CHEMISTRY

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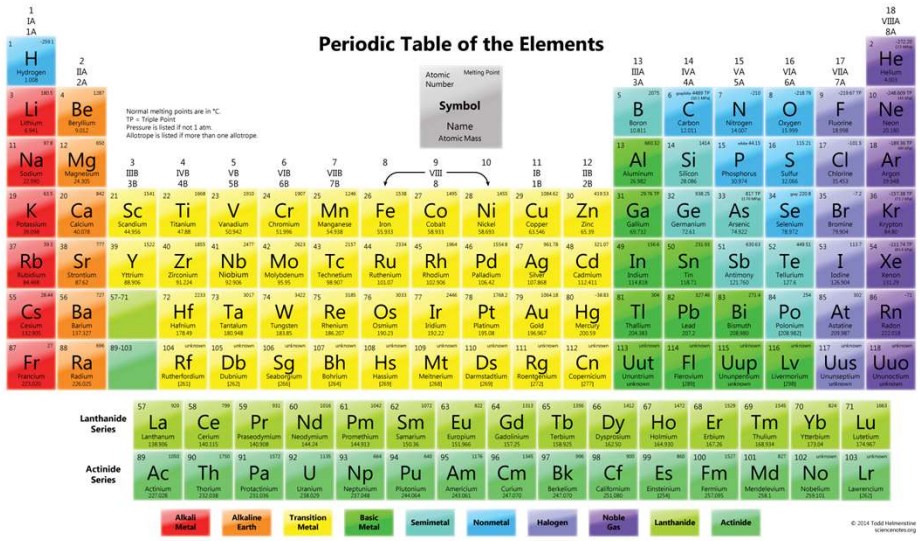
Last class..

- Periodic properties
- Slater's rule

In this class….

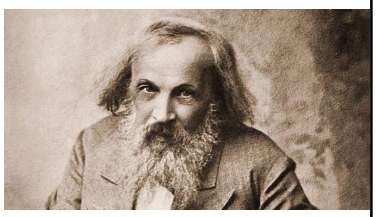
- Slater's rule, continuation
- Applications

Periodic properties



Mendeleev (1834–1907)

- Ordered elements by atomic mass
- Saw a repeating pattern of properties
- **Periodic law** – when the elements are arranged in order of increasing atomic mass, certain sets of properties recur periodically
- Put elements with similar properties in the same column & Used pattern to predict properties of undiscovered elements
- Saw this in his dream



Mendeleev' periodic law

- Mendeleev's periodic law allows us to predict **what** the properties of an element will be based on its position on the table.
- It **does not explain why** the pattern exists
- Quantum chemistry explains **why** the periodic trends in the properties exist.
  - ***Understanding why allows us to predict what***

Trends in the periodic table

- The periodic table can be used to **predict (trends)**:
  - Covalent radii (atomic size)
  - Ionic radii (ionic size)
  - Ionization energy (the energy needed to remove an electron from an atom or ion)
  - Electron affinity (as the amount of energy released when an electron is added to a neutral atom or molecule in the gaseous state to form a negative ion)
  - Electronegativity (is a chemical property that says how well an atom can attract electrons towards itself)

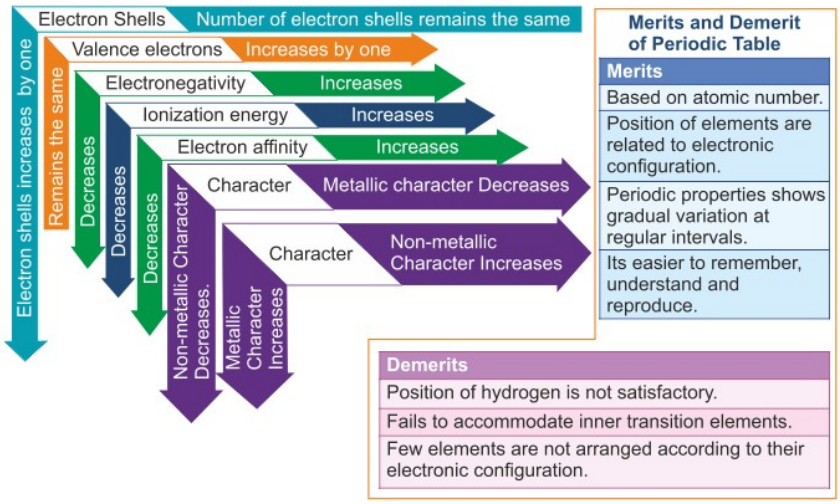
Periodicity

- Periodicity of elements means the **recurrence of similar properties of the elements after certain regular intervals** when they are arranged in the order of **increasing atomic numbers**

Cause of Periodicity of Elements?

