

Absolute electronegativity and hardness correlated with molecular orbital theory

(polarizability/visible-ultraviolet spectra/ionization potential/electron affinity)

RALPH G. PEARSON

Department of Chemistry, University of California, Santa Barbara, CA 93106

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ABSTRACT The concepts of absolute electronegativity, χ , and absolute hardness, η , are incorporated into molecular orbital theory. A graphic and concise definition of hardness is given as twice the energy gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital. Useful correlations can now be made between chemical behavior, visible-UV absorption spectra, optical polarizability, ionization potentials, and electron affinities.

The concepts of absolute electronegativity, χ , and absolute hardness, η , have recently been introduced (1, 2). The operational definitions of these quantities are

$$\chi = \frac{(I + A)}{2} \text{ and } \eta = \frac{(I - A)}{2}, \quad [1]$$

where I and A are the ionization potential and electron affinity of any chemical system, atom, ion, molecule, or radical. The usefulness of χ and η lies in their ability to help predict chemical behavior. The value of η for different systems does correlate with chemical hardness and softness defined empirically (3).

The theoretical basis for the new quantities lies in the density functional formalism (4). Since molecular orbital (MO) theory is by far the most widely used by chemists, it is important to place χ and η in a MO framework. It has already been shown (5) that the MO theory of the chemical bond contains the values of χ and η for the bonding fragments.

A much clearer and potentially more useful relationship emerges when χ and η are related to the commonly used orbital energy diagrams. Fig. 1 shows such a diagram. A molecule where $I = 10$ eV and $A = -2$ eV is arbitrarily taken as an example. The use of negative electron affinities is essential for most molecules. Fortunately it appears that these can be measured in many cases (6, 7).

Within the validity of Koopmans' theorem (17), the frontier orbital energies are given by

$$-\epsilon_{\text{HOMO}} = I \text{ and } -\epsilon_{\text{LUMO}} = A. \quad [2]$$

The value of χ , equal to 4 eV, is shown with changed sign as a dashed horizontal line in Fig. 1 (see ref. 7). It falls exactly at the energy midpoint between the HOMO and the LUMO. Negative χ is equal to the electronic chemical potential, μ (1). The value of η , equal to 6 eV, is shown as a vertical dashed line. The energy gap between the HOMO and LUMO is equal to 2η .

The above refers to a system where the HOMO is filled. Radicals, where the frontier orbital (SOMO) is half-filled, are somewhat different. Fig. 1 shows the orbital energy diagram for a radical where $I = 10$ eV and $A = +2$ eV. The energy of the SOMO (equal to -10 eV), χ ($= 6$ eV), and η ($= 4$ eV) are

shown on the figure. The (unknown) energy of the LUMO plays no role. The quantity $(I - A) = 2\eta$ is just the mean repulsion energy of two electrons in the SOMO (8).

Apart from the radical cases, it would appear that Fig. 1 offers a most graphic and concise way of defining what is meant by chemical hardness. *Hard molecules have a large HOMO-LUMO gap, and soft molecules have a small HOMO-LUMO gap.* This statement is, of course, consistent with Eq. 1, but it also agrees with the earlier, imprecise definition (3).

For example, optical polarizability in quantum theory results from a mixing of suitable excited state wave functions with the ground state wave function. The mixing coefficient is inversely proportional to the excitation energy from the ground to the excited state. A small HOMO-LUMO gap automatically means small excitation energies to the manifold of excited states. Therefore, soft molecules, with a small gap, will be more polarizable than hard molecules. High polarizability was the most characteristic property attributed to soft acids and bases.

Whether a given molecule is a Lewis acid or a base is determined by its χ value. Large χ values characterize acids and small χ values are found for bases. For any two molecules, electrons will be partially transferred from the one of low χ to that of high χ (electrons flow from high chemical potential to low chemical potential). In Fig. 1 the radical will act as a Lewis acid toward the molecule.

The general acid-base reaction can be treated by perturbation theory, as pioneered by Dewar (9) and Fukui and Fujimoto (10). The three main bonding interactions between closed-shell molecules or ions are (i) electrostatic, (ii) delocalization, and (iii) polarization. Delocalization occurs by partial transfer of electrons from the filled orbitals of one molecule to the empty orbitals of the second. For molecules of similar electronegativities, it will occur in both directions.

An approximate expression for the delocalization energy, considering only the frontier orbitals, is given by

$$\Delta E = \frac{2\beta_{12}^2}{(A_1 - I_2)} + \frac{2\beta_{21}^2}{(A_2 - I_1)}, \quad [3]$$

where the β factors are exchange integrals of the perturbation Hamiltonian over the interacting MOs. Clearly, the energy lowering is greater if A is large for both molecules and I is small. This means that both energy gaps should be small for best bonding, or both molecules should be soft.

