.17 ^a	0.349	3.29	10.57
H-PH ₂	0.235	75.84	0.557	3.97	5.89
H-CH ₃	0.194	51.45 ^a	-0.044	2.72	11.30
H-CH ₂ F	0.197	47.83	0.008	4.48	12.77
H-CH ₂ Cl	0.171	45.46	0.047	5.66	10.22
H-CH ₂ CN	0.146	44.90	0.056	8.16	11.58
H-CH ₂ NO ₂ ^b	0.125	43.03	0.074	12.24	9.34
H-CH ₂ COOH ^b	0.113	46.17	0.033	9.16	10.89
H-CH ₂ CHO ^b	0.132	47.67	0.020	6.14	8.28
H-CH ₂ OCH ₃ ^b	0.107	48.85	0.007	2.44	9.92
H-COH	0.224	48.88	0.019	6.29	9.33
H-COCH ₃	0.133	49.39	0.002	8.12	4.33
H-CONH ₂	0.159	48.30	0.017	8.18	10.13
H-OCOCH ₃	0.085	17.60	0.628	2.48	4.63
H-CH=CH ₂	0.154	49.89 ^a	-0.017	5.67	7.42
H-CCH	0.205	41.92 ^a	0.136	7.08	9.90
H-C ₆ H ₅	0.076	49.76 ^a	-0.020	6.92	6.06

^a From ref 4. ^b Average value for CH₃ hydrogens.

TABLE 6: Electronegativity (χ_G) and Hardness (η_G) Calculated by the Atomic Resolution Method for Molecular Fragments, Group Volumes (V_G) and Charges (q_G) Calculated by Integration of Electron Densities over Atomic Basins and Fukui Indices (K_G) Calculated from Atomic Volumes

group	molecule	K_G	V_G (au)	q_G	χ_G (V)	η_G (V/e)
-CH	CH ₃ F	0.762	202.69	0.742	3.67	10.58
-CH ₃	CH ₃ Cl	0.711	207.94	0.318	4.77	8.95
-CH ₃	CH ₃ CN	0.607	206.12	0.367	6.81	10.14
-CH ₃	CH ₃ NO ₂	0.523	196.28	0.635	10.00	8.16
-CH ₃	CH ₃ COOH	0.487	210.32	0.178	7.64	9.57
-CH ₃	CH ₃ CHO	0.548	227.34	0.089	5.14	7.28
-CH ₃	CH ₃ OCH ₃	0.432	204.40	0.651	2.20	8.80
-CH ₃	CH ₄	0.806	202.69	0.044	2.44	10.04
-F	CH ₃ F	0.238	98.95	-0.742	0.923	3.33
-F	HF	0.692	130.44	-0.779	1.73	4.40
-Cl	CH ₃ Cl	0.289	219.54	-0.318	1.42	3.94
-Cl	HCl	0.648	235.98	-0.273	4.22	7.49
-CN	CH ₃ CN	0.393	237.18	-0.367	1.42	3.40
-CN	HCN	0.749	246.74	-0.242	3.42	5.84
-NO ₂	CH ₃ NO ₂	0.477	276.05	-0.635	1.22	2.28
-COOH	CH ₃ COOH	0.513	295.38	-0.178	1.72	3.40
-CHO	CH ₃ CHO	0.452	230.24	-0.089	3.72	3.78
-CHO	NH ₂ CHO	0.527	216.76	0.546	4.10	5.96
-CHO	HCHO	0.776	238.96	-0.019	3.08	5.29
-NH ₂	NH ₂ CHO	0.463	171.10	-0.548	4.3	6.46
-NH ₂	NH ₃	0.783	201.98	-0.349	2.38	7.55
-OH	CH ₃ COOH	0.245	135.59	-0.687	1.54	3.20
-OH	H ₂ O	0.749	168.80	-0.628	2.48	7.53
>CO	HCHO	0.551	190.08	-0.037	1.78	3.66
>CO	CH ₃ CHO	0.319	180.85	-0.091	1.87	3.53
>CO	CH ₃ COOH	0.267	159.79	0.500	1.89	3.58
>CO	NH ₂ CHO	0.368	168.46	0.530	2.36	4.18
-OCH ₃	CH ₃ OCH ₃	0.568	301.88	-0.651	1.84	7.35
-OCOCH ₃	CH ₃ COOH	0.915	488.10	-0.628	4.80	6.56
-COCH ₃	CH ₃ COOH	0.840	370.11	0.687	5.59	7.44
-COCH ₃	CH ₃ CHO	0.867	398.21	-0.002	3.94	5.91
-CONH ₂	NH ₂ CHO	0.841	339.56	-0.017	3.45	5.46
-NHCHO	NH ₂ CHO	0.872	362.45	-0.455	1.40	3.00
-NH-CO-	NH ₂ CHO	0.722	314.16	-0.472	2.91	4.81

