Global Hardness Evaluation Using Simplified Models for the Hardness Kernel

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Two simplified models of the hardness kernel, $\eta(\mathbf{r},\mathbf{r}') \cong 1/|\mathbf{r} - \mathbf{r}'|$ and $\eta(\mathbf{r},\mathbf{r}') \cong \delta(\mathbf{r} - \mathbf{r}')$, have been tested to calculate the global hardness for a set of 18 molecules using the hybrid B3LYP functional. It is found that the simplest model, $\eta(\mathbf{r},\mathbf{r}') \cong \delta(\mathbf{r} - \mathbf{r}')$, yields the best ordering of the systems by hardness when compared to experimentally available hardnesses. However, it is worth noting that this approximation provides correct estimates of global hardnesses only after empirical corrections. Finally, it is also shown that the B3LYP method gives results close to conventional ab initio correlated methods.

I. Introduction

In recent years, density functional theory (DFT)[1] has attracted a great deal of attention because it provides accurate calculations of large molecular systems incorporating electron correlation effects at a much lower cost than conventional ab initio correlated methods. Another important aspect of DFT, besides computational advantages, is the fact that many common chemical concepts, such as the electronegativity or the hardness (and its counterpart, the softness), receive a precise mathematical definition.[1] In this respect, DFT provides a bridge that connects some traditional empirical concepts with quantum mechanics.

Hardness[2] is a measure of the resistance of a chemical species to change its electronic configuration. Within the DFT formalism, the hardness (η) is defined as the second-order partial derivative of the total electronic energy E with respect to the total number of electrons N at a fixed external potential $v(\vec{r})$,[3]

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

This definition has been used to rationalize important chemical reactivity principles such as the hard and soft acids and bases principle (HSAB)[2−4] and the maximum hardness principle (MHP).[2,5] By applying the finite difference approximation to eq 1 and assuming that the energy varies quadratically with the number of electrons, one gets the operational definition of η:[1,6−9]

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

where I and A are the vertical ionization energy and electron affinity, respectively. Indeed, experimental hardnesses are not derived from the exact eq 1 but from the approximate eq 2 and using the available experimental values of I and A. These quantities can be approximated in molecular orbital calculations by using the Koopmans' theorem. For closed-shell species, one obtains[6]

$$\eta \cong \epsilon_{\mathrm{LUMO}} - \epsilon_{\mathrm{HOMO}} \tag{3}$$

ϵ_{HOMO} and ϵ_{LUMO} being the energies of the highest occupied molecular orbital and the lowest unoccupied molecular orbital, respectively. For open-shell systems, an average of the HOMO−LUMO gaps for the α and β spins is usually taken.

Calculation of hardness from eqs 2 and 3 is subject to several error sources,[10] the most important being the fact that the finite difference approximation in eq 1 has been used to derive eqs 2 and 3 and this approximation can only be strictly applied using an integer number of electrons ($\Delta N = \pm 1$). For this reason, it is very important to explore new ways to compute more accurate hardness values. An alternative to eqs 2 and 3 is to use the following expression first derived by Ghosh[11] and later on mathematically demonstrated by Chattaraj et al.:[12]

$$\eta = \int\int f(\vec{r})\cdot\eta(\vec{r},\vec{r}')\cdot f(\vec{r}')\cdot \mathrm{d}\vec{r}\cdot\mathrm{d}\vec{r}' \tag{4}$$

In this equation, $f(\vec{r})$ is the Fukui function and $\eta(\vec{r},\vec{r}')$ is the hardness kernel,[13] from which most reactivity parameters in DFT can be readily defined.[14]

The Fukui function[1] is a reactivity index that connects the frontier orbital concepts of Fukui[15] with DFT. It was defined in the 1980s by Yang and Parr[16] as the partial derivative of the electron density with respect to the total number of electrons at constant external potential, that is,

$$f(\vec{r}) = \left(\frac{\partial \rho(\vec{r})}{\partial N}\right)_v \tag{5}$$

The Fukui function describes the local changes in the electron density of the system due to the perturbation in the global number of electrons, so it reflects the character of a molecule to accept (donate) electrons from (to) another system. For a molecular or atomic system, the derivative in eq 5 is discontinuous with the number of electrons. Because of that, Parr and Yang[16] associated different physical meanings to the left, right, and central derivatives, corresponding to a reactivity index for nucleophilic ($f^+(\vec{r})$), electrophilic ($f^-(\vec{r})$), and radical ($f^0(\vec{r})$) attacks on the system, respectively. By applying a finite difference approximation to eq 5, these three approximate Fukui functions can be written as

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$$f^{+}(\vec{r}) = \rho_{N+1}(\vec{r}) - \rho_{N}(\vec{r}) \quad (6)$$

$$f^{-}(\vec{r}) = \rho_{N}(\vec{r}) - \rho_{N-1}(\vec{r}) \quad (7)$$

$$f^{0}(\vec{r}) = \frac{1}{2}[\rho_{N+1}(\vec{r}) - \rho_{N-1}(\vec{r})] \quad (8)$$

where $\rho_{N+1}(\vec{r})$, $\rho_N(\vec{r})$, and $\rho_{N-1}(\vec{r})$ are the electron densities of the system with $N + 1$, N, and $N - 1$ electrons, respectively. From eq 5, it can be easily demonstrated that the integration of the Fukui function over all space equals one electron.

