Chapter 7

Periodic Properties of the Elements

I) Development of the P.T.

Generally, the electronic structure of atoms correlates w. the prop. of the elements

- reflected by the arrangement of the elements in the P.T.

A number of elements were discovered based on expected prop. of the "missing" elements.

A) Noble Gases

ns^2np^6 - very stable

B) Representative Elements

"last" e^- added to s & p orbitals

distinct & fairly regular variations in prop. w. changes in atomic #

C) d-Transition Elements

e^- added to d orbitals

$$ns^2(n-1)d^x$$

II) Effective Nuclear Charge

Net (+) charge attracting an e^-

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

S = screening constant

- avg. number of e^-'s between nucleus & any particular e^-

- depends on specific orbitals

Subsets of e^-:

1) core e^-

2) valence e^-

Inner e^- screen or shield outer e^- from full (+) charge

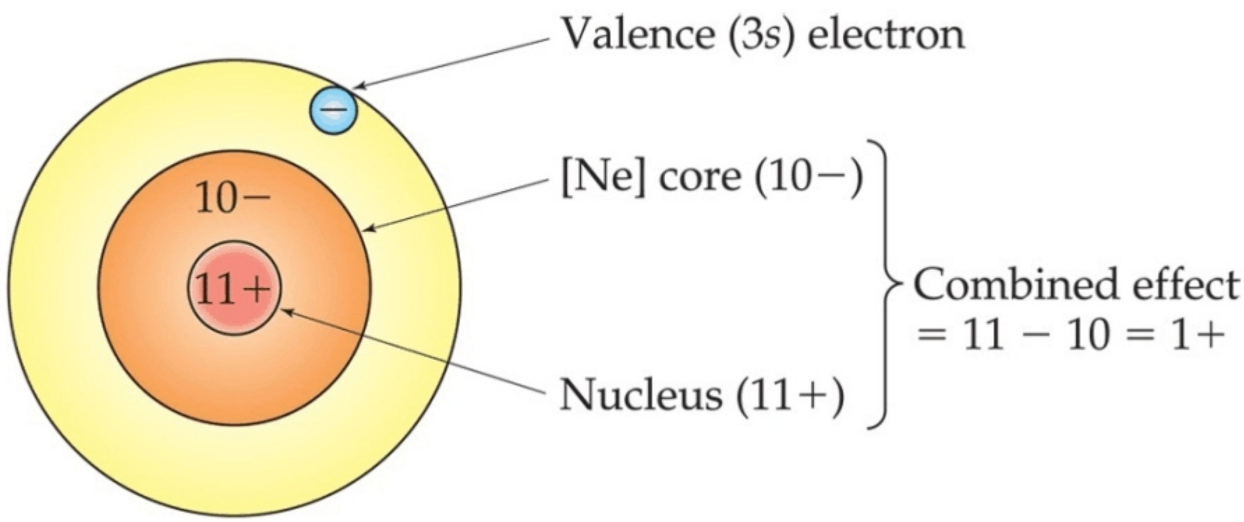
Primary interaction of e^- & nucleus is due to charge:

Coulomb's Law:

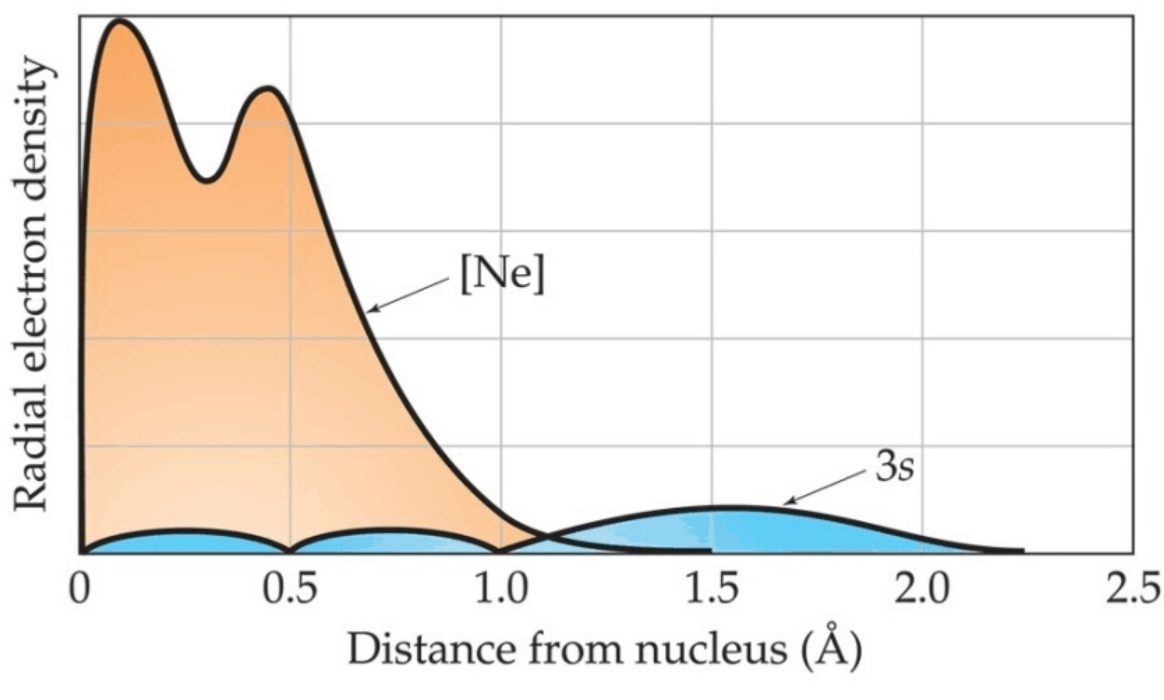
$$F = \frac{k\,(Q_e Q_n)}{r^2}$$

However, valence shell e^- do not experience full nuclear charge

- partially shielded by the core e^-


Valence (3s) electron
10−
11+
[Ne] core (10−)
Combined effect
= 11 − 10 = 1+
Nucleus (11+)

(a)


Radial electron density
[Ne]
3s
0
0.5
1.0
1.5
2.0
2.5
Distance from nucleus (Å)

(b)

Value of S is usually close to # core e^-

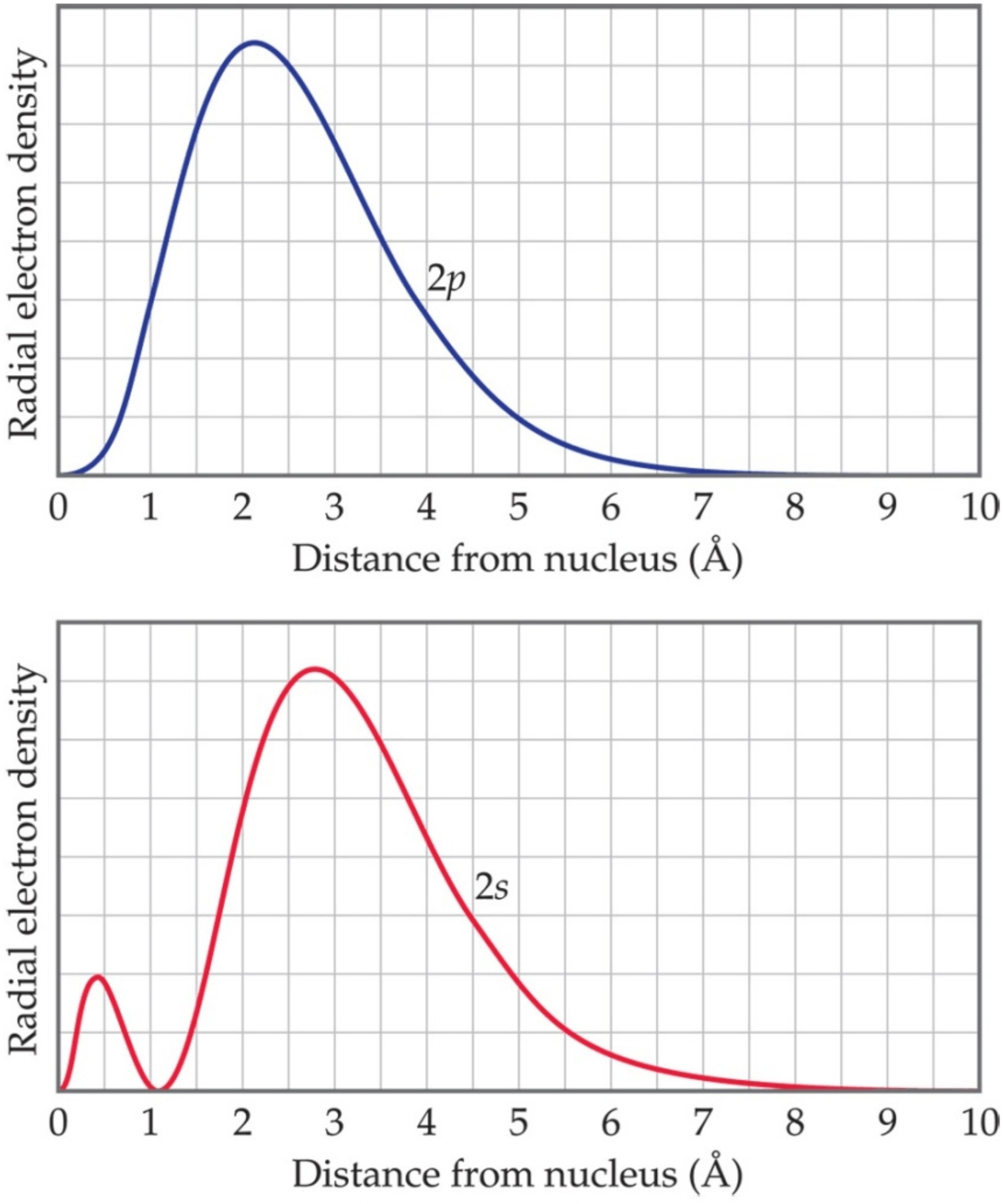
Valence shell e^- do not screen each other effectively.

