Chemical hardness and the electronic chemical potential

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Abstract

The properties of the electronic chemical potential, μ and the chemical hardness, η, are summarized. Rules-of-thumb are given for predicting the changes in μ and η when small subsystems are combined to form larger systems. In general, the hardness increases when the energy decreases. Covalent bonding and ionic bonding give rather different results in both μ and η.

Introduction

Density functional theory (DFT) has many important applications to chemistry [1]. Some of these depend on the use of two important quantities which help to characterize any chemical system. There are the electronic chemical potential, μ [2], and the chemical hardness, η [3]. A chemical system is any collection of nuclei and electrons; this may be an atom, a molecule, an ion or a radical, or two of these particles interacting with each other. The nuclei are held in fixed position, and the electrons are at equilibrium.

The definitions of these quantities are

$$\mu = (\partial E/\partial N)_v \text{ and } 2\eta = (\partial \mu/\partial N)_v \tag{1}$$

where E is the energy, N the number of electrons and v is the potential due to the fixed nuclei. The name electronic potential comes from the thermodynamic equation

$$\mu = (\partial E/\partial N)_{s, v} \tag{2}$$

In the case of the ordinary chemical potential of thermodynamics, N is the number of molecules.

Both the electronic and the thermodynamic chemical potential must be constant everywhere in the system, if at equilibrium. In spite of these superficial similarities, there is little relationship between the two properties. The μ of eqn. (1) is *not* the electronic part of the thermodynamic μ. For a molecule, the latter is defined as the total energy of the molecule at absolute zero, minus the energy of the constituent atoms. It is by far the largest part of the thermodynamic chemical potential.

The electronic chemical potential is not a simple function of the state of the system. Instead it also depends on certain constraints. For example, if a system can only lose electrons, a good approximation to μ is the negative of the ionization potential, $-I$. If it can only gain electrons, the approximation is $\mu = -A$, the electron affinity [4]. When no constraint is indicated, the approximation $\mu = -(I+A)/2$ is used. By Koopman's theorem, I and A can be replaced by $-\epsilon_{HOMO}$ and $-\epsilon_{LUMO}$, the orbital energies of the two frontier orbitals [5].

Unlike the thermodynamic μ, the electronic μ need not be a minimum value at equilibrium. The only requirement is that it be constant. What the electronic μ measures is, not stability in the sense of the chemical μ, but the tendency of a system to gain or lose electrons. A large negative μ means a good electron acceptor, and a small negative μ implies an electron donor.

Because of this, $-\mu$ can be called the absolute electronegativity.

$$-\mu = \chi_{abs} = (I+A)/2 = \chi_M \tag{3}$$

Note the close relationship of x_{abs} to the Mulliken definition of electronegativity [6]. They are not quite the same, though, since Mulliken mean that I and A were for suitable valence states, not the ground state.

There is another good reason to call χ the absolute electronegativity. If two systems are brought together, there will be a flow of electron density from one to the other until μ is constant throughout the combined systems. But this just corresponds to electrons flowing from the system of low χ to that of high χ. In other words, the electronegativities are equalized. This equalization, originally assumed by Sanderson [7], is intuitively a very appealing property of electronegativity.

The hardness measures the rate of change of μ with ρ, the electron density function. A hard system is one

where a small change in ρ produces a large change in μ. The hardness acts as a resistance to change in the electron density, for a given change in μ. Hence the name hardness, meaning resistance to deformation. DFT does not require that η be constant everywhere in the system. Instead it has local values, $\bar{\eta}$ [8]. The average of these local values over the molecule then gives the global value, η. The softness, σ, is the reciprocal of the hardness.

The local values are important for determining the most reactive sites within the molecule. In general, the reactivity is greatest where the local hardness is small, or the local softness, $\bar{\sigma}$, is large. The reactivity also depends on the wave functions for the HOMO and the LUMO. There is complete agreement between frontier orbital theory and DFT [9].