The other quantity required in eq 4 is the hardness kernel that is defined as the second-order functional derivative of Hohenberg−Kohn universal density functional ($F[\rho]$) with respect to the density,

$$\eta(\vec{r},\vec{r}') = \frac{\delta^2 F[\rho]}{\delta\rho(\vec{r})\delta\rho(\vec{r}')} \quad (9)$$

$F[\rho]$ is an unknown and presumably very complicated functional that contains the kinetic energy density functional, the classical electron−electron Coulomb repulsion functional, and the exchange-correlation functional:

$$F[\rho] = T[\rho] + J[\rho] + E_{xc}[\rho] \quad (10)$$

The lack of exact expressions for $T[\rho]$ and $E_{xc}[\rho]$ is the main impediment for obtaining accurate hardnesses from eq 4. Because the leading term in the hardness kernel comes from the Coulombic contribution,[13b,17−22] the hardness kernel can be approximated as

$$\eta(\vec{r},\vec{r}') \cong \frac{1}{|\vec{r} - \vec{r}'|} \quad (11)$$

Introducing this approximation into eq 4, one obtains

$$\eta \cong \int\int f(\vec{r})\cdot\frac{1}{|\vec{r} - \vec{r}'|}\cdot f(\vec{r}')\cdot d\vec{r}\cdot d\vec{r}' \quad (12)$$

Equation 12 was used by Liu, Proft, and Parr[22] for the calculation of the global hardness of the first 54 neutral atoms. The authors showed that eq 12 generates reasonable atomic global hardness values.

A more severe approximation to the hardness kernel could be (see Appendix A for the connection of eq 13 with formal DFT expressions):

$$\eta(\vec{r},\vec{r}') \cong \delta(\vec{r} - \vec{r}') \quad (13)$$

leading to the following very simple and computationally cheap form for the hardness:

$$\eta \cong \int f^2(\vec{r})\cdot d\vec{r} \quad (14)$$

The most important aim of this work is to examine the validity of eq 14 to calculate the hardness. This research was motivated by the particular properties of the so-called self-similarity value or average electron density,[23,24] $\int\rho^2(\vec{r})\cdot d\vec{r}$. We demonstrated that this quantity is a precise indicator of charge concentration for systems having the same number of electrons.[23] Thus, in a series of N electron molecules, we found that as the charge density became more concentrated, the self-similarity measure became larger.[23] Given that the Fukui function is a difference of densities that for all species integrates to one electron, the Fukui self-similarity values ($\int f^2(\vec{r})\cdot d\vec{r}$) should tell us whether this electron is more or less concentrated. In addition, one can assume according to the definition of hard and soft species,[2,5,25] that soft systems have more diffuse Fukui functions and therefore smaller Fukui self-similarity values than hard species. As a simple example, Figure 1 compares the Fukui radical $f^0(\vec{r})$ function for F^- and Cl^-, for Li^+, Na^+, and K^+, and for N_2 and F_2.[26] It is clearly seen in the figure that the Fukui functions for the softer Cl^-, K^+, and N_2 systems are more diffuse.

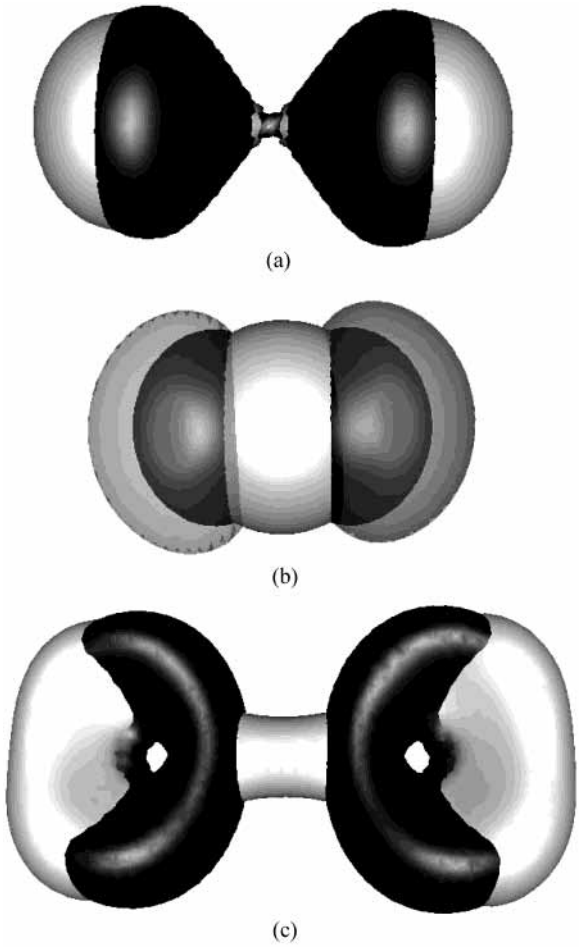

Figure 1. Three-dimensional contour plot of the Fukui function f^0 at 0.01 au for (a) the F^- (black) and Cl^- (grey) anions and (b) Li^+ (light gray), Na^+ (black), and K^+ (dark gray) cations and (c) countour plot of the Fukui function f^0 at 0.02 au for N_2 (grey) and F_2 (black) at a fixed internuclear distance of 1.258 Å.

