AN OPERATIONAL DEFINITION OF RELATIVE HARDNESS

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It is a privilege to participate in honoring Professor Jaroslav Koutecký, a very distinguished scientist and a good friend for many years.

After a brief review of polarizability, charge capacity and hardness, we look at some of the consequences of the requirement, in density functional theory, that the chemical potential and hardness be evaluated with the nuclear potential being held constant. The effects of this can be quite significant, one of them being that some molecules, especially closed-shell, may have zero chemical potentials. We propose that hardness be defined operationally through its inverse relationship to polarizability. Drawing upon correlations found earlier for the latter property, we present a formula for relative hardness in terms of the volume of a molecule and the average local ionization energy on its surface. The formula can also be applied to molecular components, e.g. functional groups, and we show – within the context of this approach – how their contributions combine to yield the hardness of the molecule. This involves a leveling-off effect that explains the relatively small range of hardness values obtained for a group of 33 molecules.

Keywords: Polarizability; Hardness; Charge capacity; Chemical potential; Group hardness; Density functional theory.

Polarizability, Charge Capacity and Hardness

Polarizability, α, is a fundamental property of atoms and molecules, a physical observable. It determines the first-order response of the system's charge distribution to an external electric field ϵ [1,2]

$$\mu(\epsilon) = \mu(0) + \alpha\epsilon \tag{1}$$

$\mu(\epsilon)$ and $\mu(0)$ are the dipole moments in the presence and absence of the field. α is a six-component tensor, which can be represented by a 3×3 ma-

trix. If this is diagonalized, the scalar (or average) value of $\boldsymbol{\alpha}$ can be expressed in terms of the resulting diagonal elements

$$\alpha = \langle \boldsymbol{\alpha} \rangle = \frac{1}{3}(\alpha_{ii} + \alpha_{jj} + \alpha_{kk}). \tag{2}$$

α_{ii}, α_{jj} and α_{kk} are the components of $\boldsymbol{\alpha}$ along the i, j and k axes. They can sometimes differ quite significantly, as will then the corresponding components of $\boldsymbol{\mu}(\boldsymbol{\epsilon})$. For our present purposes, however, it will be sufficient to focus on α $(= \langle \boldsymbol{\alpha} \rangle)$.

The importance of polarizability with respect to both covalent and noncovalent interactions has long been recognized, even though the word itself was not always used. In 1963, Pearson[3,4] proposed his hard and soft acid/base theory, which was able to rationalize a considerable amount of known reactive behavior. In this context, hardness and softness indicate low and high polarizability, respectively. At about the same time, the concept of charge capacity was emerging, particularly through the work of Huheey[5,6]. If one wishes to account for the change in an atom's electronegativity χ as it gains or loses electronic charge in the process of forming a molecule, a convenient approach is to write

$$\chi(Q) = \chi(0) + \frac{Q}{\kappa} \tag{3}$$

where $\chi(Q)$ is the electronegativity of the interacting atom with charge Q and $\chi(0)$ is the intrinsic neutral atom value. The parameter κ is the "charge capacity", which determines how much χ is affected by a transfer of charge. A small κ means that χ decreases (increases) rapidly with a gain (loss) of electronic charge, thereby diminishing the driving force of the process; alarge κ has the opposite effect. Thus, κ is the capacity to accommodate a positive or negative charge, which must depend upon how well the system can adapt to it, i.e. its polarizability. The existence of a correlation between κ and α was indeed anticipated by Huheey[6], and supporting evidence was later found[7]. The concept of charge capacity has been used to explain a variety of experimental observations, for functional groups as well as atoms; for a review, see Politzer et al.[8]

An alternative form of Eq. (3) can be obtained by expanding $\chi(Q)$ in a Taylor series around $Q = 0$ and truncating it after the first-order term

$$\chi(Q) = \chi(0) + Q\left(\frac{\partial \chi}{\partial Q}\right)_{Q=0}. \tag{4}$$

From Eqs (*3*) and (*4*)

$$\frac{1}{\kappa} = \left(\frac{\partial \chi}{\partial Q}\right)_{Q=0}. \tag{5}$$

Equation (*5*) will now be shown to link charge capacity to the density functional formulation of hardness.