Another equation from classical thermodynamics is of interest in discussing the hardness.

$$(\partial\mu/\partial N)_{T, v} + - V^2(\partial P/\partial V)_{T, v}/N^2 = V/N^2\kappa \qquad (4)$$

Here N is the number of molecules, and κ is the compressibility. Since the mechanical hardness is also equal to $1/\kappa$, times a number density factor, there is a nice correspondence between chemical and mechanical hardness [10].

Since v is held constant in eqn. (1), it follows that η depends on the changes in the kinetic energy and the electron–electron repulsion energies with changes in N, or in the electron density [8]. The method of finite differences gives the approximations {3, 5}

$$\eta = (I - A)/2 \cong (\epsilon_{LUMO} - \epsilon_{HOMO})/2 \qquad (5)$$

The relationship to the frontier orbital energies is particularly useful. It means that in the usual MO energy level diagram, the hardness is simply half the gap between the HOMO and the LUMO (in filled subshell cases). This gap also defines the energy difference between the ground state and the lowest excited state of the same multiplicity, in simple MO theory. A hard molecule has a large energy gap, and a soft molecule has a small gap.

Quantum mechanically speaking, many molecular processes occur by a mixing of excited state wave functions with ground state wave functions. A small energy gap is favorable for easy mixing. Thus we conclude that soft molecules are more polarizable than hard molecules, in agreement with an earlier definition of hardness and softness [11].

We can also conclude that soft molecules are more reactive, in general, than hard molecules. For unimolecular reactions, nuclear motions occur easily because the electron density can be readily changed. For reactions between molecules, easy electron transfer occurs between the HOMOs and LUMOs of both molecules, if both are soft.

Fortunately, in recent years many values of I and A have been determined [12]. Usually these are reported as adiabatic values (if A is positive). Actually what are needed are vertical values of I and A, since the nuclei should be held fixed in position to agree with eqn. (1). The error is usually small for I values, but can be large for positive A. Most stable molecules, in fact, have negative electron affinities. As measured, these are vertical values [13].

There is a special problem with both cations and anions. These are clearly cases where $(I+A)/2$ and $(I-A)/2$ are not good approximations. The reason is that cations are almost pure electron acceptors and anions are electron donors. Special methods have been used in these cases [14], but the problems are by no means solved.

For neutral atoms, radicals and molecules, many values of μ and η are now available [12, 13, 15]. Their usefulness has been amply demonstrated [15, 16]. Still, it is obvious that chemists can make new molecules faster than their I and A values can be measured. Therefore procedures for estimating μ and η for a new system will always be needed.

One method would be to consider a new system as made up of two or more simpler systems, where μ and η are already known. What can be said about the expected changes in the electronic chemical potential and the hardness as simple systems come together to form larger aggregates? The rest of this article will address this question.

Changes in μ

We will first see what theory has to say about changes in the electronic chemical potential, and then compare with experimental results, of which there are many. As already indicated, a favorable chemical reaction, for which ΔE is a large negative number, can be accompanied by either an increase or a decrease in μ without violating any basic laws. Still the theory has something to say about the changes.

If two systems C and D, are brought together, as in a reaction, they must form a single system with a constant value of μ. There is a transfer of electrons from the less electronegative to the more electronegative system. The fractional number of electrons transferred, ΔN, is given by [3]

$$\Delta N = \frac{(\chi_C - \chi_D)}{2(\eta_C + \eta_D)} \qquad (6)$$

After this initial equalization of electronegativities, there are further changes in electron density corresponding to covalent and ionic bonding [17]. Equation (6) only

gives the initial interaction between the two reactants. Nevertheless it seems reasonable to assume that a large value of ΔN means a strong, favorable interaction between C and D. This can indicate a strong bond between C and D, or a lowering of an activation barrier in other cases. Tests of this assumption, using experimental values of I and A for the reactants, have given strong confirmation [15]. However only reactions involving similar orbitals can be compared.

Knowing ΔN, it is a simple matter to calculate the new equilibrium value, μ_{CD} of the composite system [18].

$$\mu_{CD} = \frac{(\mu_C \sigma_C + \mu_D \sigma_D)}{(\sigma_C + \sigma_D)} \tag{7}$$

The new value is an average of the original values, weighted by the softness.

Another result may be calculated for the case where unequal numbers of the original reactants are combined. An example might be a metal complex.

$$M + nL \longrightarrow ML_n \tag{8}$$

$$\mu = \frac{(\mu_M \sigma_M + n \mu_L \sigma_L)}{(\sigma_M + n \sigma_L)} \tag{9}$$

While (7) and (9) seem quite reasonable, they do not include the effects of the further changes due to bonding.

An easy test of the importance of these secondary changes are the experimental results for $\Delta \mu$ in the cases where the reactants are the same, as in the formation of a homonuclear diatomic molecule.

$$2X \longrightarrow X_2 \tag{10}$$

In this reaction ΔN is zero, and eqn. (7) gives no change in μ.

Table 1 gives the changes in μ and in η for a number of such reactions. The changes in μ are not large, in general. The electronic chemical potential for the molecule is usually somewhat more positive than for the constituent atoms. The main exception is C_2, which has a large positive value for its adiabatic electron affinity. If the vertical value were used, as the theory requires, μ would be more positive.

Apparently pure covalent bonding does not affect the electron density greatly, and μ is relatively little changed. Table 2 gives some results for a number of examples where the reactants differ. The comparison is between the final value of μ calculated from eqns. (7) or (9), and the value of μ for the product from measured I and A data.

The examples are of two kinds. In one group, each atom or radical contributes an electron to form a bond. In the second group, the bond is a coordinate covalent one. In the first group we see that very large differences exist between calculated and experimental values of μ, if the bonding is largely covalent. The experimental values are always more positive than those from eqn. (7) and (9).

Paradoxically, the agreement is better for bonds that are highly ionic. One would expect that this maximum change in electron density would have produced the largest changes in μ. An explanation for this difference between covalent and ionic bonding will be given in the next section.

The examples of coordinate covalent bonding give much better agreement between μ_{calc} and μ_{exp}. Presumably, this is because eqns. (6) and (7) give a much better description of the bonding interactions. The best agreement is for one or two ligands on the metal atom. In cases like $Cr(CO)_6$ of $Fe(CO)_5$, interactions between the ligands can become important.

While Table 2 has only two examples, it offers some hope for estimating the effect of ligands on a metal

TABLE 1. Changes in the dimerization reaction $2X \rightarrow X_2$

X	$-\mu_x$ (eV)	$-\mu_{x_2}$ (eV)	η_x (eV)	η_{x_2} (eV)
H	7.2	6.7	6.4	8.7
Li	3.0	2.8	2.4	2.4
C	6.3	7.7	5.0	4.4
N	7.3	7.0	7.3	8.9
O	7.5	6.3	6.1	5.9
F	10.4	9.6	7.0	6.3 (7.3)[a]
Na	2.9	2.7	2.3	2.2
Al	3.2	3.6	2.8	2.5[b]
Si	4.8	4.8	3.4	2.6[c]
Cl	8.3	6.9	4.7	4.6 (5.2)[a]
K	2.4	2.3	1.9	1.8
Br	7.6	7.1	4.2	4.0 (4.3)[a]
I	6.8	6.4	3.7	3.4 (3.8)[a]

Data from ref. 12. [a]Hardness when vertical I and A values are used. [b]Ref. 19. [c]Ref. 20.

TABLE 2. Changes in μ for reactions between unlike reactants

Reaction	$-\mu_{calc}$ (eV)	$-\mu_{exp}$ (eV)
Li + F = LiF	4.9	5.9
Na + Cl = NaCl	4.7	4.8
Li + H = LiH	4.1	4.1
C + O = CO	6.8	4.1
H + F = HF	8.7	5.0
H + OH = H_2O	7.4	3.1
H + CH_3 = CH_4	5.9	2.5
CH_3 + Cl = CH_3Cl	6.7	3.8
Ni + CO = NiCO	4.4	4.4[a]
Cr + $2C_6H_6$ = $Cr(C_6H_6)_2$	2.7	2.6[b]
Cr + 6CO = $Cr(CO)_6$	5.4	3.9[c]
Fe + 5CO = $Fe(CO)_5$	5.5	4.4[c]

[a]Theoretical value, ref. 21. [b]Ref. 22. [c]Ref. 23.