- The cause of periodicity of the properties of elements is the **repetition of similar electronic configuration of their atoms in the outermost energy shell** (or valence shell) after certain regular intervals.
- Is it that simple ?

Trends in the periodic table



Merits and Demerit of Periodic Table

Merits
Based on atomic number.
Position of elements are related to electronic configuration.
Periodic properties shows gradual variation at regular intervals.
Its easier to remember, understand and reproduce.

Demerits
Position of hydrogen is not satisfactory.
Fails to accommodate inner transition elements.
Few elements are not arranged according to their electronic configuration.

Periodicity, example

Table of electronic configurations of Alkali Metals

Element	Atomic No.	Electronic configuration
Li	3	$1s^2\ 2s^1$
Na	11	$1s^2\ 2s^2\ 2p^6\ 3s^1$
K	19	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$
Rb	37	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}4s^2 4p^6 5s^1$
Cs	55	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6 3d^{10}4s^2 4p^6 4d^{10}5s^2 5p^6 6s^1$
Fr	87	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}4s^2 4p^6 4d^{10}5s^2 5p^6 6s^2 4f^{14}5d^{10}6p^6 7s^1$

Electron configuration

- Quantum theory describes the behavior of electrons in atoms
- The electrons in atoms exist in orbitals
- A description of the orbitals occupied by electrons is called an **electron configuration.**

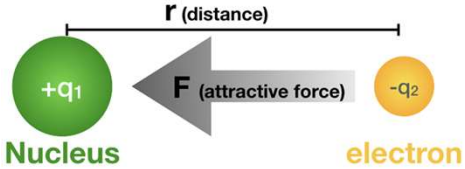
H $1s^1$ ← Number of electrons in orbital

Orbital

Coulomb's Law

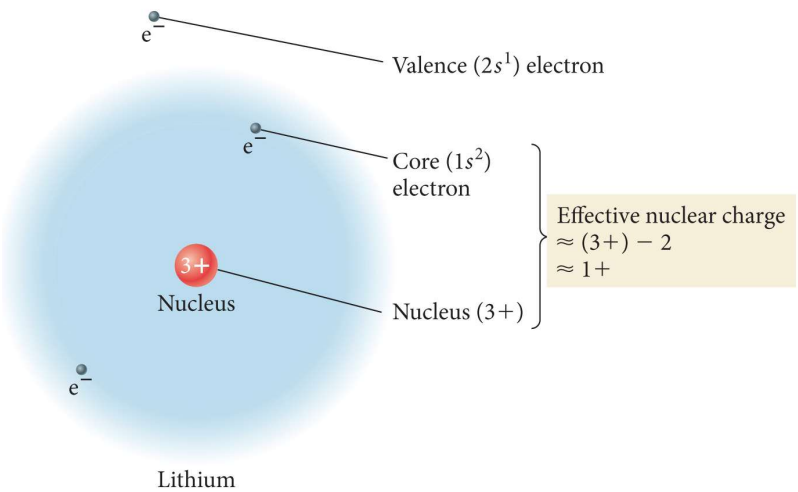
- According to Coulomb's law, the attraction of an electron to a nucleus depends only on three factors:
- the charge of the nucleus (+Z), the charge of the electron (-1), and the distance between the two (r).
- Coulomb's law works well for predicting the energy of an electron in a hydrogen atom (H has only two particles: one nucleus and one electron).

$$F = k\,\frac{Q_1 Q_2}{r^2}$$



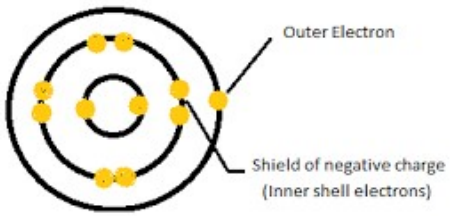
Where F is the force, k is Coulomb's constant, q1 and q2 are the charges on the two particles, and r is the distance between the particles.

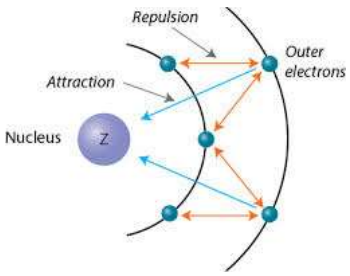
Screening and Effective Nuclear Charge



Shielding

- The ***shielding effect is the decrease in attraction between an electron and the nucleus in any atom***.
- Outer electrons are **shielded** from the nucleus by the core electrons.
  - **Screening or shielding effect**
  - Outer electrons do not effectively screen for each other and **not** experience the full strength of the nuclear charge.





Shielding

- In a multielectron system, electrons are simultaneously attracted to the nucleus and repelled by each other
- Outer electrons are **shielded** from the nucleus by the core electrons.
  - **Screening or shielding effect**
  - Outer electrons do not effectively screen for each other
- The shielding causes the outer electrons to **not** experience the full strength of the nuclear charge.

What is Nuclear Charge?

It is the charge on the nucleus with which it attracts the electrons of the atom. Basically, the Nuclear Charge is said to be equal to the atomic Number (**i.e, . the Number of protons**) in an atom. It is denoted by the symbol **Z.**

What is Shielding Effect?

Shielding Effect is defined as a measure of the extent to which the intervening electrons shield the outer electrons from the nuclear charge. It is denoted by the symbol **S.**

What is Effective Nuclear Charge ?

Effective Nuclear Charge **is the actual charge felt by the outer electrons** after taking into account shielding of the electrons. It is denoted by the symbol **Z^* or Z_{eff}** $Z_{effective} = Z - S$

Effective Nuclear Charge

- The effective nuclear charge is a net positive charge that is **attracting a particular electron.**
- **Z** is the nuclear charge, and **S** is the number of electrons in lower energy levels.
  - Electrons in the same energy level contribute to screening but since their contribution is so small they are not part of the calculation.

$$Z_{effective} = Z - S$$

Slater's rule

- **J.C. Slater** proposed a set of semi-empirical rules to understand the concept of effective nuclear charge and to **calculate the screening constant or shielding constant**
- Proposed a formula for calculation of effective nuclear charge

$$Z_{eff} = Z - S$$

where S is the Slater's screening constant ,

Z is the Nuclear charge

Slater's Rules:

Step 1 : Write the electron configuration for the atom using the following design;

(1*s*)(2*s*,2*p*)(3*s*,3*p*) (3*d*) (4*s*,4*p*) (4*d*) (4*f*) (5*s*,5*p*) (5d) (5f) (6s,6p)……. etc.

the electrons are arranged into a sequence of groups in **order of increasing principal quantum number n, and for equal n in order of increasing azimuthal quantum number l,** except that **s- and p- orbitals are kept together.**

Step 2: Identify the electron of interest, **and ignore all electrons in higher groups (to the right in the list from Step 1**). These do not shield electrons in lower groups

Slater's Rules

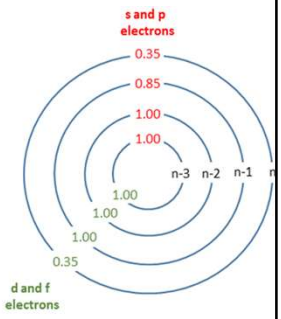
Step 3: Slater's Rules is now broken into two cases:

the shielding experienced by an ***s- or p- electron***

- electrons within same group shield **0.35**, except the 1*s* which shield **0.30**
- electrons within the n-1 group shield **0.85**
- electrons within the n-2 or lower groups shield **1.00**

the shielding experienced by ***nd or nf*** valence electrons

- electrons within same group shield **0.35**
- electrons within the lower groups shield **1.00**



Shielding constant for 2p electron in N

- Determine the electron configuration of nitrogen, then write it in the appropriate form. Use the appropriate Slater Rules to calculate the shielding constant for the electron.