On the basis of such considerations, it follows that eq 14 may be a good approximation for the calculation of hardnesses, despite the fact that the use of such an approximation produces some inconsistencies (see Appendix A). The study of the validity of this equation to calculate hardness values is the main goal pursued in this paper. In addition, we aim to extend the use of eq 12 to molecular systems and to compare the results of hardness values derived from eqs 12 and 14 and those calculated from eqs 2 and 3. Calculations are carried out with the B3LYP method. However, MP2 and QCISD calculations will be also performed to discuss the reliability of the B3LYP method in this kind of computation.

II. Computational Details

Integrals involved in eqs 12 and 14 can be written in a general form as

$$\eta \cong \int\int f(\vec{r})\cdot\Theta(\vec{r},\vec{r}')\cdot f(\vec{r}')\cdot d\vec{r}\cdot d\vec{r}' \quad (15)$$

From this equation, three types of hardnesses for electrophilic, nucleophilic, and radical attacks can be defined,[12] corresponding to the three definitions of Fukui functions, eqs 6−8. Considering $f^-(\vec{r})$ and using eqs 15 and 7, one gets

$$\begin{aligned}\eta_{f^-f^-}(\Theta) &\cong \int\int f^-(\vec{r})\cdot\Theta(\vec{r},\vec{r}')\cdot f^-(\vec{r}')\cdot d\vec{r}\cdot d\vec{r}' \\ &\cong \int\int (\rho_N(\vec{r}) - \rho_{N-1}(\vec{r}))\cdot\Theta(\vec{r},\vec{r}')\cdot(\rho_N(\vec{r}') - \\ &\qquad \rho_{N-1}(\vec{r}'))\cdot d\vec{r}\cdot d\vec{r}' \\ &= \int\int \rho_N(\vec{r})\cdot\Theta(\vec{r},\vec{r}')\cdot\rho_N(\vec{r}')\cdot d\vec{r}\cdot d\vec{r}' + \\ &\qquad \int\int \rho_{N-1}(\vec{r})\cdot\Theta(\vec{r},\vec{r}')\cdot\rho_{N-1}(\vec{r}')\cdot d\vec{r}\cdot d\vec{r}' - \\ &\qquad 2\cdot\int\int \rho_N(\vec{r})\cdot\Theta(\vec{r},\vec{r}')\cdot\rho_{N-1}(\vec{r}')\cdot d\vec{r}\cdot d\vec{r}' \\ &= Z_{\rho_N\rho_N}(\Theta) + Z_{\rho_{N-1}\rho_{N-1}}(\Theta) - 2\cdot Z_{\rho_N\rho_{N-1}}(\Theta) \qquad (16)\end{aligned}$$

where $Z_{\rho_A\rho_B}(\Theta)$ is the so-called quantum molecular similarity measure (QMSM) between two molecules A and B of densities $\rho_A(\vec{r})$ and $\rho_B(\vec{r})$.[27,28] The QMSM gives a measure of how similar one molecule is to another, and it is a useful parameter in studies of charge density redistributions[29] and QSAR analysis.[30] Overlap-like QMSMs are obtained when the $\Theta(\vec{r},\vec{r}')$operator in $Z_{\rho_A\rho_B}(\Theta)$ is chosen as the Dirac delta function, $\delta(\vec{r}-\vec{r}')$, while use of the operator $1/|\vec{r}-\vec{r}'|$ gives rise to Coulomb-like QMSMs. In the particular case that $\rho_A(\vec{r}) = \rho_B(\vec{r})$, one gets $Z_{\rho_A\rho_A}(\Theta)$, which is the so-called self-QMSM.[23] Equation 16 shows that evaluation of integrals such as those appearing in eqs 12 and 14 involves the calculation of three Coulomb-like and three overlap-like QMSM, respectively. Integrals such as those appearing in eq 14 have been already used to evaluate molecular similarity in a previous work.[31]

Likewise for $f^+(\vec{r})$ and $f^0(\vec{r})$, we can write

$$\eta_{f^+f^+}(\Theta) \cong Z_{\rho_{N+1}\rho_{N+1}}(\Theta) + Z_{\rho_N\rho_N}(\Theta) - 2\cdot Z_{\rho_{N+1}\rho_N}(\Theta) \quad (17)$$

$$\eta_{f^0f^0}(\Theta) \cong \frac{1}{4}[Z_{\rho_{N+1}\rho_{N+1}}(\Theta) + Z_{\rho_{N-1}\rho_{N-1}}(\Theta) - 2\cdot Z_{\rho_{N+1}\rho_{N-1}}(\Theta)] \quad (18)$$

In this work, we have used the Gaussian 98 program[32] to perform correlated calculations with the hybrid density functional B3LYP,[33] second-order Møller−Plesset (MP2),[34] and singles and doubles quadratic configuration interaction (QCISD)[35] calculations of vertical *I* and *A*, HOMO and LUMO orbital energies, and electron densities.

Including electron correlation effects is very important when comparing results from species with different numbers of electrons.[36] Indeed, in the calculation of *I* and *A* values, it is highly advisable to go beyond the Hartree−Fock method.[10,37] Less-relevant seems to be the effect of electron correlation in calculated Fukui functions,[38] and in particular, the B3LYP method provides excellent Fukui functions according to De Proft and co-workers.[39] The 6-31++G** basis set[40] has been used throughout.

