Theoretical Interpretation of Atomic and Ionic Size

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Introduction

DeKock, Strikwerda, and Yu showed in 2012 how an atom’s atomic size relates to its average valence ionization energy according to the formula

$$r_n = n_a \frac{r_n}{F}$$  \hspace{1cm} (1)

where $r_n$ is the effective atomic radius, $n$ is the principal quantum number of the valence electrons in the atom, $a_0$ is the bohr radius, $F_n$ is the ionization energy of the hydrogen atom, and $r_n$ is the atom’s average valence ionization energy [1]. The radius obtained from this equation using experimental ionization energy values correlate well with other measures of atomic size, in particular the theoretical $r_{max}$, 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. 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 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 $r_{max}$, the maximum of the radial probability distribution function; $<r>$, the expectation value of $r$; and $\sqrt{<r^2>}$, the root 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 $r_{max}$ and $r_{\alpha 0}$, 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 $r_{max}$, $r_{\alpha 0}$, and $r_{\alpha 0}$, corresponding to the radius where 95, 98, or 99 percent 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 1-20 (H-Ca) in order to explore trends across the periodic table.

Results

Central to an understanding of electronic behavior upon ionization in atoms is the qualitative concept of atomic and ionic size. Previously, we related the effective radius, $r_n$, of an atom to the average valence ionization energy, $F_n$.

$$r_n = n_a \frac{r_n}{F}$$

In this formula, $n$ is the principal quantum number of the valence electrons in the atom; $F_n$ is the ionization energy of the hydrogen atom, and $r_n$ is the bohr radius. If an atom obeys the arithmetic progression, then it can be easily shown that the ratio of the squares of the neutral atom’s radius with $N$ valence electrons to that of its ion with charge $\alpha$ is given by the following equation.

$$\left( \frac{r_n}{r_i} \right)^2 = \frac{N(N+1) - \alpha(\alpha+1)}{N(N+1)}$$  \hspace{1cm} (2)

Representative ratios computed by equation 2 are given in Table 2. These values agree well with our Hartree-Fock data, reflecting a shrinking cationic radius. In contrast, evoking the frozen orbital approximation demands these radius ratios to be one. The concept of relaxation compensation, however, is consistent with a shrinking cationic radius like that predicted from equation 2.

Table 1: Values of $r_{max}$ and $r_{\alpha 0}$, for the fluorine atom and its singly-charged ions, in Angstrom units.

<table>
<thead>
<tr>
<th>Species</th>
<th>$r_{max}$</th>
<th>$r_{\alpha 0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>0.40</td>
<td>1.86</td>
</tr>
<tr>
<td>F+</td>
<td>0.39</td>
<td>1.63</td>
</tr>
<tr>
<td>F-</td>
<td>0.38</td>
<td>1.44</td>
</tr>
</tbody>
</table>

Figure 1a: The radial probability density of the fluorine cation, fluorine atom, and fluorine anion as a function of the distance from the center of each species. Figure 1b: The radial probability density of the fluorine atom labeled with several different measures of size.

Figure 2a: The radial probability density of the sodium atom and cation plotted against the distance from the center of each species. Figure 2b: A closer view of the radial probability density of sodium atom’s 3s electron to the radial probability density.

Table 2: Neutral to cation radius ratios, as obtained from Hartree-Fock calculations (column 2) and computed from the effective radius equation (column 3), for neon cations Ne$^+$, Ne$^{2+}$, and Ne$^{3+}$.

<table>
<thead>
<tr>
<th>Neon</th>
<th>Hartree-Fock</th>
<th>Equation 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne</td>
<td>1.10</td>
<td>1.11</td>
</tr>
<tr>
<td>Ne$^+$</td>
<td>1.11</td>
<td>1.22</td>
</tr>
<tr>
<td>Ne$^{2+}$</td>
<td>1.34</td>
<td>1.33</td>
</tr>
</tbody>
</table>

Conclusion

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 atomic radii best correlate with 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.

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References

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