observed for such groups as CN, CHO, CO, and COCH₃. On the other hand, small groups like OH and NH₂ change their volumes substantially upon bonding, with no clear relationship to the charge. Although all groups listed in Table 6 are

transferable in the common chemical sense, only the groups (and atoms) that retain at least their volume parameters can be considered topologically transferable. It is important to note that topologically transferable groups may have variable group charge (CH₃, CHO), a characteristic feature for the disjoint fragments.

Electronegativity and hardness parameters provide even more subtle insight into the properties of an atom in its actual local environment. Electronegativity of a hydrogen atom (Table 5) reaches a maximum for HCH₂NO₂, HCN, and HF, (12.24, 12.32, and 12.39 V, respectively) with no correlation to its atomic charge (0.074, 0.242, and 0.779, respectively). This suggests that the proposed electronegativity parameter reflects not only the effects of ionic bonding but also contains contributions from the covalent bonding character which is particularly strong in these molecules. High electronegativity of a hydrogen atom may suggest high reactivity toward electron donors. This hypothesis was tested on the hydrocarbons methane, ethylene, and acetylene. The energy gain upon the charge transfer between hydrogen in each of these molecules and a molecule of water was calculated according to the formula for charge transfer affinity (CTA):²⁷

$$CTA = \frac{(\chi_1 - \chi_2)^2}{4(\eta_1 + \eta_2)} \quad (22)$$

Resulting CTA energies (eV) are 0.020, 0.098, and 0.234 for CH₄, C₂H₄, and C₂H₂, respectively, and match the known order of the increasing dissociative properties of these molecules in water.

Electronegativities of groups (Table 6) provide further evidence for the relationship between χ and the bonding character of the group. The electronegativity of the methyl group in CH₃G increases in the series G = H, F, Cl, CN, and NO₂ ($\chi_G = 2.44, 3.67, 4.77, 6.81,$ and 10.00 V, respectively), which parallels the order of increasing electron withdrawing power of these substituents. The methyl group is the more electronegative end of the molecule in the series except for CH₄ where electronegativities of the hydrogen ($\chi_H = 2.72$) and the methyl ($\chi_{CH_3} = 2.44$) are nearly equal, in accordance with the accepted nonpolar character of the C-H bond in methane.

The hardness of a bonded hydrogen atom provides an illustration of the well-known phenomenon of symbiosis or hardness borrowing.²⁸ The harder the free atom (group) to which a hydrogen is attached, the harder the hydrogen. The experimentally well-established relative hardnesses for the selected pairs of substituents show that F > Cl, F > CH₃, OH > SH, and NH₂ > PH₂.²⁸ Calculated hardness parameters for hydrogen (Table 5) are completely consistent with this: hydrogens bonded to the harder group are in all instances harder. Since reliable sequence of experimental hardness for a wider selection of groups has not yet been established, the hardness parameters given in Table 5 for hydrogens in different environments serve as a relative hardness scale for the given groups, η_H being an ordering parameter. Thus, the η_H listed suggest the following sequence of decreasing hardness: F > CN > CH₃ > Cl > CHO. Symbiosis is also observed for groups in Table 6; for example, the hardness of the methyl group in CH₃F (10.58) is considerably larger than that in CH₃Cl (8.95) and supports the trend shown by η_H in Table 5. No relationship between hardness and charge is detectable for either H or the various groups listed in Table 6.

