

## 1.4.4: Covalent and Ionic Radii

### Measurement of Radius

There are several methods that can be used to determine radii of atoms and ions:

- **Nonpolar atomic radii:** The radius of an atom is derived from the bond lengths within nonpolar molecules; one-half the distance between the nuclei of two atoms within a covalent bond.
- **van der Waals radius:** The radius of an atom is determined by collision with other atoms.
- **Crystal radii:** The atomic or ionic radius is determined using electron density maps from X-ray data.

The measurement of atomic or ionic size will depend on a number of factors, including the covalent character of bonding in any particular molecule, coordination number, physical state (liquid, solid, gas), the identity of nearby atoms/ions, variation in crystal structure, and distortions within regular crystal structures. You should keep in mind that the size of an atom or ion is a "fuzzy" measure, and the radius under a different set of conditions will probably change slightly.

Regardless, measured atomic and ionic radii reveal obvious trends across the periodic table and between atoms and ions. The relative atomic sizes shown in Figure 1.4.4.1 were derived from crystallographic data.<sup>1</sup>

### Trends in Atomic Radius

Atomic size generally decreases gradually from left to right across a period of elements. As nuclear charge ( $Z$ ) increases, we expect the effective nuclear charge ( $Z^*$ ) of the valence electrons to also increase. Increasing  $Z$  pulls electrons closer to the nucleus. However, with each additional unit of  $Z$ , there is also an additional electron. The change in size is a balance of a compression caused by increasing  $Z$  and an expansion in the number of electrons. As a result, the atomic radius decreases *gradually* across a period.

Atomic size generally increases going down a group. As valence electrons occupy higher level shells due to the increasing quantum number ( $n$ ), size increases despite the fact that  $Z$  and  $Z^*$  are increasing going down the group.

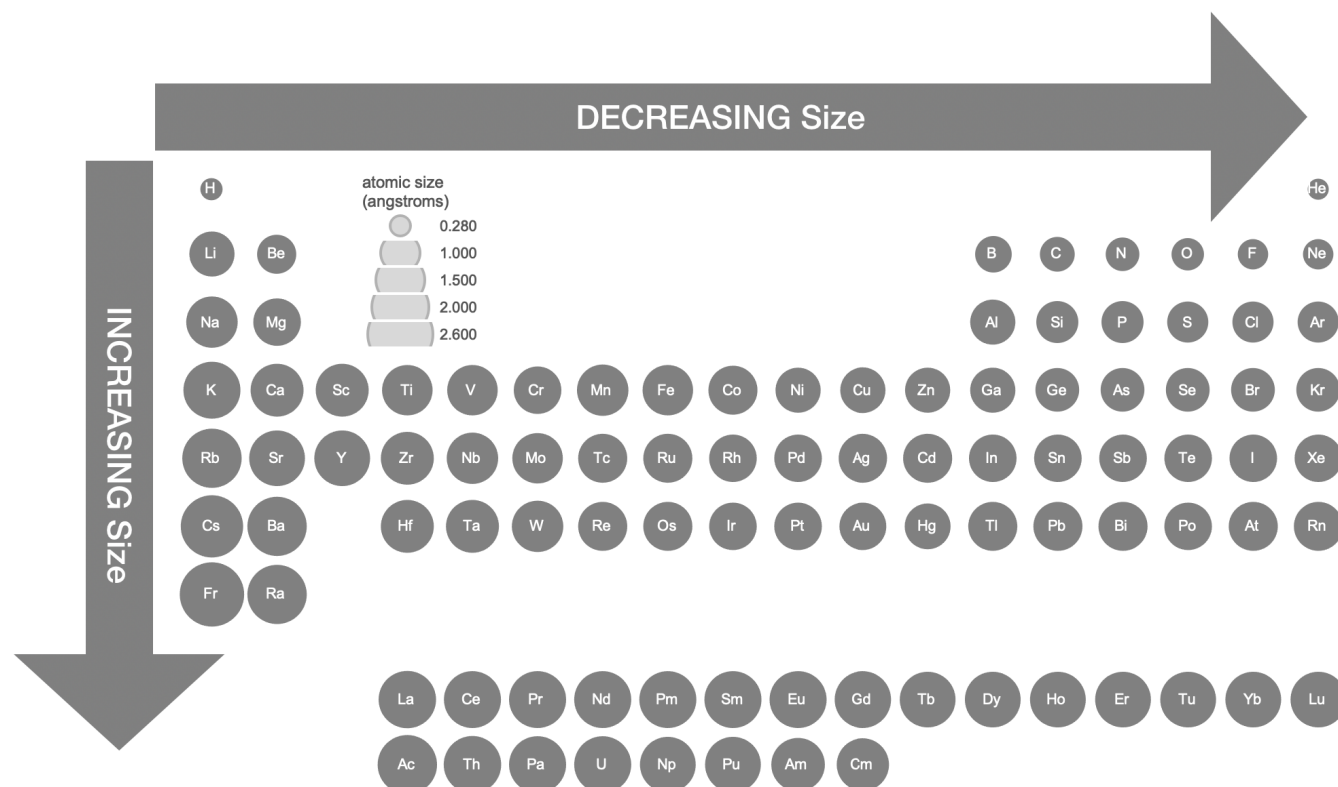


Figure 1.4.4.1. Atomic Radii Calculated from Crystallographic Data. Data from Cordero, Beatriz, Verónica Gomez, Ana E. Platero-Prats, Marc Reves, Jorge Echeverría, Eduard Cremades, Flavia Barragan, and Santiago Alvarez. "Covalent Radii Revisited." *Dalton Transactions*, no. 21 (2008): 2832–38. doi:10.1039/b801115j. (Kathryn Haas; CC-NC-BY-SA)



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## References

1. Cordero, Beatriz, Veronica Gomez, Ana E. Platero-Prats, Marc Reves, Jorge Echeverria, Eduard Cremades, Flavia Barragan, and Santiago Alvarez. "Covalent Radii Revisited." *Dalton Transactions*, no. 21 (2008): 2832–38. doi:10.1039/b801115j.
2. R. D. Shannon (1976). "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides". *Acta Crystallogr A*. **32** (5): 751–767. Bibcode:1976AcCrA..32..751S. doi:10.1107/S0567739476001551.
3. Wikipedia articles on [Atomic Radius](#) and [Ionic Radius](#).

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