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Using Sanderson's Principle to Estimate Global Electronic Properties and Bond Energies of Hydrogen-Bonded Complexes

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In this paper, we use Sanderson's geometric mean equalization principle for electronegativity (χ) to derive expressions for molecular hardness (η) and its derivative (γ) that are used to estimate the electronic properties of 14 molecules and bimolecular hydrogen-bonded complexes. Beyond the determination of electronic properties, it is shown that Sanderson's scheme can be very useful as a method for rationalizing chemical reactions when both N and v change. We have found that the conditions of maximum hardness and minimum polarizability complement the minimum energy criterion for stability of molecular aggregates. Finally, we propose a new scheme for obtaining molecular properties from the isolated fragments that produces results that are in excellent agreement with those determined through Sanderson's scheme.

1. Introduction

A formation reaction results from the combination of constituent fragments. The resulting system, a molecule or an aggregate, presents properties that, in many cases, can be rationalized in terms of the properties of the isolated constituent fragments. The main problem that arises when using this approximation to estimate molecular properties is that the bonding potential and redistribution of the electron density among the fragments are not considered, and structural relaxation due to new specific through-bond and through-space interactions is not allowed within this scheme. In fact, the approach of using the properties of rigid isolated fragments to estimate the corresponding properties of a system made up of these fragments entails errors such as the completeness of the basis sets and the mixing of electronic states. The effects of such errors are not considered at all in fragment addition schemes, and therefore, the quantities determined in this way are not expected to be very accurate. However, the use of addition rules to estimate global properties of composite systems is attractive mainly because they may be useful in predicting qualitative features. In this paper, we investigate whether one can safely estimate global molecular properties from the corresponding values associated with the constituent fragments through the application of Sanderson's principle of electronegativity equalization.[1−3] Also, we explore how these electronic properties can be related to bond energies involved in molecule and aggregate formation processes.

Within the frame of density functional theory (DFT),[4−6] a complete characterization of an N-particle wave function requires knowledge of only N and the external potential $v(\vec{r})$. The response of the system to any external perturbation is measured by the electronic chemical potential (μ) and the hardness (η) when N is varied for a fixed $v(\vec{r})$. Complementary to this, the polarizability (α) can be used in understanding the behavior of the system for changing $v(\vec{r})$ at constant N.[7] In DFT, μ is the Lagrange multiplier associated with the normalization constraint that the electron density integrates to N; the association with classical structural chemistry is achieved by the identification of μ as the negative of the electronegativity (χ). Definitions of χ (or μ) and η were given by Parr et al.[8] and Parr and Pearson,[9] respectively. Chemical potential (electronegativity) and hardness are global electronic properties that are implicated in the reactivity of molecular systems, and they are well-established quantities that have evoked considerable research activity in the last years.[10−14]

The product of a chemical reaction can be seen as resulting from the combination and redistribution of atom's or fragment's electron densities, giving rise to a new electronic distribution from which the electronic properties of the new molecule or aggregate are derived. It is well-known by now that molecular electron densities exhibit local topological features that makes it possible to recognize atomic or fragment shapes within the molecule.[15−17] In this context, it is important to characterize the effect of combination and redistribution of electron densities on global electronic properties that have been defined as the response of the system to external perturbations.

To relate the molecular electronegativity to those of the constituent atoms or fragments, Sanderson proposed a geometric mean equalization principle, that defines the molecular electronegativity as the geometric mean of the electronegativities of the constituent atoms or fragments.[1−3] In recent papers, we have extended this approach to estimate molecular hardness from the corresponding property of the constituent atoms or fragments.[18,19] In this paper, we go further by estimating for the first time numerical values of γ [$\gamma \equiv (\partial\eta/\partial N)_v$] in molecules, obtaining expressions for η and γ from the geometric mean of χ (or μ), and then investigating how these properties, together with the polarizability α, might be related to the energy of conventional and hydrogen bonds.

This study concerns the formation of four molecules of the type HCX−YH from radicals HCO, HCS, OH, and SH and 10 cyclic hydrogen-bonded bimolecular complexes of the type HCX−YH···HCY−XH formed by combinations of the HCX−

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YH species (X, Y = O, S). Our main goal in this paper is to discuss the validity of Sanderson's addition scheme and to investigate whether this approach can be used to discuss reordering of electronic density due to the bonding process.

2. Theoretical Background

Within the framework of DFT, the chemical potential and hardness for an N-particle system with total energy E and external potential $v(\vec{r})$ are defined as follows:[4-6]

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{v(\vec{r})} = -\chi \tag{1}$$

and

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial^2 N}\right)_{v(\vec{r})} = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_{v(\vec{r})} \tag{2}$$

In numerical applications, μ and η are calculated through the following approximate versions of eqs 1 and 2, based upon the finite-difference approximation and Koopman's theorem:[5]

$$\mu \approx -\frac{1}{2}(I + A) \simeq \frac{1}{2}(\epsilon_L + \epsilon_H) \tag{3}$$

and

$$\eta \approx \frac{1}{2}(I - A) \simeq \frac{1}{2}(\epsilon_L - \epsilon_H) \tag{4}$$

where I is the ionization potential, A is the electron affinity, and ϵ_H and ϵ_L are the energies of the highest-occupied molecular orbital (HOMO) and the lowest-unoccupied molecular orbital (LUMO), respectively. In this paper, μ and η will be calculated using the MO energies.

The energy involved in forming a molecule or aggregate from n_f non-bonded constituent fragments is given by

$$\Delta E_{n_f} = E - E^\circ_{n_f} \tag{5}$$

where E is the energy of the fully optimized resulting molecule or aggregate and $E^\circ_{n_f} = \sum_x^{n_f} E_x$, with E_x the energy of the fragment x duly optimized. Note that, in our applications, the energy of the bimolecular complexes can be estimated from the energy of two (E°_2) and four (E°_4) fragments. It is important to point out here that both basis set superposition and the mixing of electronic states are source of errors in the estimation of ΔE_{n_f}; however, attempts to evaluate them are beyond the scope of this paper.

Sanderson's equalization principle states that the electronegativity of a molecule is given by the geometric mean of the electronegativities of the isolated atoms (or fragments)[1-3]

$$\mu^\circ_{n_f} = -\left(\prod_x^{n_f} |\mu^\circ_x|\right)^{1/n_f} \tag{6}$$

where μ°_x is the chemical potential of fragment x. Note that the larger the value of n_f, the less accurate the result because of the number of bonds and bonding potentials not being considered in the calculations of $\mu^\circ_{n_f}$.

Within this scheme, the hardness is obtained by differentiating $\mu^\circ_{n_f}$ with respect to N,[18,19] thus obtaining

$$\eta^\circ_{n_f} = \left(\frac{\partial \mu^\circ_{n_f}}{\partial N}\right)_{v(\vec{r})} = \frac{\mu^\circ_{n_f}}{n_f}\sum_x^{n_f}\frac{\eta^\circ_x}{\mu^\circ_x} \tag{7}$$

η°_x is the hardness of fragment x. The difference between the approximate values ($\mu^\circ_{n_f}$ and $\eta^\circ_{n_f}$) and the actual values obtained using eqs 3 and 4 from the ab initio calculations (μ and η) can be attributed to relaxation of the electron density after bonding. Quantification of this difference may help in developing an understanding of the reordering of the electron density as the reaction takes place.

The derivative of the hardness with respect to N at constant external potential was defined previously as the third-order property γ; it was numerically studied only in atoms and atomic ions with the result that, in most cases, it is smaller than μ and η.[20] Within the Sanderson scheme, we obtain from eq 7

$$\gamma^\circ_{n_f} = \left(\frac{\partial \eta^\circ_{n_f}}{\partial N}\right)_{v(\vec{r})} = \frac{(\eta^\circ_{n_f})^2}{\mu^\circ_{n_f}} - \frac{\mu^\circ_{n_f}}{n_f}\sum_x^{n_f}\left(\frac{\eta^\circ_x}{\mu^\circ_x}\right)^2 + \frac{\mu^\circ_{n_f}}{n_f}\sum_x^{n_f}\frac{\gamma^\circ_x}{\mu^\circ_x} \tag{8}$$

This provides an analytic expression to estimate γ from atomic (or fragment) chemical potentials and hardnesses. Notice that $\eta^\circ_{n_f}$ and $\gamma^\circ_{n_f}$ have been defined by dropping, from the original definitions, the numerical factors $^1/_2$ and $^1/_3$, respectively.

3. Computational Methods

Although restricted Hartree−Fock (RHF) calculations are not expected to give accurate hydrogen-bond energies, it has been recently shown that they are highly consistent with DFT/B3LYP results.[19] Therefore, all calculations were performed at the RHF level of theory with the standard 6-311G** basis set using the Gaussian 94 package.[21] Radical fragments were calculated using the UHF theory. The electronic chemical potential and molecular hardness have been calculated by applying eqs 3 and 4, respectively, with ϵ_H and ϵ_L obtained from the RHF/UHF calculations of the fully optimized species.

In Table 1, we display reference values of energy, chemical potential, and hardness of the initial isolated radical species HCX and XH (X = O, S). Formation of molecules HCO−OH (**M1**), HCS−OH (**M2**), HCO−SH (**M3**), and HCS−SH (**M4**) from the two constituent radicals involves a change in energy and electronic properties mainly due to formation of a covalent C−X bond (X = O, S). Thus, in comparing $\mu^\circ_{n_f}$ and $\eta^\circ_{n_f}$ with respect to the actual values of μ and η determined from ab initio calculations on the fully optimized molecule, we will obtain, as a qualitative result, the effect of the bonding potential on these specific electronic properties.

Among many possible bimolecular structures, we will review here only cyclic complexes that are estabilized by two hydrogen bonds.[19] Combinations of monomeric units of formic (HCO−OH), thione−formic (HCS−OH), thiol−formic (HCO−SH), and dithioformic (HCS−SH) acids leads to 10 cyclic bimolecular complexes, **C1**−**C10** (see Table 2). To build them, two approaches have been considered: (**a**) formation from two neutral molecules ($n_f = 2$) where the ab initio optimized values of E, μ, and η of each HCX−YH (X, Y = O, S) species are used to produce E°_2, μ°_2, and η°_2 (note that these quantities do not contain the hydrogen-bonds potentials); and (**b**) formation from four isolated radical fragments ($n_f = 4$). The latter approach leads to E°_4, μ°_4, and η°_4 values in which the effect of two covalent and two hydrogen-bond potentials are not included. In Table 2, we define the species under study and quote the values of $E^\circ_{n_f}$, together with the reaction energies ΔE_2 and ΔE_4,

TABLE 1: Energy, Chemical Potential, and Hardness for the Fully Optimized Radical Structures Determined at the Ab Initio UHF/6-311G Level**[a]

fragment	E	μ	η
CHO	−113.2802	−0.1327	0.2450
OH	−75.4107	−0.1906	0.3153
CHS	−435.9153	−0.1492	0.1852
SH	−398.0929	−0.1907	0.1864

[a] All values are in atomic units.

which should be proportional to the bond energies involved in forming the molecules and aggregates.

4. Results and Discussion

Estimating C−X Bond Energies. We note in Table 2 that all ΔE_{n_f} values are negative, indicating that formation of molecules (**M1**−**M4**) and bimolecular complexes (**C1**−**C10**) are favorable processes. Note that, in formation reactions, $E^{\circ}_{n_f}$ and E are the total energies of reactants and products, respectively. For our purposes, the most relevant feature appearing in the formation energy of **M1** and **M2** is that their ΔE_2 values can be identified with the energy of a single C−O bond, the average value determined from Table 2 being $\langle \Delta E_2 \rangle_{CO} \approx 0.12$ au. Note that the average value of the experimental C−O bond energy has been estimated to be 0.13 au,[22] in reasonable agreement with our estimate. In the formation of **M3** and **M4**, $-\Delta E_2$ is mainly attributed to formation of a single C−S bond, for which the average experimental bond energy is 0.10 au;[22] our estimation is $\langle \Delta E_2 \rangle_{CS} \approx 0.08$ au. Although the numerical values may differ to some extent, our results show that the C−O bond is correctly estimated as being stronger than the C−S bond by about 0.04 au, in qualitative agreement with the experimental data.[22]

When the complexes are formed from four isolated fragments ($n_f = 4$), the reaction energies can be related to the energies of the bonds being formed. Table 2 shows that, in **C1**, **C2**, and **C3**, the ΔE_4 values goes from −0.28 au (**C1**) up to −0.25 au (**C3**); these values correspond to the approximate contribution of the two C−O bonds being formed ($\Delta E_4 \approx 2\langle \Delta E_2 \rangle_{CO}$). In **C4**−**C7**, we find that the average value of ΔE_4 is 0.21 au, with quite a small dispersion. This can be associated with the energetic contribution due to formation of one C−O and one C−S bond ($\Delta E_4 \approx \langle \Delta E_2 \rangle_{CO} + \langle \Delta E_2 \rangle_{CS}$). In **C8**−**C10**, we find that $\Delta E_4 \approx -0.16$ au, which is the energetic contribution due to formation of two C−S bonds ($\Delta E_4 \approx 2\langle \Delta E_2 \rangle_{CS}$).

Estimating Hydrogen-Bond Energies. It is important to mention that, although Hartree−Fock calculations are not expected to be very accurate in estimating hydrogen-bond energies, our ΔE_2 values follow the correct qualitative trend and compare satisfactorily well with other theoretical estimates.[23] Recent DFT/B3LYP calculations on the complexes we are discussing here led to hydrogen-bond energies that are in very good agreement with the HF results (see Figure 8 of ref 19). Concerning the comparison with experimental data, we note that our energies quantitatively match the available experimental data. For example, $\Delta E_2 = -0.0233$ au for **C1**[24] (compared with $\Delta E_2 = -0.0231$ au from Table 2), and the energy of a single hydrogen bond in **C10** was measured to be 0.0016 au,[25] which is very close to one-half of our ΔE_2 value given in Table 2 ($\Delta E_2/2 = 0.0019$ au), where the factor $^1/_2$ is introduced for proper comparison as **C10** contains two hydrogen bonds. This latter result suggests that hydrogen-bond energies for the series of systems we are studying here might be rationalized in terms of the sum of individual H-bond energies present in the complex.

