

Saving Sanderson's Principle? Order of Magnitude Improvements by Equalizing Mulliken Valence-State Electronegativities χ_{VS} Instead of DFT-Based Chemical Potentials μ

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Conceptual DFT operationally assumes $\mu = -\frac{1}{2}(I_0 + A_0) = -\chi$, with I_0 and A_0 being the ground-state ionization energy and electron affinity, respectively. However, a recent empirical test of 210 molecules discloses that most molecules seriously disobey Sanderson's electronegativity equalization (ENE) principle and the μ -equalization principle [1]. In more than 150 cases, the molecular μ_{mol} falls outside the range spanned by the μ_{at} of the constituent atoms, $\min \{\mu_{\text{at}}\} \leq \mu_{\text{mol}} \leq \max \{\mu_{\text{at}}\}$ [1].

I here discuss elementary thermodynamic cycles revealing the conditions for ENE and/or μ -equalization in arbitrary diatomic and selected polyatomic molecules. The cycles explain why the DFT-based operational μ is equalized in exceptional cases only, as for the H_2 molecule. A proof is given that the diatomic $\chi(\text{XY})$ and $\mu(\text{XY})$ cannot be generally calculated from atomic data alone, but necessarily require molecular input data, specifically, the bond dissociation energies, D_0 , of molecular ions, e. g., XY^+ and XY^- . Using ground-state I_0 and A_0 frequently violates the Wigner-Witmer correlation rules [2] necessary for proper molecular symmetry. According to the correlation rules Mulliken's valence-state ionization energies, I_{VS} , electron affinities, A_{VS} , and electronegativity, χ_{VS} , [3] have to be employed for molecules and atoms alike. The differences between the molecular $\chi_{VS, \text{mol}} = \frac{1}{2}(I_{VS} + A_{VS})$ and $-\mu_{\text{mol}}$ and the corresponding averages from atomic values, $\langle \chi_{VS, \text{at}} \rangle$ and $\langle -\mu_{\text{at}} \rangle$, are expressed by observed differences in D_0 . Such differences frequently cancel and an order of magnitude improvement of accuracy in ENE is achieved by the consistent use of Mulliken's valence-state χ_{VS} as opposed to the commonly used ground-state EN, or μ values. The study shows that the Mulliken electronegativity and the DFT-based chemical potential have to be accepted as two separate and distinct properties characterizing chemical systems. For conceptual DFT a **paradigm shift** is in order by replacing the dominance of ground-states and emphasising valence-states.

[1] Datta, D., Shee, N., von Szentpály, L. *J. Phys. Chem. A* 117, 200-206, 2013.

[2] Wigner, E., Witmer, E. E. *Z. Phys.* 51, 859-886, 1928.

[3] (a) Mulliken, R. S. *J. Chem. Phys.* 2, 782-793, 1934; (b) Mulliken, R. S. *J. Chem. Phys.* 3, 573-585, 1934; (c) Mulliken, R. S. *J. Chim. Phys. (France)* 46, 497-542, 1949. (English version: 1948/49 ONR Report on MO Theory).