Calculated *A* and *I* are always vertical values computed using the B3LYP/6-31++G** geometry of the neutral forms. All calculations have been done within the restricted formalism except for open-shell systems that have been calculated using the unrestricted approach. In some open-shell systems such as HF^+, CH_3F^+, HCl^+, CH_3Cl^+, and CO^-, the UB3LYP/6-31++G** density loses the full molecular symmetry because of frontier orbital degeneracy. These symmetry problems can be solved by performing CASSCF calculations, although we have preferred here to keep the B3LYP/6-31++G** level of theory throughout. Further, the errors in B3LYP/6-31++G** vertical *A* and *I* when compared to QCISD/6-31++G** values are not larger for the abovementioned systems than for the rest of the systems that do not present degeneracy problems.

TABLE 1: Experimental and Calculated Hardness for the 18 Lewis Bases Studied[a]

			Coulomb		overlap		
molecule	η_1	η_2	$\eta_{f^-f^-}(\Theta)$	$\eta_{f^0f^0}(\Theta)$	$\eta_{f^-f^-}(\Theta)$	$\eta_{f^0f^0}(\Theta)$	expt
HF	10.77	17.04	24.66	24.08	25.61	25.49	22.0
CH_3F	9.44	13.79	15.28	14.42	16.46	16.43	18.8
HCl	8.38	13.35	16.62	17.55	14.25	14.31	16.0
CH_3Cl	7.76	11.94	13.53	13.22	13.64	13.54	15.0
H_2O	8.07	13.41	20.43	20.39	19.33	19.13	19.0
CH_3OH	7.32	11.55	14.93	14.20	16.37	16.32	17.0
CH_3OCH_3	6.95	10.62	12.64	11.74	15.96	15.94	16.0
H_2S	6.66	10.99	14.53	14.94	13.11	13.04	12.4
CH_3SH	6.06	10.01	12.63	12.64	12.97	12.87	
CH_3SCH_3	5.80	9.34	11.36	10.84	12.92	12.82	12.0
NH_3	6.84	11.55	17.68	17.36	15.49	15.39	16.4
NH_2CH_3	6.22	10.24	14.20	13.41	14.57	14.50	14.4
$NH(CH_3)_2$	5.87	9.46	12.35	11.43	14.32	14.28	
$N(CH_3)_3$	5.64	8.95	11.03	10.22	14.16	14.16	12.6
PH_3	7.20	11.20	13.39	13.25	12.55	12.47	12.0
AsH_3	7.21	11.12	12.69	12.37	12.26	12.18	12.2
C_2H_4	7.31	11.41	13.24	12.90	13.11	13.05	12.4
CO	9.34	15.52	17.81	23.12	14.22	15.23	15.8
STD[b]	8.22	3.85	1.93	2.92	1.46	1.39	

[a] η_1 is obtained using eq 3, η_2 is calculated from eq 2, while $\eta_{f^-f^-}(\Theta)$ and $\eta_{f^0f^0}(\Theta)$ are derived from the Coulomb and overlap Fukui self-similarities for the Fukui functions f^- and f^0, respectively (eq 19). Experimental values are from ref 2 obtained using eq 2. Units are eV. [b] STD is the standard deviation defined as

$$\left(\sum_{i=1}^{N}\frac{(\eta_i - \eta_i^{expt})^2}{N-1}\right)^{1/2},$$

where η_i and η_i^{expt} are the calculated and experimental hardness, respectively, and N is the number of Lewis bases for which η_i^{expt} is known ($N = 16$).

QMSMs have been obtained from the Gaussian 98 electron densities using the Messem program[41] developed in our group. MP2 and QCISD generalized densities[42] and B3LYP electron densities calculated from self-consistently converged Kohn−Sham orbitals have been used for the calculation of QMSMs.

III. Results and Discussion

The methodology described in the previous section has been applied to the ground state of a series of 18 Lewis bases. Table 1 collects the B3LYP hardness values of the different molecules calculated with the operational expressions given by eqs 2 and 3 and with the alternative procedure represented by eqs 16 and 18 with $\Theta(\vec{r},\vec{r}') = \delta(\vec{r}-\vec{r}')$ (overlap-like Fukui self-similarity, OFSS) and $\Theta(\vec{r},\vec{r}') = 1/|\vec{r}-\vec{r}'|$ (Coulomb-like Fukui self-similarity, CFSS). Equation 17 has not been used here to compute hardnesses given the fact that the molecules chosen do not undergo nucleophilic attacks because of their inherent basic character. We have included in our study the CH_3SH and $(CH_3)_2NH$ molecules for which experimental values are not available to discuss the effect of successive substitution of hydrogen atoms in H_2S and NH_3 by methyl groups.

