REVISITING PEARSON'S HSAB PRINCIPLE: THE HARDNESS OF CATIONS AND ANIONS FROM ATOMIC POLARIZABILITIES

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Pearson's hard and soft acids and bases (HSAB) principle remains a cornerstone of coordination chemistry for rationalizing coordination preferences [1]. We noted however that its quantitative implementation through absolute hardness, $\eta = (I - A)/2$, can yield chemically misleading trends for some metal ions. Here we analyze systematic inconsistencies in Pearson-type hardness values, focusing on trivalent lanthanides and first-row transition-metal ions. For the lanthanide series, η derived from ionization potentials and electron affinities displays pronounced anomalies for La^{3+}, Gd^{3+}, and Lu^{3+} (empty, half-filled, and filled 4f shells) and an extreme outlier for Y^{3+}, despite their well-

known smooth and closely-related coordination chemistry. Similar electronic-configuration artifacts are observed for 3d ions, leading to counterintuitive predictions such as Mn^{2+} being slightly harder than Mn^{3+}. To overcome these limitations, we adopt a physically transparent route that links global hardness to ionic size and polarizability. Building on density-functional arguments relating α, the Fukui function, and radial charge distributions, we employ the simple expression $\eta = r^2/\alpha$, where r is an effective ionic radius. Dipole polarizabilities are obtained from high-level scalar-relativistic CCSD(T) calculations (DKH2), and r is extracted consistently from the maxima of the computed radial distribution functions. The resulting hardness values recover smooth, chemically meaningful trends across the lanthanides and transition metals, and—critically—provide a practical avenue to estimate η for anions, for which reliable electron affinities are generally unavailable. This framework offers an improved quantitative descriptor for HSAB-guided ligand design and reactivity analysis.

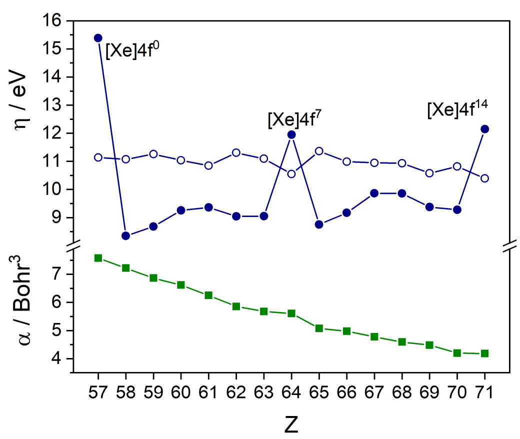

Figure 1. Values of η obtained using Pearson's definition (closed circles), values of η obtained from atomic radii and polarizabilities (open circles) and polarizabilities (squares) calculated for the Ln^{3+} ions.

[1] Parr, R. G.; Pearson, R. G. Absolute Hardness: Companion Parameter to Absolute Electronegativity. *J. Am. Chem. Soc.* **1983**, *105* (26), 7512–7516. https://doi.org/10.1021/ja00364a005.