To explore this idea, we use the ΔE_2 values for the dimers **C1** and **C10**, which present only H···O or H···S bonds, as reference values defining the energy of the respective bonds: i.e., $E(\mathrm{H\cdots O}) = \Delta E_2(\mathbf{C1})/2 = -0.01155$ au and $E(\mathrm{H\cdots S}) = \Delta E_2(\mathbf{C10})/2 = -0.00185$ au. Using these values, we approximate the ΔE_2 values for the remaining eight complexes as $\Delta E_2^{(a)} = \sum_X E(\mathrm{H\cdots X})$, simply the sum of energies of H-bonds present in the system. The results are included in Table 3. We note that this estimation of ΔE_2 is rather crude, exhibiting considerable errors that go up to 70% (**C3**). Thus, the rough estimation of the H-bond energies from the reference systems **C1** and **C10** is not accurate enough to get an adequate description of the remaining ΔE_2 values.

A considerably better approach to ΔE_2 can be obtained if we consider not only the corresponding H-bonds but also the effect that the neighboring heteroatom may have, thus defining the energy of fragments X−H···Y (X, Y = O, S). To do so, we use as a reference four dimers (**C1**, **C3**, **C8**, and **C10**) that present the desired fragments: $E(\mathrm{OH\cdots O}) = \Delta E_2(\mathbf{C1})/2 = -0.01155$ au; $E(\mathrm{OH\cdots S}) = \Delta E_2(\mathbf{C3})/2 = -0.00595$ au; $E(\mathrm{SH\cdots O}) = \Delta E_2(\mathbf{C8})/2 = -0.00445$ au; and $E(\mathrm{SH\cdots S}) = \Delta E_2(\mathbf{C10})/2 = -0.00185$ au. Note that the presence of a sulfur atom adjacent to the H-bond makes the H-bond weaker than it would be in the presence of oxygen. Now we define $\Delta E_2^{(b)} = \sum_{X,Y} E(\mathrm{XH\cdots Y})$; the results are shown in Table 3 and compared with ΔE_2 and $\Delta E_2^{(a)}$. It can be seen that the deviations with respect to the calculated ΔE_2 values are now very small; they go up to 0.82 kcal/mol in **C6** (the larger deviation of $\Delta E_2^{(a)}$ with respect to ΔE_2 was found in **C8** and was 8.91 kcal/mol). This indicates that the effect of the heteroatom adjacent to the H-bond is very important in characterizing the different H-bond energies. In summary, we estimate the H···O bond energy to be 0.0080 ± 0.0036 au and the H···S bond energy to be 0.0039 ± 0.0021 au, the H···O bond being about twice as strong as the H···S bond.

Force Constants and Hydrogen-Bond Energies. In bimolecular systems when the energy is estimated using $n_f = 2$, the quantity $\Delta E_2 = E - E_2^{\circ}$ gives an estimate of the hydrogen-bond energies, because the larger ΔE_2 is, the stronger the pair of hydrogen bonds being formed is expected to be. Table 3 shows that the bond energy decreases with the number of electrons and that the O···H bonds are stronger than the S···H bonds. The strength of a chemical bond is usually represented by its force constant; in our case, we expect ΔE_2 to be related with the force constants k associated with the pair of hydrogen bonds of the complex. These force constant values have been determined through ab initio frequency calculations on the optimized structure of the complexes, and the results are displayed in Figure 1a, where a good linear correlation can be observed between ΔE_2 and k for the 10 complexes identified by their total number of electrons, the correlation factor being 0.980. Because there are four systems having 64 electrons (**C3**, **C5**, **C6**, and **C8**), two with 72 electrons (**C7** and **C9**), and two with 56 electrons (**C2** and **C4**), we plot the average of their ΔE_2 and k values, obtaining an enhanced correlation, as is apparent in Figure 1b ($R = 0.996$). Thus, the ab initio force constants are consistent with expectations based on the energetic results: the stronger the hydrogen bond, the higher its $|\Delta E_2|$ value.

Chemical Potential. Equation 6 has been used to obtain the chemical potential within Sanderson's scheme. The estimates for **M1**−**M4** require the ab initio data (μ_x and η_x) for the isolated radicals x = CHO, OH, CHS, and SH that are quoted in Table

TABLE 2: Total and Reaction Energies of Molecular Systems and Formation Processes[a]

system		$-E$	$-E_2^\circ$	$-E_4^\circ$	$-\Delta E_2$	$-\Delta E_4$
HCOOH	(**M1**)	188.8205	188.6910		0.1295	
HCSOH	(**M2**)	511.4454	511.3260		0.1194	
HCOSH	(**M3**)	511.4493	511.3731		0.0762	
HCSSH	(**M4**)	834.0867	834.0082		0.0785	
HCOOH···HCOOH	(**C1**)	377.6641	377.6410	377.3819	0.0231	0.2822
HCOOH···HCSOH	(**C2**)	700.2840	700.2659	700.0170	0.0181	0.2670
HCSOH···HCSOH	(**C3**)	1022.9027	1022.8908	1022.6520	0.0119	0.2507
HCOOH···HCOSH	(**C4**)	700.2847	700.2698	700.0641	0.0149	0.2206
HCOOH···HCSSH	(**C5**)	1022.9176	1022.9072	1022.6992	0.0104	0.2184
HCOSH···HCSOH	(**C6**)	1022.9068	1022.8947	1022.6992	0.0121	0.2076
HCSSH···HCSOH	(**C7**)	1345.5389	1345.5320	1345.3342	0.0069	0.2047
HCOSH···HCOSH	(**C8**)	1022.9076	1022.8987	1022.7463	0.0089	0.1613
HCSSH···HCOSH	(**C9**)	1345.5425	1345.5360	1345.3813	0.0065	0.1612
HCSSH···HCSSH	(**C10**)	1668.1770	1668.1733	1668.0164	0.0037	0.1606

[a] All values are in atomic units.

TABLE 3: Double Hydrogen-Bond Energies of Bimolecular Aggregates[a]

complex	N	$-\Delta E_2$	$-\Delta E_2^{(a)}$	$-\Delta E_2^{(b)}$
C1	48	0.0231	0.0231	0.0231
C2	56	0.0181	0.0134	0.0175
C3	64	0.0119	0.0037	0.0119
C4	56	0.0149	0.0231	0.0160
C5	64	0.0104	0.0134	0.0104
C6	64	0.0121	0.0134	0.0134
C7	72	0.0069	0.0134	0.0078
C8	64	0.0089	0.0231	0.0089
C9	72	0.0065	0.0134	0.0063
C10	80	0.0037	0.0037	0.0037

[a] All values are in atomic units.

1. The effect of relaxation and redistribution of the electronic density on the chemical potential due to formation of covalent and hydrogen bonds can be quantitatively characterized by the numerical values of $\mu_{n_f}^\circ$ with reference to the calculated chemical potential; numerical values are listed in Table 4. We note that the deviations of $\mu_{n_f}^\circ$ with respect to the reference ab initio values are reasonably small; in most cases, μ_2° approaches the reference value better than μ_4° does. As for the energy, the chemical potential seems to be quite dependent on the number of fragments used.

