Unit 2

Atomic Structure and Properties
&
Chemical Bonding

Blueprint question

http://www.spectro-oil.com/laboratory-services-aviation.html

http://news.commercialaircraft.bombardier.com/wp-content/gallery/engine-run/right_engine.jpg

Learning Objectives

After mastering this unit you will be able to:

- Define the terms valence and core electrons
- Determine the number of valence electrons and core electrons based on electron configuration for atoms and ions
- Define, in words or using equations, effective nuclear charge (Z_{eff}), atomic and ionic radius, ionization energy, and electron affinity.
- Rank elements and ions according to their Z_{eff}, atomic size, ionization energy, and electron affinity.
- Rationalize the periodic trends of radii, relative ionization energies and electron affinities of atoms and ions based on nuclear charge and/or electron configurations.

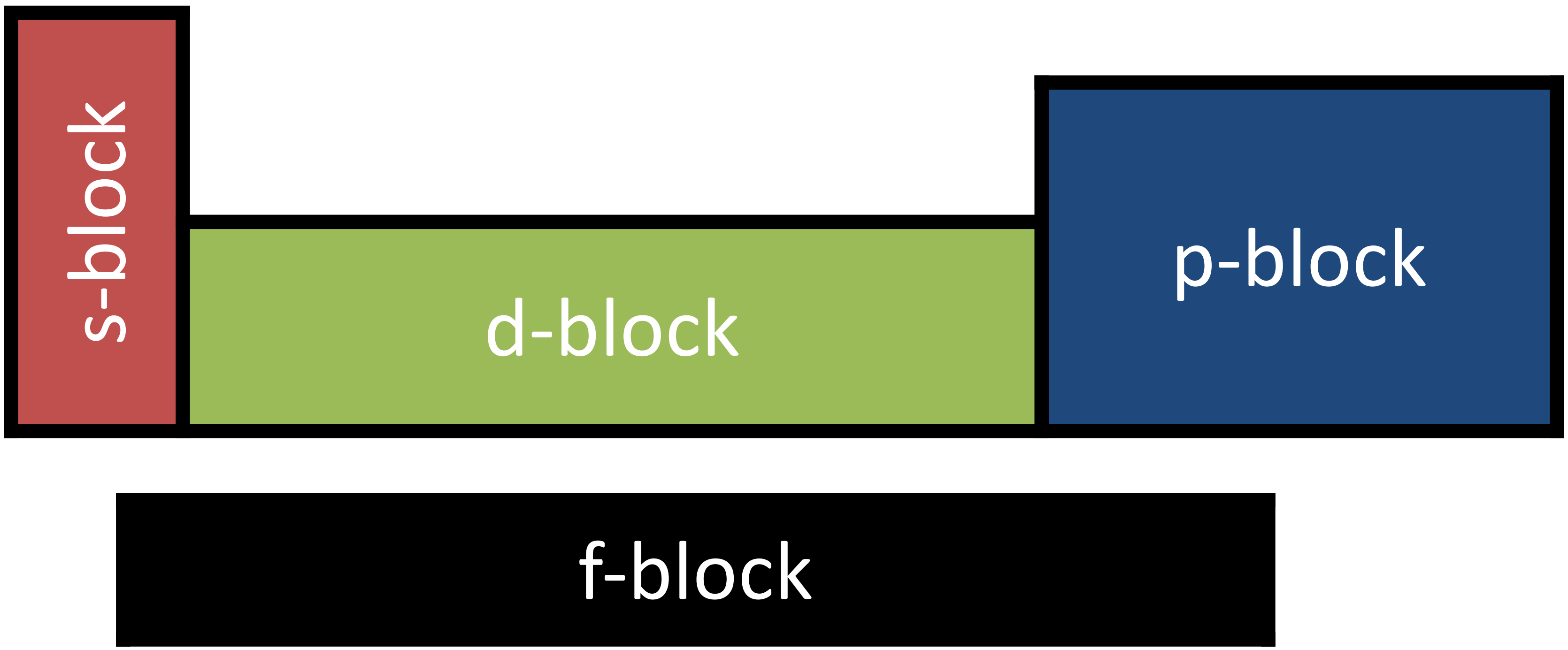
Learning Objectives (continued)

- Describe the nature of ionic and covalent bonds.
- Define electronegativity and describe how electronegativity varies with position in the periodic table.
- Predict the nature of a chemical bond (ionic/covalent, polar/nonpolar) and justify your prediction by comparing the relative electronegativities of the atoms involved.
- Predict lattice energy trends in ionic solids & justify your predictions.