atom. For example, take the reaction

$$Pt \; + \; 2P(CH_3)_3 \longrightarrow Pt(P(CH_3)_3)_2 \qquad (11)$$

$-\mu$	5.4 eV	2.8 eV	?
η	3.3	5.9	?
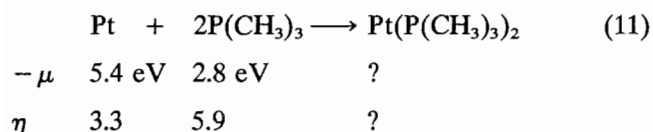
Use of eqn. (9) gives a predicted value of $-\mu = 3.8$ eV for $Pt(P(CH_3)_3)_2$. This seems a reasonable result, since the phosphine ligands, by donating electron density to the metal, will make the metal a better electron donor.

The principle of maximum hardness

There is no theoretical equation to estimate the hardness of a composite system from the known hardnesses of its parts. There has been some study of the derivative $(\partial \eta / \partial N)$ [24], but this information by itself may not be enough. The assumption that η_{CD} is some weighted average of η_C and η_D also does poorly.

Indeed, there are reasons to believe that the secondary effects of covalent and ionic bonding produce larger changes in η than in μ.

This can be illustrated, using simple MO theory, and the fact that maximum hardness means a maximum energy gap between the HOMO and the LUMO. Consider a movement of nuclei in a system along a reaction coordinate, and the resulting orbital interactions. Assume the HOMO and the LUMO play the dominant role in these interactions. This is the basic premise of frontier orbital theory [25]. Figure 1(a) shows the interaction of the frontier orbitals. The lower energy orbital, the HOMO, goes down in energy. The higher energy orbital, the LUMO, goes up in energy, more than the HOMO goes down. There is a net energy lowering, and also the HOMO–LUMO gap increases.

Figure 1(b) shows the case where the main interaction of the HOMO is with another filled orbital of similar energy. Now the HOMO goes up in energy, and the

net effect for both orbitals is an increase in energy. The LUMO is not involved in the major orbital interaction. But it will mix with other empty orbitals, which will lower its energy, as shown. Since LUMO is empty, there is no net energy effect.

For both Fig. 1(a) and (b), we can always reverse the reaction coordinate, to raise the energy in (a) and lower it in (b). For example, the reverse of Fig. 1(a) could be the dissociation of an atom or radical from the rest of the system. The reverse of Fig. 1(b) could be the relief of repulsive forces by the separation of two parts of the system. To summarize, when the energy is decreasing, the HOMO–LUMO gap increases; when the energy is increasing, the gap decreases. When the energy is at a minimum for the system, the gap will be a maximum.

This is the result for orbital interactions, or covalent bonding. What about ionic bonding? Consider a cation and an anion approaching each other, with a decrease in energy. The HOMO will be an atomic orbital on the anion, and the LUMO will be an orbital of the cation. As the ions approach, the potential of the cation will lower the orbital energy of the anion, and the potential of the anion will raise the orbital energy of the cation. The HOMO and LUMO will move apart, just as in Fig. 1(a).

This result is general, for any collection of charged spheres. If the spheres move to raise the potential energy, the HOMO and LUMO move towards each other in energy. When the energy has a minimum value, the HOMO–LUMO gap will be maximum, just as for covalent bonding.