When two fragments are brought into contact, electrons will flow from the one of higher chemical potential to that of lower μ, the amount of flowing charge being proportional to the difference in the chemical potentials of the fragments.[8] A qualitative estimation of the charge transfer (ΔN) involved in the formation process of a two-fragment reaction can be determined through the following expression:[5,8,10,12]

$$\Delta N = \frac{1}{2}\frac{(\mu_x - \mu_y)}{(\eta_x + \eta_y)} \tag{9}$$

with x and y representing the different fragments used in the formation of the desired product. The values of ΔN are quoted in Table 5, where it is interesting to note that reactions involving formation of covalent bonds are accompanied with high positive values of ΔN whereas, in bimolecular complex formation, we find smaller values of ΔN. According to eq 9, the amount of charge (δN_{n_f}) that is not relaxed in the formation process from the rigid fragments must be proportional to $\Delta\mu_{n_f} = (\mu - \mu_{n_f}^\circ)$. Thus, we simply define $\delta N_{n_f} \equiv \Delta\mu_{n_f}$ and quote its values in Table 5. It is interesting to note, for bimolecular complexes, that formation from four fragments in most cases implies higher values of this index than formation from two fragments, thereby implying that reordering of the electron density becomes increasingly important with the number of fragments.

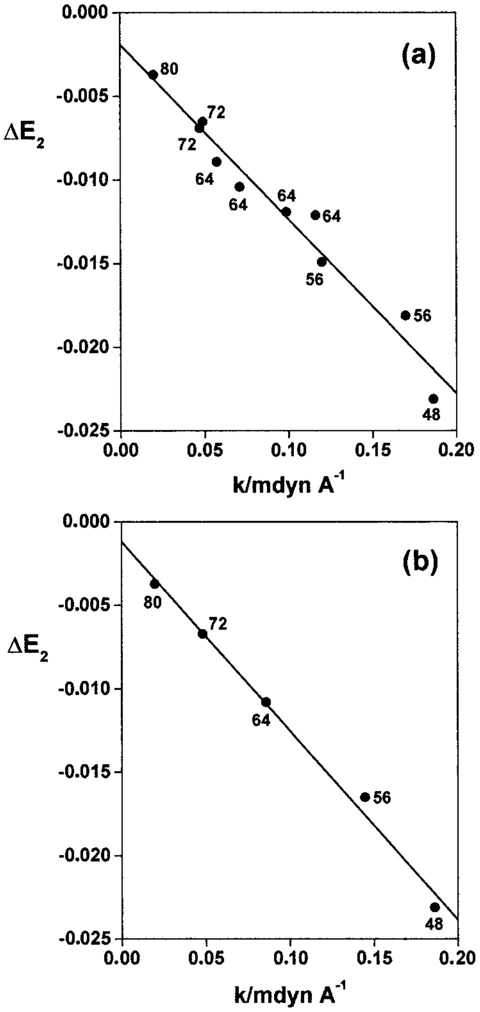

Figure 1. (a) Correlation between hydrogen-bond energies and H-bond force constants of bimolecular aggregates identified by their number of electrons. (b) Same as in panel a but using the average values of ΔE_2 and k in systems presenting the same number of electrons.

Molecular Hardness. Within Sanderson's scheme, we have determined the molecular hardness using eq 7; the results that are quoted in Table 4 must be compared with the reference ab initio values also included in the table. It is interesting to note that hardness can be approached using either η_2° or η_4°, depending on the specific system, both approaches represent

TABLE 4: Calculated and Estimated Electronic Properties of Isolated Molecules and Molecular Aggregates[a]

system	μ	μ_2°	μ_4°	η	η_2°	η_4°	γ_2°	γ_4°
M1	−0.1554	−0.1590		0.3138	0.2783		0.0247	
M2	−0.1402	−0.1686		0.2206	0.2441		0.0214	
M3	−0.1391	−0.1591		0.2608	0.2246		0.0431	
M4	−0.1532	−0.1687		0.1996	0.1872		0.0062	
C1	−0.1503	−0.1554	−0.1590	0.3204	0.3138	0.2783	0.0317	0.0247
C2	−0.1411	−0.1476	−0.1638	0.2251	0.2652	0.2619	0.0303	0.0269
C3	−0.1462	−0.1402	−0.1686	0.2169	0.2206	0.2441	0.0153	0.0214
C4	−0.1402	−0.1470	−0.1590	0.2609	0.2863	0.2515	0.0281	0.0380
C5	−0.1601	−0.1543	−0.1638	0.2021	0.2563	0.2342	0.0398	0.0326
C6	−0.1320	−0.1397	−0.1638	0.2215	0.2408	0.2342	0.0231	0.0326
C7	−0.1604	−0.1466	−0.1687	0.1966	0.2108	0.2157	0.0148	0.0187
C8	−0.1331	−0.1391	−0.1591	0.2607	0.2608	0.2246	0.0240	0.0431
C9	−0.1511	−0.1460	−0.1638	0.2000	0.2319	0.2065	0.0288	0.0289
C10	−0.1576	−0.1532	−0.1687	0.1965	0.1996	0.1871	0.0084	0.0064

[a] All values are in atomic units.

TABLE 5: Estimation of Charge Transfer (ΔN) in Formation of Molecular Systems and Bimolecular Complexes

system	ΔN	δN_2	δN_4
M1	0.0516	0.0036	
M2	0.0414	0.0284	
M3	0.0672	0.0200	
M4	0.0558	0.0155	
C1	0.0	0.0051	0.0087
C2	−0.0142	0.0065	0.0227
C3	0.0	−0.0060	0.0224
C4	−0.0142	0.0068	0.0188
C5	−0.0021	−0.0058	0.0037
C6	0.0011	0.0077	0.0318
C7	−0.0155	−0.0138	0.0083
C8	0.0	0.0060	0.0260
C9	−0.0153	−0.0051	0.0127
C10	0.0	−0.0044	0.0111

TABLE 6: Comparison of Hardness Determined through Different Methods[a]

system	η[b]	eq 7[c]	ref 26	ref 27
M1	0.3138	0.2783	0.2757	0.2779
M2	0.2206	0.2441	0.2333	0.2417
M3	0.2608	0.2246	0.2117	0.2137
M4	0.1996	0.1872	0.1858	0.1858
C1	0.3204	0.3138	0.3138	0.3138
C2	0.2251	0.2652	0.2591	0.2631
C3	0.2169	0.2206	0.2206	0.2206
C4	0.2609	0.2863	0.2849	0.2861
C5	0.2021	0.2563	0.2440	0.2503
C6	0.2215	0.2408	0.2390	0.2399
C7	0.1966	0.2108	0.2096	0.2098
C8	0.2607	0.2608	0.2608	0.2608
C9	0.2000	0.2319	0.2261	0.2282
C10	0.1965	0.1996	0.1996	0.1996

[a] All values are in atomic units. [b] η is the reference ab initio value. [c] Equation 7 is used with $n_f = 2$.