- same distance from nucleus

The "p" e^- do not screen "s" e^-

The "s" e^- do screen "p" e^- somewhat due to a probability for these e^- to be nearer the nucleus

- penetration


Radial electron density
2p
0 1 2 3 4 5 6 7 8 9 10
Distance from nucleus (Å)
Radial electron density
2s
0 1 2 3 4 5 6 7 8 9 10
Distance from nucleus (Å)

A) General Trends

1) Across Row

Z_{eff} inc. by ~1 as each atom has added 1 proton to nucleus and 1 e^- to valence shell (which does not screen)

→

Z_{eff} inc.

2) Down Column

Z_{eff} inc. slightly as valence shell e^- can penetrate better

III) Atomic and Ionic Radii

A) Atomic Radii

1) Nonbonding

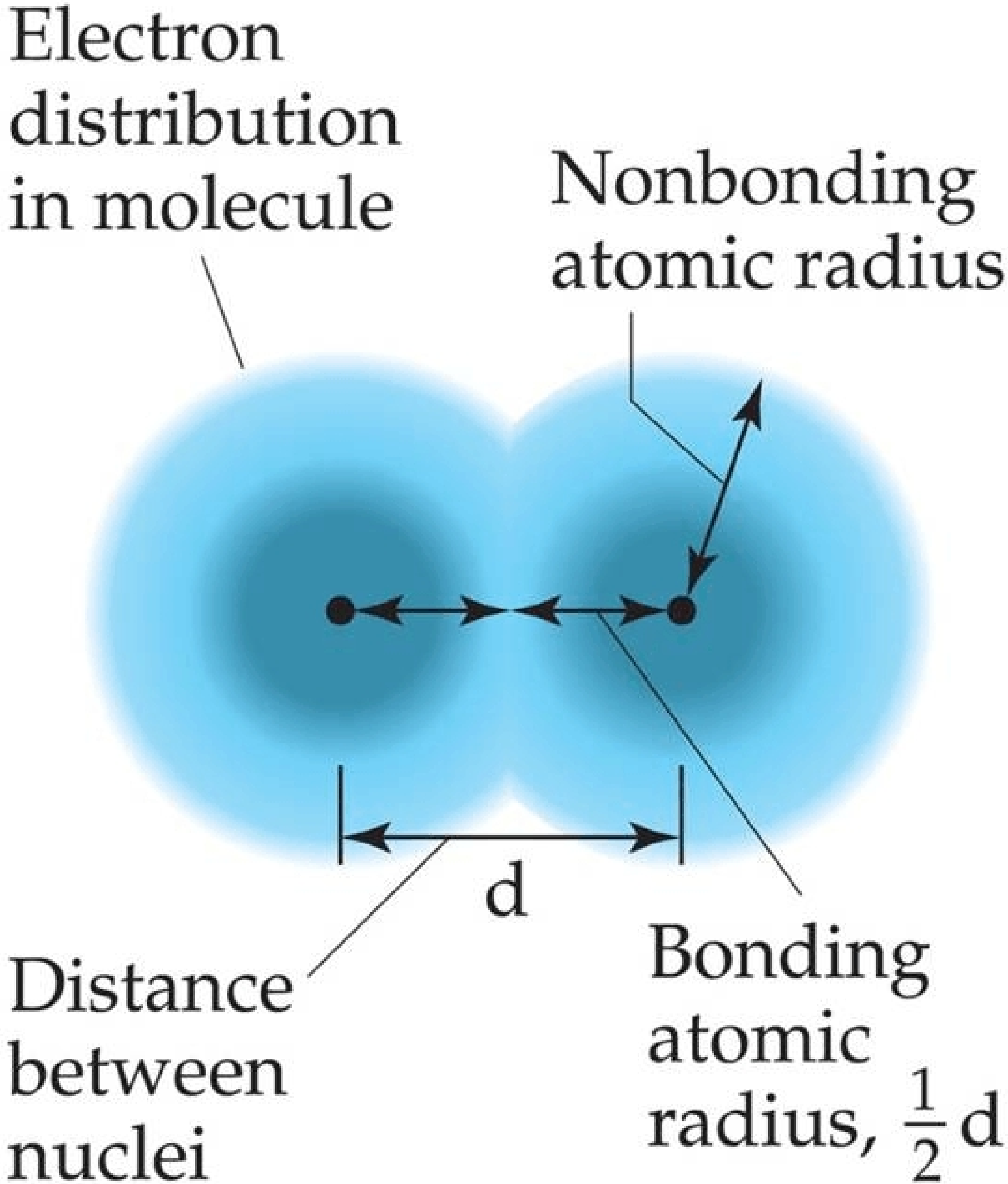
Closest approach of atoms based on gas phase collisions or crystal structures

