The Relationship Between Atomic Size and Charge
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DeKock, Strikwerda, and Yu showed in 2012 how an atom’s atomic size relates to its average valence ionization energy according to the formula \( r_e = n a_\text{0} \sqrt{\frac{I_H}{I_v}} \) where \( r_e \) is the effective atomic radius, \( a_\text{0} \) is the bohr radius, \( I_H \) is the ionization energy of the hydrogen atom, and \( I_v \) is the average valence ionization energy [1]. This effective atomic radius corresponds to the theoretical \( r_{\text{max}} \) that we will discuss below. The radii obtained from this equation using experimental ionization energy values correlate well with other measures of atomic size. In our present work, we seek to explore this equation further using theoretical ionization energies from Hartree-Fock theory. In addition, we examine other ways of calculating atomic size that correlate with covalent or van der Waals radii [2] and how these values change when comparing neutral atoms to their ions. In doing this work, we seek to gain insight into the electronic structure of atoms.

We employed the quantum chemistry software GAMESS (General Atomic and Molecular Electronic Structure System) [3] to obtain theoretical results that include the binding energy and radial size. Our studies were done for elements 1-20 (H-Ca) in order to explore trends across the periodic table. Theoretical \( I_v \) calculations were done using RHF (Restricted Hartree-Fock) or Restricted Open Shell Hartree-Fock (ROHF), depending upon whether the atom or ion was closed shell or open shell.

We mentioned one measure of atomic size in the opening paragraph, but there are many different ways to measure the “radius” of an atom. We were interested in two different groups of radii, those that align closely with either experimentally-determined covalent radii or van der Waals radii. The covalent radii were computed as weighted averages of the individual radius measures of each species' valence atomic orbitals. These radii include \( r_{\text{max}} \), the maximum of the radial probability distribution function; \( <r> \), the expectation value of \( r \); and \( \sqrt{\langle r^2 \rangle} \), the root mean square radius. The van der Waals radii were determined from taking the radius at certain points in the total electron density curve. These radii include \( r_{0.001} \) and \( r_{0.002} \), corresponding to the points where electron density is equal to 0.001 or 0.002 atomic units, and \( r_{95\%} \), \( r_{98\%} \), and \( r_{99\%} \), corresponding to the radius where 95, 98, or 99 percent of the integration of electron density is contained, respectively.

From these studies we were able to conclude that when chemists refer to neutral and ionic radii, they are referring to very different ways of determining atomic radius. Our results show that neutral radii best match the covalent radii. Ionic radii, on the other hand, show more agreement with our van der Waals radii. Slater discussed this nature of atomic radii in a 1930 paper [4], however, this idea of different size measurements being used for different species has not made its way into the chemistry literature and textbooks.

This research experience has been a great benefit to me. I enjoyed being able to combine chemistry with mathematics, physics, and computer science on a project that explores the foundations of the electronic structure of atoms. I also have gained valuable scientific writing and presentation experience that will benefit me in my future academic and professional work. I am very grateful for this opportunity.

References:
(4) Slater, J. C. Physical Review 1930, 36, 57-64.