Parr et al.[9] have identified electronegativity with the negative of the chemical potential, μ

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{v(\mathbf{r})}. \tag{6}$$

In Eq. (*6*), E is the energy of a ground-state atom or molecule, N is its number of electrons and $v(\mathbf{r})$ is the nuclear potential. Equation (*6*) can be viewed as a more rigorously-based version of Iczkowski and Margrave's[10]

$$\chi = \left(\frac{\partial E}{\partial Q}\right)_{Q=0} \tag{7}$$

although it should be noted that Eq. (*7*) refers to an interacting atom (E is the valence-state energy). Parr and Pearson[11] subsequently gave a quantitative definition of hardness, η

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{v(\mathbf{r})} = -\frac{1}{2}\left(\frac{\partial \chi}{\partial N}\right)_{v(\mathbf{r})}. \tag{8}$$

η can be rewritten in terms of Q by invoking, for an atom, $Q = Z - N$; then from Eq. (*8*)

$$\eta = -\frac{1}{2}\left(\frac{\partial \chi}{\partial N}\right)_{v(\mathbf{r})} = \frac{1}{2}\left(\frac{\partial \chi}{\partial Q}\right)_{v(\mathbf{r})}. \tag{9}$$

Combining Eqs (*5*) and (*9*)[7]

$$2\eta = \frac{1}{\kappa}. \tag{10}$$

It is fair to say, therefore, that the concept of charge capacity anticipated the density functional hardness. It should be emphasized, however, that the former focuses upon an interacting atom (or functional group), whereas

μ and η are defined for atomic and molecular ground states. (For a relevant discussion in the context of electronegativity, see Politzer et al.[12].)

As the preceding discussion has pointed out, hardness and charge capacity have a long-standing association with polarizability, first qualitatively[3,4,6] and then quantitatively[7,13–19]. Our primary interest in this paper is the connection between η and α. However, since the former is simply the derivative of the chemical potential, μ shall enter the discussion as well.

Evaluation of Hardness

We are looking at two related quantities – polarizability and hardness – only the first of which is a measurable physical observable. How can the other be evaluated? η is commonly expressed as[11]

$$\eta = \frac{1}{2}(I - A) \tag{11}$$

where I and A are the system's ionization energy and electron affinity. Equation (*11*) can be obtained by (i) assuming a quadratic dependence of E upon N; (ii) expanding E in a Taylor series around $N = N_0$ (the number of electrons in the neutral system) and truncating it after the second-order term; and (iii) a finite-difference approximation of $(\partial^2 E/\partial N^2)_{v(\mathbf{r})}$[8,11,20,21]. Analogous approaches yield a formula for the chemical potential and electronegativity

$$\chi = -\mu = \frac{1}{2}(I + A)\ . \tag{12}$$

Equations (*11*) and (*12*) are widely used for both atoms and molecules[21,22].

A significant question that is associated with these derivations as well as with Eqs (*6*) and (*8*) is the validity of treating $E(N)$ as a continuous, differentiable function, given that the number of electrons of a free atom or molecule can only change by integral amounts. This issue has been addressed on a number of occasions, as reviewed by Parr and Yang[21]; see also the citations by Politzer et al.[8]. The problem does not arise with regard to Eqs (*3*)–(*5*) and Eq. (*7*), because it is quite normal to think of interacting atoms as having continuously variable numbers of electrons.

We have recently demonstrated that if one is willing to view $E(N)$ as being continuous, then Eqs (*11*) and (*12*) are reasonably good representations of η and μ for most of the free atoms of groups IIA and IVA–VIIIA[23] (oxy-

gen being a notable exception). *However, the arguments that were presented are applicable only to neutral atoms.* Furthermore, in extending these equations to polyatomic entities, an additional factor must be taken into account, which we will now consider.