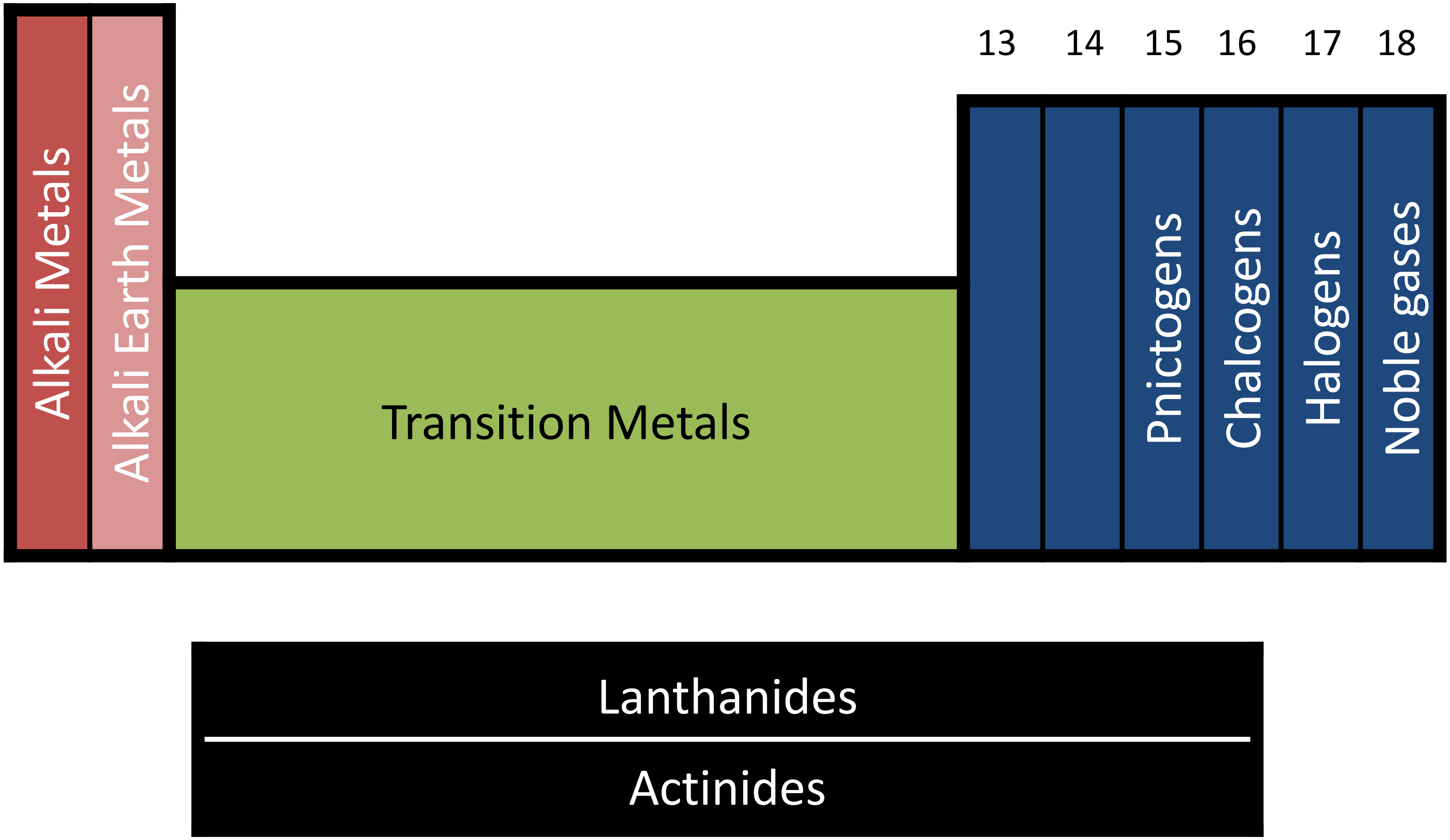
The Periodic Table

Columns in the periodic table are called groups.

Rows in the periodic table are called periods.



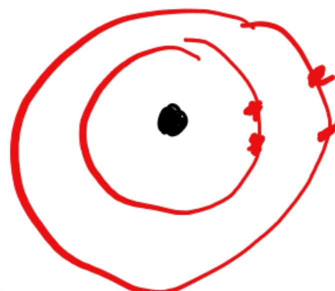
The Periodic Table



Clicker Question

Which of the following represents the best analogy for the structure of an atom?

a) Solar system



structure ok ?

flat ✗

b) Cotton ball

e^- cloud ✓

no nucleus

c) Billiard Ball

- collisions, spherical ✓

hard edge ?

no e^- structure

d) Onion

clouds? shells ✓

spherical ✓

no nucleus

e) Dumbbell

maybe excited atoms?

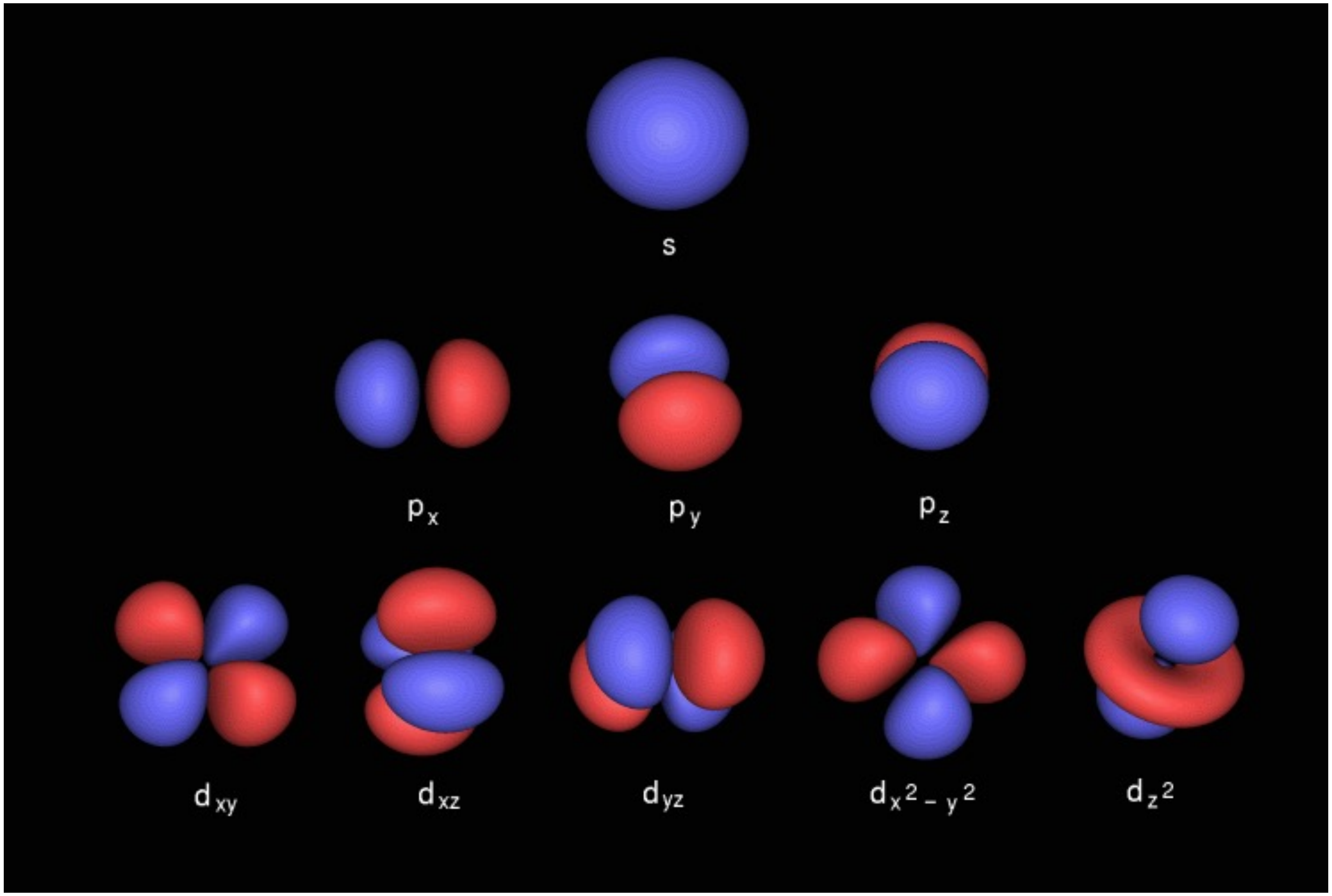
no shells, no nucleus.

Salient Features of Quantum Mechanics

Small objects, like electrons, behave as both particles and waves which means they can interfere, diffract and spread. Orbitals give the probability for finding electrons at particular points in space.

Quantum mechanics is the theory explaining why energies and angular momenta of atoms and molecules are quantized, that is only have certain discrete values.

Hydrogenic Orbitals



Electronic Structure

Electrons have negative charge but are also tiny magnets. Spin is our way of describing the orientation of the poles of these magnets ("spin up ↑" or "spin down ↓").

↑ 2s

↑↓ 1s

The Pauli Principle states a maximum of 2 electrons can be assigned to any one orbital, and the electrons must have opposite spins (↑↓).

