

## Chapter 9

### The Periodic Table and some Atomic Properties

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Orbital Diagrams

Remember the “orbital diagrams” from the previous chapter? They determine the magnetic properties of an atom.

#### Electron Spins and Magnetic Properties

- The spin quantum number  $m_s$  gives the electron the ability to interact with magnetic fields.
- The electron acts as a tiny magnet, and it aligns its spin so that there is an attractive force between the source of the magnetic field and the electron.

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Orbital Diagrams

“Wait, what? I don’t see anything about orbital diagrams, electron spin, and magnetic properties at the beginning of Ch. 9 of the textbook”, you say?

The book discusses those at the end of this chapter (instead of the “Electrons in Atoms” chapter)

Not unreasonable, as this chapter is about “atomic properties”, after all

But instead of discussing it at the end of the chapter like the book does, we will discuss it at the beginning

... before the orbital diagrams fade from our memory 🌀

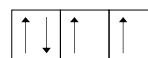
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Orbital Diagrams

#### Paramagnetism

If an atom has one or more unpaired electrons (at least one orbital occupied by a single electron)



2 unpaired electrons

it is **attracted to a magnetic field**.

Then the atom is paramagnetic.

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Orbital Diagrams

#### Diamagnetism

If all the electrons in an atom are paired (all orbitals are occupied by two electrons of opposite spins)



their spins cancel out, and the atom is **repelled by a magnetic field**.

Then the atom is diamagnetic.

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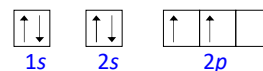
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Orbital Diagrams

#### Example

Determine if a gas-phase carbon atom is paramagnetic

Carbon:  $1s^2 2s^2 2p^2$



Carbon has 2 unpaired electrons in 2p orbitals, therefore it is paramagnetic.

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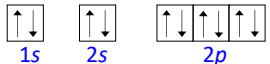
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Orbital Diagrams

**Example**

Determine if atoms of neon gas is paramagnetic

Neon:  $1s^2 2s^2 2p^6$



Neon has no unpaired electrons, therefore it is diamagnetic.

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Orbital Diagrams

Electron configurations and paramagnetism/diamagnetism discussed here are for isolated atoms.

When bonded, even to another atom of the same element, electron configurations and the resulting paramagnetism/diamagnetism change.

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**Trends in the periodic table**

We will study the periodic trends of the following:

- Ionization Energy
- Electron Affinity
- Atomic Radius

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**Trends in the periodic table**

**Why do we see trends?**

- Trends across a period (left to right) can be explained by increasing effective nuclear charge
- Trends from top to bottom in a group can be explained by increasing distance from the nucleus

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Trends in the periodic table

**Ionization Energy**

Energy required to remove an electron from a gaseous atom or ion.

$$X(g) \rightarrow X^+(g) + e^-$$

$$Mg(g) \rightarrow Mg^+(g) + e^- \quad \Delta E = 735 \text{ kJ}$$

Ionization energy of Mg = 735 kJ/mol

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Trends in the periodic table

**Electron Affinity**

- Energy change for an atom when it gets an electron  
 $X(g) + e^- \rightarrow X^-(g)$
- $e^-$  can only attach to an atom if  $\Delta E$  for that process is negative (energy is released).
- If electron affinity is listed as a (+) value, it is the magnitude of the energy released.
- The extra electron is repelled by the electrons in the atom, but is attracted to the nucleus.  
—Usually favorable overall, releasing energy

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Trends in the periodic table

### Atomic Radius

- Atomic radius is the size of the largest occupied orbitals (which is in the valence shell) in an atom.
- As such, its precise value depends on how we define the “size” of the electron cloud in those orbitals.
- But the trends in the atomic radius don’t depend on the specific definition used

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Trends in the periodic table

### To understand trends, we need to remember:

Protons in the nucleus are (+) charged

Electrons in the surrounding shells are (–) charged

Protons and electrons attract

Stronger attraction pulls electrons closer to the nucleus (smaller radius)

Stronger attraction makes it harder to remove an electron from the atom (larger ionization energy)

Stronger attraction makes it more favorable to add an electron to the atom (larger electron affinity)

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Trends in the periodic table

### The concept of “shielding”

Other electrons in the same atom counteract the attractive force exerted by the nucleus on an electron, because electrons repel each other.

If an electron provides full shielding to another electron, it’s as if that second electron is feeling one less proton in the nucleus.

Each electron is “shielded” from the nucleus by other electrons to some extent.