A frequently neglected aspect of Eqs (*6*) and (*8*), which define the chemical potential and hardness, is the requirement that the nuclear potential be held constant. For atoms and monoatomic ions, this is of course trivial; for molecules, on the other hand, it can be much more significant. If one wishes to apply Eqs (*11*) and (*12*) to polyatomic systems, then the constant $v(\mathbf{r})$ stipulation means that vertical, not adiabatic, ionization energies and electron affinities should be used. This is often not done.

The importance of observing the restriction to vertical I and A depends upon the molecule. Table I presents our computed adiabatic and vertical I and A for several molecules, most of them open-shell. The calculations were at the density functional B3PW91/6-311++G(3df,3pd) level. The adiabatic values are in very good agreement with the corresponding experimental ones, the average absolute difference being just 0.2 eV. This provides reassurance concerning the computational procedure.

For the molecules in Table I, the calculated adiabatic and vertical ionization energies tend to be quite similar, except for NH_2 and especially NO_2. The electron affinities, however, show more significant differences between the adiabatic and the vertical, the largest being for F_2, Cl_2 and again NO_2. For these molecules, using adiabatic rather than vertical I and A in Eqs (*11*) and (*12*) affects η and μ substantially, by 1–2 eV.

TABLE I
Experimental[a] and computed[b] (adiabatic and vertical) ionization energies, I, and electron affinities, A (in eV)

Molecule	I(exp)	I(calc,adiab)	I(calc,vert)	A(exp)	A(calc,adiab)	A(calc,vert)
OH	13.0170	13.1	13.2	1.827670	1.6	1.7
CN	13.5984	14.0	14.2	3.862	3.9	3.9
O_2	12.0697	12.6	13.0	0.451	0.52	–0.04
F_2	15.697	15.6	15.8	3.08	3.5	0.09
Cl_2	11.480	11.4	11.5	2.38	2.7	0.90
CH_3	9.843	10.4	10.0	0.08	–0.02	–0.58
NH_2	11.14	11.2	12.1	0.771	0.60	0.60
NO_2	9.586	9.7	13.1	2.273	2.1	1.2

[a] Ref.[24]; [b] B3PW91/6-311++G(3df,3pd).

Except for CH_3, all of the molecules in Table I have $A(calc,vert) > 0$. This seems to often not be the case, however, especially for closed-shell molecules (many of which may not form stable negative ions). In a 1988 compilation of experimental data for 65 representative organic and inorganic molecules[22], 46 of them – all closed-shell – had $A(exp,vert) < 0$. They included saturated and unsaturated hydrocarbons, halides, benzene derivatives, nitriles, aldehydes, amines, etc. (It is certainly not being implied that all closed-shell molecules have $A(vert) < 0$, as can be seen from the examples of F_2 and Cl_2 in Table I.)

Having $A(vert) < 0$ raises an interesting possibility with regard to the chemical potential. It means that the function $E(N)$ might have a minimum for the neutral molecule and therefore, by Eq. (*6*), μ would equal 0. *Thus some molecules, particularly closed-shell, may have zero or near-zero chemical potentials.* This brings to mind the much broader argument of Ganguly[25], that μ = 0 for the stationary state of any neutral atom or molecule; this is also predicted by Thomas–Fermi theory[21].

The consequences of $A(vert) < 0$ for molecular hardness, as defined by Eq. (8), are difficult to assess. However, it seems justified to question the derivation of Eq. (*11*), which was in the context of a monotonically decreasing $E(N)$ [21,26], for molecules for which $E(N)$ is known to have a minimum near the neutral system. We will therefore consider now the quantitative representation of molecular hardness.

Hardness and Polarizability Relationships

It seems intuitively reasonable that hardness should be related to polarizability[3,4,6,7,11,21]. This expectation is supported by both theoretical and empirical studies, primarily involving atoms and atomic clusters[16–19]; using η calculated with Eq. (*11*), $η = 0.5(I – A)$, it was found that $η \sim α^{-1/3}$. Thus for 18 main group atoms, for which our earlier work provides some justification for utilizing Eq. (*11*)[23], we obtain $η \sim α^{-1/3}$ with linear $R^2 = 0.868$.

