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Universal Potential Function and Electronegativity Equalization: Transferable Bond Energies from a Charge-consistent Model.

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Bond energy additivity and transferability are puzzling characteristics of bonds, and the source of Pauling's definition of electronegativity difference, $\Delta\chi$. Most of the difficulties in rationalizing Pauling's relation, $D(XY)=½[D(XX)+D(YY)]+c(\Delta\chi)^2$, lie in the fact that the term bond energy, D, carries two different connotations: an empirical and a theoretical. Attempts to link Pauling's relation to electronegativity equalization and a self consistent charge (SCC) bond model have failed because of their insistence on empirical bond energies. By doing so, the ionic bond energy, δ^2/R, seems to outweigh the average of the covalent contributions. We have developed a Valence State PEC, which describes the molecule as being formed from atoms in their promoted MO-theoretical valence state.[1] The asymptotic reference energy defines a theoretical bond energy, D_{vs}, which is transferable from homonuclear to heteronuclear bonds. Notably, the SC charges obtained by energy minimization are very close to those from electronegativity equalization. The missing link between the Iso-electronegativity Principle and Pauling's thermochemical scale is one of the byproducts of the universal Valence State PEC. Incidentally, the Pearson+Parr Hard-Soft-Acid-Bases (HSAB) Principle is rationalized on the same grounds.

1. (a) L. v. Szentpaly, Chem. Phys. Lett. **245** (1995) 209. (b) D. Gardner, L. v. Szentpaly, J. Phys. Chem. A **103** (1999) 9313.