

What exactly is the size of an atom?

One important periodic property of the elements is the size of atoms and ions. We often think of atoms and ions as hard, spherical objects. According to the quantum mechanical model, however, atoms and ions do not have sharply defined boundaries. The edges are a bit “fuzzy” because most of an atom’s volume is occupied by an electron cloud with no distinct boundary to separate inside from outside. Yet, in many respects atoms do behave like ordinary objects, bouncing off each other as if hard boundaries did exist. Chemists measure atomic radius as one-half the average distance between the centers of adjacent atoms in a solid. The atomic radius of an atom does vary slightly depending on which other atoms that atom is bonded to.

Size trend in columns

Within each column (family or group) atomic radius tends to increase as we proceed from top to bottom. This trend occurs because the number of *occupied* energy levels increases from top to bottom. Additional occupied energy levels mean that the *valence* electrons are further from the nucleus, which of course means the atom will be larger. (Do NOT say that the atom is larger simply because of more electrons, rather, it is important to comment on how/where those electrons are arranged/located.)

Size trend in rows

You might think that the size of the atom gets larger as you go across the chart because of the increasing number of electrons, but as you move across the chart the electrons are added into the same energy level no further from the nucleus, thus the atom does *not* get larger. Next you might be inclined to think that the size of the atom would stay the same because each electron is added into the same energy level, however, atomic measurements show that the atom actually gets *smaller across the row*. The major factor influencing this decrease in size is the increase in the positive pull from the nucleus. You must remember that every time an atom gets an extra electron, it also gets an extra proton. Thus as moving across the chart the increasing nuclear charge steadily draws the electrons that are in the same energy level, closer to the nucleus, causing the radius to decrease.

		1A	2A											3A	4A	5A	6A	7A	8A		
1		25 H		radius in picometers ($\# \times 10^{-12}$ meters)																32 He	1
2		145 Li	105 Be											85 B	70 C	65 N	60 O	50 F	45 Ne	2	
3		180 Na	150 Mg											125 Al	110 Si	105 P	102 S	99 Cl	97 Ar	3	
4		220 K	180 Ca	160 Sc	140 Ti	135 V	140 Cr	140 Mn	140 Fe	135 Co	135 Ni	135 Cu	135 Zn	130 Ga	125 Ge	119 As	116 Se	114 Br	110 Kr	4	
5		235 Rb	200 Sr	180 Y	155 Zr	145 Nb	145 Mo	135 Tc	130 Ru	135 Rh	140 Pd	160 Ag	155 Cd	155 In	145 Sn	140 Sb	138 Te	136 I	130 Xe	5	
6		260 Cs	215 Ba	175 Lu	155 Hf	145 Ta	135 W	135 Re	130 Os	135 Ir	135 Pt	135 Au	150 Hg	190 Tl	180 Pb	160 Bi	155 Po	150 At	148 Rn	6	

So what are the forces on electrons that affect the amount of space those electrons need within the atom, which results in the size (atomic radius) of the atom?

To more completely understand the size issue, we must consider what are the forces, and what affects those forces within an atom. There are two opposing forces: the $+/-$ attraction between the protons and electrons (which causes the electrons to draw in closer to the nucleus), and there is the $-/-$ repulsion between electrons themselves (which causes the electrons to push apart).

Coulomb’s law of electrostatic attraction:
$$F = \frac{q^+ q^-}{d^2}$$

Coulombs law says that the strength of the interaction between two electrical charges (the + proton, and the – electron) depends on the size of the total nuclear charge, q^+ (+ 1, +2, etc) and the square of the distance, d between the nucleus and the electron of interest.

The total + charge (force) of the nucleus does not all “get out” to the valence electrons. Some of the positive force is blocked or *shielded* by the *inner core* of electrons. Thus the force of attraction between a valence electron and the protons depends on the amount of positive nuclear charge that actually “gets out” to the valence electrons, this is called *effective nuclear charge*. (ENC)

Secondly the average distance between the nucleus and those electrons is very important, as electrons are further from the nucleus, the attractive force decreases. The force of attraction increases as the number of protons increases, and decreases as the electron moves farther from the nucleus.

Furthermore, electrons repel each other and if there were no + pull acting on them, they would fly away from each other. It is the resulting balance between these two opposing forces ($+/-$ attraction and $-/-$ repulsion) that results in the size of the atom.

Like the size of the atom, the size of an ion depends on the number of protons, the number of electrons, and the orbitals in which the outer energy level electrons reside. The ions follow the same periodic trends as the atoms. Let's take a closer look at the effect on the size of a particle when the atom gains or loses electrons and turns into a charged particle.

Positive ions

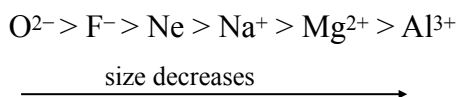
When atoms lose electrons, positive ions result. The formation of a cation (positive ion) removes the outermost (valence) electrons usually eliminating the outermost energy level, which would obviously make the resulting ion smaller than its *parent* atom.

Negative ions

When an atom gains electrons, a negative ion results. Anions (negative ions) are always larger than their parent atom. Adding an electron(s) to an atom increases the electron/electron repulsion in the outer most energy level resulting in an ion that will be larger than its *parent* atom.

Comparing particles that all have the same number of electrons – *isoelectronic* particles

The effect of varying nuclear charge on ionic radii is seen in the variation of the radius of an isoelectronic series of ions. The term *isoelectronic* means possessing the *same* number of electrons. For example, each ion in the series O^{2-} , F^{-} , Ne , Na^{+} , Mg^{2+} , Al^{3+} has 10 electrons, and thus these particles are isoelectronic. The nuclear charge in this series increases steadily in the order listed, and the ionic size decreases steadily as the effective nuclear charge draws the electrons in more tightly.



Relative Sizes of some atoms and ions. (You may find it beneficial to view this colored image on your computer)

In this diagram,

- Atoms are represented in as gray half-circles.

- Positive ions (atoms that lost electrons) are shown in pink and have the same periodic trends as atoms:
(check on line for the colored version of this note sheet)

- larger down the table
- smaller across the table

Positive ions are always smaller than their parent atom.

- Negative ions (atoms that gained electrons) are shown in blue and have the same periodic trends as atoms:

- larger down the table
- smaller across the table

Negative ions are always larger than their parent atom.

Radius of atoms and their respective ions

radius in picometers ($\# \times 10^{-12}$ meters)

Group 1A		Group 2A		Group 3A		Group 6A		Group 7A	
Li^{+}	Li	Be^{2+}	Be	B^{3+}	B	O	O^{2-}	F	F^{-}
68	145	31	105	23	85	60	140	50	133
Na^{+}	Na	Mg^{2+}	Mg	Al^{3+}	Al	S	S^{2-}	Cl	Cl^{-}
97	180	66	150	51	125	102	140	99	133
K^{+}	K	Ca^{2+}	Ca	Ga^{3+}	Ga	Se	Se^{2-}	Br	Br^{-}
133	220	99	180	62	130	116	198	114	196
Rb^{+}	Rb	Sr^{2+}	Sr	In^{3+}	In	Te	Te^{2-}	I	I^{-}
147	235	113	200	81	155	138	221	136	220