good approximations of the actual ab initio result. Qualitative consistency between η_2° or η_4° indicates that eq 7 is a reliable expression for estimating molecular hardness. There are a few different ways to estimate η from fragment values: the arithmetic average for softness[26] ($S = 1/\eta$) and the geometric mean principle for hardness[27] are among the most relevant treatments for determining hardnesses. In Table 6, we compare the numerical values of η calculated using eq 7 with values determined using the above-mentioned treatments. We note that the comparison is quite satisfactory, with only very small deviations among the values obtained through the different methods being observed. This result adds evidence for an important feature of hardness: it is a quite stable property. This attribute, in combination with the principle of maximum hardness (PMH),[28−30] which states that molecular systems at equilibrium tend to states of highest hardness, suggest that, for systems in which the energy is difficult to obtain, knowledge of η may open the way for obtaining energetic information.[18]

Relation Between Energy and Hardness. The connection between energy and hardness through the PMH prompted us to investigate the relation between the formation energies ΔE_2 and ΔE_4 of the bimolecular complexes and the corresponding hardnesses η_2° and η_4°, determined using eq 7. Panels a and b of Figure 2 show good linear correlations between ΔE_{n_f} and $\eta_{n_f}^\circ$ for the complexes identified by their total number of electrons. These correlations are substantially improved when we use the average value of the properties of complexes with the same number of electrons ($N = 56$, 64, and 72), as shown in Figure 2c,d. As dictated by the PMH, we see that the more stable the complex is, the harder it appears to be.

There have been few interesting and useful attempts to relate electronic properties to reaction energies.[14,31,32] Pearson[31] proposed an empirical method for ranking the order of Lewis acids and bases in terms of their hardness at their reaction sites. More recently, Gázquez[32] proposed an expression for the bond energy in terms of the chemical potential, the hardnesses, and the condensed Fukui functions of the isolated species. In our search for a relation between the hydrogen-bond energies and the electronic properties of the isolated species, we have tested the Gázquez expression with the result that it overestimates the H-bond energies although it indicates correctly that the main contribution to the bond energy comes from the change in the hardness of the system.

To close this discussion, it is interesting to note that the analysis of Figures 1 and 2 suggests that hardness and the H-bond force constants must be related. In Figure 3, we show the nice linear relations connecting these properties. It can be seen that the stronger the bond being formed, the harder the complex. This result confirms the fact that there is direct proportionality between hardness and force constants, as correctly pointed out recently by Arulmozhiraja and Kolandaivel.[33]

Polarizability of Hydrogen-Bonded Systems. Along with the PMH, Chattaraj et al. have proposed a minimum polarizability principle (MPP), which states that the natural direction of evolution of any system is toward a state of minimum polarizability.[34] In general, the conditions of maximum hardness and minimum polarizability complement the minimum energy criterion for molecular stability.[35] The polarizability of the isolated molecules and those of the hydrogen-bonded systems determined through the ab initio calculations are quoted in Table 7, together with the best approach to the polarizability of the hydrogen-bonded systems: the simple addition of the polariz-

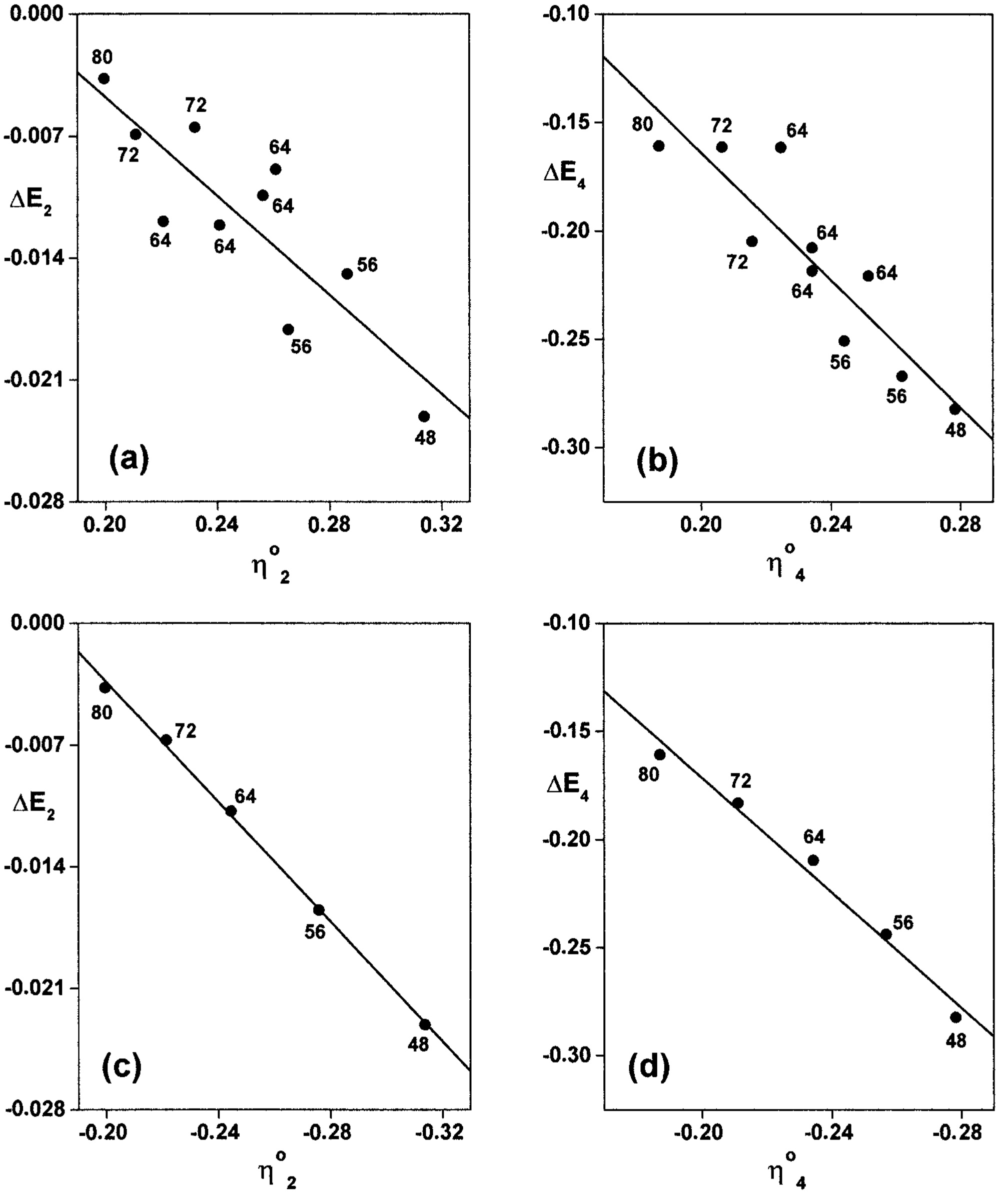

Figure 2. Correlation between bond energy and hardness of the product determined from the Sanderson approximation with (a) $n_f = 2$ and (b) $n_f = 4$. (c) and (d) Same as in panels a and b but using the average values in systems presenting the same number of electrons.

abilities of the constituent monomeric units (α_2°, the fourth column of Table 7). Figure 4a shows the excellent quality of this approach. Our results suggest that the polarizability of a composite system is given by the sum of the n_f individual polarizabilities

$$\alpha_{n_f}^\circ = \sum_{x}^{n_f} \alpha_x^\circ \tag{10}$$

where α_x° stands for the polarizabilities of the monomeric units. The above expression is not an attempt to define an addition scheme for polarizabilities; it simply comes from the empirical observation of the present results.