The trends presented for electronegativity and hardness reproduce, albeit qualitatively, the experimental trends in the corresponding properties of the bonded groups studied, including transferability of the relative order of hardness. (The numerical

values for χ and η cannot, however, be assumed to be quantitatively significant.) Table 6 provides ample examples of a variety of χ and η for each group; even for topologically transferable groups such as, e.g., CH₃, χ and η vary considerably depending on the actual H₃C–X bonding. This suggests a possible use of χ and η for characterization of properties of bonded groups, since the indices reflect not only the property of the group but also the effect of the molecular environment. No attempt has yet been made to produce intrinsic of χ and η for free groups by the method applied in this work.

Conclusion

In general, molecular fragments have not been sufficiently studied to establish their electronegativity and hardness parameters. There is an abundant literature on group electronegativity scales (refs 10, 11, and 18, and references cited therein); however, only a few comprehensive accounts for the two parameter (χ , η) description of chemical substituents have been reported. The first and most intuitive approach, that of Huheey, originated before the notion of hardness was related to its quantitative measure.²⁹ It has been continued by Politzer *et al.*,³⁰ using the original notion of the charge capacity instead of inverse hardness (softness). Another important contribution was provided by Bergman and Hinze.³¹ Both the Huheey and Bergman–Hinze analyses were based on an electronegativity equalization procedure, using charge flow as a fitting parameter; a similar method has also been recommended by Mortier *et al.* for other purposes.²¹ The Bergman–Hinze method is much improved over Huheey's earlier effort because it includes valence state adjustment and complete orbital resolution. An original set of data (χ , η) for groups has been proposed by Komorowski *et al.*,¹⁸ without referring to electronegativity equalization. It has been pointed out that, in addition to χ and η parameters, the charge transfer ΔN and/or the charge transfer affinity (energy) provide a proper measure of the group action, and this has been demonstrated by correlation with the Hammett constants for the substituents. Another original approach to group parameters was recently proposed by Geerlings *et al.*³² The trivial definitions of χ and η (eq 2) were adopted, with I and A for the free, radical group calculated by an *ab initio* method using the geometry typical for this group as a substituent. Although different in principle, all these sets of group parameters share a common feature: they are deemed to be inherent parameters for "free" groups, corresponding to the well-known electronegativity and hardness of free atoms, ions, and molecules.

Our approach represents quite a different viewpoint: χ_G and η_G parameters are "local", i.e., derived for groups and atoms bonded in molecules. As such, it is related to the recent concept by Cioslowski *et al.*^{33,34} The latter authors derived bond hardness parameters for bonds between the *in situ* molecular fragments (Bader basins), using charge transfer as a main variable. This very well founded work could not yield meaningful indices for the basins themselves. In a separate approach Cioslowski calculated Fukui indices for atomic basins, as frontier orbital density.³⁵ Results obtained at various levels of *ab initio* calculations compare favorably with those reported in this work for two cases where comparison is possible. The average value of f^+ and f^- for a hydrogen atom in HCOH ranges from 0.272 to 0.362 for different calculations in ref 35, while 0.224 is obtained in this present work; for the hydrogen atom in C₂H₄O the numbers are 0.113–0.228³⁵ and 0.132 (this work).

The present work combines a simplicity of analysis with a focus on bonded atoms, rather than bonds. The use of purely s-bonded hydrogen as a reference, and the availability of

experimental values χ_M and η_M for the molecules which are used for input data, make the calculated parameters for groups as nearly transferable as possible. As a result, qualitative trends in group electronegativities and hardnesses have been reliably predicted. However, χ and η parameters which are quantitatively transferable will require further study. In conclusion, our work has demonstrated how the basic quantifying descriptors of group properties, namely, electronegativity and hardness, may be conveniently obtained from the calculated properties of atoms in molecules.

Acknowledgment. The authors gratefully acknowledge the financial support of the Natural Sciences and Engineering Research Council of Canada in the form of grants and a Foreign Researcher Award which made this work possible during visits by L.K. at Dalhousie University. L.K. also acknowledges sponsorship by the Polish Committee for Scientific Research (KBN) through the Technical University of Wroclaw Grant No. 341 343.