2) Bonding Atomic Radius

Bond Length:

Distance between atoms in a covalently bound cmpd., averaged over many cmpds.

b.a.r = ½ bond length


Electron distribution in molecule
Nonbonding atomic radius
d
Distance between nuclei
Bonding atomic radius, $\frac{1}{2}$d

3) Size inc. down a group

e^- occupy a higher energy level w. each element down a group & n determines size of orbital and avg. radius

∴ Inc. n ⇛ Inc. atomic size

4) Size generally dec. across a period from left to right

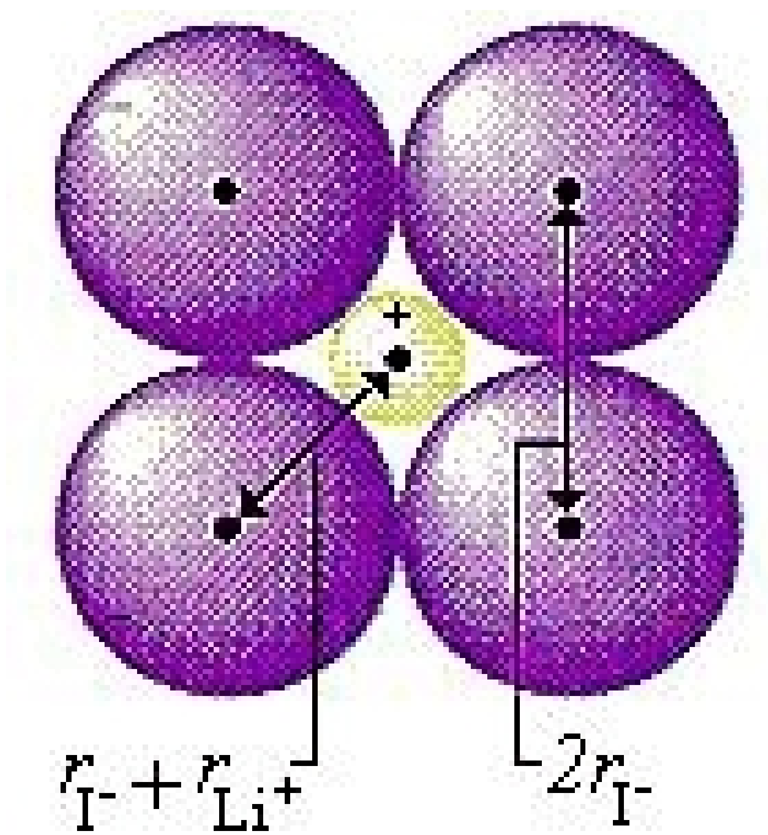
- e^- added to same shell
- nuclear charge, Z_{eff}, inc. which pulls whole shell closer

5) <u>Overall Trend</u>

B) Ionic Radii

Determined from crystal structure of ionic cmpds.