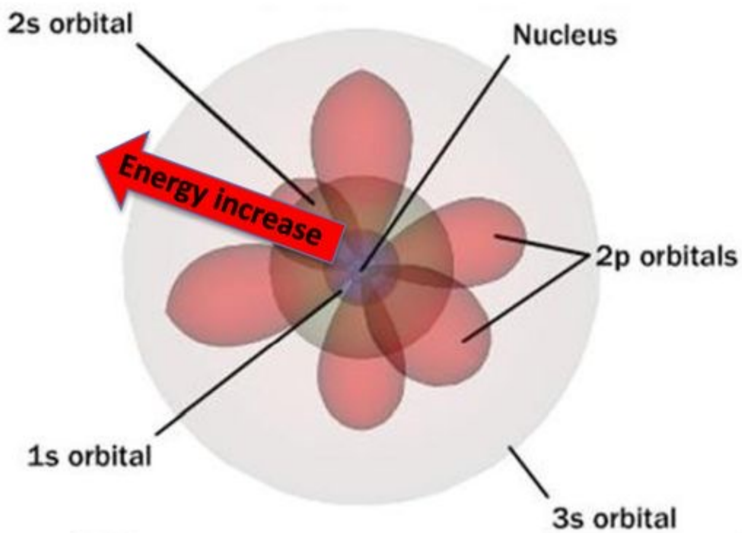
principle quantum #

Orbitals are arranged in shells, labelled by n and sub-shells. Each shell contains only certain orbitals. Starting with the lowest shell, n=1, electrons are assigned to s, p, d orbitals until they are all accounted for. Note: orbitals get bigger as n increases (a 2s orbital is bigger than a 1s orbital) thus forming the shell structure of atoms.

sub-shells

Shell Structure of Atoms

Orbitals become larger as the energy level increases



n=1 1st shell
1 subshell 1s
n=2 2nd shell
2 subshell 2s 2p
n=3 ..... 3s 3p 3d

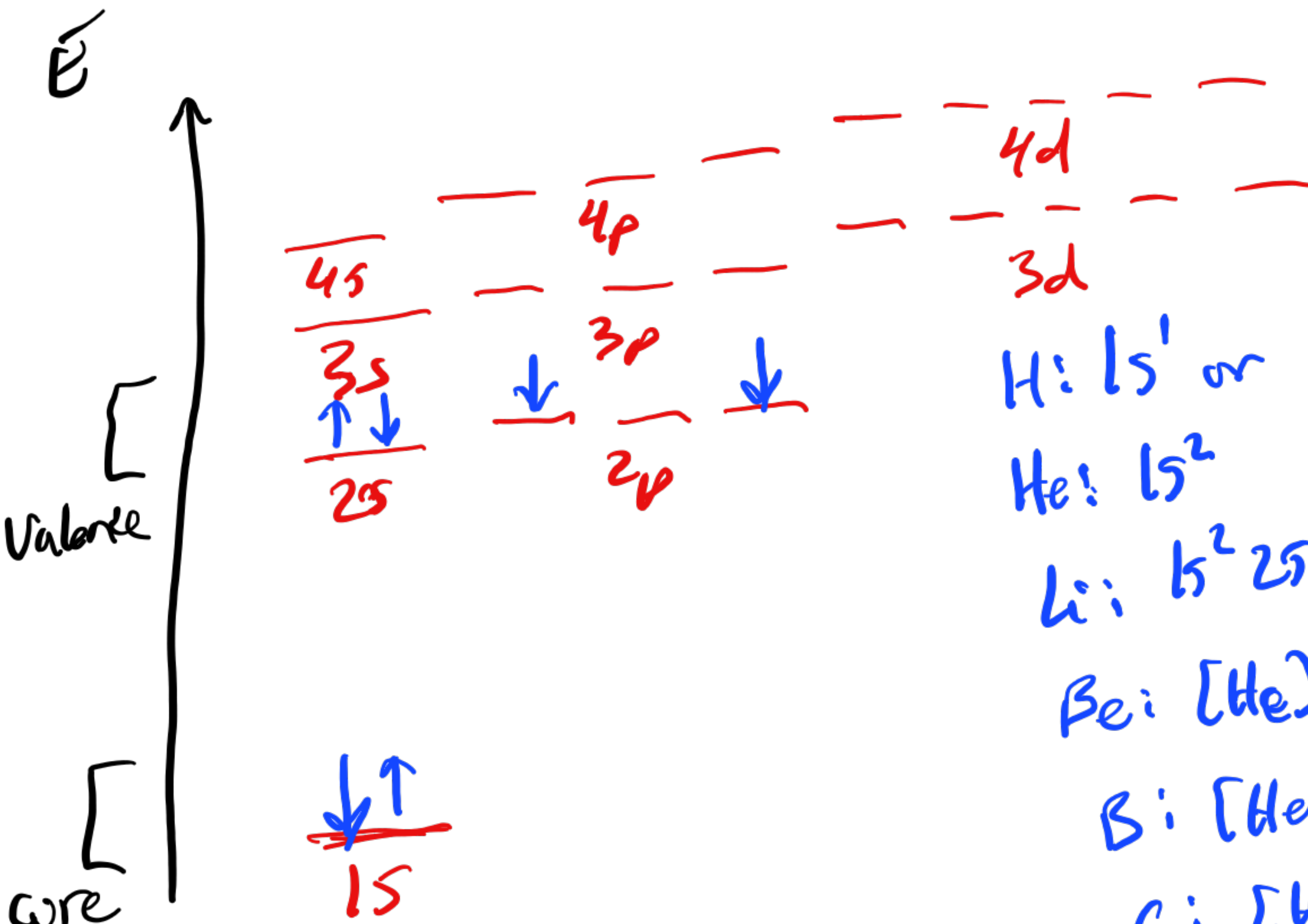
- **Electrons filling order : 1s, 2s 2p, 3s**
- **Orbitals** arranged in order of **increasing energy: 1s, 2s 2p, 3s**
- **Orbitals** arranged in **increasing size: (smallest) 1s <2s <2p < 3s (largest)**

Shells and subshells

Shell (n)	Sub-shells	Max. # e^- in subshells	
1	s	2	$2(1)^2 = 2$
2	s, p	2 + 6 = 8	$2(2)^2 = 8$
3	s, p, d	2 + 6 + 10 = 18	$2(3)^2 = 18$
4	s, p, d, f	2 + 6 + 10 + 14 = 32	$2(4)^2 = 32$

[redacted]

Electron Configurations: Idea - put e^- in orbitals to give the lowest energy → ground state



