Effective Atomic Size Concept: A Dilemma
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Introduction

In 2012, the DeKock Research Group derived the following equation [1] from Slater-Zener theory [2], relating effective “size” to average valence ionization energy:

\[ r_e = n a_0 \sqrt{\frac{H}{E_v}} \]

where:
- \( r_e \) = Effective size
- \( n \) = Principal quantum number
- \( a_0 \) = The bohr radius
- \( H = \text{Ionization energy of hydrogen} \)
- \( E_v = \text{Average valence ionization energy} \)

\[ r_e = n a_0 \sqrt{H/E_v} \]

The bohr radius vs \( n \)

<table>
<thead>
<tr>
<th>( n )</th>
<th>( r_e )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<tr>
<td>2</td>
<td>1.0582</td>
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<tr>
<td>3</td>
<td>1.5873</td>
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<tr>
<td>4</td>
<td>2.1164</td>
</tr>
<tr>
<td>5</td>
<td>2.6455</td>
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</tbody>
</table>

The bohr radius vs \( n \)

As shown in Figure 1, the equation agrees with atomic radii from Hartree-Fock theory (Waber-Cromer radii) [3] for the first two rows of the periodic table, but the discrepancy increases significantly for rows three, four and five.

\[ r_e \text{ vs } r_{WC} \]

Herein lies the dilemma, how can Equation 1 be “fixed” while staying well rooted in theory?

Data Analysis

Figure 2 shows the relationship between the true core-valence repulsion energy (\( V_{ee} \)-core-valence), and the core-valence repulsion energy needed to get atomic size results that agree well with Waber-Cromer radii energy (\( V_{ee} \)-core-valence), for group 2 of the periodic table. The correlation is very strong and as the equation suggests, about 91% of the term is needed to get accurate results. This was repeated for group 18 and row 2 of the periodic table, which both suggested 91% as well.

\[ y = 0.9136x \quad R^2 = 0.9988 \]

The resulting average ionization energies from equation 2, with 91% of the core-valence repulsion energy, were then compared with experimental ionization energies. For each of the fifteen atoms, an “adjustment factor” was found. This was simply what the experimental \( I_e \) values need to be multiplied by to give \( I_e' \) values, which are based on 91% of \( V_{ee} \)-core-valence. These adjustment factors were found to correlate strongly with the ratio of core to valence electrons for the given atom (Figure 3). Thus, an adjustment factor could be found for every atom in the periodic table using the linear regression equation. When comparing final results for the entire periodic table to theWaber-Cromer radii, using 90% of \( V_{ee} \)-core-valence actually worked the best.

\[ y = 0.1473x + 1.0373 \quad R^2 = 0.9933 \]

Theory and Method

We examine Equation 1 through the eyes of Hartree-Fock theory. There is a fundamental problem that arises when relating ionization energy to atomic size. To wit, when ionizing the valence electrons of an atom, 100% of the repulsion energy between the core and the valence electrons is lost. In other words, ionization assigns all of the core-valence repulsion energy to the valence shell. It seems fundamentally incorrect to associate all of the core-valence repulsion with the valence shell when measuring atomic size.

With this in mind, we modeled the effect of associating less than 100% of the core-valence repulsion energy with the valence shell. To do this, we used the software package GAMESS (General Atomic and Molecular Electronic Structure System) [4], to break down fifteen elements (He-Mg, Ar, Ca, Kr, and Sr) into their core energy (\( E_{core} \)), valence energy (\( E_{valence} \)), and core-valence repulsion energy (\( V_{ee} \)-core-valence). Using these terms, total valence ionization energy can be described by the following equation:

\[ I_{total} = -E_{valence} - V_{ee} \text{-core-valence} \]

Thus, the ionization energy, and corresponding atomic size (eqn. 1) could be monitored as the core-valence repulsion term is changed.

Results

As shown above (Figure 4), the results of this correction method, \( r_e' \) (90%), agree very well with Hartree-Fock radii.

Conclusion

Relating ionization energy to atomic size makes a false assumption that atomic size should associate 100% of the core-valence repulsion with valence shell. As theory suggests, associating some of this energy with the core, and less with the valence, gives much better results. It is important to note that this is merely a qualitative argument and theory, and not a quantitative one. There is nothing special about 90%. When comparing to other radii, slightly different percentages were suggested.

References