Averaged interatomic distance from multiple cmpds.



1) Cations

always smaller than parent atom

Cs^{+} smaller than Cs

a) Size decreases with increasing ionic charge

$Fe^{3+} < Fe^{2+}$; $Cu^{2+} < Cu^{+}$

2) Anions

always larger than parent atom

$Br^{-} > Br$ $S^{2-} > S$

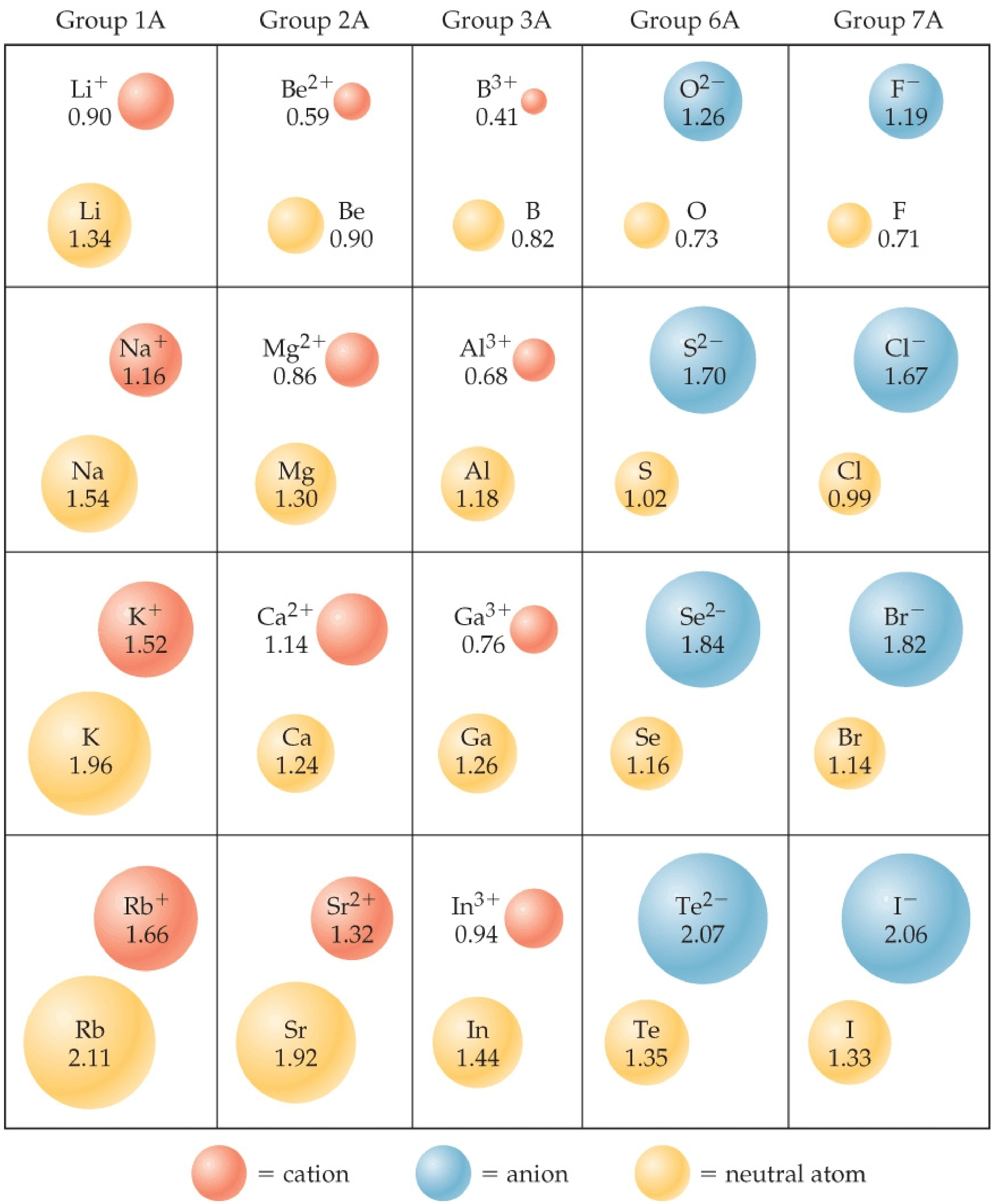
3) Isoelectronic Series

Same # e^{-}

${}_{16}S^{2-} > {}_{17}Cl^{-} > {}_{19}K^{+} > {}_{20}Ca^{2+}$

$\longrightarrow$

Z_{eff} inc., radius dec.