e^- config for He then add

H: $1s^1$ or $1s$

He: $1s^2$

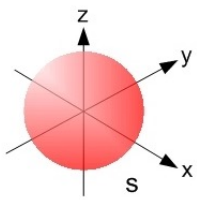
Li: $1s^2 2s$ = $[He]\,2s$

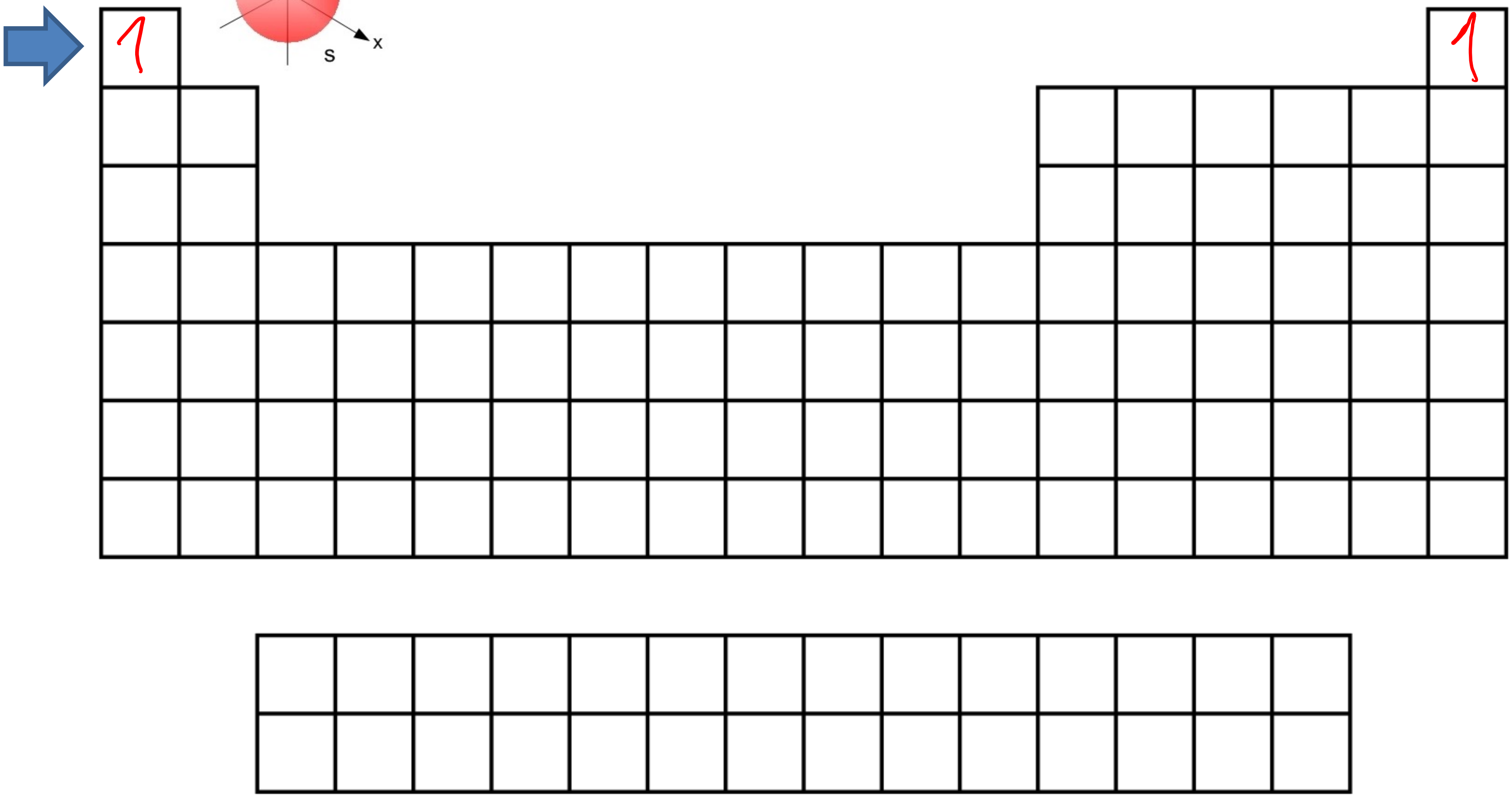
Be: $[He]\,2s^2$

B: $[He]\,2s^2 2p$

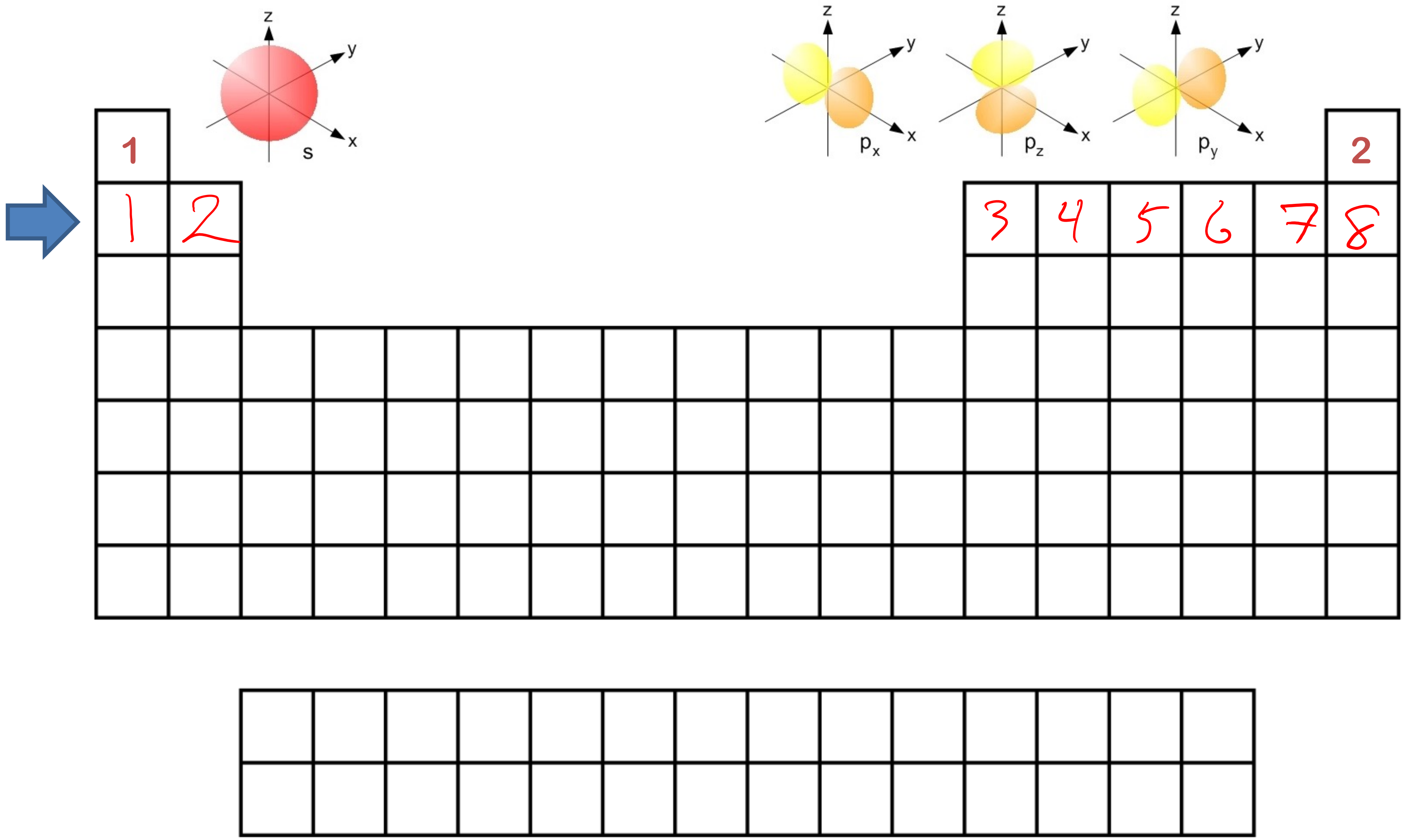
C: $\underbrace{[He]}_{\text{core}}\,\underbrace{2s^2 2p^2}_{\text{valence}}$