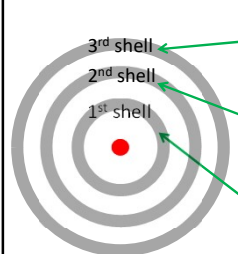
The more of an electron’s “cloud” lies between the other electron and the nucleus, the more shielding it provides.

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Trends in the periodic table

In order to shield another electron from the nuclear charge, an electron’s cloud must lie between the nucleus and the other electron.



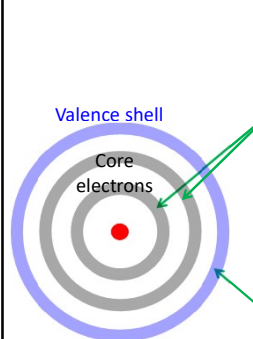
- 3<sup>rd</sup> shell
  - Is shielded by the 1<sup>st</sup> and 2<sup>nd</sup> shells
  - Does not shield the 1<sup>st</sup> and 2<sup>nd</sup> shells
- 2<sup>nd</sup> shell
  - Shields the 3<sup>rd</sup> shell from the nucleus
  - Does not shield the 1<sup>st</sup> shell
  - Is shielded by the 1<sup>st</sup> shell
- 1<sup>st</sup> shell
  - Almost completely exposed to the nuclear charge
  - Not shielded by the outer electrons
  - Shields 2<sup>nd</sup> and 3<sup>rd</sup> shells (cancels the effect of two protons)

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Trends in the periodic table

### “Shielding” of the valence electrons



- Shells closer to the nucleus (“core electrons”) almost completely shield the valence electrons from the protons that came with the core electrons. e.g. the valence electron of Na (Z=11) feels very little of the 10 protons that came with the 10 core electrons.
- Valence electrons are partially shielded by other valence electrons. They do **partially feel** the protons that were added when other valence electrons were added to build the atom.

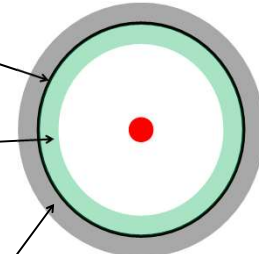
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Trends in the periodic table

### Understanding the “partial shielding” of the valence electrons by other valence electrons

For a given electron in a shell:



- Only a part (about a third) of other valence electrons’ “cloud” is closer to the nucleus than the given electron. That part provides “shielding” — like the core electrons do
- Part of the other electrons’ cloud is farther out. That part provides no shielding

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Trends in the periodic table

### Vertical trends in the periodic table

Understood in terms of:

- Distance from the nucleus, and
- “Core” electrons completely canceling the effect of an equal number of protons in the nucleus
  - Outermost shell’s distance from the nucleus won’t be affected much by the protons that came with the earlier, “core” electrons
- Each time we go down in the periodic table, a new valence shell starts getting populated
- The valence shell is the farthest from the nucleus

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Trends in the periodic table

### Vertical trends in the periodic table

Going downward in a group:

- Atomic size is determined by the farthest shell. So it gets larger as we travel down the periodic table in a given group
- Removing an electron from a farther-out shell costs less energy (smaller plus-minus attraction)
  - smaller ionization energy
- Adding an electron to farther-out shells releases less energy (smaller plus-minus attraction)
  - smaller electron affinity

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Trends in the periodic table

### Vertical trends in the Periodic Table

Ionization Energy  
Electron Affinity

large

↓ decrease

small

Atomic Radius

small

↓ increase

large

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Horizontal trends in the periodic table

### Horizontal trends in the periodic table

All horizontal trends are explained by this:

Incomplete shielding by electrons in the valence shell leads to **increasing effective nuclear charge** felt by each of them as we go from left to right across a period.

Effective nuclear charge

Periodic table

→ increase →

→ increase →

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Horizontal trends in the periodic table

### Understanding “increasing effective nuclear charge”

Across a period, each new atom adds a proton in the nucleus and an electron in the valence shell.

But the added electron does not fully cancel the effect of the accompanying proton on the other valence electrons.

As more valence electrons are added (going across a period), more of those “only partially shielded protons” are added with them.

Increasing number of “only partially shielded protons” lead to **increasing effective nuclear charge**.

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Horizontal trends in the periodic table

Increasing effective nuclear charge explains all horizontal trends. Across a period:

Atomic radius decreases

- Stronger attraction by the nucleus pulls the valence electrons closer and closer

Ionization energy increases

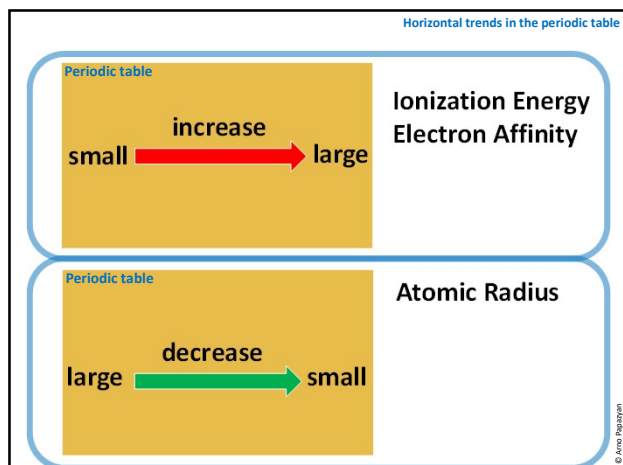
- Stronger attraction by the nucleus raises the energy cost of removing an electron

Electron affinity increases

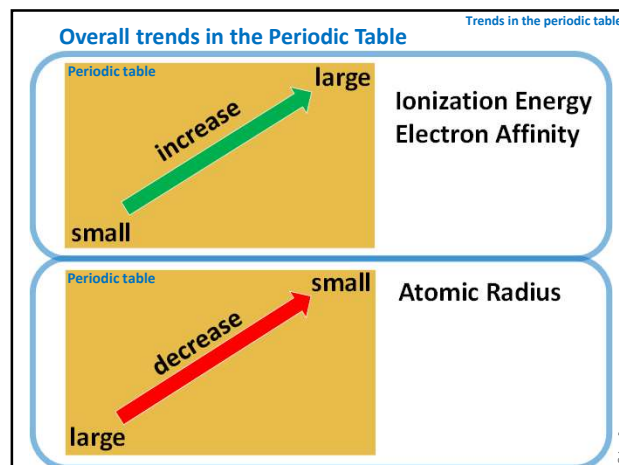
- Stronger attraction by the nucleus makes the energy of the added electron lower, releasing more energy

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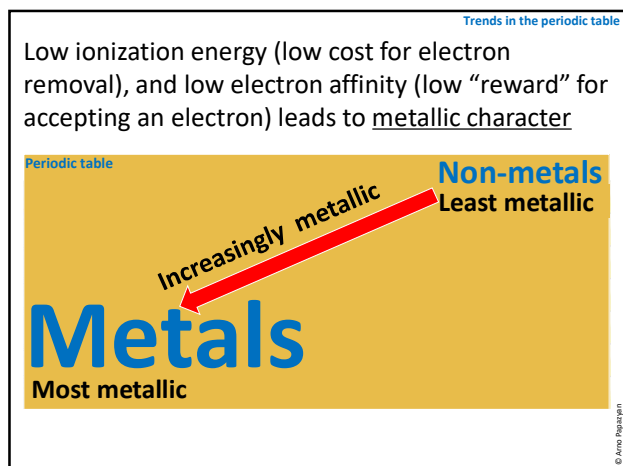
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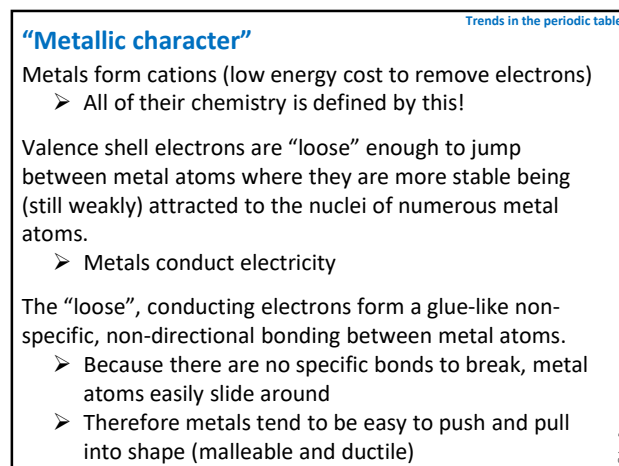
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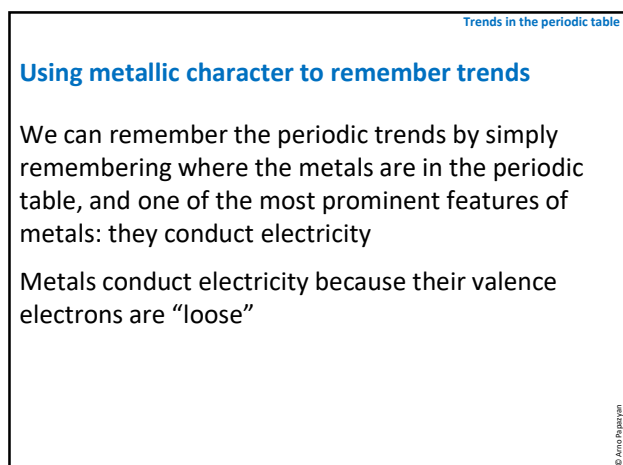
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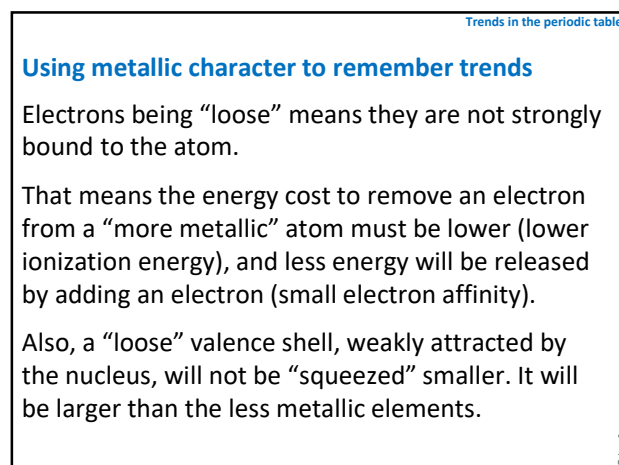
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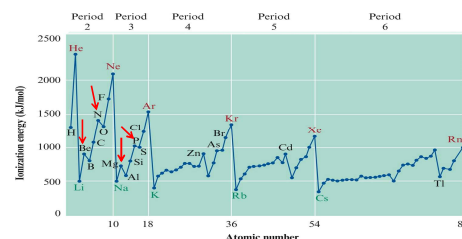
In the next few slides, we will take a closer look at the three properties (ionization energy, electron affinity, atomic radius) whose periodic trends we considered.