- Step A N: $1s^2\ 2s^2\ 2p^3$. N: $(1s^2)(2s^2,2p^3)$

- Step B There are 4 other electrons in the same ns, np group @ 0.35: $(2s^2,2p^3)$.
- There are 2 electrons in the n-1 groups @ 0.85: $(1s^2)$

$$S[2p] = \underbrace{0.85(2)}_{\text{the 1s electrons}} + \underbrace{0.35(4)}_{\text{the 2s and 2p electrons}} = 3.10$$

Slater's Rules

Calculate Z^* for a valence electron in fluorine (Z = 9).

1. Electronic configuration of fluorine is $1s^2,2s^2,2p^5$
2. Grouping it acc. to slater's rule : $(1s^2)(2s^2,2p^5)$
3. Rule 2 does not apply;
4. Now, one electron out of the 7 valence electrons becomes the electron of interest. The other remaining 6 valence electrons will contribute 0.35 each towards shielding.
5. The electrons in (n – 1) orbitals i.e. 1s orbital will contribute 0.85 each towards shielding.

Slater's Rules

S = 0.35 x (No. of electrons in the same shell i.e. n orbital) + 0.85 x (No. of electrons in the (n – 1) shell)

S = 0.35 x 6 + 0.85 x 2
= 2.1 + 1.7
= 3.8

$Z^* = Z - S$

= 9 – 3.8 = 5.2 for a valence electron.

Slater's Rules

Calculate Z* for a 4s electron in Zinc (Z of Zinc is 30)

- $\mathbf{1s^2 2s^2} 2p^6 \mathbf{3s^2} 3p^6 3d^{10} \mathbf{4s^2}$
- $(1s^2)(2s^2,2p^6)(3s^2,3p^6)(3d^{10})(4s^2)$
- (0.35 x 1) + (0.85 x 18) + (10 x 1.00) = 25.65
- **Z* = 30 – 25.65 = 4.35 for a valence electron.**

Slater's Rules

What is the shielding constant experienced by a 3d electron and 4p electron in the bromine atom and calculate Z_{eff}? Z of Bromine is 35

Solution A Br: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^5$

Br: $(1s^2)(2s^2,2p^6)(3s^2,3p^6)(\mathbf{3d^{10}})(4s^2,4p^5)$

Ignore the group to the right of the 3d electrons. These do not contribute to the shielding constant.

Solution S[3d] = 1.00(18) + 0.35(9) = 21.15

$Z^* = Z - S = 35 - 21.15 = 13.85$ for a 3d electron

Effective nuclear charge felt by a 4p electron of bromine

- $(1s)^2\ (2s^2, 2p^6)\ (3s^2, 3p^6)\ (3d^{10})\ (4s^2, 4p^5)$
- There are 6 other electrons in the same ns, np group.
- There are 18 electrons in the n-1 groups. (3s, 3p and 3d)
- There are 10 electrons in the n-2 and lower groups. (1s, 2s and 2p)
- **S = 6(0.35)+18(0.85)+10(1.00) , S= 27.4**
- Bromine's atomic number is 35

$Z^* = Z - S = 35 - 27.4 = 7.6$ for a 4p electron

Slater's rule

Calculate Z^* for a 4s and a 3d electron in Iron (Z = 26).

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$

$$4s \quad : s = 0.35 \times 1 + 0.85 \times 14 + 1.00 \times 10 = 22.25 \Rightarrow Z_{\text{eff}}(4s) = 26.00 - 22.25 = 3.75$$

$$3d \quad : s = 0.35 \times 5 + 1.00 \times 18 = 19.75 \Rightarrow Z_{\text{eff}}(3d) = 26.00 - 19.75 = 6.25$$

Transition elements: reviewing the rules: electrons in the same (nd) group contribute 0.35 towards the overall shielding. Elements in all groups to the left in the Slater configuration format contribute 1.00 towards overall shielding. Electrons in all groups to the right in the slater configuration contribute nothing towards overall shielding.