Adding electrons to a system will increase its polarizability because α is proportional to N; our results concerning the hydrogen-bonded complexes confirm this proportionality, as shown in Figure 4b. On the other hand, we have shown recently[19] that the H-bond energy is proportional to N; therefore, one should expect ΔE_2 be related to the polarizability. However, Figure 5a shows a very scattered plot of ΔE_2 against the reaction polarizability $\Delta\alpha_2$ (fifth column in Table 7), where this latter quantity is defined as the difference between the polarizabilities of the product (the H-bonded system) and reactants (the sum of monomeric units). The expected consistency in our results is achieved when the polarizability of the reactants is defined as the arithmetic mean of the polarizabilities of the monomeric units, thus defining the reaction polarizability as $\Delta\bar{\alpha}_2 = \alpha - (\sum_x \alpha_x)/2$, which is given in Table 7. Figure 5b shows a quite good linear correlation in which it is apparent that the lower the reaction energy, the lower the reaction polarizability. This result suggests the possibility of extending the validity of the MPP to allow for comparisons of relative energies and polarizabilities. Furthermore, ΔE_2 displays a linear correlation with the polarizability of the product, as shown in Figure 5c. In summary, the more stable the product species, the harder and less polarizable it was found to be.

We have mentioned that the polarizability can be used to understand the behavior of the system when the external potential is changed at constant N.[7] Formally, the chemical potential is a function of N and a functional of the external

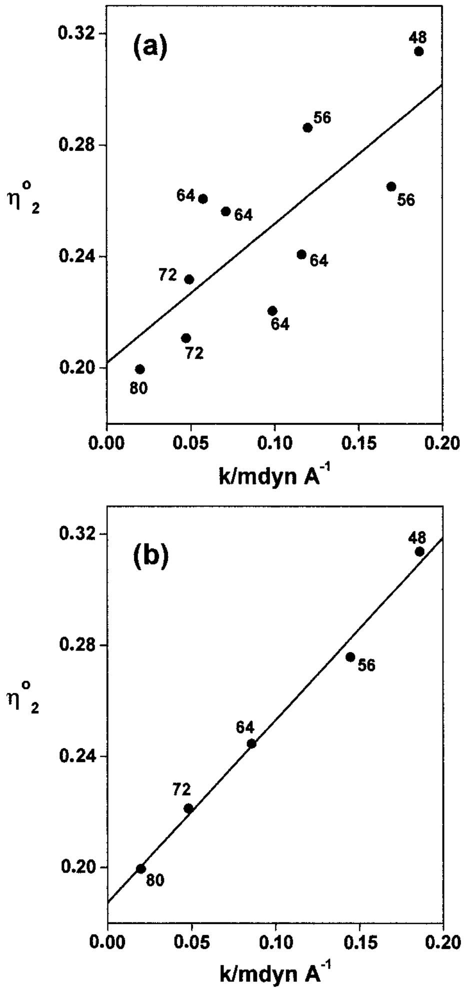

Figure 3. (a) Correlation between hardness and H-bond force constants of bimolecular aggregates. (b) Same as in panel a but using the average values in systems presenting the same number of electrons.

TABLE 7: Calculated and Estimated Polarizabilities of Isolated Molecules and Molecular Aggregates[a]

system	N	α	α_2°	$\Delta\alpha_2$	$\Delta\bar{\alpha}_2$
M1	24	15.1733			
M2	32	28.2873			
M3	32	27.7830			
M4	40	43.4183			
C1	48	30.9583	30.3466	0.6117	15.7850
C2	56	45.7427	43.4606	2.2821	24.0124
C3	64	60.5700	56.5746	3.9954	32.2827
C4	56	43.6490	42.9563	0.6927	22.1709
C5	64	60.9957	58.5916	2.4041	31.6999
C6	64	58.0750	56.0703	2.0047	30.0399
C7	72	75.0847	71.7056	3.3791	39.2319
C8	64	56.3013	55.5660	0.7353	28.5183
C9	72	72.9003	71.2013	1.6990	37.2997
C10	80	88.6140	86.8366	1.7774	45.1957

[a] All values are in atomic units.

potential $v(\vec{r})$, so we can write $\mu \equiv \mu[N,v(\vec{r})]$. To relate the change of the external potential to the reaction polarizability, we differentiate eq 6 with respect to $v(\vec{r})$, thus defining the quantity $F^\circ_{n_f}$.

$$F^\circ_{n_f} \equiv \left(\frac{\delta \mu^\circ_{n_f}}{\delta v}\right)_N \approx \frac{\mu^\circ_{n_f}}{n_f}\Delta v \sum_x^{n_f}\left(\frac{f^\circ_x}{\mu^\circ_x}\right) \qquad (11)$$

Because the formal definition of $F^\circ_{n_f}$ is analogous to the Fukui function used to quantify the reactivity of specific sites on a given molecule and because it contains information on the overall change from reactants to products through Δv, we call it the Reaction Fukui Function (RFF). It can be seen from eq 11 that $F^\circ_{n_f}$ is a global property that contains the fragment reactivities through the Fukui functions $f^\circ_x = (\delta\mu^\circ_x/\delta v)_N$. Therefore, we expect $F^\circ_{n_f}$ to be a property measuring the global reactivity of the system.

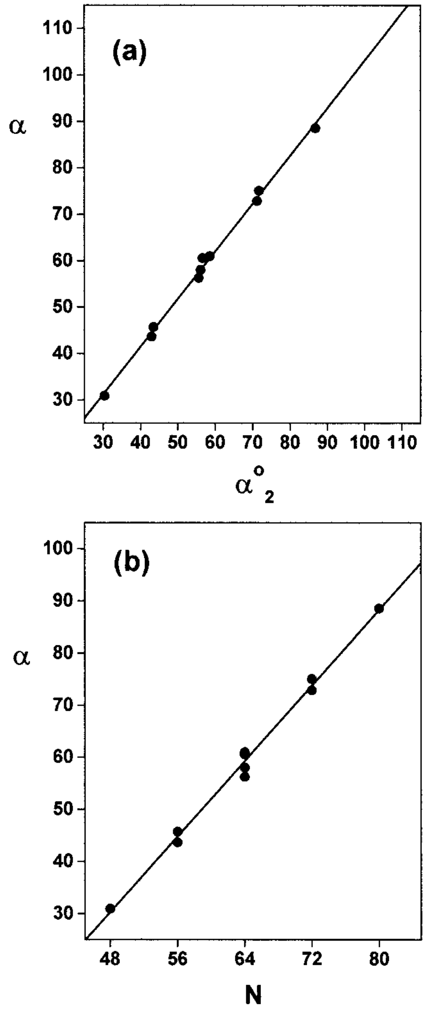

Figure 4. (a) Comparison of the calculated polarizability of the hydrogen-bonded complexes with the estimation of eq 10. (b) Characterization of the calculated polarizability with the total number of electrons of the H-bonded complexes.