Fill in electrons

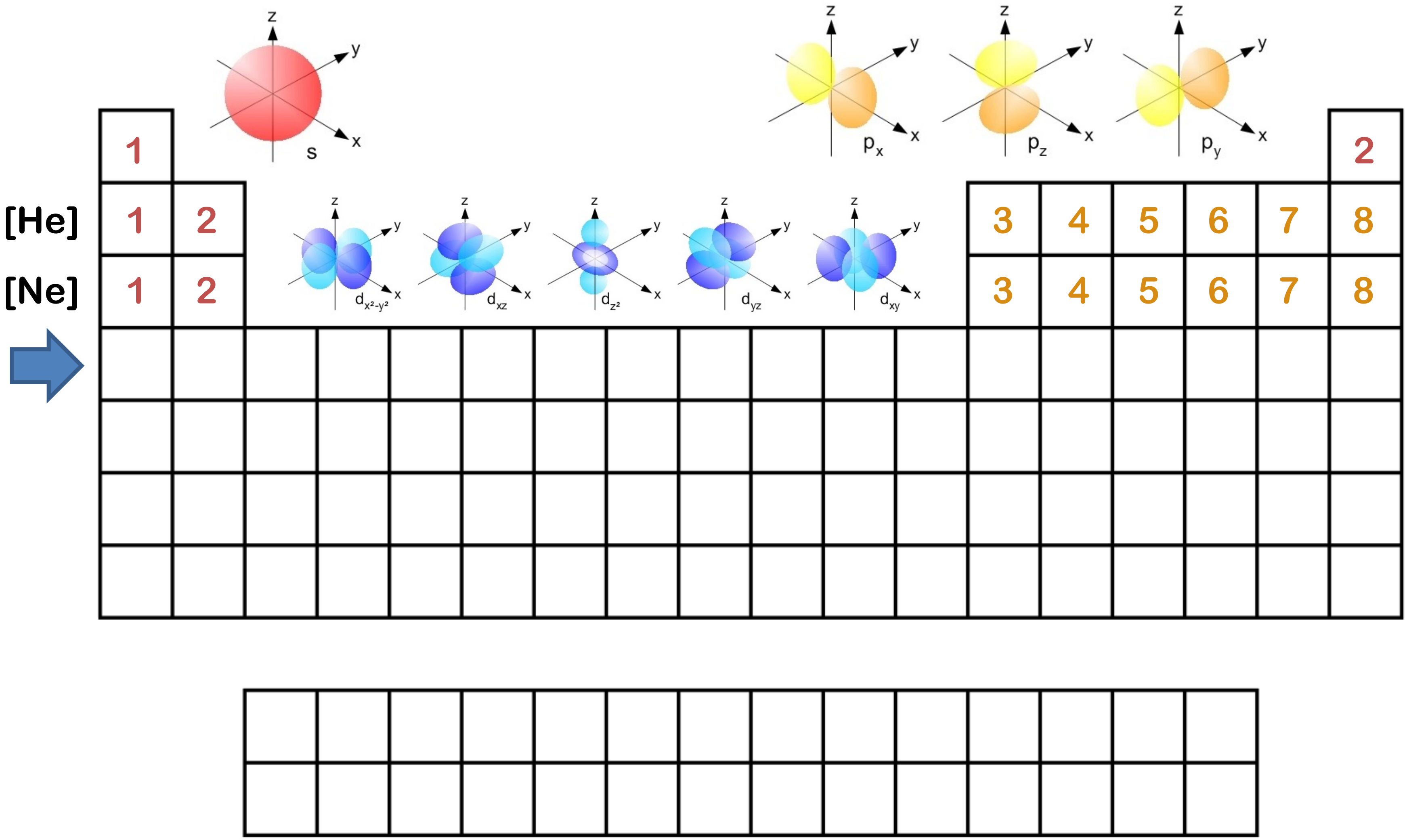




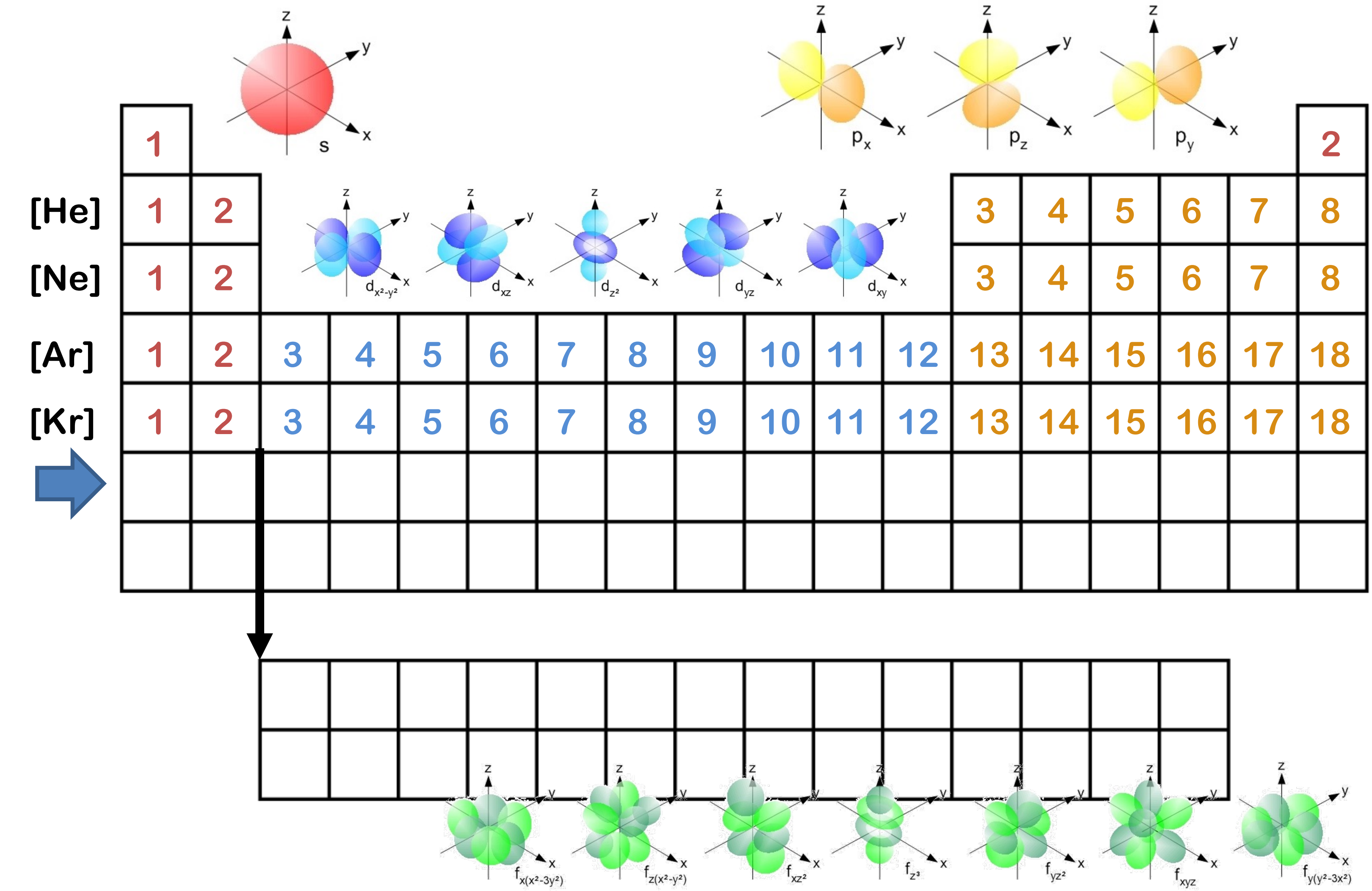
Fill in electrons



Fill in electrons

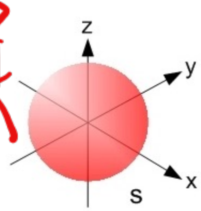


Fill in electrons

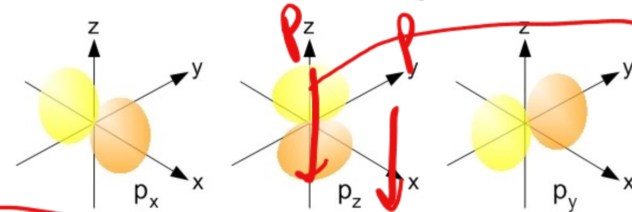


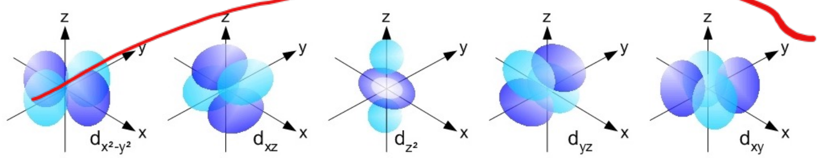
Fill in electrons

s^1 s^2



p^1 p^2





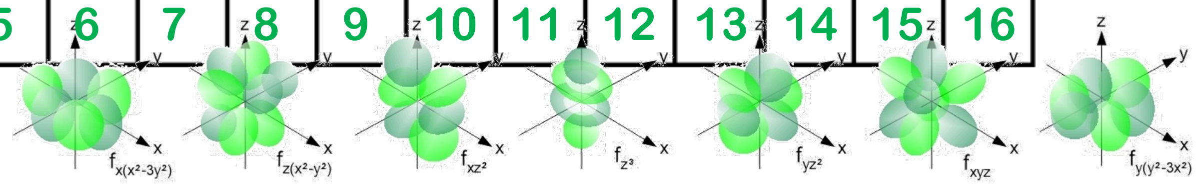
n=1	1																	2
n=2 [He]	1	2											3	4	5	6	7	8
n=3 [Ne]	1	2											3	4	5	6	7	8 ← Ar
[Ar]	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
[Kr]	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
[Xe]	1	2	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32
[Rn]	1	2	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32

Se: [Ar]$4s^2 3d^{10} 4p^4$

6 valence e's

f orbitals

3	4	5	6	7	8	9	10	11	12	13	14	15	16
3	4	5	6	7	8	9	10	11	12	13	14	15	16



Valence Electrons

For elements in the s- and p-blocks only

The electrons occupying the *s* and *p* subshells with the largest n (for the neutral element) are called valence electrons, and the collection of occupied subshells is called the valence shell.

Electrons which aren't valence electrons are called core electrons.

In solids, valence orbitals on atoms overlap to form valence bands extending throughout the material.