Workers who do MO calculations of molecular structures and energies always seem to find that the most stable structure has a maximum HOMO–LUMO gap [26]. Figure 2 illustrates this by showing an MO energy diagram for CH_4 in its stable tetrahedral form, and in an unstable planar form. The smaller gap in the latter case arises because the p_z orbital of carbon is removed
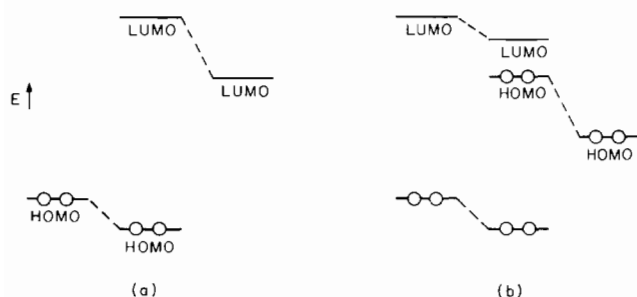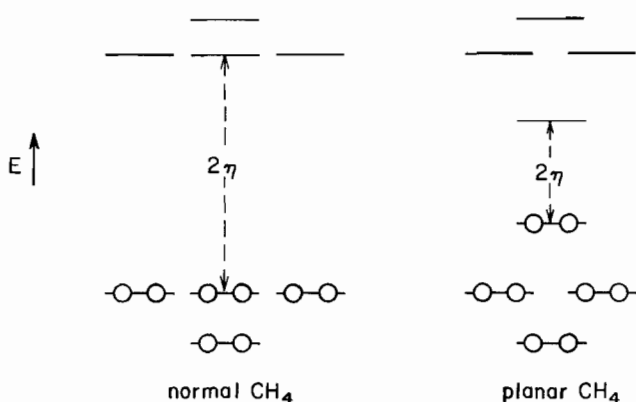

Fig. 1. Frontier orbital interactions showing energy changes of HOMO and LUMO. (a) Energy lowering interaction between HOMO and LUMO. (b) Energy raising interaction between HOMO and another filled orbital.

Fig. 2. The HOMO–LUMO gap, equal to 2η, for tetrahedral CH_4 and planar CH_4.

from bonding, while still occupied. Thus it becomes the HOMO. A linear combination of hydrogen 1s orbitals is removed from an anti-bonding MO, is lowered in energy, and becomes the LUMO.

The greater stability of the structure with the larger gap is usually explained as the result of the second-order Jahn–Teller effect [27]. A large gap means more difficult mixing of excited states with the ground state, as already mentioned.

There seems to be a rule of nature that molecules arrange themselves to be as hard as possible [28]. Parr and Chattaraj have recently given a rigorous proof that the equilibrium for a chemical system requires a maximum value for the hardness as defined in eqn. (1) [29]. However, there are constraints that T, μ and v remain constant.

The requirement of constant μ and v is very stringent, and it is hard to find examples where it can be satisfied. Fortunately, one important case does just this. Start with a molecule in its equilibrium geometry, and calculate the orbital energies at, or near, the Hartree–Fock level. Then η can be calculated from eqn. (5). Now distort the molecule a small amount along directions given by the vibrational symmetry coordinates, and recalculate the orbital energies and the new η. It turns out that for the non-totally symmetric coordinates, μ and v are constant and η is indeed a maximum [30]. For the totally symmetric coordinates, μ and v are not constant, and η is not a maximum.

If an incorrect structure is selected, such as planar methane, then μ and v are constant for the asymmetric distortions, but η is a minimum. Thus there is strong support for Parr and Chattaraj's Principle of Maximum Hardness, based on detailed calculations for NH_3 and C_2H_6 [30].

From these two examples, at least, it appears that the point group of a molecule is determined by maximum hardness, but the exact bond distances and bond angles are not. These are determined by the Hellman–Feynman electrotation theorem. The repulsive force on each nuclei, due to the other nuclei, is just balanced by the attractive force due to the electron cloud.

There are still reasons to believe that increasing hardness accompanies the approach of a chemical system to its equilibrium state. Consider the overall process

$$N(g) + 3H(g) = NH_3(g) \qquad (12)$$

which is very favorable energetically. We can calculate the overall changes in μ and η, using experimental I and A values*. We find that μ increases from -7.2 to -2.6 eV, and η increases from 6.4 to 8.2 eV.

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*To find μ and η for a mixed system, such as $N + 3H$, take the smallest value of I, and the largest positive value of A (ref. 4).

This is not an isolated case. Examination of a large number of reactions where a few atoms, or radicals, are combined to form a molecule, always seems to give the same result for η. Table 3 gives a number of examples. In all cases, η increases, the increase being larger when the bonding is ionic. Table 1 also shows small changes in η for pure covalent bonding. Sometimes η actually decreases on forming X_2 from $2X$. However, this seems to be an artifact due to using adiabatic, rather than vertical, values of A. When the known vertical electron affinities are used for halogens, η always increases.