These results are not surprising. It is well established that atomic polarizability varies inversely with the cube of the ionization energy, $α \sim I^{-3}$ (refs[27–30]). Since atomic electron affinities tend to be low (2/3 are <1.0 eV)[24], then in many cases, $0.5(I – A) \sim 0.5I$, and so the relationship of α with $0.5(I – A)$ should be very similar to that with I.

For molecules, α correlates only weakly with I. For one representative group of 29 molecules[31], we obtained $R^2 = 0.553$ for $α \sim I^{-1}$ and $R^2 = 0.523$ for $α \sim I^{-3}$. The link between α and η, as given by $0.5(I – A)$, is also not as good as it is for atoms; for 36 molecules for which Pearson quoted

A(exp,vert) [22], we find R^2 to be 0.531 for $\alpha \sim \eta^{-1}$ and 0.684 for $\alpha \sim \eta^{-1/3}$. Accordingly, if one accepts the concept that η should vary inversely with α, then it appears that Eq. (*11*) is significantly less valid for molecules than for atoms.

One factor in this may be the issue of size, which is totally neglected by Eq. (*11*). The polarizabilities of both atoms[27,32] and molecules[31,33–37] increase linearly with volume; for example, for the 29 molecules mentioned above, $\alpha \sim V$ has $R^2 = 0.960$ [31]. The fact that atomic α correlates with both I and V, but molecular α only with the latter, can be attributed to the inverse variation of I and V for atoms (but not molecules), which is well known empirically and has been explained theoretically[38,39].

However, the ionization energy does play a role with respect to molecular polarizability, especially in the form of the average local ionization energy on the molecular surface. We introduced the concept of average local ionization energy, $\bar{I}(\mathbf{r})$, in 1990, defining it within the framework of Hartree–Fock theory by[40]

$$\bar{I}(\mathbf{r}) = \sum_i \frac{\rho_i(\mathbf{r})|\varepsilon_i|}{\rho(\mathbf{r})} \tag{13}$$

in which $\rho_i(\mathbf{r})$ is the electronic density of the i-th orbital, having energy ε_i, and $\rho(\mathbf{r})$ is the total electronic density. Koopmans' theorem[41,42] provides support for interpreting $\bar{I}(\mathbf{r})$ as the average energy needed to remove an electron at the point $\mathbf{r}$ in the space of an atom or molecule. The focus is upon the specific point, not a particular orbital.

$\bar{I}(\mathbf{r})$ has proven to be very effective in predicting and ranking sites susceptible to electrophilic attack. For this purpose, we compute it on the molecular surface, taking this to be the 0.001 electrons/bohr^3 contour of $\rho(\mathbf{r})$ [43], and label it $\bar{I}_S(\mathbf{r})$. The lowest values of $\bar{I}_S(\mathbf{r})$, the $\bar{I}_{S,min}$, indicate the locations of the least tightly-held electrons, most reactive toward electrophiles. Indeed $\bar{I}_S(\mathbf{r})$ has been successfully related to the reactive behavior of aromatic and heterocyclic systems, Hammett and Taft substituent constants, protonation enthalpies and pK_a values, etc. For reviews, see Murray and Politzer[44,45]. It has been shown that Kohn–Sham density functional $\bar{I}_{S,min}$ are as effective as the Hartree–Fock for these applications[46].

The significance of $\bar{I}(\mathbf{r})$ is not limited to reactivity. It correlates with local temperature and atomic shell structure, reveals electron localization and strain in C–C bonds, and free radical character in aromatic hydrocarbons[44,45]. $\bar{I}_S(\mathbf{r})$ on the surfaces of atoms has been linked to their electronegativities[47]. Of particular relevance to the present paper is the proposed

use of $\bar{I}_S(\mathbf{r})$ as an inverse measure of local polarizability[29,31,45,48]; on a local level, the dependence of polarizability upon volume is not a factor, because the volumes being compared are all simply the elements d$\mathbf{r}$.

