

ALE 6. Atomic Radii

(Reference: Section 8.4 - Silberberg 5th edition)

How does the effective nuclear charge affect the size of an atom?

The Model: Coulomb's Law

$$F = k \frac{q_1 q_2}{r^2}$$

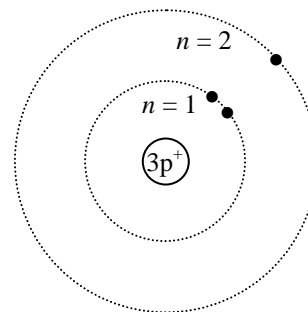
Coulomb's law, above, relates the force between two charged particles. In Coulomb's Law, k is a constant, q_1 and q_2 are the charges of the two particles, and r is the distance between the two particles. When q_1 and q_2 have opposite signs, the force between the two particles is attractive in nature. When considering the radius of an atom, we recognize that q_1 is the **effective charge of the nucleus** (represented by Z_{eff} , which is related to but not equal to the atomic number) and q_2 is the **charge of the outermost electron** (i.e., the electron that defines the size of the atom). The average distance between the nucleus and the outermost electron is r , the radius of the atom. Since all electrons have a constant charge, Coulomb's Law can be simplified as:

$$F \propto \frac{Z_{\text{eff}}}{r^2}$$

where the symbol \propto means "is proportional to".

Key Questions

1. Consider the Lithium atom. While the electrons are not in fixed orbits, the electrons in the 1s orbital are most likely to be closer to the nucleus than the electron in the 2s orbital. Suppose at some moment in time the Lithium atom looked like the Bohr model to the right (which is not drawn to scale). In the model, the central circle with "3p⁺" written in it represents the nucleus and the smaller black circles represent the electrons at their average distances from the nucleus.

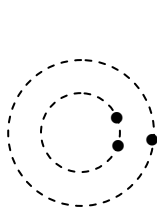


Explain why the Z_{eff} of the Lithium atom is less than the total charge of three protons.

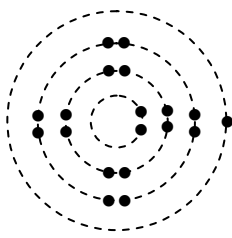
(What type of force exists between the electron in the 2nd shell and the electrons in the 1st shell? Note how the electrons in the 1st shell are drawn relative to the electron in the 2nd.)

The Model: Atomic Radii of Elements in the Same Group

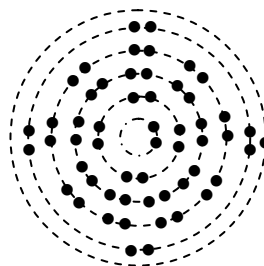
Electrons in the n^{th} shell shield electrons in the $(n+1)^{\text{th}}$ and higher shells nearly 100% effectively. That is, an electron in the outermost shell (i.e. the **valence shell**) sees a nucleus with an effective nuclear charge that is decreased by *every* electron in the core shell(s). Atoms within the same group, therefore, have nearly the same effective nuclear charge. Elements within the same group typically have similar valence electron configurations. Given these facts, the thing that makes an element with a higher Z different than that of a second element with a lower Z in the same family is the expected radius of outermost shell of electrons. Using the Alkali Metals (group 1A) as an illustration:



Li: $1s^2 2s^1$



K: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$



Cs: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^1$

Key Questions

- 2 a. What is the trend in atomic radius in a group (or column or family) as Z increases?
 - b. Explain the trend in Question 2a. (Comparing the element at the top of the group with the element at the bottom of the group, what happens to the value of n for the valence electron? What does n inform us of? What kind of force exists between an electron in the valence shell and the electrons in the core shells?)
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3. A transition element of the $6d$ block has nearly the same atomic radius as the transition element of the $5d$ block in the same family. (For example, Niobium and Tantalum each have an atomic radius of 143 pm. And some $6d$ -block transition elements are actually *smaller* than the element immediately above it on the Periodic Table!) This phenomenon is referred to as the “lanthanide contraction”. Use differences in effective nuclear charges between transition metals within the same family to explain the lanthanide contraction.

The Model: Atomic Radii of Elements in the Same Period

Electrons within the same shell do not shield each other from the nucleus 100% effectively. When determining the effective nuclear charge experienced by the outermost electron, each other electron with the same value of n typically only reduces Z_{eff} by 0.35 of a proton. Therefore, within a period of the Periodic Table, for an increase of Z of 1, Z_{eff} increases by 0.65 of a proton.

Key Questions

4. Compare the effective nuclear charge of elements in the same period of the Periodic Table. (For example, how does the Z_{eff} of Lithium compare to the Z_{eff} of Neon?)

- 5 a. According to Coulomb's Law, as the effective nuclear charge increases, what happens to the force of attraction between the nucleus and the outermost electron?

b. If the force of attraction between the nucleus and the outer-most electron were to increase, what would happen to the distance between the nucleus and that electron?

6. In going from left to right across a period on the Periodic Table, what happens to the atomic radius of an element? (Refer to [Questions 4 & 5](#) as you answer this one.)

The Model: Ionic Radii

When an atom loses one or more electrons, it becomes a cation. When an atom gains one or more electrons, it becomes an anion. Once an electron has been lost or gained by an atom, the new outermost electron no longer experiences the same amount of shielding that did the "old" electron that once defined the atom's radius. As a result, the radius of an ion is different than the radius of a neutral atom of the element.

Key Questions

- 7 a. Suppose the outermost electron is lost by an atom. What happens to the amount of shielding that is experienced by the new outermost electron? Is it the same as before, or does it decrease, or does it increase? (Circle the correct answer.)

b. As the amount of shielding that the outermost electron experiences decreases, what happens to the effective nuclear charge?

c. According to Coulomb's Law, as the effective nuclear charge increases, what happens to the force of attraction between the nucleus and the outermost electron?

- d. What happens to the radius of an atom when it becomes a cation? (Hint: Look back at your answers to [Question 7c](#) and then [Question 5b](#).)
8. What happens to the radius of an atom when it becomes an anion? Provide an explanation that involves (1) the relative amounts of shielding before and after the electron was added, and (2) what happens to the effective nuclear charge, and (3) Coulomb's Law.

Exercises

9. [Problem 8.54](#): Arrange each set in order of *decreasing* atomic size. Briefly explain your reasoning.

a.) Ge, Pb, Sn Decreasing Atomic size: > >
Reasoning:

b.) Sn, Te, Sr: Decreasing Atomic size: > >
Reasoning:

c.) F, Ne, Na: Decreasing Atomic size: > >
Reasoning:

d.) Be, Mg, Ca: Decreasing Atomic size: > >
Reasoning:

10. [Problem 8.87](#): Arrange each set of ions in order of *decreasing* size. Briefly explain.

a.) Se^{2-} , S^{2-} , O^{2-} Decreasing size: > >
Reasoning:

b.) Te^{2-} , Cs^+ , I^- Decreasing size: > >
Reasoning: