Finnish Symposium on Quantum Chemistry
June 11th –17th, 2001.

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

László v. Szentpály
Chemistry Dept. University of the West Indies, Kingston, Jamaica, and
Institut für Theoretische Chemie, Universität Stuttgart, Germany.

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, $D(XY)=\frac{1}{2}[D(XX)+D(YY)]+c(\Delta\chi)^2$, 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.