These results are consistent with Fig. 1, and the accompanying discussion. The HOMO–LUMO gap gets larger as the energy decreases. An absolute maximum may not be reached because the Hellman–Feynman theorem interposes a more powerful requirement. The small values for the increase in η with covalent bonding probably result because Fig. 1(a) is not a good representation of covalent bonding in many cases. If we start with the bond electrons in different orbitals, the Figure does not show the fact that the orbital energy of the HOMO is increased due to the greater interelectronic repulsion of the two electrons when in the same orbital.

The increase in the HOMO–LUMO gap due to ionic bonding is easily calculated, assuming pure ionic bonding. For NaCl, at the equilibrium distance of 2.36 Å, the electrostatic contribution to the gap is 6.1 eV. The observed value of 3.8 eV reflects the same factors which decrease the gap for covalent bonding.

It is interesting to note that ionic bonding predicts no change in μ. The HOMO is lowered, and the LUMO raised by exactly equal amounts. Therefore the midpoint is unchanged. For covalent bonding, the LUMO is raised more than the HOMO is lowered. Hence there

TABLE 3. Changes in η for reactions between unlike reactants

Reaction	$\eta_R{}^a$ (eV)	$\eta_P{}^b$ (eV)
$Na + Cl = NaCl$	0.8	4.8
$Li + F = LiF$	1.0	5.4
$Li + H = LiH$	2.3	3.8
$H + Cl = HCl$	4.7	8.0
$C + O = CO$	4.9	7.9
$H + OH = H_2O$	5.7	9.5
$CH_3 + F = CH_3F$	3.2	9.4
$CH_3 + Cl = CH_3Cl$	3.1	7.5
$CH_3 + Br = CH_3Br$	3.2	5.8
$CH_3 + I = CH_3I$	3.4	4.7
$Ni + CO = NiCO$	3.3	3.6
$Cr + 6CO = Cr(CO)_6$	3.1	4.5
$Fe + 2C_5H_5 = Fe(C_5H_5)_2$	2.8	3.8^c
$Cr + 2C_6H_6 = Cr(C_6H_6)_2$	3.1	3.3

^{a}Hardness of reactants. ^{b}Hardness of products. ^{c}Ref. 31.

is a small overall positive increase in μ, as shown in Fig. 1(a). This analysis agrees with the results in Tables 1 and 2.

Conclusions

While the foregoing has not provided ways of predicting values of μ and η very accurately, it does provide some useful rules-of-thumb for estimation. Restricting ourselves to the process of forming a complex system from a few simpler ones, an estimate of the new electronic chemical potential can be made from eqn. (7).

This will be a fairly good estimate for ionic bonding, or for coordinate covalent bonding. However, for covalent bonding where each unit contributes one electron, μ will be much more positive than the predicted value.

The hardness will increase for the processes considered. The increase will be small for covalent bonding and large for ionic bonding.

The rule that the hardness increases as the energy decreases, cannot be applied to the formation of a giant molecule, or a crystal of a solid. For example, consider the reaction

$$Li(g) = Li(s) \qquad (13)$$

For the atom, we have $-\mu = 3.0$ eV and $\eta = 2.4$ eV. For lithium metal, we have $-\mu = 3.1$ eV (the work function) and $\eta = 0.0$ eV. The value of η equal to zero follows because, in a metal, I and A are the same number, equal to the work function.

Thus μ is virtually unchanged but η decreases, instead of increasing. The reason for this is not hard to find. Instead of forming a HOMO and a LUMO, as in Fig. 1(a), a valence band and a condition band are formed. In a metal, the valence band is only partly filled, so the highest occupied level is virtually the same energy as the lowest empty level.

Even in an insulator the top of the filled valence band will be close to the bottom of the empty conduction band. In solid NaCl, for example, the band gap is 8.0 eV, which makes $\eta = 4.0$ eV. This may be compared to 4.8 eV for diatomic NaCl. In silicon we have $\eta = 0.55$ eV (solid) and somewhat greater than 2.6 eV for Si_2. The larger effect in silicon shows that covalent bonding is responsible for the bandwidth.

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