APPLICATIONS OF SLATER'S RULE

- It provides a quantitative justification for the sequence of orbitals in the energy level diagram
- Understand the variation of atomic radius (size)
- Understand the size of cation, anion
- Understand the variation of IE, EA and EN

APPLICATIONS OF SLATER'S RULE

- It helps to **explain the filling of ns - orbital (4s, 5s,6s etc. – orbitals) prior to the filling of (n-1)d** orbital (3d, 4d, 5d…etc.)
- **We can predict/understand this**
- Let us consider the case of **Potassium (Z = 19), in which the last electron is added to 4s orbital or 3d orbital ?**

- **Now, Let us assume that the last electron enters the 4s orbital rather than 3d orbital,**
- The configuration of **Potassium** acc. to Slater is

$$(1s^2)\ (2s^2\ 2p^6)\ (3s^2\ 3p^6)\ (4s^1)$$

- As the effective nuclear charge on electron in 4s orbital has to be calculated , the electrons in the same orbital i.e. n orbital will contribute 0.35 each, the electrons in (n – 1) orbital i.e. 3s and 3p orbitals will contribute S = 0.85 each and all the electrons in (n – 2, n – 3…. Etc) orbitals i.e. (2s , 2p, 1s) orbitals will contribute S =1.00 each.

So,

$S = 0 \times 0.35 + 8 \times 0.85 + 10 \times 1.00$

$= 16.80$

Therefore, Effective Nuclear Charge

$Z^* = Z - S = 19 - 16.80 = 2.20$

Now, Let us assume that the last electron enters the 3d orbital rather than 4s orbital,

Then the configuration acc. to Slater is

$(1s^2)(2s^2\ 2p^6)(3s^2\ 3p^6)(3d^1)$

Here the d electron is under interest, so the electrons in the same orbital i.e. 3d orbital will contribute S = 0.35 each, where as the electrons in all the other orbitals i.e. (3s,3p,2s, 2p, 1s) will all contribute S = 1.00 each.

So,

$S = 18 \times 1.00 = 18.00$

Therefore Effective Nuclear Charge

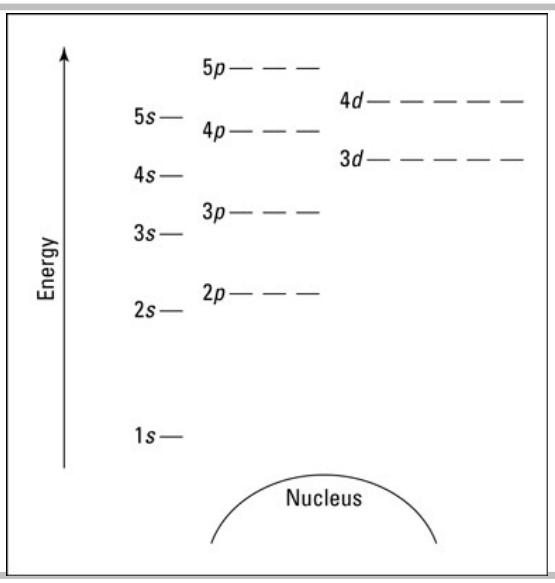
$Z^* = Z - S = 19.00 - 18.00 = 1.00$

On comparing the Effective Nuclear Charge of both 4s and 3d orbitals, we see that the 4s electron is under the influence of greater Effective Nuclear charge (Z_{eff} = 2.20) as compared to 3d electron (Z_{eff} = 1.00) in Potassium atom.

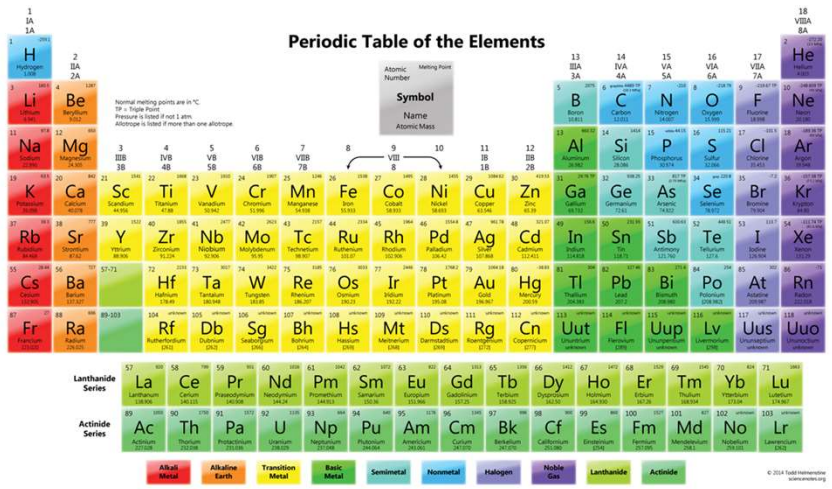
- So, **the electron in <u>4s orbital will be more attracted</u> by the nucleus and <u>will have lower energy than the 3d electron.</u>**