Group 1A
Group 2A
Group 3A
Group 6A
Group 7A
Li+ 0.90
Be2+ 0.59
B3+ 0.41
O2− 1.26
F− 1.19
Li 1.34
Be 0.90
B 0.82
O 0.73
F 0.71
Na+ 1.16
Mg2+ 0.86
Al3+ 0.68
S2− 1.70
Cl− 1.67
Na 1.54
Mg 1.30
Al 1.18
S 1.02
Cl 0.99
K+ 1.52
Ca2+ 1.14
Ga3+ 0.76
Se2− 1.84
Br− 1.82
K 1.96
Ca 1.24
Ga 1.26
Se 1.16
Br 1.14
Rb+ 1.66
Sr2+ 1.32
In3+ 0.94
Te2− 2.07
I− 2.06
Rb 2.11
Sr 1.92
In 1.44
Te 1.35
I 1.33
= cation
= anion
= neutral atom

IV) Ionization Energy, I.E.

Ionization: removal of an e^-

I.E. : energy required to remove e^- from gaseous atom or ion

$Na \rightarrow Na^+ + e^-$ 5.1 eV

$Cs \rightarrow Cs^+ + e^-$ 3.9 eV

e^- removed is from highest energy level (highest n & ℓ)

I.E. depends on avg. distance from the nucleus.

First I.E, I_1

Energy req. to remove the highest energy e^- from neutral atom

$Mg (g) \rightarrow Mg^+ (g)$ $I_1 = 738$ kJ/mol

Second I.E I_2

Energy req. to remove the next highest energy e^- from ion

$Mg^+ (g) \rightarrow Mg^{2+} (g)$ $I_2 = 1450$ kJ/mol

Successive I.E. inc. in magnitude

- # e^- dec. (less repulsion)

- Z (# p^+) same (greater attraction)

	I_1	I_2	I_3	I_4	I_5
Na	496 [Ne]	4560			
Mg	738 $3s^1$	1450 [Ne]	7730		
Al	577 $3s^2$	1816 $3s^1$	2744 [Ne]	11,600	
Si	786 $3s^2 3p^1$	1577 $3s^2$	3228 $3s^1$	4354 [Ne]	16,100
P	1060 $3s^2 3p^2$	1890	2905	4950	6270
S	999 $3s^2 3p^3$	2260	3375	4565	6950

inner-shell e^-

I.E. for removing e^- beyond valence e^- greater than energy involved in chem. rxns & bonding

- only e^- outside noble-gas core involved in chem. change

Remember:

Atoms tend to lose or gain e^- to get filled outer shell

- e^- config. of a noble gas

Note

I.E. depends on avg. distance from nucleus & Z_{eff}

$$\text{I.E.} \propto Z_{eff} \qquad\qquad \text{I.E.} \propto 1/r$$

A) Up a Group

Dec. atomic radius

e^- held more tightly

I.E. Inc.

