<u>General information Effective Nuclear Charge,</u> <u>Ionization Energies, and Electron Affinities</u>

7.2 Effective Nuclear Charge

Absorption and emission spectra shows that He^+ has energy levels that depend on *n*, just like hydrogen atom. The overall data is very different¹.

Color	Reds	Green	Blue	Indigos	violets
H atom	656.2 nm	None	486.1 nm	434.0 nm	410.1nm
He ⁺ ion	650 nm	541.4 nm	486.1 nm	498.7 nm,454.3 nm, 434.0 nm,	420.1 nm 410.1nm

Therefore, the energy levels must be different. something other than n must be a factor in the energy difference.

- 1) nuclear attractions
 - a. The Z for He is greater than the Z for H.
 - b. H is a one electron system
 - c. A higher nuclear charge increases the nucleus-electron attractions and lowers the energy of the sublevel, thus stabilizing the atom.
- 2) electron repulsions
 - a. Other atoms have more than one electron. These electron-electron interactions make the orbital energies unique for each element.
- 3) orbital shape and size
 - a. Electrons closer to the nucleus are more compact. Larger orbitals are more diffuse.
 - b. Larger *I* values have more nodes, leading to lower probabilities of finding an electron near a nucleus.

The three factors give rise to *shielding* and *penetration*.

- Shielding and penetration occur in all atoms except hydrogen.
- Shielding is also called screening.
- Penetration refers to the ability of an an electron in a higher *n* value to penetrate to a lower orbital
- Penetration has two effects:
 - It increases the nuclear attraction of a 2s electron over a 2p electron.
 - It decreases the shielding of a 2s electron by the 1s electron

¹ <u>reference for calculations</u>



• Consider the third (outer most) electron for Li. It occupies 2s orbital rather than a 2p orbital. A 2p orbital is slightly closer to the nucleus but the 2s orbital density peaks within the 1s orbital. A 2s electron spends part of its time penetrating closer to the nucleus.

Screening refers to the electron-electron repulsions that cancel a portion of the attraction of an electron to the nucleus because repulsions counteract the nuclear attractions. The outer electron feels less of the full nuclear charge.

Orbitals with higher n are not good at screening as orbitals with lower n values. This is also truce for l values when n is the same.

Electrostatic interactions determine sublevel energies:

- Greater nuclear charge lowers sublevel energy making electrons harder to remove
- Electron-electron repulsions raise sub level energy, making electrons easier to remove.
- Repulsions shield electrons from the full nuclear charge, reducing it to an effective nuclear charge, $Z_{\rm ff}$.
- Inner electrons shield outer electrons very effectively
- Penetration makes an electron harder to remove because nuclear attraction increases and shielding decreases.
- An energy level is spit into sublevels with the order s
- We account for screening with the equation $Z_{eff} = Z_{--}S$, where S is the screening constant.
 - \circ Z_{eff} increases across the representative elements.
 - \circ Z_{eff} is less evident going down a family. The Z is increasing, but the outer electron being shielded is further away.

² <u>distribution location</u>

Row 2	Li	Be	В	С	Ν	0	F	Ne
Ζ	3	4	5	6	7	8	9	10
Electron	$1s^22s^1$	$1s^22s^2$	$1s^22s^22p^1$	$1s^22s^22p^2$	$1s^22s^22p^3$	$1s^22s^22p^4$	$1s^22s^22p^5$	$1s^22s^22p^6$
configuration								
Electron	$1s^22s^0$	$1s^22s^1$	$1s^22s^2$	$1s^22s^2$	$1s^22s^2$	$1s^22s^2$	$1s^22s^2$	$1s^22s^2$
configuration	+ 1	+ 1	+ 1	+ 1 3	+ 1	+ 1	+ 1	+ 1
—1 electron								
Number of	1	2	3	4	5	6	7	8
electrons $n =$								
2								
# e affected	1	1	1	1	1	1	1	1
by shielding								

- Stadium Quantum numbers: Like locations of box seat at a sports game. The stadium (atom) is divided into sections (*n*, *level*), box (*l*, *sublevel*), row (*m*, *orbital*), and seat (*m*, *orbital*) only one person (electron) can have a unique seat.
 - Patrons further from the field "experience" less of the game because they are shielded by the seats in front of them. However, they are not blocked from vison by the patrons in the same row.
 - \circ As nuclear charge (and Z_{eff}) increases while **S** stays relatively constant, the attraction to the outer most electron increases. This is COULOMB!!