- Thus, **<u>the last electron will enter in the 4s orbital , rather than the 3d orbital in case of Potassium atom</u>.**

Energy level diagram



Trend in Atomic Radius



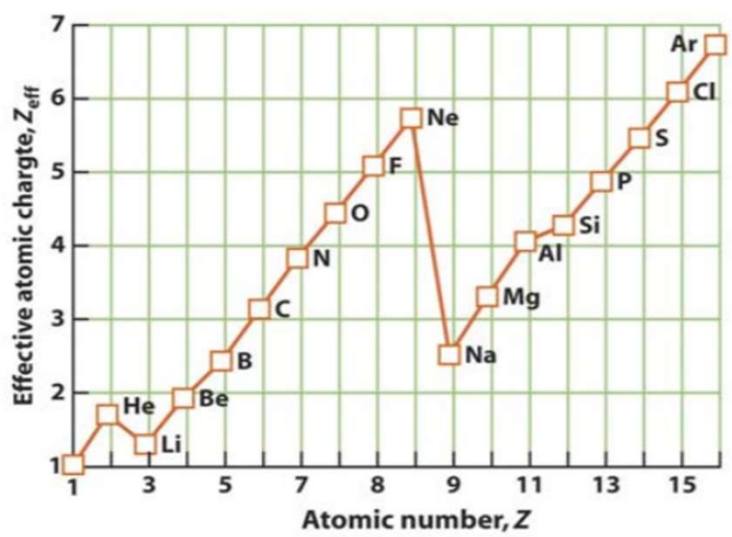
Trend in Atomic Radius

- **What happens when we move across the period ?**
- Example from Lithium to Neon
- Calculate the effective nuclear charge (valence electron) !

Lithium (L)	3	2, 1	$1s^2,2s^1$	2 x 0.85	1.7
Neon (N1)	10	2, 8	$1s^2,2s^22p^6$	2 x 0.85 + 2 x 0.35 + 5 x 0.35	4.15

Trend in Atomic Radius

Elements	Atomic number	Electronic configuration	Detailed Electronic configuration	Calculation	Screening effect constant
Lithium (L)	3	2, 1	$1s^2,2s^1$	2 x 0.85	1.7
Beryllium (Be)	4	2, 2	$1s^2,2s^2$	2 x 0.85 + 1 x 0.35	2.05
Boron (B)	5	2,3	$1s^2,2s^22p^1$	2 x 0.85 + 2 x 0.35	2.40
Carbon (C)	6	2, 4	$1s^2,2s^22p^2$	2 x 0.85 + 2 x 0.35 + 1 x 0.35	2.75
Nitrogen (N)	7	2, 5	$1s^2,2s^22p^3$	2 x 0.85 + 2 x 0.35 + 2 x 0.35	3.10
Oxygen (O)	8	2, 6	$1s^2,2s^22p^4$	2 x 0.85 + 2 x 0.35 + 3 x 0.35	3.45
Fluorine (F)	9	2, 7	$1s^2,2s^22p^5$	2 x 0.85 + 2 x 0.35 + 4 x 0.35	3.80
Neon (N1)	10	2, 8	$1s^2,2s^22p^6$	2 x 0.85 + 2 x 0.35 + 5 x 0.35	4.15



Period Trend in Atomic Radius

- The **larger the effective nuclear charge** an electron experiences, the **stronger the attraction** it will have **for the nucleus**.
- The **stronger the attraction the valence electrons** have for the nucleus, **the closer their average distance** will be to the nucleus.
- **Traversing across a period increases the effective nuclear charge on the valence electrons.**
- Quantum-mechanics **predicts the atoms should get smaller across a period**
- **Lithium atomic radius : 182 pm , Neon atomic radius : 34 pm**

Trend in Atomic Radius, Group

Group – 1 (Alkali Metals):

Elements	Atomic Number (Z)	Screening effect Constant (σ)	Effective Nuclear charge Zeff = Z – σ
Lithium (L)	3	1.7	1.3
Sodium (Na)	11	8.8	2.2
Potassium (K)	19	16.8	2.2
Rubidium (Rb)	37	34.8	2.2
Caesium (Cs)	55	52.8	2.2