We have determined numerical values of RFF approaching Δv by the electron−nuclei potential (V_{ne}) obtained from the ab initio calculations; in fact, we have used $\Delta v = [V_{ne}(\text{product}) - \sum V_{ne}(\text{reactants})]$. The f°_x values were approximated as N_x/N, with N_x being the number of electrons of fragment x and N the total number of electrons of the composite system such that $\sum_x N_x = N$. In Figure 6a, we show that the RFF is linearly related to the reaction energy, indicating that the RFF may be a measure of the exothermicity of the reaction: the lower ΔE_2, the higher the RFF value. On the other hand, Figure 6b indicates that the RFF is related to the reaction polarizability through a very good straight line. This result shows that the polarizability is the right response of the system when the external potential is changed, and it emphasizes the usefulness of determining accurate values for this property. On the other hand, it is clear that the whole procedure based upon Sanderson's scheme is a powerful tool for characterizing chemical reactions when both N and v change.

The Hardness Derivative. Hardness is now recognized as an important property for characterizing chemical processes, so

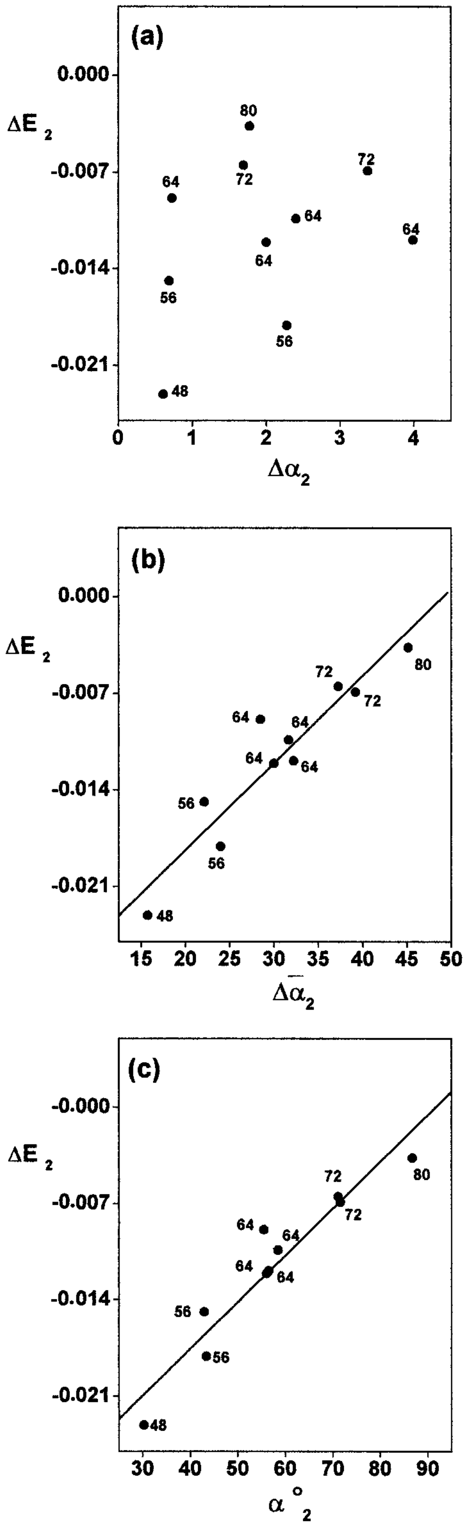

Figure 5. Representation of reaction energies ΔE_2 against (a) the reaction polarizability defined as $\Delta\alpha = \alpha(\text{product}) - \sum_x \alpha_x$, (b) the reaction polarizability defined as $\Delta\bar{\alpha} = \alpha(\text{product}) - (\sum_x \alpha_x)/n_f$, and (c) the polarizability of the bimolecular complex from eq 10. All values are in atomic units.

it is necessary to know how it changes with the number of electrons and the external potential. The quantity γ measures the change of η with N. We have used eq 8 to estimate numerical values of this property. We first note that to evaluate the third term of eq 8, we need the values of γ_x° of the isolated fragments; these were estimated from the following approximate formula proposed by Fuentealba and Parr:[20]

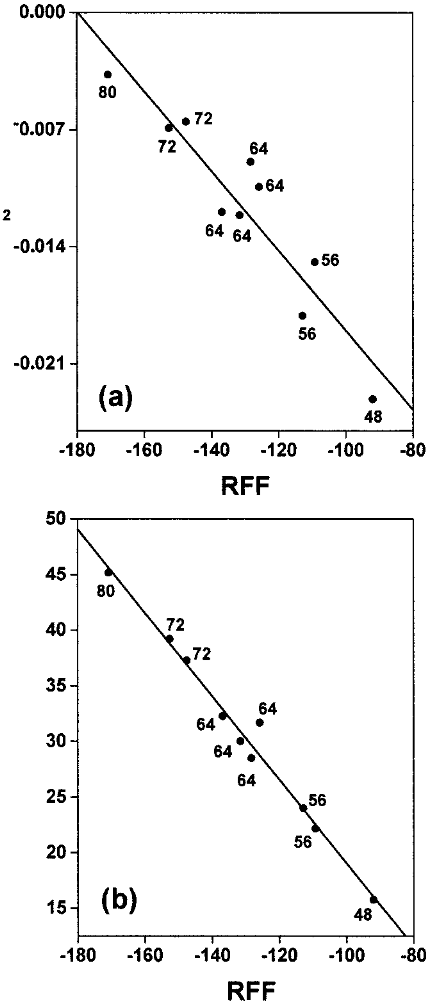

Figure 6. Characterization of the reaction Fukui function (RFF) with (a) the reaction energy and (b) the reaction polarizability. All values are in atomic units.

$$\gamma_x^\circ \approx \left[\frac{\epsilon_L}{\epsilon_L - 3\epsilon_H}\right]_x^\circ \eta_x^\circ \qquad (12)$$

Equation 8 shows a quite complex dependence of γ with respect to η that is far from being linear, as indicated by eq 12. The validity of this latter equation and its consistency with Sanderson's scheme has been tested by calculating η and γ using eqs 7 and 8 to check their possible linear relation. Values of γ_2° and γ_4° for the 14 compounds we are studying here are quoted in Table 4. We note that, in all cases, they are positive and very small. The linear dependence between γ and η could not be obtained, as is apparent in Figure 7a,b. These results are in agreement with expectations based on the very definition of γ.[20] When the atomic data of Fuentealba and Parr[20] are used to build the properties of the bimolecular complexes, thus producing η_{10}° and γ_{10}° from the 10 constituent atoms, we obtain negative values of γ and linear behavior with η, as shown in Figure 7c. It should be noted that because there are systems presenting the same atomic composition, their values of η_{10}° and γ_{10}° are the same. Thus, in Figure 7c, the systems have been ordered in terms of their total number of electrons.

