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Atomic electronegativities from electrostatic potentials

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Electronegativity is arguably the most consequential chemical property of an element. It governs the polarity of chemical bonds and their dissociation energies, dictates the reactivity of atoms and functional groups, and underpins a vast array of physical properties of both elements and compounds - from electrical conductivity and optical response to the hardness of materials. Since its introduction by Pauling in 1932 [1], the concept has become an indispensable pillar of chemical intuition.

Over the ensuing decades, a great many definitions and scales of electronegativity have been proposed. The mid-twentieth century saw a flourishing of seminal contributions: Mulliken grounded the concept in atomic spectroscopy by averaging the ionization energy and electron affinity [2]; Allred and Rochow linked it to the effective nuclear charge experienced by valence electrons at the covalent radius [3]; Martynov and Batsanov defined electronegativity as the square root of the mean valence ionization energy of an atom [4]; along the same lines later Allen defined his electronegativity as the average one-electron energy of valence-shell electrons in ground-state free atoms [5]. After this intense period of activity, many in the community came to regard electronegativity as a settled subject, with diminishing scope for fundamentally new insights, and probably superseded by the widely available quantum-mechanical and machine learning tools.

In recent years, however, there has been great resurgence of interest, fueled by a deeper understanding of chemistry, the availability of large thermochemical datasets (including theoretical), and the growing body of weird phenomena discovered under pressure and demanding explanations. Together with Tantardini, we have constructed a comprehensive thermochemical electronegativity scale optimized to reproduce bond polarities and bond energies in molecules across the periodic table [6] – for that, we had to modify Pauling's formula, recognizing its shortcomings. Subsequently, with Kostenko, we developed a simple electronegativity-based model that successfully predicts compound stability using only elemental electronegativities and an additional descriptor, which we called the chemical mismatch parameter [7]. Paper [7] gives a refined Pauling-like scale of electronegativities. Together with Dong and co-workers, we modified the Mulliken definition to make it applicable to nonzero pressures, and the resulting scale easily explained many high-pressure chemical anomalies [8]. These modern efforts demonstrate that electronegativity continues to evolve as a first-principles, environment-aware descriptor.

Analyzing perhaps too numerous electronegativity scales, I suggest to give preference to those based on observable quantities, such as molecular dissociation energies, heats of formation, orbital energies, ionization potentials, and electron affinities. Another important consideration is that different electronegativity scales carry different physical dimensions – ranging from electron-volts (eV) to $\mathrm{eV}^{1/2}$ to purely dimensionless numbers – and, strictly speaking, cannot be the same physical quantity. Yet, these different scales correlate well with each other. Furthermore, some scales are defined for isolated free atoms, while others pertain to atoms embedded in molecules or crystals, and consequently different scales are best applied in different situations. Therefore, we are likely to have multiple (perhaps 3–5) scales, reflecting different aspects of the behavior of atoms and applicable in different situations, rather than converge on a single one.

A new chapter in this long history has now been written by Zheng, who introduces an electronegativity scale derived from the atomic mean inner potential (AMIP) [9]. The AMIP is the volume average of the electrostatic Coulomb potential within an atom - a fundamental, quantum-mechanical property that is accessible both from first-principles electronic-structure calculations and