Trend in Atomic Radius

- **Group – 2 (Alkaline Earth Metals):**

Elements	Atomic Number (Z)	Screening effect Constant (σ)	Effective Nuclear charge Zeff = Z – σ
Beryllium (B)	4	2.05	1.95
Magnesium (Mg)	12	9.15	2.85
Calcium (Ca)	20	17.15	2.85
Strontium (Sr)	38	35.15	2.85
Barium (Ba)	56	53.15	2.85

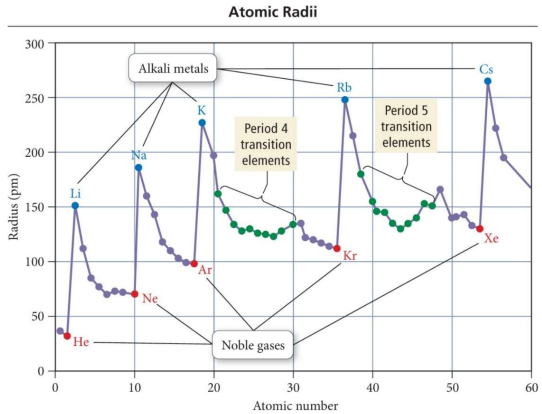
- It is observed that in a subgroup of normal elements the magnitude of effective nuclear charge remains almost the same.

Group Trend in Atomic Radius

- The size of an atom is related to the distance the valence electrons are from the nucleus.
- The larger the orbital an electron is in, the farther its most probable distance will be from the nucleus, and the less attraction it will have for the nucleus.
- **Traversing down a group adds a principal energy level.**
- **The larger the principal energy level an orbital is in, the larger its volume.**
- Quantum-mechanics **predicts the atoms should get larger down a column.**

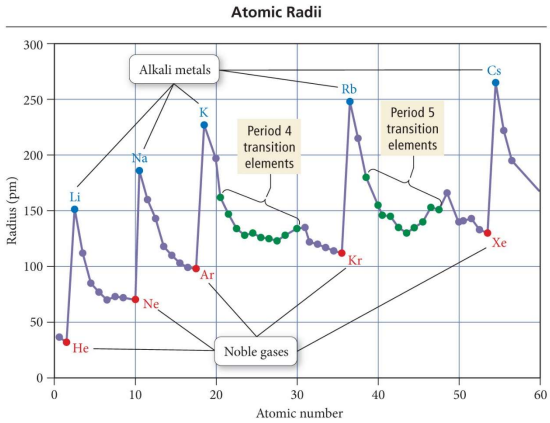
Trend in Atomic Radius

- **Atomic radius decreases across period (left to right)**
  - Adding electrons to same valence shell
  - Effective nuclear charge increases
  - Valence shell held closer



Trend in Atomic Radius

- **Atomic radius increases down group**
  - Valence shell farther from nucleus
  - Effective nuclear charge fairly close



Trend in Ionic size

- Example of **Lithium atom** and **Lithium ion (Li^+) – What do you expect size wise and why ?**
- **It helps to explain why size of a cation is always smaller than its neutral atom.**

The Electronic configuration of **Lithium atom** is $1s^2\ 2s^1$

Write it according to Slater's $(1s^2)\ (2s^1)$

As 2s orbital has only one electron , it becomes the electron of interest.

- Only the 1s electrons will contribute towards shielding

  S = 2 x 0.85 = 1.70

  $\mathbf{Z_{eff} = Z - S}$ = 3 – 1.70 = **1.30**

In case of Lithium (Li^+) Ion

- The Electronic Configuration of Li^+ is $1s^2$
- Grouping acc. to Slater : $(1s^2)$
- In Case of Li^+ , one of the 1s electrons becomes electron of interest and the other 1s electron contributes towards shielding. **S = 1 x 0.30 = 0.30**

  $\mathbf{Z_{eff} = Z - S}$ = 3 – 0.30 = **2.70**

- **Comparison of the Effective Nuclear Charge of Li atom**

(Z_{eff} = 1.30) and Li^+ ion (Z_{eff} = 2.70), shows that effective nuclear charge of Li^+ ion is more than Li atom. So , the size of Li^+ ion is smaller than Li atom.