In contrast to what Liu and co-workers found using CFSS measures for atoms,[22] we find that hardnesses obtained from eqs 16 and 18 using both OFSS and CFSS measures are clearly underestimated as compared to experimental values based on eq 2. In the case of the CFSS hardness values, we attribute the

larger errors found for molecules to the fact that experimental values of hardnesses are more reliable for atoms than for molecules (vide infra). For the OFSS hardness values, it is important to remark that the proposed model yields inaccurate absolute values, as expected from the inconsistencies arising from the approximation given by eq 13 (see Appendix A), although it provides the correct relative ordering by hardness of the series of molecules studied in this work. Given the large errors in absolute hardnesses shown by the OFSS measures, the values of hardness in Table 1 obtained from Fukui self-similarity measures are not those obtained directly from the calculation of integrals in eqs 16 and 18, but those calculated from eq 19 that were derived from a linear regression using the CFSS or the OFSS measures and the experimental values as the y and x components. The resulting equations are (in au) as follows:

$$\eta_{f^-f^-}(1/|\vec{r}-\vec{r}'|) = 1.788\int\int f^-(\vec{r})\cdot\frac{1}{|\vec{r}-\vec{r}'|}\cdot f^-(\vec{r}')\cdot d\vec{r}\cdot d\vec{r}' - 0.071; \quad r^2 = 0.705$$

$$\eta_{f^0f^0}(1/|\vec{r}-\vec{r}'|) = 3.807\int\int f^0(\vec{r})\cdot\frac{1}{|\vec{r}-\vec{r}'|}\cdot f^0(\vec{r}')\cdot d\vec{r}\cdot d\vec{r}' - 0.230; \quad r^2 = 0.509$$

$$\eta_{f^-f^-}(\delta(\vec{r}-\vec{r}')) = 5.712\int\int f^-(\vec{r})\cdot\delta(\vec{r}-\vec{r}')\cdot f^-(\vec{r}')\cdot d\vec{r}\cdot d\vec{r}' + 0.403; \quad r^2 = 0.806$$

$$\eta_{f^0f^0}(\delta(\vec{r}-\vec{r}')) = 23.474\int\int f^0(\vec{r})\cdot\delta(\vec{r}-\vec{r}')\cdot f^0(\vec{r}')\cdot d\vec{r}\cdot d\vec{r}' + 0.398; \quad r^2 = 0.822 \quad (19)$$

Because of the use of experimental hardnesses, the coefficients present in eqs 19 are empirical and not necessarily transferable to other sets of molecules. However, it is very important to have methods that give the correct ordering by hardness for a series of molecules. Indeed, application of the HSAB and the MHP principles only requires knowing whether the hardness of some species is greater or smaller than that of a certain system of reference. We will show at this point that the use of OFSS measures is a good method to order molecules by hardness.

Electronegativity is an old concept originally introduced by Pauling[43,44] that describes the capacity of an atom or a molecule to attract electrons. From arguments based on the electronegativity concept, we can expect the following relations among several Lewis bases analyzed here:

$$\eta(HF) > \eta(HCl); \quad \eta(H_2O) > \eta(H_2S); \quad \eta(NH_3) > \eta(PH_3) > \eta(AsH_3); \quad \eta(HF) > \eta(H_2O) > \eta(NH_3); \quad \eta(HCl) > \eta(H_2S) > \eta(PH_3) \quad (20)$$

Alkyl groups[45] are usually regarded as electron-donating ($+I$) substituents. Thus, substitution of a hydrogen atom in water by a methyl group to give methanol will increase the electron density of the central atom. Because the oxygen atom will be richer in electrons, it will more easily transfer these electrons, and therefore, methanol will be softer than water. As a consequence, one can expect the following ordering in hardnesses:

$$\eta(HF) > \eta(CH_3F); \quad \eta(HCl) > \eta(CH_3Cl); \quad \eta(H_2O) > \eta(CH_3OH) > \eta(CH_3OCH_3); \quad \eta(H_2S) > \eta(CH_3SH) > \eta(CH_3SCH_3); \quad \eta(NH_3) > \eta(NH_2CH_3) > \eta(NH(CH_3)_2) > \eta(N(CH_3)_3) \quad (21)$$

Experimental hardnesses in Table 1 have been obtained from eq 2 using the experimental values of I and A.[2] With the exception of the hardness for PH_3 and AsH_3, the qualitative ordering predicted above is followed by the experimental values of hardness. The difference in hardness between PH_3 and AsH_3 is only 0.2 eV, and given the approximate nature of eq 2, one can only assert that the hardnesses of these two molecules are very similar. This is in agreement with the fact that the Pauling electronegativity of P and As differs by only 0.31 eV[46] and with previous calculations by Chattaraj and Schleyer who found that the hardness of PH_3 is larger than that of AsH_3 by only 0.02 eV.[47]

Among the different theoretical methods used to compute hardness, the use of eq 3 to compute η_1 leads, not unexpectedly, to two errors in the qualitative ordering shown in eqs 20 and 21: $\eta_1(NH_3) < \eta_1(PH_3)$ and $\eta_1(H_2S) < \eta_1(PH_3)$. Equation 2 reproduces also the erroneous order for H_2S and PH_3. The rest of the theoretical methods yield the qualitative ordering predicted by eqs 20 and 21. All methods also yield the expected larger difference in hardness between water and methanol than between methanol and dimethyl ether.

More difficult for the theoretical methods employed is to place correctly the CO and C_2H_4 molecules as compared to the experimental ordering of hardnesses. Experimentally, C_2H_4 is a rather soft molecule, while CO has an intermediate character. Values of η_1 obtained with eq 3 yield a CO molecule harder than water and only softer than HF and CH_3F, whereas C_2H_4 is as hard as CH_3OH. HOMO and LUMO energies in DFT do not usually provide good estimates for I and A.[48] Therefore, the poor results obtained with eq 3 are not unexpected. The values of hardness for CO and C_2H_4 calculated with eq 2, that is, η_2, are qualitatively similar and do not improve the overall picture obtained with η_1. This result is more surprising, especially if one takes into account, first, that the experimental values in Table 1 are obtained from the same eq 2 using experimental I and A and, second, that according to De Proft and Geerlings[10] the mean absolute deviation of B3LYP/6-311++G(3df,2p) hardnesses is only 0.08 eV when compared to experimental values for a set of atoms that have positive electron affinities. As can be seen in Table 1, the deviations of B3LYP/6-31++G** hardnesses in the molecules studied in this work are much larger.