Valence electrons are fundamental to chemistry because they are involved in the formation of bonds. Core electrons are not involved in chemical bonding.

Valence electrons for neutral elements

1												EXCEPTION					2
1	2											3	4	5	6	7	8
1	2											3	4	5	6	7	8
1	2											3	4	5	6	7	8
1	2											3	4	5	6	7	8
1	2											3	4	5	6	7	8

0?

Clicker Question

How many valence electrons does Li have?

a) 0
b) 1
c) 2
d) 8
e) 4

Clicker Question

How many valence electrons does Li^+ have?

a) 0
b) 1
c) 2
d) 8
e) 4

$Li: 1s^2 2p$

$Li^+: 1s^2$

still are

empty valence shell

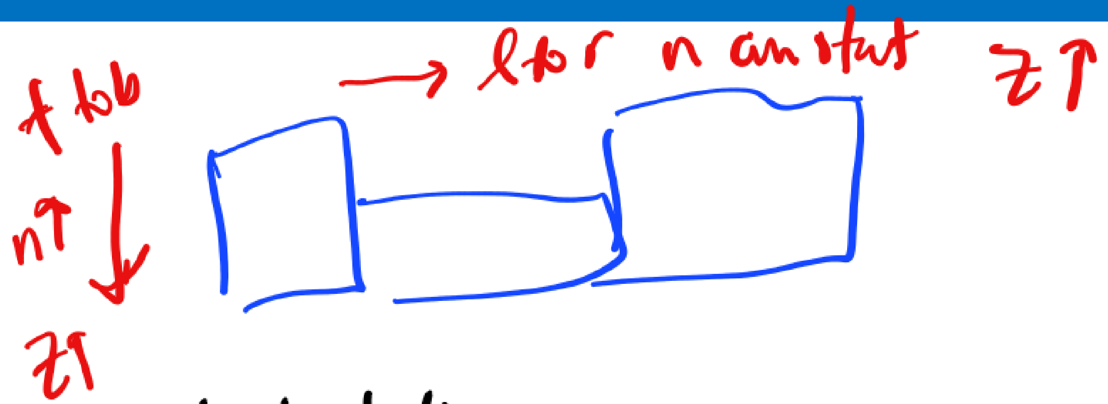
Lab Connection

EXPT. 22 – *Using WebMO to understand* Periodic/ atomic/ molecular properties

- Effective nuclear charge
- Atomic radius/ ionic radius/ metallic radius
- Ionization energy
- Electron affinity
- Electronegativity
- Orbitals – wave representations of the space with highest probability of finding the electron
- Types and sizes of orbitals – s, p, d, f and variation based on the “n” value and type of species (atom, cation, anion)

Periodic Properties

- Atomic radius
- Effective nuclear charge (Z_{eff})
- Ionization energy
- Electron affinity
- Electronegativity (EN)