7.3 Sizes of Atoms and Ions



³ the p-electrons do not effectively shield each other, so are not considered for this conceptual model of shielding. We do count them in Slater Rules. If you are interested in learning more about Slater Rules, see the handout in the Chapter 7 section of lecture notes on my website.

⁴ <u>Atomic radii reference</u>

- Nonbonding distance: How close one electron lies next to one another without bonding compared to **bonding distance: t**he distance between atomic nuclei in an element and dividing by 2.
- Within a group, radii increase downward-quantum effect of increasing *n* value.
 - The probability of outer electrons spending most of their time farther away increases.
- Within a period, radii decrease across due to increase in Z_{eff}. There are some minor exceptions.

				,				
Row 2	Li	Be	В	С	Ν	0	F	Ne
Ζ	3	4	5	6	7	8	9	10
Electron	$1s^22s^1$	$1s^22s^2$	$1s^22s^22p^1$	$1s^22s^22p^2$	$1s^22s^22p^3$	$1s^22s^22p^4$	$1s^22s^22p^5$	$1s^22s^22p^6$
configuration								
Shielding	$1s^2+\uparrow$	$1s^2+\uparrow$	$1s^22s^2+\uparrow$	$1s^22s^2+\uparrow$	$1s^22s^2+\uparrow$	$1s^{2}2s^{2}+\uparrow$	$1s^{2}2s^{2}+\uparrow$	$1s^22s^2+\uparrow$
Radius	167	112	87	67	56	48	42	38

• Outer electron pulled closer to nucleus, size decreases

NOTATION: $1s^2 + \uparrow$ means core electrons and 1 electron (\uparrow). This electron is the one we are considering to determine the size. Also note that the core electrons don't change in the shielding. Electrons in the same sublevel do not sufficiently shield each other, and, therefore, are not considered. They are not shown. (see footnote) Ionic Radius:

Same idea as atomic radius, however, the charge is a factor, and we must consider the loss or gain of electrons as it affects Zeff.



Row 2	Li	Be	В	С	Ν	0	F	Ne
Ζ	3	4	5	6	7	8	9	10
#e in shell	2	2	2	10	10	10	10	10
Ion formed	Li ⁺	Be ²⁺	B ³⁺	C4	N^{3-}	O^{2-}	F ⁻	No ion
Electron	$1s^2$	$1s^2$	$1s^2$	$1s^22s^22p^6$	$1s^22s^22p^6$	$1s^22s^22p^6$	$1s^22s^22p^6$	$1s^22s^22p^6$
configuration				-	-	-	-	-
Shielding	1s ¹	$1s^1+\uparrow$	$1s^{1}+\uparrow$	$1s^22s^22p^5$	1s ² 2s ² 2p ⁵	1s ² 2s ² 2p ⁵	1s ² 2s ² 2p ⁵	$1s^22s^22p^5$
	$+\uparrow$			+↑ 5	$+\uparrow$	$+\uparrow$	$+\uparrow$	$+\uparrow$
Number of	0	0	0	6	6	6	6	6
electrons $n =$								
2								
Radius	76	35	23		171	140	133	no

• As positive charge increases, ionic radius decreases. The parent radius > ionic radius

• As negative charge increase, ionic radius increases. The parent radius < ionic radius

Isoelectronic Series: same number of electrons, varies in Z and charge

ion	C4	N ^{3—}	O^{2-}	F-	Ne	Na	Mg ²⁺	Al ³⁺
Z	6	7	8	9	10	11	12	13
# e in shell	10	10	10	10	10	10	10	10
		171	140	133	38	116	86	68

 Which one of the following isoelectronic ions would you expect to have the largest radius and why? Mn⁷⁺, P³⁻, S²⁻, Sc³⁺, Ti⁴⁺