To analyze the origin of the large standard deviation in the hardnesses computed using eq 2, which is as large as 3.85 eV, we have compared the calculated and experimental ionization potentials and electron affinities for the whole series of studied systems. In previous works,[10,49,50] it was found that B3LYP ionization energies and positive or close to zero electron affinities have relatively small average absolute deviations from experiment. In line with these results, we found that the maximum deviation in the B3LYP/6-31++G** ionization potential of the molecules in Table 1 is 0.6 eV, the B3LYP ionization potentials being of the same quality if not better than MP2 or QCISD estimates. In contrast, calculated electron affinities in systems with very negative electron affinities such

as H_2O, NH_3, CH_3F, CH_3OH, or HF are in error by about 5 eV, the experimental values being more negative than the B3LYP/6-31++G** ones. For instance, the experimental vertical electron affinity of water is −6.4 eV,[51] while the theoretical B3LYP/6-31++G** estimate is −0.67 eV and the QCISD/6-31++G** result is −0.95 eV. Because the experimental determination of negative electron affinities is complex and the QCISD/6-31++G** results are quite reliable, one can assume that the reason for this large discrepancy may be found in experimental electron affinities. Despite the fact that different experimental methods and solvents may lead to quite different results of electron affinities,[52] the large differences found between experimental and theoretical electron affinities seems to indicate that for the aforementioned systems the experimental electron affinities should be revised. However, because the experimental hardnesses values given by Pearson yield the expected order for the systems considered, we have decided to work with these values despite the fact that some experimental hardness values in Table 1 can be overestimated.

To return to the discussion of the position of CO and C_2H_4 in the series, the use of equations based on CFSS measures improves the results for C_2H_4 but not for CO. Remarkably, the results from equations based on OFSS place the CO and C_2H_4 in the expected zone. Finally, from a quantitative point of view, the hardness values calculated with eqs 2 and 3 systematically underestimate the experimental hardness, whereas the theoretical hardnesses calculated from eq 19 based on CFSS and OFSS measures are much closer to the experimental results.

According to experimental values, the ordering of the molecules by hardness is as follows:

$$\eta(\mathrm{HF}) > \eta(\mathrm{H_2O}) > \eta(\mathrm{CH_3F}) > \eta(\mathrm{CH_3OH}) > \eta(\mathrm{NH_3}) > \eta(\mathrm{CH_3OCH_3}) = \eta(\mathrm{HCl}) > \eta(\mathrm{CH_3Cl}) > \eta(\mathrm{NH_2CH_3}) > \eta(\mathrm{N(CH_3)_3}) > \eta(\mathrm{H_2S}) = \eta(\mathrm{C_2H_4}) > \eta(\mathrm{AsH_3}) > \eta(\mathrm{PH_3}) = \eta(\mathrm{CH_3SCH_3}) \quad (22)$$

The classification of the molecules given in eq 22 is not followed precisely by any of the theoretical methods employed. As said before, the experimental ordering is based on hardnesses calculated with eq 2, which is an approximation to the exact definition of hardness given by eq 1. For this reason, it is more rational to discuss general trends than to analyze the exact position of each molecule given by the different methods. It seems reasonable to consider that we have three main groups of molecules, the hardest being HF, H_2O, CH_3F, and CH_3OH, the softest being $N(CH_3)_3$, H_2S, C_2H_4, AsH_3, PH_3, and CH_3SCH_3, and the rest can be considered as molecules with intermediate hardnesses.

With this experimental grouping in mind, values from Table 1 indicate that η_1 hardnesses calculated with eq 3 have several errors. For instance, the CO molecule, which belongs to the group of molecules with intermediate hardness, is considered as a hard molecule, whereas a hard molecule such as CH_3OH shows the same hardness as soft molecules such as C_2H_4, PH_3, and AsH_3. The ordering obtained from η_2 hardnesses calculated with eq 2 exhibits slight differences, but the main problems observed with η_1 remain. There is a minor improvement when the CFSS measures, $\eta_{f^-f^-}(1/|\vec{r} - \vec{r}'|)$, are used to calculate hardnesses, but still a number of errors are apparent. As an example, with this method H_2S is found to be almost as hard as CH_3OH. The results worsen when the $\eta_{f^0f^0}(1/|\vec{r} - \vec{r}'|)$ values are used. Finally, when OFSS measures are used, most molecules are positioned correctly with respect to the three groups aforementioned, with the possible exception of the CH_3Cl, which is predicted to be softer than experimentally found, despite the fact that the difference between experimental and OFSS hardness for this molecule is rather small. Clearly, the ordering obtained from OFSS measures is the closest to the experimental sequence.