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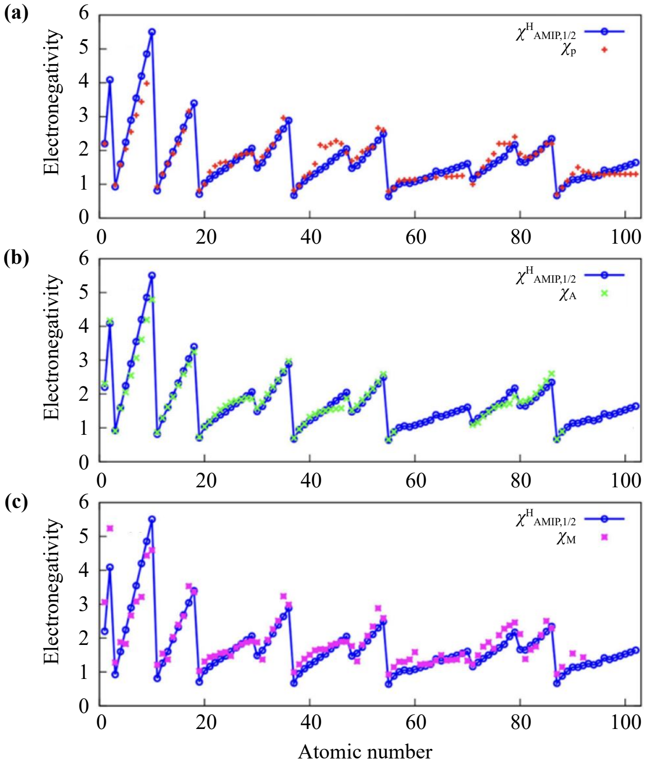

Fig. 1 Comparison of Zheng's electronegativities with **(a)** Pauling's, **(b)** Allen's, and **(c)** Mulliken's scales.

from electron-scattering experiments such as off-axis electron holography.

Zheng's scale, denoted $\chi_{\rm AMIP,1/2}$, contains a constant K and is an analytic function of just three ground-state atomic descriptors: the principal quantum number n_q, the forward electron-scattering factor $f^{(e)}(0)$ (which is proportional to the second moment of the total charge density), and the mean valence atomic radius r_v. The resulting expression

$$\chi_{\rm AMIP,1/2} = \sqrt{\frac{v_0}{n_q}} = \sqrt{K\frac{f^{(e)}(0)}{n_q\Omega_a}} = \sqrt{\frac{K}{4\pi}\frac{\langle r_t^2\rangle}{n_q r_v^3}}$$

contains no empirical parameters, carries explicit units of $\mathrm{V}^{1/2}$, and can be normalized to the Pauling value for hydrogen to yield a scale directly comparable with conventional tabulations.

Benchmarking against established scales reveals excellent agreement. For main-group elements, the coefficient of determination R^2 is 0.88 with the Pauling scale, 0.98 with the Allen scale, and 0.87 with the Mulliken scale (Fig. 1). Importantly, the AMIP-based scale correctly places the canonical metalloids (B, Si, Ge, As, Sb, Te) on the metal–nonmetal boundary, satisfying the stringent "Si rule" benchmark.

Beyond replicating known trends, $\chi_{\rm AMIP,1/2}$ proves to be a powerful predictive tool. Zheng demonstrates that it accurately determines Lewis acid strengths across more than 14 000 coordination environments ($R^2 = 0.93$) and correlates strongly with the full width at half maximum of positron–electron annihilation γ-ray spectra for 36 elements ($R^2 = 0.97$), outperforming previous electronegativity descriptors. The AMIP formalism also cleanly separates metallic, covalent, and ionic bonding in a triangular diagram of 358 binary compounds, achieving a quality score on par with the best historical scales.

Because every quantity in the AMIP definition is a well-defined quantum-mechanical observable, the scale is parameter-free, computationally efficient, and physically transparent. Its direct connection to the Coulomb potential — the fundamental force responsible for electron attraction — establishes a unified and predictive framework for electronic structure and chemical behavior across the periodic table. The work may be extended to high-pressure conditions, where the charge density and atomic volume respond sensitively, opening a pathway toward a pressure-dependent electronegativity scale derived from the same first-principles foundation.

In summary, Zheng's AMIP-based electronegativity scale represents a significant advancement in the long quest to quantify the most central concept of chemistry. It bridges the gap between empirical thermochemical scales and the underlying quantum mechanics of the Coulomb potential, providing a fresh perspective that is both experimentally grounded and theoretically rigorous. As the family of electronegativity scales continues to expand, this new addition stands out for its elegance, predictive power, and deep physical insight.

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