7.4 Ionization Energies

Ionization energy: the minimum energy needed to remove an outer most electron from an atom or ionic in the ground. The atom or ion is in the gaseous form so that there are no other interactions interfering with the process

Energy
$$+X_{(g)} \rightarrow X^{+}_{(g)} + e^{-}$$

- The first ionization energy (IE) is always the lowest.
 - $\circ~$ IE increases with increasing $\rm Z_{eff}$. As subsequent electrons are removed, IE increases because shielding decreases.
 - Removing an electron from an atom reduces the repulsions between the remaining electrons.
 - $\circ~$ The nuclear charge remains constant, but shielding is reduced, so $\rm Z_{eff}$ increases and the size of the cation decreases.

⁵ the p-elelctrons do not effectively shield each other, so are not considered for this conceptual model of shielding. For the purpose of showing the movement of the electron gained, I have put them in the notations for N, O, F and Ne.

- \circ The parent atom is always larger than any subsequent cation created. Ionization energies increase when more electrons are removed. This means that $I_1 < I_2 < I_3$ and so on.
- IE tends to decreases down a group.
 - As *n* and therefore size increases, it is easier to remove an electron as the outer electrons are the most unstable.
- IE tends to increase across a group
 - Exceptions: in n=2 and n=3,
- IE explains the trend that metals tend to form cations in nature.
- In the ionization process, cations are always made and electrons are lost.

Ionization energies for period 3 representative elements									
Element	IE ₁	IE ₂	IE ₃	IE ₄	IE ₅	IE ₆	IE ₇		
Na	498	4560	6910	9540	13,400	16,600	20,100		
Mg	736	1445	7730	10,600	13,600	18,000	21,700		
Al	577	1815	2740	11,600	15,000	18,310	23,290		
Si	787	1575	3220	4350	16,100	19,800	23,800		
Р	1063	1890	2905	4950	6270	21,200	25,400		
S	1000	2260	3375	4565	6960	8490	27,000		
Cl	1255	2295	3850	5160	6560	9360	11,000		
Ar	1519	2665	3945	5770	7230	8780	12,000		

Anomalies:

group 3A shows a dip in IE. These are the first *np* electrons and are easy to remove because the resulting ion has a filled (stable *ns*) sublevel.



Al⁺Isoelectronic with magnesium

• Group 6A shows a dip in O and S, these atoms have a 4th electron in *np*. Electron-electron pair repulsions raise the orbital energy. Removing an electron relieves the repulsions and leaves a half fill shell (stable)



1. Why doesn't a Li²⁺ ion form in nature? The formation of the Li²⁺ ion comes at a high-energy cost, yet Be²⁺ does form. Explain the energy jump.

- 2. The ionization energies show anomalies for oxygen in the 1st ionization energies. Draw the box diagram of ground state nitrogen and oxygen. Draw the box diagram of the P⁺ and S⁺. What happens to the orbital stability for the phosphorus and sulfur atoms vs the orbital stability the respected ions? There is a similar trend for Be and B.
- Choose the orbital in which an electron would experience the highest Z_{eff}, effective nuclear charge (least shielded), and the highest I₁. Na (3s) Mg (3s) Al (3p) P (3p) S (3p)
- 4. Match the following electron configurations with the appropriate ionization energies (I₁). a) $1s^2 2s^2 3p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^1$ b) $1s^2 2s^2 3p^6 3s^2 3p^6 4s^2$ c) $1s^2 2s^2 3p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$ ii) 595 kJ/moliii) 409 kJ/mol

PULLING IT ALL TOGETHER:

Atomic radius: When shielding (S) stays relatively constant, and Z increases, Z_{eff} increases. The attraction of the electron to the nucleus increases, and radius decreases.

Ionic radius: In successive removal of electrons: When atomic number (Z) stays relatively constant, and S increases, Z_{eff} increases. The attraction of the electron to the nucleus increases, as the charge of the ion becomes more positive, the radius decreases. CONSEQUENCE: Ionization Energy goes up because the electron is more attracted to the nucleus.