On the molecular level, the dominant relationship is between α and V, as stated above. It is improved, however, by taking $\bar{I}_S(\mathbf{r})$ into account. For our database of 29 molecules, R^2 increases from 0.960 for $\alpha \sim V$ to 0.984 for $\alpha \sim V/\bar{I}_{S,ave}$ (ref.[31]), where $\bar{I}_{S,ave}$ is the average of $\bar{I}_S(\mathbf{r})$ over the molecular surface. We have shown that $V/\bar{I}_{S,ave}$ can also be used to estimate the relative polarizabilities of components of molecules, e.g. functional groups[49,50]; for this purpose, V and $\bar{I}_{S,ave}$ are evaluated only for the portion of the molecule that is of interest.

An Operational Definition of Relative Hardness

In 1990, Nagle[15] pointed out the fundamental nature of polarizability, and showed that it could be the basis for quantifying electronegativity. We suggest that hardness also be quantified in terms of polarizability. In view of the results obtained by us and by others for atoms, mentioned in the previous section, we propose $\eta \sim \alpha^{-1/3}$. Further, since it has been shown that for molecules $\alpha \sim V/\bar{I}_{S,ave}$ with $R^2 = 0.984$, then for polyatomic systems, our operational definition of relative hardness, η^{rel}, would be

$$\eta^{rel} = \left[\frac{\bar{I}_{S,ave}}{V} \right]^{1/3}. \tag{14}$$

Equation (*14*) allows η^{rel} to be calculated for molecules for which α is not known, and it also permits η^{rel} to be determined for components of molecules, by means of the procedure that we have introduced for predicting group and component polarizabilities[49,50].

The issue of group (or component) hardness is an important one because hardness, unlike the chemical potential, is not expected to be uniform throughout a molecule in its ground state[21]. However, Eq. (*11*), $\eta = 0.5(I - A)$, even if it could be shown to be valid, would face the problem of obtaining I and A for components of molecules. It is not sufficient to use the I and A of the gas phase radicals corresponding to functional groups, e.g. NO_2 or NH_2, because this ignores the influence of the molecular environment as well as the requirement that the overall $v(\mathbf{r})$ of the molecule be held constant. Thus a significant feature of Eq. (*14*) is its capacity for addressing the relative hardnesses of molecular components.

In Table II are presented the relative hardness values that are produced by Eq. (*14*) for the database of 29 representative molecules mentioned earlier. The V and $\bar{I}_{S,ave}$ are taken from Jin et al.[31]; they were obtained at the HF/6-31G*//STO-3G* computational level. The molecular surfaces were taken to be the 0.001 electrons/bohr^3 contours of the electronic densities[43]. The volumes were determined by enclosing each molecule in a box and excluding those points with $\rho(\mathbf{r}) < 0.001$.

The molecular η^{rel} values in Table II cover a rather small range; overall, they vary by less than a factor of two. In contrast, the polarizabilities and volumes of these molecules vary by factors of eight and five, respectively[31].

Also included in Table II are the estimated relative hardnesses, via Eq. (*14*), for nine common molecular components. The V and $\bar{I}_{S,ave}$ are again HF/6-31G*//STO-3G* and are from Jin et al.[50]. For each component, the V and $\bar{I}_{S,ave}$ are the results of averaging over at least 25 molecules that contain it. The partitioning procedure is described elsewhere[49,50]. When these data were used to estimate relative group polarizabilities, by means of $\alpha \sim V/\bar{I}_{S,ave}$, these correlated well with Miller's absolute values[51], with $R^2 = 0.963$ [50]. As would be anticipated, the largest η_i^{rel} is that of fluorine, with its small size and tightly-bound electrons[50]. It should be emphasized that the component η_i^{rel} in Table II are for them in molecular environments; they are not for the corresponding free radicals.

