

The Chemical Reference Atom and its Ionization: the Role of Fictitious Atomic States

Regan L. Farrell

Mentor: Professor Roger L. DeKock

Department of Chemistry and Biochemistry, Calvin College, Summer 2017

The focus of the DeKock group since 2012 has been the electronic structure of atoms, that is, using quantum chemistry to investigate the behavior of electrons in the atom. One such behavior results in the qualitative concept of electronegativity. As defined by Pauling, electronegativity is based on how attractive atoms are to electrons.¹ One interpretation by Allen and coworkers is called configuration energy and is the weighted average of the valence s and p electron ionization energies.² Another, by Politzer, et al., is the weighted electron density of an orbital multiplied by the absolute value of its orbital energy, called the average local ionization energy.³ There are other interpretations of as well.

My research this summer was to compute chemical reference (CR) ionization energies for elements helium through xenon and correlate the values with the various measures of electronegativity, experimental and theoretical. Our goal was to show how the CR atom and ion comprise a new perspective on electronegativities. To do this, we used Amsterdam Density Functional (ADF) software, which utilizes Kohn-Sham Density Functional Theory (KS-DFT).⁴ ADF allows for fractional electronic occupancies in orbitals, a feature necessary for our work with the CR atom.

The CR atom differs from a real atom because it has spin and angular momentum both equal to zero, 1S term symbol. This requires using an equal number of spin up and spin down electrons, for both the neutral atom and its cation. Furthermore, the valence electrons need to be “smeared” among the requisite subshells. Finally, in order to get at the concept of electronegativity we require that the electron that is ionized be fractionally removed from all valence orbitals, weighted according to occupancies.

CR ionization energies show very strong correlations through xenon with Allen’s configuration energies and Politzer’s average local ionization energies, indicating that CR ionization could perhaps be a new, albeit theoretical, interpretation of electronegativity. CR ionization also varies smoothly across the periodic table, unlike first ionization energies, since it removes electrons equally from all valence orbitals. This suggests that CR ionization may be a new, fundamental way to examine atoms and ions.

This summer was my first time participating in scientific research on any level and it taught me a great deal. First, I learned about several computational chemistry programs and their uses. I also took part in the scientific writing process, which has improved my written and graphical communication skills. Giving presentations has enhanced my speaking skills, and I have learned—often through error—how to communicate ideas clearly and efficiently. Working with peers and mentors has taught me collaboration

¹ Linus Pauling, “THE NATURE OF THE CHEMICAL BOND. IV. THE ENERGY OF SINGLE BONDS AND THE RELATIVE ELECTRONEGATIVITY OF ATOMS,” *J. Am. Chem. Soc.* 54, (September 1, 1932): 3570–82.

² Joseph B. Mann, Terry L. Meek, and Leland C. Allen, “Configuration Energies of the Main Group Elements,” *J. Am. Chem. Soc.* 122, (2000): 2780–83.

³ Peter Politzer et al., “Average Local Ionization Energies as a Route to Intrinsic Atomic Electronegativities,” *J. Chem. Theory Comput.* 7, February 8, (2011): 377–84.

⁴ADF2017, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, <http://www.scm.com>.

skills and has been enjoyable as well. I am very thankful that I have been given this research opportunity, and I'm thankful for Calvin College as well.