Ionic radii across the PT: When shielding (S) stays relatively constant, and Z increases, Z_{eff} increases. When shielding (S) increases, and Z increases, Z_{eff} decreases, and radii decrease

The larger the positive charge, the smaller the radius for an **ISOELECTRONIC SERIES**. The larger the negative charge, the larger the radius for an **ISOELECTRONIC SERIES**

Electron configurations of ions

CATIONS

Representative elements:

- Removal of sequential electrons: come from the highest *nl. ns<np<nd<nf*
- Generally, to make the stable cation, enough electrons are removed to make the noble gas shell.
- Report the cation thusly: Na⁺ [He] 2s²2p⁶ NOT Na⁺ [Ne]

Transition elements:

Watch it! It might seem that you take them out of the *d* orbitals first, but NO they come out of the *ns* orbital.

How to avoid the mistake

- 1. Co [Ar] $4s^23d^7$ this is the fill order based on the periodic table of the **ATOM**
- 2. Put in energy order: Co [Ar] $3d^74s^2$
- 3. Remove the electron from the highest energy orbital to make the correct charge.
- 4. Co^{2+} [Ar] 3d^7

ANIONS

Representative elements:

• Addition of sequential electrons: come into the highest *nl. ns<np<nd<nf*

• Generally, to make the stable cation, enough electrons are added to make the noble gas shell. Report the cation thusly: F^- [He] $2s^22p^6$ NOT [Ne]

7.5 Electron Afinity

Electron Affinity: Measures the affinity or attraction of an electron to an atom. In general, this is an exothermic process. Energy is released because of the high potential energy to hold the electron away from the atom. This process occurs in the gas phase.

- EA decreases with increasing addition of electrons because shielding (and repulsions) increase.
 - \circ EA₁ is usually negative. EA₂ is usually positive.
 - \circ Trends are not as regular as those for size and IE₁
- EA decreases down a family. this means the number becomes less negative. Less energy is released for the process. A smooth trend is seen in 1A, but not all representative groups. Group 2A elements increase in magnitude, going from positive values to negative.
- EA shows a regular increase across the period with some similar anomalies as seen in ionization energy.
 - Atomic size is decreasing and a higher Z_{eff} should attract the electron.
 - Groups 6A and 7A have large negative electron affinities.
 - \circ This makes sense. These elements have high ionization energies, because of a small atomic radius and large Z_{eff} . This supports them forming negative ions in the ionic form.

Anomalies: Adding electron and destabilizing the shells

group 5A shows a rise in EA_1 . Nitrogen has a half filled shell. Adding an electron makes it isoelectronic with oxygen, increasing the electron repulsions, increasing shielding, and lowering Z_{eff} .



- Group 2A shows a rise in EA₁. Beryllium has a filled shell very stable. When an extra electron is added to the Be atom, it goes in as the first *np* electron. Electron-electron pair repulsions raise the orbital energy increasing the electron repulsions, increasing shielding, and lowering Z_{eff}. As the *n* value increases, the energy difference between the *ns* and *np* subshells decreases, making it easier to add an electron.
- Other anomalies are explained by increased shielding due to *nd* and *nf* sub levels.

\mathbf{v}_{1}	Be	$\downarrow\uparrow$	$\downarrow\uparrow$			
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In the following questions, choose the best answer, and explain your choice.

- 1. Which species of each pair has the higher ionization energy?
 - a) Mg or Mg^{2+}
 - b) $O \text{ or } O^{2-}$
 - \dot{c} K⁺ or Cl⁻
 - d) P^{3-} or S^{2-}
- 2. Order the following groups from largest to smallest radii.
 - a) Ar, Cl₋, K+, S^{2}_{-}
 - b) C, Al, F, Si
 - c) Na, Mg, Ar, P
 - d) I-, Ba^{2+} , Cs^+ , Xe
- 3. 13. For each of the following pairs, which of the two species is larger?
 - a) N^{3-} or F^{-}
 - \dot{b} Mg²⁺ or Ca²⁺
 - c) Fe^{2+} or Fe^{3+}
- 4. 14. For each of the following pairs, which of the two species is smaller?
 - a) K^+ or Li^+
 - b) Au^+ or Au^{3+}
 - c) P^{3-} or N^{3-}