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### Ionization energy trends have “bumps”

Atoms with **filled or half-filled subshells** appear to have anomalously high ionization energies (**more stable than the atoms on their left or right**)

- Half-filled or filled subshells are relatively stable
- It takes more energy to pry away an electron



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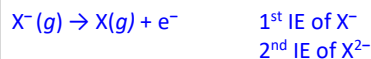
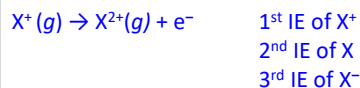
### Second, third, etc. ionization energies for an element can tell us how many valence electrons it has

Element	$I_1$	$I_2$	$I_3$	$I_4$	$I_5$	$I_6$	$I_7$
Na	495	4560					
Mg	735	1445	7730				
Al	580	1815	2740	11,600			
Si	780	1575	3220	4350	16,100		
P	1060	1890	2905	4950	6270	21,200	
S	1005	2260	3375	4565	6950	8490	27,000
Cl	1255	2295	3850	5160	6560	9360	11,000
Ar	1527	2665	3945	5770	7230	8780	12,000

- From the **jump** in successive ionization energies, we can tell when we are **starting to dig into the lower shell**, having to lift the electron from a lower level.
- So we can tell which periodic table group the atom belongs to.

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“Ionization energy” can refer to removing an electron from entities other than a neutral atom



etc.

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### More on Electron Affinity

- Adding an  $e^-$  to an atom is not the reverse of removing an electron from a neutral atom.
- Removing an  $e^-$  from an atom creates a charge separation that always requires energy (ionization energy)
- But adding an  $e^-$  to a neutral atom (electron affinity) doesn't combine or separate charges.

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### More on Electron Affinity (cont.)