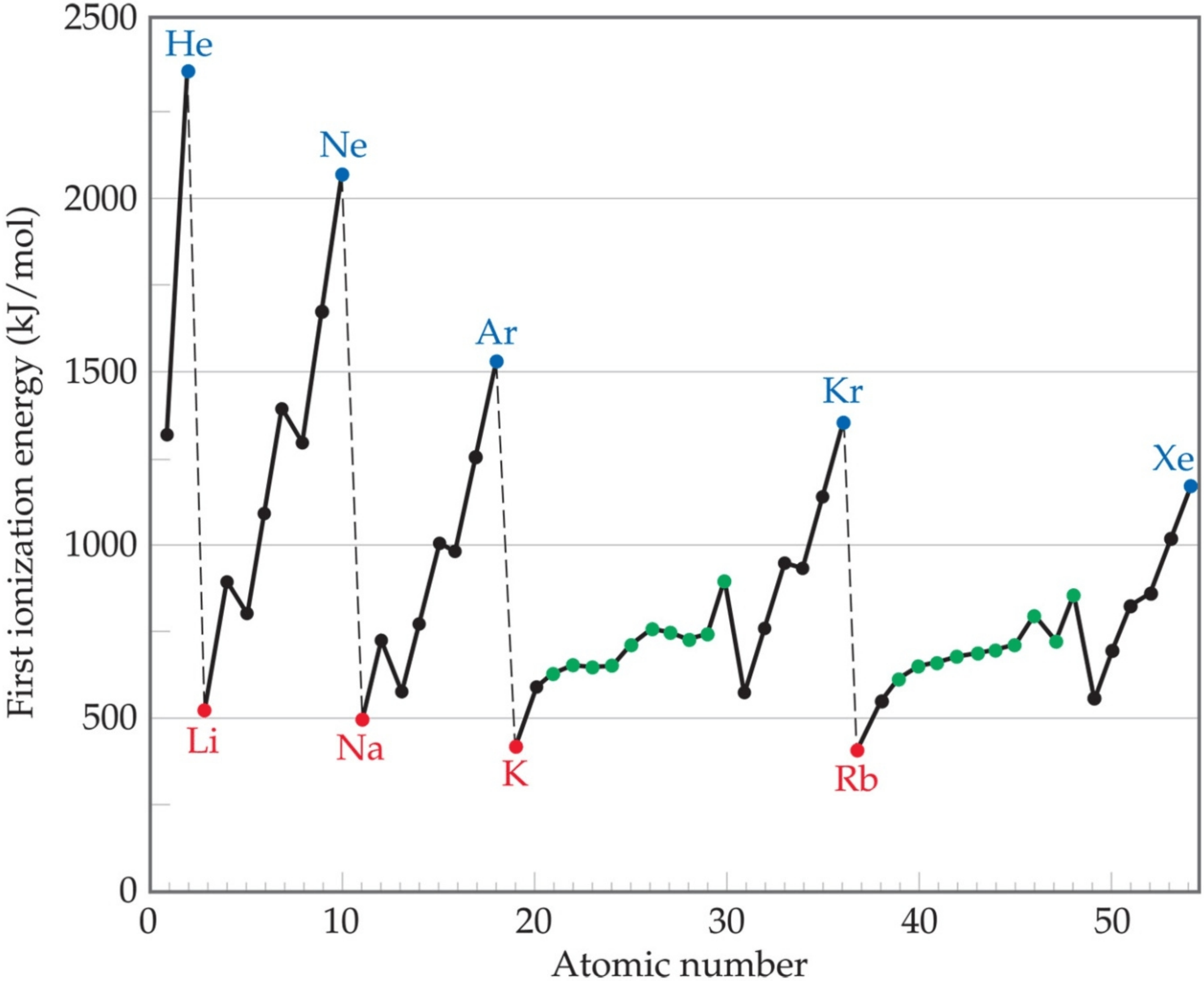
B) Across a Period

Dec. atomic radius

Z_{eff} inc. e^- held more tightly

I.E. Inc

C) Summary



He
Ne
Ar
Kr
Xe
Li
Na
K
Rb
2500
2000
1500
1000
500
0
First ionization energy (kJ/mol)
0
10
20
30
40
50
Atomic number

D) Irregularities

e^- config. accounts for irregularities

Li → Ne, generally inc.

However,

Be ($1s^2\ 2s^2$) > B ($1s^2\ 2s^2\ 2p^1$)

N ($1s^2\ 2s^2\ 2p^3$) > O ($1s^2\ 2s^2\ 2p^4$)

½-filled & filled subshells more stable

Elements at end of each transition series, Zn, Cd & Hg have higher I.E. than following element

pseudo-noble-gas

Highest I.E. for noble gases

- filled s & p subshells

E) Electron Config. of Ions

1) Representative Ions

a) Metals

Form Cations

1) s - block

Groups 1A & 2A

All valence e^- removed

- noble-gas config.

Na $1s^2\ 2s^2\ 2p^6\ 3s^1$

Na^+ $1s^2\ 2s^2\ 2p^6$ [Ne]

1) p - block

Groups 3A - 5A

Lose p e^- fairly readily

(group # - 2)

Often req. too much energy to remove all val. e^-

(group #)

Pb [Xe] $4f^{14}\ 5d^{10}\ 6s^2\ 6p^2$

Pb^{2+} [Xe] $4f^{14}\ 5d^{10}\ 6s^2$

Pb^{4+} [Xe] $4f^{14}\ 5d^{10}$

Pb^{2+} more common than Pb^{4+}

b) NonMetals

Monatomic anions

charge = (group # - 8)

- add e^- to obtain noble-gas e^- config.