Not only hardnesses based on OFSS measures are ordered better but also they are computationally cheaper than those obtained from CFSS values. The reason for the excellent behavior of OFSS measures is attributed to the fact that, as said before, the self-similarity measure[23] is an excellent indicator of charge concentration. As a consequence, harder species with more electronegative atoms lead to small and more compact Fukui functions and have larger OFSS measures.

Standard deviations also show that the methods based on OFSS measures are superior to both the traditional methods of eqs 2 and 3 and the method based on CFSS measures. Both the equation based on electrophilic OFSS measures, $\eta_{f^-f^-}(\delta(\vec{r} - \vec{r}'))$, and that using the radical OFFS values, $\eta_{f^0f^0}(\delta(\vec{r} - \vec{r}'))$, provide excellent results. According to the values of standard deviations and the linear regression coefficients in eqs 19, the method giving the best results is $\eta_{f^0f^0}(\delta(\vec{r} - \vec{r}'))$.

One may wonder whether the use of OFSS and CFSS measures in a multilinear regression can improve the results significantly. For the Fukui electrophilic $f^-(\vec{r})$ function, we have found the following equation (in au):

$$\eta_{f^-f^-} = 3.384 \int\int f^-(\vec{r})\cdot\delta(\vec{r} - \vec{r}')\cdot f^-(\vec{r}')\cdot \mathrm{d}\vec{r}\cdot\mathrm{d}\vec{r}' + 0.422 \int\int f^-(\vec{r})\cdot\frac{1}{|\vec{r} - \vec{r}'|}\cdot f^-(\vec{r}')\cdot \mathrm{d}\vec{r}\cdot\mathrm{d}\vec{r}' + 0.318; \quad r^2 = 0.829 \quad (23)$$

that leads to a standard deviation of 1.23 eV. If one compares this standard deviation with those found using OFSS measures (Table 1), it is seen that the results do not improve markedly despite the fact that the computing time increases significantly because of the need to calculate CFSS values.

Equation 19 and Table 1 show that OFSS calculations are the best in terms of accuracy and computational cost. For this reason, we have analyzed the reliability of the B3LYP method in this kind of calculation by performing OFSS calculations using the conventional correlated MP2 and QCISD methods. Results in Table 2 show that all methods yield similar results, the conclusions resulting from the MP2 and QCSID values being the same as those derived from the B3LYP hardnesses. Not surprisingly, QCISD results are better than B3LYP ones. More unexpected are the excellent results obtained with the MP2 method.

Finally, it is worth noting that OFSS measures (eq 14) by themselves do not provide accurate values of hardnesses, and therefore, experimental values are needed to derive expressions such as those in eq 19. However, it is important to remark that for the application of the HSAB or the MHP principles one only needs to know whether the hardness of some species is greater or smaller than that of a certain system of reference. In this sense, it is relevant to note that OFSS measures give the most correct ordering among all expressions used in this work to calculate the hardness.

IV. Conclusions

In this paper, we have tested two approximate hardness kernels, $\eta(\mathbf{r},\mathbf{r}') \cong 1/|\mathbf{r} - \mathbf{r}'|$ and $\eta(\mathbf{r},\mathbf{r}') \cong \delta(\mathbf{r} - \mathbf{r}')$, for the evaluation of the global hardness in a series of 18 Lewis bases. The intuitive order of hardness supported by electronegativity

TABLE 2: Experimental and Calculated Hardness Obtained from the Overlap Fukui Self Similarities with the Fukui Functions f^- and f^0 at the B3LYP, MP2, and QCISD Levels of Theory[a]

	B3LYP		MP2		QCSID		
molecule	$\eta_{f^-f^-}(\Theta)$	$\eta_{f^0f^0}(\Theta)$	$\eta_{f^-f^-}(\Theta)$	$\eta_{f^0f^0}(\Theta)$	$\eta_{f^-f^-}(\Theta)$	$\eta_{f^0f^0}(\Theta)$	expt
HF	25.61	25.49	23.95	23.91	24.59	24.55	22.0
CH_3F	16.46	16.43	19.42	19.39	17.73	17.69	18.8
HCl	14.25	14.31	13.92	13.90	14.21	14.18	16.0
CH_3Cl	13.64	13.54	13.73	13.59	13.97	13.82	15.0
H_2O	19.33	19.13	18.22	18.08	18.75	18.62	19.0
CH_3OH	16.37	16.32	17.07	17.05	17.00	16.97	17.0
CH_3OCH_3	15.96	15.94	16.59	16.58	16.77	16.77	16.0
H_2S	13.11	13.04	12.85	12.73	13.12	13.01	12.4
CH_3SH	12.97	12.87	12.82	12.67	13.10	12.95	
CH_3SCH_3	12.92	12.82	12.79	12.68	13.09	12.95	12.0
NH_3	15.49	15.39	14.93	14.81	15.35	15.24	16.4
NH_2CH_3	14.57	14.50	14.57	14.48	14.87	14.78	14.4
$NH(CH_3)_2$	14.32	14.28	14.35	14.29	14.71	14.66	
$N(CH_3)_3$[b]	14.16	14.16	14.11	14.10			12.6
PH_3	12.55	12.47	12.37	12.23	12.64	12.51	12.0
AsH_3	12.26	12.18	12.09	11.95	12.34	12.21	12.2
C_2H_4	13.11	13.05	12.63	12.99	12.95	13.30	12.4
CO	14.22	15.23	14.76	15.54	14.02	14.80	15.8
STD[c]	1.46	1.39	1.08	1.08	1.18	1.13	