Some elements don't have an EA because the  $\Delta E$  for adding an  $e^-$  is (+). The element cannot form an anion in vacuum because there is no barrier to simply spitting out the added electron in order to attain a lower energy (basically the  $e^-$  bounces off the atom)

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"Closer Look"

### Electron Affinity trends have many exceptions

Atoms with filled subshells (Group 2, 12, 18) have anomalously small (or zero) electron affinities  
 — Added electron has to go to a higher-energy subshell

Atoms with half-filled subshells (Groups 7, 15) have anomalously small (or zero) electron affinities  
 — Configuration with added electron lacks the stabilization of the half-filled subshell

Second period elements have smaller (or zero) EA than the element below them, violating the trend  
 — Their small size makes it more difficult to squeeze in an extra electron

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"Closer Look"

### Electron Affinity trends have many exceptions

From chem.libretexts.org/Bookshelves/General\_Chemistry/Map%3A\_Chemistry\_-\_The\_Central\_Science\_(Brown\_et\_al\_107)\_Periodic\_Properties\_of\_the\_Elements/7%3A\_Electron\_Affinities

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"Closer Look"

### Atomic Radii trends of the main group elements have no serious exceptions

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### Practice

Which of the following elements has the smallest atomic radius?

a) P  
**b) Cl**  
 c) S  
 d) Na  
 e) Si

All in the same Period, Cl is the rightmost

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### Practice

Which of the following elements has the highest ionization energy?

**a) Li**  
 b) Na  
 c) K  
 d) Rb  
 e) Cs

All in the same group, Li is the topmost

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### Practice

Which of the following elements has the smallest ionization energy?

a) P  
 b) Cl  
 c) S  
**d) Na**  
 e) Si

All in the same Period, Na is the leftmost

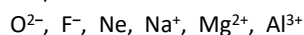
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### Isoelectronic Series

A series of ions/atoms containing the same number of electrons.

For example:



Consider what happens to the number of electrons when we form the ions above, and how they would compare with Ne.

Now think of other isoelectronic series. Write a few of them.

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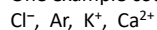
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### Practice:

Choose an alkali metal, an alkaline earth metal, a noble gas, and a halogen so that they constitute an isoelectronic series when the metals and halogen are written as their most stable ions.

- What is the **electron configuration** for each species?
- **Determine the number of electrons** for each species.
- **Determine the number of protons** for each species.

One example could be:



- The electron configuration for each species is  $1s^2 2s^2 2p^6 3s^2 3p^6$ .
- The number of electrons for each species is 18.
- $\text{Cl}^-$  has 17 protons, Ar has 18 protons,  $\text{K}^+$  has 19 protons,  $\text{Ca}^{2+}$  has 20 protons

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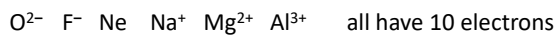
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### Why think about isoelectronic series?

Same number and configuration of electrons  
Increasing number of protons (increasing nuclear charge)

We can easily guess how their sizes vary!

For example:



Z: 8 9 10 11 12 13

Increasing nuclear charge →

Decreasing radius →

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We will be considering the energetics of ionic bonds and ionic compounds later, and ion sizes are important in that regard.

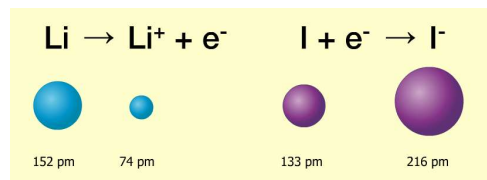
So, understanding isoelectronic series helps.

But we need to study the periodic trends of ionic radii more directly as well.

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### Ionic Radii



Cations are smaller than the parent atom

- because the valence shell is lost

Anions are larger than the parent atom

- because the extra electron-electron repulsion makes the valence shell puff up

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### Ionic Radii

#### Group IA

Atom	Ion
Li 152 pm	$\text{Li}^+$ 74 pm
Na 186 pm	$\text{Na}^+$ 102 pm
K 227 pm	$\text{K}^+$ 138 pm
Rb 248 pm	$\text{Rb}^+$ 149 pm
Cs 265 pm	$\text{Cs}^+$ 170 pm

- Ionic radius increases as we go down in a group,  
— Just like the atomic radius for the neutral atoms of elements
- Each period has one more shell than the previous one, making the ion larger than the one above it in the same group  
— Just like the atomic radius for the neutral atoms of elements

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### Ionic Radii

Period 3

Atom	Na	Mg	Al	P	S	Cl
	186 pm	160 pm	143 pm	110 pm	103 pm	99 pm
Ion	Na <sup>+</sup>	Mg <sup>2+</sup>	Al <sup>3+</sup>	P <sup>3-</sup>	S <sup>2-</sup>	Cl <sup>-</sup>
	102 pm	72 pm	53 pm	212 pm	184 pm	181 pm

Isoelectronic (10 e<sup>-</sup>)      Isoelectronic (18 e<sup>-</sup>)

Considering cations and anions **separately**:

- Ionic radius decreases across a period
- There is a big jump in ionic radius between the last metal cation in the period and the first non-metal anion

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