This is part of the reason for the principle of hard and soft acids and bases (3). Another contribution to the added stability of a soft acid-soft base complex comes from the mutual polarization effect. A small energy gap favors easy polarization for both molecules. Note, however, that this chemical polarizability is not exactly the same as optical polarizability, since different excited states may be involved.

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Abbreviations: MO, molecular orbital; HOMO, highest occupied MO; LUMO, lowest unoccupied MO; SOMO, singly occupied MO.

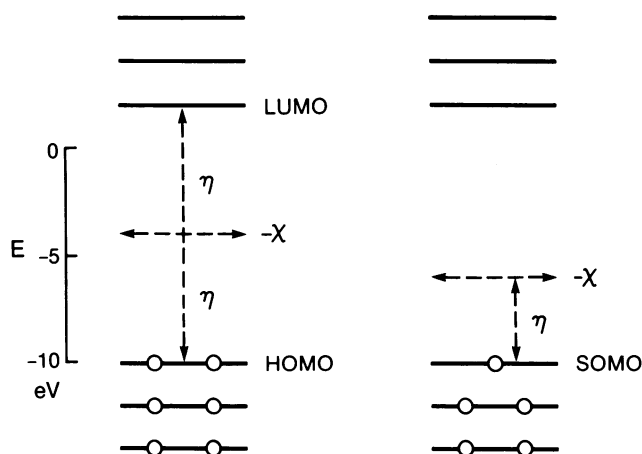


FIG. 1. Orbital energy diagrams for a molecule (*Left*) and a radical (*Right*). HOMO, highest occupied MO; LUMO, lowest unoccupied MO; SOMO, singly occupied MO.

Two hard molecules will not benefit as much from the above two processes. However, strong bonding can still exist from the electrostatic interactions. This completes the explanation for the principle.

Fig. 1 can be used to correlate chemical behavior with visible-UV spectra. A small energy gap means that absorption bands are shifted toward the visible. For example, H_2O , H_2S , H_2Se , and H_2Te have their first absorption maxima at 1655, 1950, 1970, and 2000 Å, respectively (11). We can be reasonably sure that H_2O is much harder than H_2S , which is somewhat harder than H_2Se and H_2Te . Since the value of η for H_2S can be measured directly (12), whereas that for H_2O cannot, this is useful, if incomplete, information.

It would be convenient if we could evaluate $(I - A)$ from measured visible-UV spectra. But this is not easy to do. For example, for H_2S the absorption maximum mentioned above corresponds to an energy of 6.4 eV. But the measured value of $(I - A)$ is equal to 12.6 eV. The difference arises from the extra electron-electron repulsion that results from adding an electron. Spectroscopic excitation energies are generally about one half of $(I - A)$ (6).

It should also be mentioned that the first absorption band of a molecule may be due to a Rydberg state and have little to do with the energy of the LUMO. Also, the promoted electron may come from an occupied MO other than the HOMO.

We can draw a new conclusion from Fig. 1. Soft molecules will undergo unimolecular reactions more readily than hard molecules. Processes such as dissociation and isomerization proceed by mixing excited state wave functions with ground state wave functions [second-order Jahn-Teller effect (13)]. A small energy gap is favorable for easy reaction. A textbook example is given by the rearrangement energies of halogen-aromatic hydrocarbon charge-transfer complexes (14).

In short, soft molecules are more reactive than hard molecules if electron transfer or rearrangement is necessary for the reaction. Hard molecules resist changes in their electron number and distribution. MO theory is useful in the application of chemical hardness in one further way. Unlike the electron chemical potential ($\mu = -\chi$), which is constant everywhere in the molecule, the hardness varies from atom to atom (15). This is most easily discussed by defining the softness, σ , of a molecule as the inverse of its hardness, $\sigma = 1/\eta$. Then the local softness, $\bar{\sigma}$, is given by (see ref. 16)

$$\bar{\sigma} = \sigma\rho_{\text{HOMO}} \text{ OR } \bar{\sigma} = \sigma\rho_{\text{LUMO}} \quad [4]$$

The ρ factors are the normalized electron densities of the frontier orbitals. The HOMO is used if the reaction is with an electrophile, or Lewis acid, and the LUMO is used if reaction is with a nucleophile, or base.

The local softness is important in understanding the chemistry of large, delocalized molecules or ions. Usually $(I - A)$ is rather small for such systems, so that the global σ is large. But $\bar{\sigma}$ may be quite small for some atoms in the molecule. An example is the phenolate anion, $\text{C}_6\text{H}_5\text{O}^-$, where the oxygen atom is hard (low $\bar{\sigma}$) and the aromatic ring is soft.

The concepts of absolute electronegativity and absolute hardness are thus quite compatible with MO theory. Indeed they complement it in a way that seems to be potentially very useful.

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