The Relationship Between Atomic Size, Charge, and Polarizability
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Introduction
DeKock, Strikwerda, and Yu showed in 2012 how an atom’s “effective” atomic size, \( r_e \), relates to its average valence ionization energy according to the formula

\[
r_e = n_0 \sqrt{\alpha_0 / \alpha}
\]

where \( n \) is the principal quantum number of the valence electrons in the atom, \( n_0 \) is the bohr radius, \( \alpha_0 \) is the ionization energy of the hydrogen atom, and \( \alpha \) is the atom’s average valence ionization energy [1]. The radii obtained from this equation using experimental ionization energy values correlate well with other measures of atomic size, in particular the theoretical \( r_{\text{max}} \) that we will discuss below. In our present work, 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. We also explore other uses of this effective radius equation including ratios of size between neutral atoms and their cations, atomic polarizability, and polarizability ratios between neutral atoms and cations. In doing this work, we seek to gain insight into the electronic structure of atoms.

Theory and Method
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 with 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: \( \langle r \rangle \), the expectation value of \( r \); and \( \langle r^2 \rangle \), the mean square radius. The van der Waals radii comprise two different kinds of calculations that are both based on the total electron density curve. One kind of these radii includes \( r_{\text{coval}} \) and \( r_{\text{ion}} \), corresponding to the points where the total electron density is equal to 0.001 or 0.002 atomic units. The other kind of van der Waals radii includes \( r_{\text{coval}} \) and \( r_{\text{ion}} \), corresponding to the radius where 95%, 99, or 99% of the integration of radial probability density is contained, respectively.

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 1-36 (H-Kr) minus the transition metal elements in order to explore trends across the periodic table. Results are shown in Figure 1.

Results
The effective size concept can be applied to cations as well to obtain neutral to cation radius ratios. To obtain a simplified equation, we note that successive ionization energies of atoms roughly follow an arithmetic progression. If this arithmetic progression is assumed, we can derive the ratio

\[
r_e = n_0 \sqrt{\alpha_0 / \alpha} \left( \frac{N(N+1) - \gamma(N+1)}{(N-\gamma)(N+1)} \right)^{1/2}
\]

where \( N \) is the number of valence electrons in the neutral atom and \( \gamma \) is the charge on the cation. Radius ratios were calculated using this formula and compared to actual radius ratios from theoretical radii, and results are given in Table 2. Note the excellent agreement between the two ratios depicted in Table 2.

Polarizability
Our work is also directly related to atomic polarizability, \( \alpha \). Polarizability is a fundamental property of atoms that is important in van der Waals interactions. It has been shown to correlate with the cube of atomic size. By cubing our effective atomic radii, we obtained effective atomic polarizability, \( \alpha_e \), and these results are shown compared to experiment in Figure 2. Cubing Equation 2 results in an equation that can be used to estimate the ratio of polarizabilities of a neutral atom compared to its cation:

\[
\frac{\alpha}{\alpha'} = \left( \frac{r_e}{r_{\text{ion}}} \right)^3 \left( \frac{N(N+1) - \gamma(N+1)}{(N-\gamma)(N+1)} \right)^{3/2}
\]

We have completed theoretical studies of polarizability ratios using this equation, compared them to experimental polarizations, and found reasonable agreement between the two methods. There has been recent interest in polarizability [4,5], and our work can provide new insight into this property and its relationship to atomic size and ionization energy.

Atomic and Ionic Size Ratios
The effective size concept can be applied to cations as well to obtain neutral to cation radius ratios. To obtain a simplified equation, we note that successive ionization energies of atoms roughly follow an arithmetic progression. If this arithmetic progression is assumed, we can derive the ratio

\[
r_e = n_0 \sqrt{\alpha_0 / \alpha} \left( \frac{N(N+1) - \gamma(N+1)}{(N-\gamma)(N+1)} \right)^{1/2}
\]

where \( N \) is the number of valence electrons in the neutral atom and \( \gamma \) is the charge on the cation. Radius ratios were calculated using this formula and compared to actual radius ratios from theoretical radii, and results are given in Table 2. Note the excellent agreement between the two ratios depicted in Table 2.

Conclusion
When chemists refer to neutral and ionic radii, they are referring to very different ways of determining atomic radius. Neutral atomic radii correlate best with the theoretical covalent radii, namely, the first three types depicted in Figure 1b. Ionic radii, on the other hand, show better agreement with the theoretical van der Waals radii, namely, the last five types depicted in Figure 1b. Our formula for neutral to cation radius ratios correlates well with actual ratios from theoretical radii. Effective polarizabilities obtained from cubing our effective radii were shown to agree well with experimental atomic polarizabilities.

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References