

# ACCOUNTS OF CHEMICAL RESEARCH®

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## COMMENTARY

### Electronegativity Scales

This Commentary is meant as a supplement to the one of the same title by Professor Ralph Pearson (*Acc. Chem. Res.* 1990, 23, 1). Since the turn of the century, electronegativity differences have been identified with bond polarity, and Pauling's classic 1932 paper<sup>1</sup> provided a set of semiquantitative free-atom values whose differences gave rough numerical estimates of polarities across bonded atoms in molecules and solids. In the succeeding 58 years, prediction of bond polarity has continued to be the motivation for the many alternative scales proposed,<sup>2</sup> and during this time, Pauling's scale<sup>1</sup> and that of Allred and Rochow<sup>3</sup> have proved to be the overwhelming preference of practicing experimental chemists and physicists. A new definition,  $\chi_{\text{spectroscopic}}$  ( $\chi_{\text{spec}}$ ), the average one-electron energy of the valence-shell electrons in ground-state free atoms,<sup>4</sup> obtains its values from the National Bureau of Standards high-resolution atomic energy level tables, and it has no adjustable parameters (other than the scale units).  $\chi_{\text{spec}}$  has a different origin than other scales, but yields numbers strikingly close to the Pauling and Allred and Rochow sets as shown in Figure 3 of ref 4. In addition, translation of the new free-atom definition into a quantum mechanical operator has been shown to yield chemically meaningful bond polarities between atoms in molecules<sup>5</sup> and thus the first quantitative quantum mechanical realization of Pauling's description of  $\chi$  as "the power of an atom in a molecule to attract electrons to itself". Bond polarity characterizes the static, nonuniform charge distribution in a molecule or solid, and its definition as the energy difference of average electrons in atoms A and B is conceptually equivalent to a bond dipole moment. It may be visualized also as the difference in the static force an electron experiences at the radius of atom A and at the B atom radius. This collection of simple, pictorial images

has been cleanly and fruitfully identified with electronegativity throughout its development over nearly a century.

Parr and co-workers, through the use of density functional theory, have introduced another chemical property, the electronic chemical potential,  $\mu$ , which they approximate by  $(I + A)/2$ , where  $I$  and  $A$  are the ground-state first-ionization potential and electron affinity, respectively.<sup>6</sup> Figure 6 and the associated text in ref 4 contrast this energy with the very different behavior of  $\chi_{\text{spec}}$ .

In accord with the traditional meaning of chemical potential, Parr et al. find that when two systems C and D, with  $\mu_C$  different from  $\mu_D$ , are put in contact, the combined system will equilibrate to a new common value of  $\mu$  differing from either of the original values.<sup>6</sup> Equalization is another aspect of  $\mu$  that strongly differs from  $\chi_{\text{spec}}$ . First, as shown in Figure 1, in going from free atoms to hydrides,  $\chi_{\text{spec}}$  values are compacted, but not equalized.<sup>7</sup> These in situ values are in compliance with the fundamental empirical observation that atoms retain their identity when combined into molecules or solids. This contrasts with  $\mu$ , where any arbitrary selection of electron groups has the same electronic chemical potential, making it unnecessary to invoke the concept of atoms in molecules.<sup>8,9</sup> Second, in density functional theory, a pair of different atoms, in equilibrium with a reservoir, but infinitely separated from

(6) Parr, R. G.; Donnelly, R. A.; Levy, M.; Palke, W. E. *J. Chem. Phys.* 1978, 68, 3801. Donnelly, R. A.; Parr, R. G. *J. Chem. Phys.* 1978, 69, 4431. Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford Univ. Press: New York, 1989.

(7)  $\chi_{\text{spec}}^A - \chi_{\text{spec}}^H$  values for free-atom F, O, and N calculated at 6-31G\* are -0.453, -0.162, and -0.073 hartree, respectively.  $EI_A - EI_H$  values for F, O, and N in FH, OH<sub>2</sub>, and NH<sub>3</sub> are -0.055, -0.028, and -0.010 hartree. All numbers are on a per bond basis. A formula for  $EI_A$  is given in ref 4.

(8) The density functional theory of electronegativity forces a very specific definition of an atom in a molecule (Parr, R. G. *Int. J. Quantum Chem.* 1984, 26, 687), an "atom in a molecule will be a species bearing a nonintegral number of electrons". However, it frequently occurs that different types of atoms have differing chemical behavior even though they have almost exactly the same charge. Thus, this definition is neither necessary nor sufficient.

(9) Politzer, P.; Weinstein, H. *J. Chem. Phys.* 1979, 71, 4218.

(10) This footnote was deleted on revision.

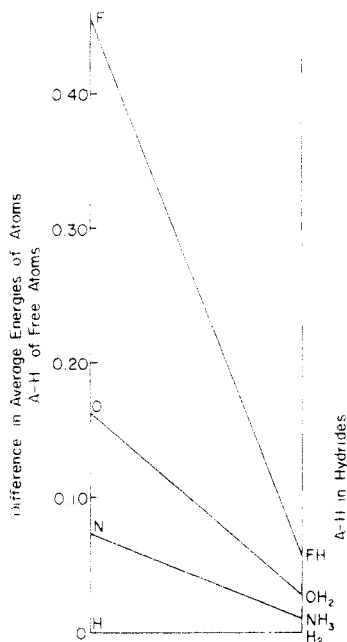
(1) Pauling, L. *J. Am. Chem. Soc.* 1932, 54, 3570. Updated by: Allred, A. L. *J. Inorg. Nucl. Chem.* 1961, 17, 215.

(2) Allen, L. C. A review of electronegativity to be submitted to *Chem. Rev.*

(3) Allred, A. L.; Rochow, E. G. *J. Inorg. Nucl. Chem.* 1958, 5, 264.

(4) Allen, L. C. *J. Am. Chem. Soc.* 1989, 111, 9003.

(5) Allen, L. C.; Egolf, D. A.; Knight, E. T.; Liang, C. Bond Polarity Index. *J. Phys. Chem.*, in press.



**Figure 1.** Differences in average valence-shell energies between atoms A and the H atom (hartree). Left side: Free atoms F, O, and N relative to H as zero reference. Right side: Atoms F, O, and N in their hydrides relative to H in  $H_2$  as zero reference. Values for both left and right sides are per bond (pattern shown is not qualitatively altered if whole-molecule energies are employed). If the electronic chemical potential,  $\mu$ , were plotted in the same manner, the left side would be approximately the same, but the right side would be a single point at the reference line,  $H_2$ . Equalization of electronegativity does not occur.

each other, are required to have a common chemical potential,<sup>11</sup> in contrast to  $\chi_{\text{spec}}$  and other definitions of  $\chi$ ,

(11)  $\mu = -(I_{\text{min}} + A_{\text{max}})/2$ , where  $I_{\text{min}}$  and  $A_{\text{max}}$  are the minimum and maximum of the two  $I$  and  $A$  values, respectively. Perdew, J. P.; Parr, R. G.; Levy, M.; Balduz, J. L. *Phys. Rev. Lett.* **1982**, *49*, 1691. Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford Univ. Press: New York, 1989; Chapter 10.

which have free-atom values at infinite internuclear separation.

It is well-known that almost all chemical bonding phenomena can be at least qualitatively explained within the framework of the Hartree-Fock approximation (including the periodic table and the successes of molecular orbital theory), and thus it is a surprise that density functional  $\mu$  cannot be obtained uniquely at this level of approximation.  $\chi_{\text{spec}}$  contrasts sharply in that almost all of the useful chemical information is obtained at the Hartree-Fock level for most molecules.<sup>4,5</sup> Likewise, in Pearson's Commentary referred to previously, he has pointed out that  $\mu$  does not give reliable estimates of bond polarity nor conform to Pauling's description of electronegativity.<sup>12</sup>

In conclusion, it seems obvious that the electronic chemical potential,  $\mu$ , as developed and applied by Parr, Pearson, et al., is an entirely different chemical quantity than the concept of electronegativity,  $\chi$ , which chemists and physicists have consistently associated with bond polarity. Thus, it creates unnecessary confusion to equate  $\chi$  with  $-\mu$ . For a very long time, electronegativity has been regarded by many scientists as a somewhat "fuzzy" and ill-defined idea, and misappropriation of the word electronegativity would be an unfortunate setback just as a more precise and broadly applicable formulation is beginning to emerge.

(12) In a *Coord. Chem. Rev.* article (in press), Pearson states in regard to his and Parr's identification of  $\mu$  with  $-\chi$ , "But this is a new electronegativity that has been created. It not longer applies to atoms in a molecule so much, but to the entire molecule, radical or ion. Perhaps the word electronegativity should not have been preempted, and the term electronic chemical potential used instead."

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## ARTICLES

### Mechanistic Studies of Light-Induced Charge Separation at Semiconductor/Liquid Interfaces<sup>†</sup>

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The energy crisis of the early 1970s stimulated numerous investigations of semiconductor/liquid junctions for the conversion and storage of solar energy.<sup>1-3</sup> Al-

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though similar in concept to solid-state photovoltaic devices, semiconductor/liquid junctions offered the potential for inexpensive, chemically based energy-conversion devices, with the accompanying potential to effect the direct conversion of light into chemical fuels.

<sup>†</sup> Contribution No. 8056.

(1) *Semiconductor Liquid-Junction Solar Cells*; Heller, A., Ed.; Electrochemical Society: Princeton, NJ, 1977.

(2) *Semiconductor Electrodes*; Finklea, H. O., Ed.; Elsevier: Amsterdam, 1988.

(3) Rajeshwar, K. *J. Appl. Electrochem.* **1985**, *15*, 1.