S [Ne] $3s^2\ 3p^4$

S^{2-} [Ne] $3s^2\ 3p^6$

Cl [Ne] $3s^2\ 3p^5$

Cl^- [Ne] $3s^2\ 3p^6$

2) Transition Metal Ions

Generally, only highest energy e^- lost

Outer s-subshell e^-

Many tran. metals form +2 cations

- lose both s-subshell e^-

For ions of higher charge
d-subshell e^- are lost

a) Ex 1:

Group 2B

Zn, Cd, Hg

$$(n-1)d^{10}\ ns^2 \rightarrow (n-1)d^{10}$$

Zn^{2+}, Cd^{2+}, Hg^{2+}

b) Ex 2:

Fe [Ar] $4s^2\ 3d^6$

Fe^{2+} [Ar] $3d^6$

Fe^{3+} [Ar] $3d^5$

V) Electron Affinity, EA

Energy associated with the gain of an e^- by a gaseous atom or ion

A) First EA

$Cl\,(g) + e^- \rightarrow Cl^-\,(g)$ EA = −349 kJ/mol

Energy released for most neutral atoms & all positive ions

greater attraction for e^- ⇒ more neg. EA

B) Second EA

$O^-\,(g) + e^- \rightarrow O^{2-}\,(g)$ EA = +710 kJ/mol

2nd e^- must be forced onto a neg. charged ion which requires energy

H −73							**He** > 0
Li −60	**Be** > 0	**B** −27	**C** −122	**N** > 0	**O** −141	**F** −328	**Ne** > 0
Na −53	**Mg** > 0	**Al** −43	**Si** −134	**P** −72	**S** −200	**Cl** −349	**Ar** > 0
K −48	**Ca** −2	**Ga** −30	**Ge** −119	**As** −78	**Se** −195	**Br** −325	**Kr** > 0
Rb −47	**Sr** −5	**In** −30	**Sn** −107	**Sb** −103	**Te** −190	**I** −295	**Xe** > 0
1A	2A	3A	4A	5A	6A	7A	8A

A) Periodic Trends in EA

Generally, parallels variation
in atomic size

- not as well-established
as other trends (exceptions)

e^- placed into outer shell

- closer it gets to nucleus
& greater Z_{eff}

larger neg. EA

C) Summary

1) Exceptions

a) 2nd period

F: –328 kJ/mol   Cl: –349 kJ/mol

True for other 2nd period elements

Small size of 2nd period elements

e^- enters small outer shell

Adding an e^- places it very close to other 2s and 2p e^- resulting in stronger e^- - e^- repulsions.

b) Other Exceptions

Adding an e^- to stable e^-- config.

1) Group 2A

full s subshell

added e^- goes into p subshell

2) Group 5A

½ - filled p valence subshell

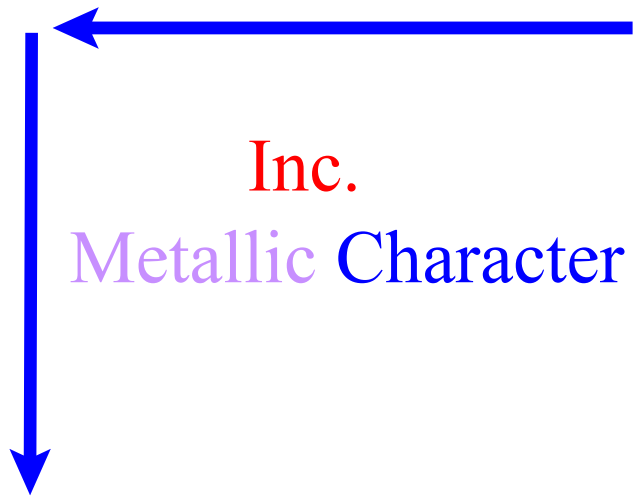
added e^- pairs w. another e^- in occupied p orbital & experiences repulsions

3) Group 8A

filled valence shell

e^- goes into next higher shell

VI) Metals, Nonmetals, Metalloids



metals		nonmetals
Low IE	B, Si, Ge, As, Sb, Te, Po, At	Large IE
Low EA		Large EA
form cations		form anions
oxides are basic		oxides are acidic

Summary of Periodic Trends