Since molecular volumes can be treated as sums of component contributions V_i [35,52], and polarizability is proportional to volume, then it might be reasonable to write

$$\alpha \approx \sum_i \alpha_i \tag{15}$$

where α_i are average atomic (valence state), group and/or bond polarizabilities. The approximate validity of Eq. (*15*) has been confirmed[35,36,50,51,53]. If one accepts $\eta \sim \alpha^{-1/3}$, it follows from Eqs (*14*) and (*15*) that

$$\eta^{rel} = \left[\sum_i \left(\frac{1}{\eta_i^{rel}} \right)^3 \right]^{-1/3}. \tag{16}$$

Equation (*16*) is tested in Table III for five molecules that are combinations of the components in Table II. The average difference between the η^{rel} obtained from Eqs (*14*) and (*16*) is 1.7%. This is quite satisfactory, considering that η_i^{rel} for each component is an average for it in many different mo-

TABLE II
Relative hardness values for molecules and molecular components, using Eq. (*14*)

Molecule[a]	η^{rel}	Component[b]	η_i^{rel}
Naphthalene	0.441	SH	0.721
p-$C_6H_4(NO_2)(CH_3)$	0.460	Br	0.747
Cyclohexanol	0.474	NO_2	0.755
$C_6H_5CH_3$	0.479	CN	0.761
$(C_2H_5)_2S$	0.479	Cl	0.787
$C_6H_5NH_2$	0.488	CH_3	0.804
$(C_2H_5)_2NH$	0.498	NH_2	0.876
C_6H_6	0.508	OH	0.998
Pyridine	0.520	F	1.201
Thiophene	0.520		
C_6F_6	0.520		
1,4-Dioxane	0.521		
C_2H_5SH	0.543		
Pyrrole	0.545		
$(CH_3)_2S$	0.546		
n-C_3H_7OH	0.548		
Furan	0.561		
C_2H_5Cl	0.566		
$(CH_3)_2CO$	0.569		
$(CH_3)_2O$	0.600		
C_2H_5OH	0.603		
CH_3COOH	0.610		
CH_3CHO	0.629		
C_2H_2	0.683		
CH_3OH	0.689		
CH_4	0.728		
CH_2O	0.732		
NH_3	0.779		
CO	0.789		

[a] $\bar{I}_{S,ave}$ and V values are from ref.[31]. [b] $\bar{I}_{S,ave}$ and V values are from refs[49,50].

lecular environments; it indicates a reasonable level of transferability for the η_i^{rel}.

It is notable that the η_i^{rel} of the components in Table II cover a greater range and are, for the most part, larger in magnitude than the η^{rel} of the molecules in Table II as well as those composed of these components (Table II). This of course follows from Eq. (*16*), which shows that the hardness of a molecule represents a leveling-off of the contributions of its components.

Table III
Comparison of η^{rel} as predicted by Eqs (*14*) and (*16*)[a]

Molecule	V, Å^3	$\bar{I}_{\text{S,ave}}$, eV	η^{rel}, Eq. (*14*)	η^{rel}, Eq. (*16*)[b]
CH_3NO_2	72.41	17.84	0.627	0.617
$BrNH_2$	63.83	15.92	0.629	0.636
$ClCN$	64.24	16.23	0.632	0.614
FSH	50.42	16.19	0.685	0.675
CH_3OH	51.27	16.75	0.689	0.699

[a] V and $\bar{I}_{\text{S,ave}}$ were computed at HF/6-31G*//STO-3G* level. [b] Computed using η_i^{rel} from Table II.

CONCLUSIONS

The density functional definitions of the chemical potential and hardness require that the nuclear potential be held constant. We have pointed out that this can have substantial implications for μ and η; in particular, it can result in the chemical potential being zero for some molecules, especially those with closed shells.

We suggest that hardness be defined operationally in terms of its inverse relationship with polarizability, and propose Eq. (*14*) as a formula for estimating the relative hardnesses of molecules and also their components, e.g. functional groups. In the context of this approach, Eq. (*16*) shows how the contributions of the components combine to produce the hardness of the molecule, with a leveling-off effect that explains the relatively small range found for a group of molecular hardnesses.

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