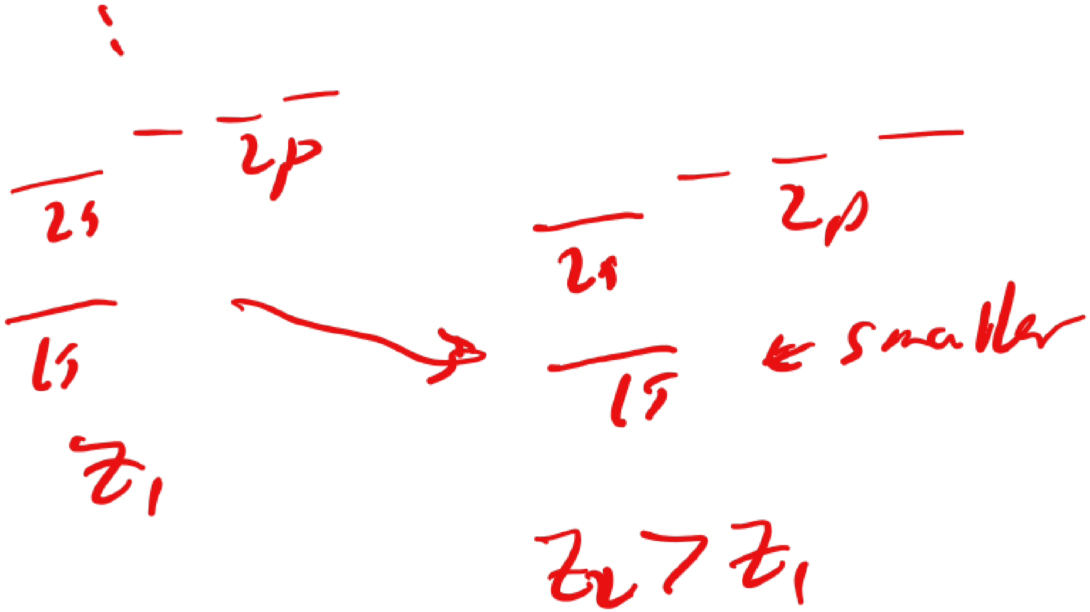


1. ↑n → bigger orbitals, E↑
2. Z↑ (fixed n)

electrostatics

e^- repel each other

e^- attracted to nucleus (Z)



l to r n constant Z↑

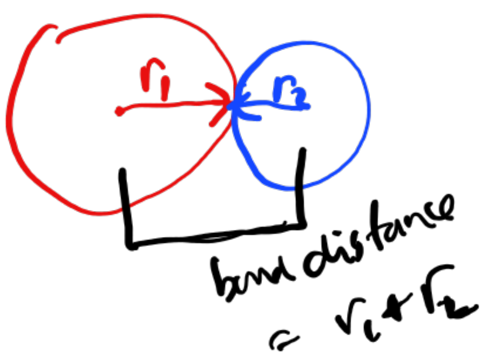
expect smaller orbitals, ↓ orbital energies

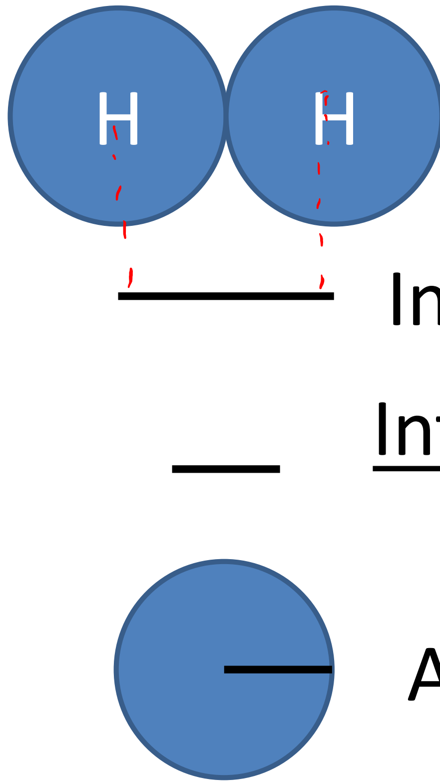
t to b n↑ Z↑

compete against each other, which wins out?

→ experiment

Atomic Radius





Internuclear distance

$$\frac{\text{Internuclear distance}}{2}$$

Atomic Radius

Atomic radius is calculated by measuring the internuclear distance and dividing by 2

Atomic Radius (across a period)

ℓ for r gets smaller

$Z\uparrow$ is causing orbitals to shrink

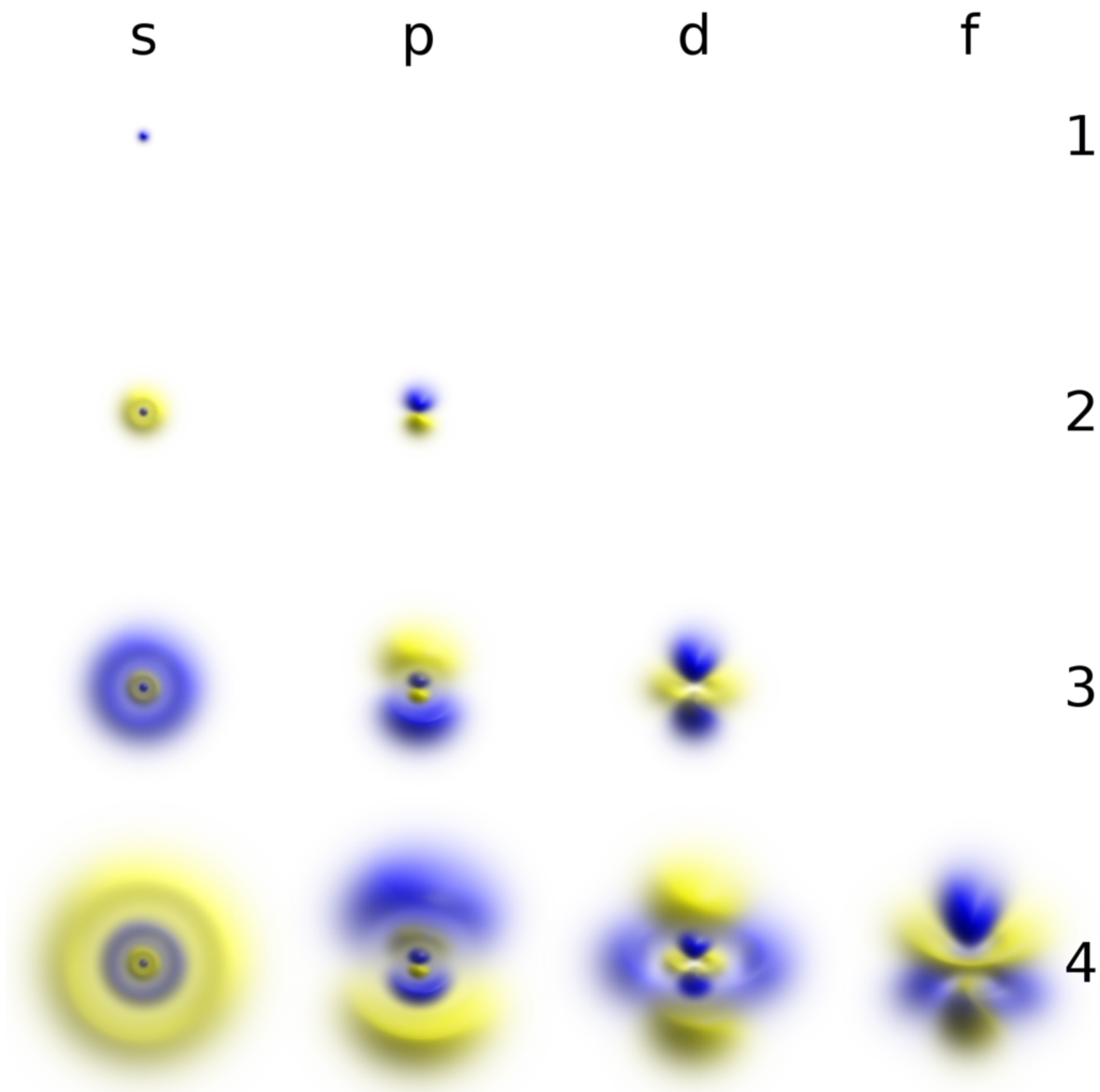
Element	Radius (Å)
Be	0.96
B	0.84
C	0.76
N	0.71
O	0.66
F	0.57
Ne	n/a