References and Notes

- (1) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Clarendon Press: Oxford, U.K., 1989.
- (2) Parr, R. G. *Annu. Rev. Phys. Chem.* **1983**, *34*, 631.
- (3) Bader, R. F. W. *Atoms in Molecules. A Quantum Theory*; Clarendon Press: Oxford, U.K., 1990.
- (4) Bader, R. F. W.; Popelier, P. L. A.; Keith, T. A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 620.
- (5) Bader, R. F. W. *J. Chem. Phys.* **1986**, *85*, 3133.
- (6) Parr, R. G. *J. Chem. Phys.* **1986**, *85*, 3135.
- (7) Bader, R. F. W. *Phys. Rev. B* **1994**, *49*, 13348.
- (8) Bader, R. F. W.; Carroll, M. T.; Cheeseman, J. R.; Cheng, C. J. *Am. Chem. Soc.* **1987**, *109*, 7968.
- (9) Bader, R. F. W. *Chem. Rev.* **1991**, *91*, 893.
- (10) Boyd, R. J.; Edgecombe, K. E. *J. Am. Chem. Soc.* **1988**, *110*, 4182.
- (11) Boyd, R. J.; Boyd, S. L. *J. Am. Chem. Soc.* **1992**, *114*, 1652.
- (12) Knop, O.; Boyd, R. J.; Choi, S. C. *J. Am. Chem. Soc.* **1988**, *110*, 7299.
- (13) Boyd, R. J.; Choi, S. C. *Chem. Phys. Lett.* **1985**, *120*, 80.
- (14) Boyd, R. J.; Choi, S. C. *Chem. Phys. Lett.* **1986**, *129*, 62.
- (15) Chattaraj, P. K.; Parr, R. G. *Struct. Bonding* **1993**, *80*, 11.
- (16) Parr, R. G.; Pearson, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 1503.
- (17) Komorowski, L.; Lipiński, J. *Chem. Phys.* **1991**, *157*, 45.
- (18) Komorowski, L.; Lipiński, J.; Pyka, M. J. *J. Phys. Chem.* **1993**, *93*, 3166.
- (19) Gasquez, J. L.; Ortiz, E. *J. Chem. Phys.* **1984**, *81*, 2741.
- (20) Komorowski, L. *Chem. Phys.* **1987**, *114*, 55.
- (21) Baekelandt, B. G.; Mortier, W. J.; Schoonheydt, R. A. *Struct. Bonding* **1993**, *80*, 187.
- (22) Borkman, R. F. *J. Chem. Phys.* **1969**, *51*, 5596.
- (23) Borkman, R. F.; Parr, R. G. *J. Chem. Phys.* **1968**, *48*, 1116.
- (24) Ghosh, S. K.; Parr, R. G. *Theor. Chim. Acta* **1987**, *72*, 379.
- (25) Vogel, I. *J. Chem. Soc.* **1948**, 1833.
- (26) Pearson, R. G. *Inorg. Chem.* **1988**, *27*, 734.
- (27) Komorowski, L. *Struct. Bonding* **1993**, *80*, 45.
- (28) Huheey, J. F. *Inorganic Chemistry: Principles of Structure and Reactivity*; Harper & Row: New York, 1983.
- (29) Huheey, J. E. *J. Org. Chem.* **1966**, *31*, 2365.
- (30) Politzer, P.; Huheey, J. E.; Murray, J. S.; Grodzicki, M. J. *Mol. Structure (THEOCHEM)* **1992**, *259*, 99.
- (31) Bergman, D.; Hinze, J. *Struct. Bonding* **1987**, *66*, 145.
- (32) De Proft, F.; Langenaecker, W.; Geerlings, P. *J. Phys. Chem.* **1993**, *97*, 1826.
- (33) Cioslowski, J.; Mixon, S. T. *J. Am. Chem. Soc.* **1993**, *115*, 1084.
- (34) Cioslowski, J.; Stefanov, B. *J. Chem. Phys.* **1993**, *99*, 5151.
- (35) Cioslowski, J.; Martinov, M.; Mixon, S. T. *J. Phys. Chem.* **1993**, *97*, 10948.