[a] Experimental values from ref 2 obtained using eq 2. Units are eV. [b] QCISD calculations on $N(CH_3)_3$ were not performed due to computational limitations. [c] STD is the standard deviation defined as

$$\left(\sum_{i=1}^{N}\frac{(\eta_i-\eta_i^{\text{expt}})^2}{N-1}\right)^{1/2},$$

where η_i and η_i^{expt} are the calculated and experimental hardness, respectively, and N is the number of Lewis bases for which η_i^{expt} is known (B3LYP and MP2 $N = 16$, QCSID $N = 15$).

arguments and given by eqs 20 and 21 is correctly reproduced by the methods based on both OFSS and CFSS measures but not by methods based on the common operational expressions (eqs 2 and 3). A comparison with experimental hardnesses shows that the simplest and computationally cheapest model, $\eta(\mathbf{r},\mathbf{r}') \cong \delta(\mathbf{r}-\mathbf{r}')$, affords the most reasonable ordering of the molecules.

Because the common operative expressions to calculate the hardness of a system are quite approximate, it is very important to explore new methods to calculate hardnesses. We have shown here that eq 14 is a very good alternative to the operational recipes, especially if one wants to know whether a system is harder or softer than a molecule of reference, as required by the MHP and HSAB principles. The success of OFSS measures to order molecules by hardness has been attributed to the particular properties of Fukui self-similarity measures, which are smaller for soft systems having more diffuse Fukui functions.

However, it is important to remark that despite the success of the simple $\eta(\mathbf{r},\mathbf{r}') \cong \delta(\mathbf{r}-\mathbf{r}')$ model in ordering the molecules by hardness, this approximation does not provide correct estimates of global hardnesses. Therefore, further work should be devoted to find more refined models of the hardness kernel that may yield accurate global hardness values from eq 4. In this direction, attempts such as that by Chattaraj, Cedillo, and Parr[53] are very promising and should be pursued. Additional work on this issue is presently in progress in our laboratory.

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V. Appendix A

In this appendix, we show how the $\eta(\mathbf{r},\mathbf{r}') \cong \delta(\mathbf{r}-\mathbf{r}')$ approximation can be formally derived from conceptual DFT expressions and how this approximation leads to some inconsistencies.

Let us start considering a density functional composed by the Thomas−Fermi form[54] for the kinetic energy density functional,

$$T^{\text{TF}}[\rho] = c_{\text{T}}\int \rho^{5/3}(\vec{r})\,\mathrm{d}\vec{r} \tag{A.1}$$

and the Dirac exchange energy functional[55] for the exchange-correlation functional,

$$E_{\text{xc}}[\rho] = c_{\text{X}}\int \rho^{4/3}(\vec{r})\,\mathrm{d}\vec{r} \tag{A.2}$$

Now, taking into account the well-known exact form of the classical Coulomb repulsion functional,

$$J[\rho] = \frac{1}{2}\int\int \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}\,\mathrm{d}\vec{r}\,\mathrm{d}\vec{r}' \tag{A.3}$$

one gets from eq 9 the following expression for the hardness kernel:[17]

$$\eta(\vec{r},\vec{r}') = \frac{1}{|\vec{r}-\vec{r}'|} + \frac{10}{9}c_{\text{T}}\rho^{-1/3}(\vec{r})\delta(\vec{r}-\vec{r}') + \frac{4}{9}c_{\text{X}}\rho^{-2/3}(\vec{r})\delta(\vec{r}-\vec{r}') \tag{A.4}$$

Equation A.4 reveals that the hardness kernel can be plausibly approximated as[14]

$$\eta(\vec{r},\vec{r}') \cong \frac{1}{|\vec{r}-\vec{r}'|} + g(\vec{r})\delta(\vec{r}-\vec{r}') \tag{A.5}$$

From eq (A.5), one can derive eq 13 by just approximating the Coulombic term, $1/|\vec{r}-\vec{r}'|$, to a Dirac delta function, $\delta(\vec{r}-\vec{r}')$, and assuming that $g(\vec{r})$ is a constant.

The use of such an approximation produces some inconsistencies. For instance, only when the Fukui function is constant and equal to the global hardness of the system, the approximation given by eq 13 conforms to the inverse relation between the hardness and softness kernels (eq A.6).[13a,19] This can be easily demonstrated by inserting eq 13 into

$$\int s(\vec{r},\vec{r}'')\eta(\vec{r}'',\vec{r}')\,\mathrm{d}\vec{r}'' = \delta(\vec{r}-\vec{r}') \tag{A.6}$$

which gives

$$s(\vec{r},\vec{r}') = \delta(\vec{r}-\vec{r}') \tag{A.7}$$

However, taking into account that[19]

$$s(\vec{r}) = \int s(\vec{r},\vec{r}')\,\mathrm{d}\vec{r}' \tag{A.8}$$

one finds from eq A.7 that $s(\vec{r}) = 1$, which according to the relationship between the local softness and the global softness[19]

implies that the global softness cannot be defined, a result that is contradictory with the inverse relationship between the global hardness and the global softness. Remarkably, a similar approximation to that of eq A.7 for the softness kernel that satisfies some of the basic properties of the static density linear response function was proposed by Gázquez and Vela some years ago.[56]

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