What happens in anion vs. neutral atom ?

It explains why a anion is always larger than its neutral atom

- Taking the example of **Chlorine atom** and **Chlorine ion (Cl^-).**
- In case of **Chlorine atom (Z = 17),** the electronic configuration is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$
- Grouping it acc. to Slater's rule $(1s^2)\ (2s^2\ 2p^6)\ (3s^2\ 3p^5)$

S = 6 x 0.35 + 8 x 0.85 + 2 x 1.00 = 10.90

Z_{eff} = Z – S = 17 – 10.90 = 6.10

In case of Chlorine ion Cl^-

- The electronic configuration is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$
- Grouping it acc. to Slater's rule

$(1s^2)\ (2s^2\ 2p^6)\ (3s^2\ 3p^6)$

S = 7 x 0.35 + 8 x 0.85 + 2 x 1.00 = 11.25

Z_{eff} = Z – S = 17 – 11.25 = 5.75

- Comparison of the **Effective Nuclear Charge of Cl atom**

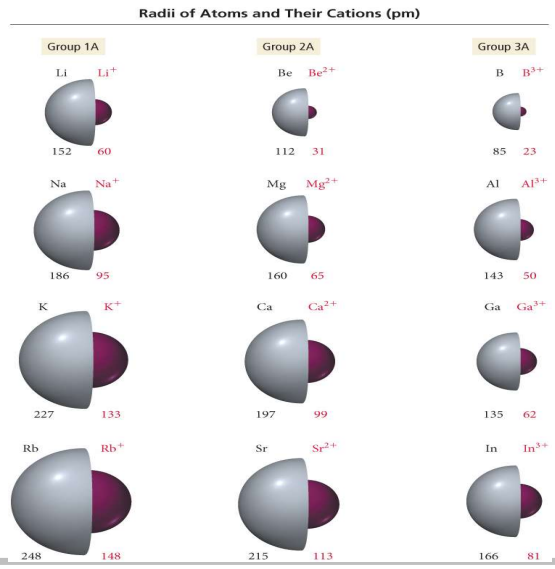
(Z_{eff} = 6.10) and Cl^- ion (Z_{eff} = 5.75), shows that the Effective nuclear charge on Cl atom is more than Cl^- ion.

- So , the size of Cl^- ion is larger than Cl atom

Trends in Ionic Radius

- Ions in the same group have the same charge
- Ion size increases down the column.
  - Higher valence shell, larger
- Cations are smaller than neutral atoms; anions are larger than neutral atoms.
- Cations are smaller than anions.
- Larger positive charge = smaller cation
- Larger negative charge = larger anion

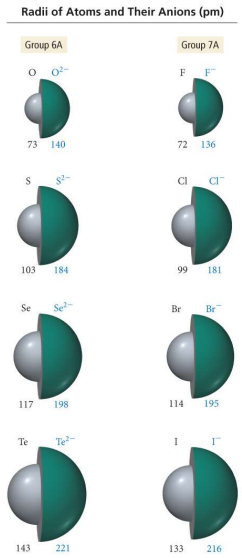
Periodic trends in cationic radius



Explanation for the Trends in Cation Radius

- When atoms form cations, the valence electrons are removed.
- The farthest electrons from the nucleus are the *p* or *d* electrons in the (n − 1) energy level.
- This results in the cation being smaller than the atom.
- These "new valence electrons" also experience a larger effective nuclear charge than the "old valence electrons," shrinking the ion even more.
- **Traversing down a group increases the (n − 1) level, causing the cations to get larger.**
- **Traversing to the right across a period increases the effective nuclear charge, causing the cations to get smaller.**

Periodic trends in anionic radius



Explanation for the Trends in Anion Radius

- When atoms form anions, electrons are added to the valence shell.
- These "new valence electrons" experience a smaller effective nuclear charge than the "old valence electrons," increasing the size.
- The result is that the anion is larger than the atom.
- **Traversing down a group increases the *n* level, causing the anions to get larger.**
- **Traversing to the right across a period decreases the effective nuclear charge, causing the anions to get larger.**

Thank you all for your attention

Information presented here were collected from various sources – textbooks, articles, manuscripts, internet and newsletters. All the researchers and authors of the above mentioned sources are greatly acknowledged.