A New Additivity Scheme for μ and η. In this section, we propose a new additivity scheme for the chemical potential and hardness that is based upon dimensional analysis of eq 11, which shows that it is possible to define the inverse of the chemical potential of a composite system as

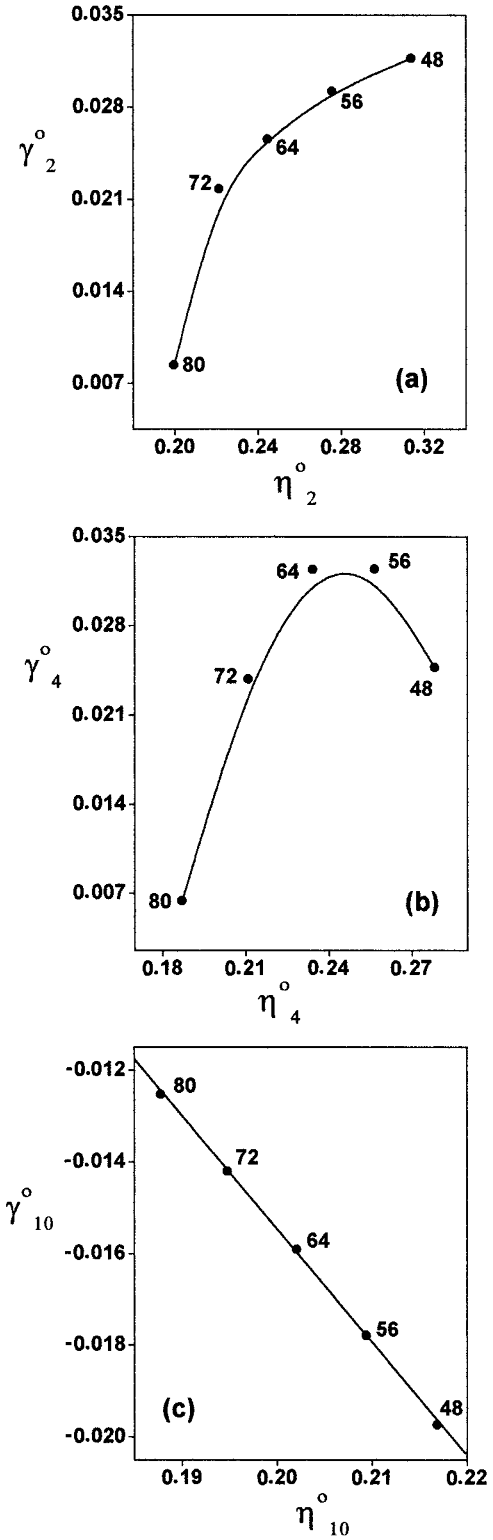

Figure 7. Relationship between $\eta^\circ_{n_f}$ and $\gamma^\circ_{n_f}$ of the H-bonded systems ordered in terms of their total number of electrons: (a) $n_f = 2$, (b) $n_f = 4$, and (c) $n_f = 10$ (from atomic data in ref 20). All values are in atomic units.

$$\frac{1}{\mu'_{n_f}} \approx \sum_x^{n_f} \left(\frac{f^\circ_x}{\mu^\circ_x}\right) \tag{13}$$

Determination of the chemical potential of a composite system from the properties of the isolated fragments by means of eq 13 produces results that are in very good agreement with those determined using eq 6. This can be verified in Figure 8, where we compare both approaches for estimating the chemical potential of the 10 bimolecular complexes using $n_f = 2$. Moreover, we have verified that, in all cases studied here, μ'_{n_f} provides a better approach to the reference ab initio value than does $\mu^\circ_{n_f}$ determined from eq 6; this was verified for $n_f = 2$, 4, and 10. These results show that eq 13 represents a valid alternative to the original Sanderson's formulation. It is interesting to note that this new expression contains the electronic population of the isolated fragment, a local quantity, together with the chemical potential, a global property of the fragment.

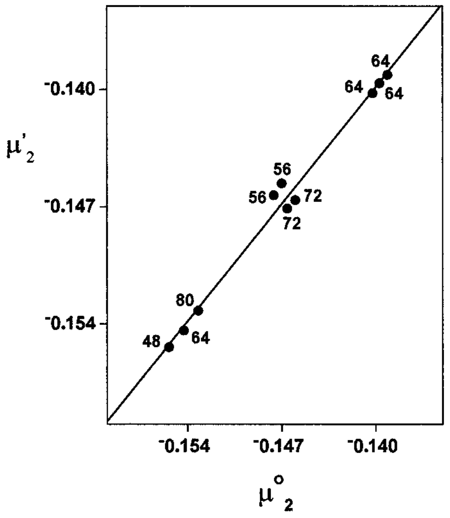

Figure 8. Comparison of chemical potentials determined through eqs 6 and 13. All values are in atomic units.

Characterization of higher-order derivatives of eq 13 is straightforward. In the new framework the hardness is given by

$$\eta'_{n_f} = \left(\frac{\partial \mu'_{n_f}}{\partial N}\right)_{v(\vec{r})} = (\mu'_{n_f})^2 \sum_x^{n_f} \frac{1}{(\mu^\circ_x)^2}[f^\circ_x \eta^\circ_x - h^\circ_x \mu^\circ_x] \tag{14}$$

where h°_x is a measure of the fluctuation of the chemical hardness due to a change in the external potential. Alternatively, through the Maxwell relation, h°_x can be seen as the response of the Fukui function to a change in the total number of electrons.

$$h^\circ_x = \left(\frac{\delta \eta^\circ_x}{\delta v}\right)_N = \left(\frac{\partial f^\circ_x}{\partial N}\right)_v \tag{15}$$

Recently, Parr et al.[36] have defined the electrophilicity index as $W = \mu^2/2\eta$. In analogy with this definition, we can define a nucleophilicity index from eq 14 as

$$\frac{\eta'_{n_f}}{(\mu'_{n_f})^2} = \sum_x^{n_f} \frac{1}{(\mu^\circ_x)^2}[f^\circ_x \eta^\circ_x - h^\circ_x \mu^\circ_x] \tag{16}$$

which is a positive defined quantity. The above set of equations containing local and global properties opens a method for characterizing the reactivity and selectivity concepts in an unified perspective.

5. Concluding Remarks

We have used Sanderson's Principle to estimate the first, second, and third derivative of the energy with respect to the total number of electrons. The results for $\mu^\circ_{n_f}$ and $\eta^\circ_{n_f}$ show that, in the cases treated here, Sanderson's geometric mean equalization principle is adequate for predicting these electronic properties of composite systems. Numerical values for the third-order property, γ, were found to be very small and positive, in agreement with the expected behavior.

Numerical results for bond energies at the RHF/6−311G** level were qualitatively satisfactory and quantitatively in agreement with the available bond-energy data. We have found that principles of maximum hardness and minimum polarizability are operative for rationalizing the formation of molecules and bimolecular aggregates. Sanderson's scheme has been shown to be very useful not only in determining electronic properties but also in rationalizing chemical reactions when both N and v change. Finally, we have proposed a new scheme for obtaining molecular properties from the isolated fragments with quite encouraging results for chemical potentials. In this approach, local and global properties play equivalent roles, which may lead to methods for simultaneously characterizing the reactivity and selectivity concepts in chemical processes.

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