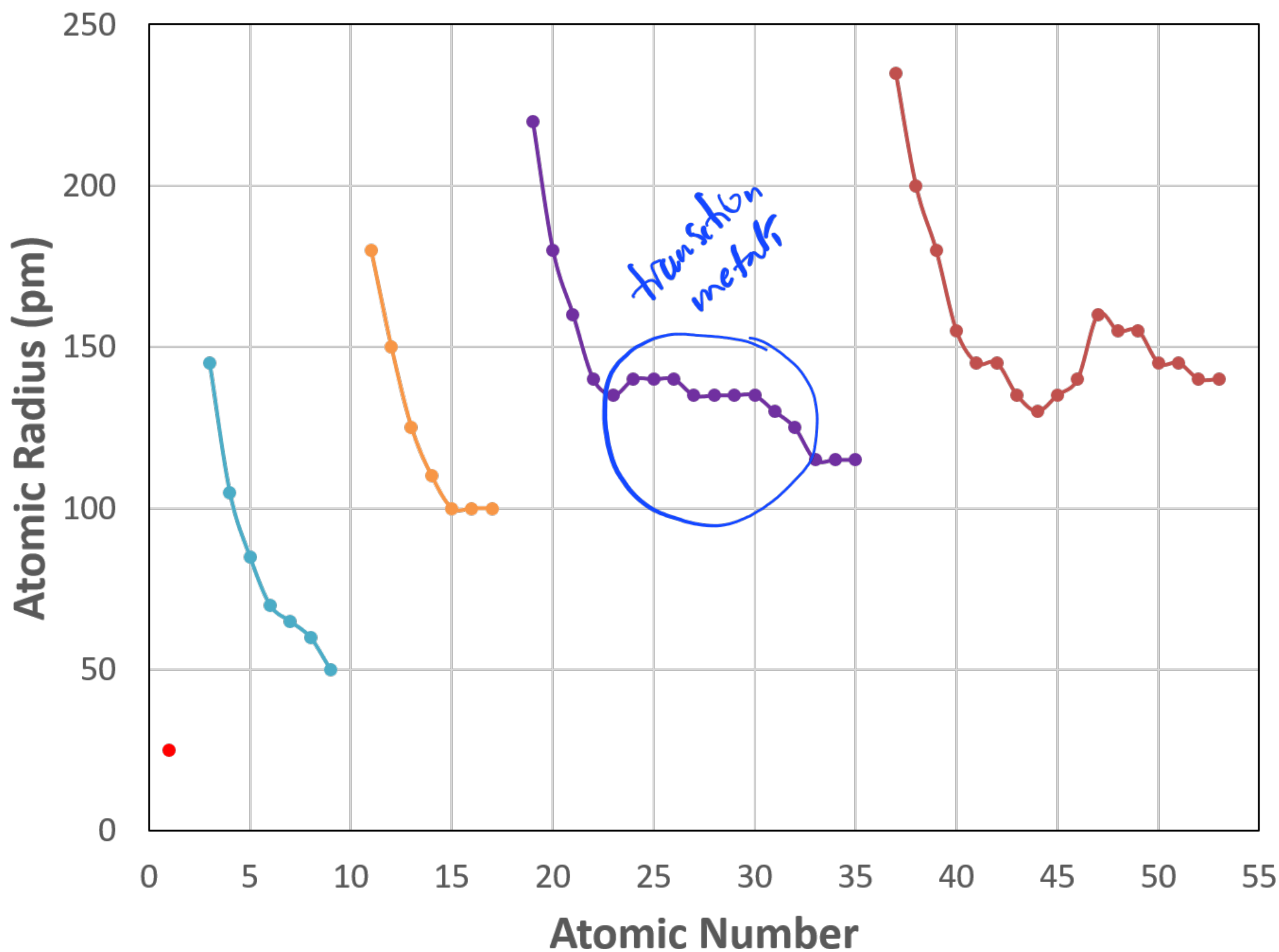
Atomic radius (down a group)

t to b
radius $\uparrow$
so $\uparrow n$ wins
over $Z \uparrow$

Element	Radius (Å)
Li	1.28
Na	1.66
K	2.03
Rb	2.20
Cs	2.44
Fr	n/a

Relative Orbital Sizes

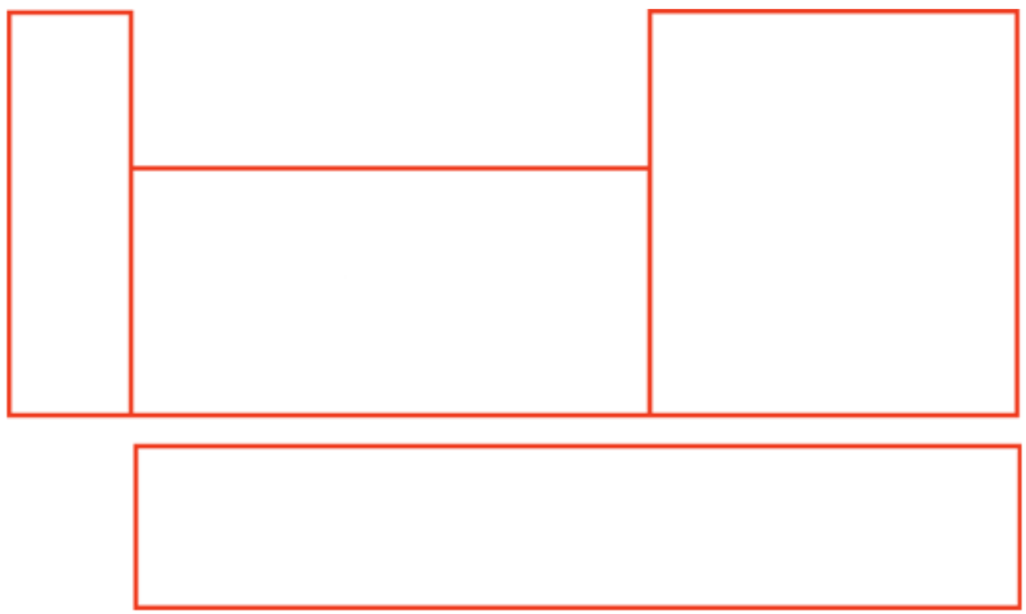




250
200
150
100
50
0
0
5
10
15
20
25
30
35
40
45
50
55
Atomic Radius (pm)
Atomic Number
transition
metals

Worksheet Question #3

Draw arrows to explain the trends of Z_{eff} and size on the periodic table below.



Worksheet Question #4

Calculate the atomic radius of silicon (one of the most important elements in the microelectronics industry), given the following information:

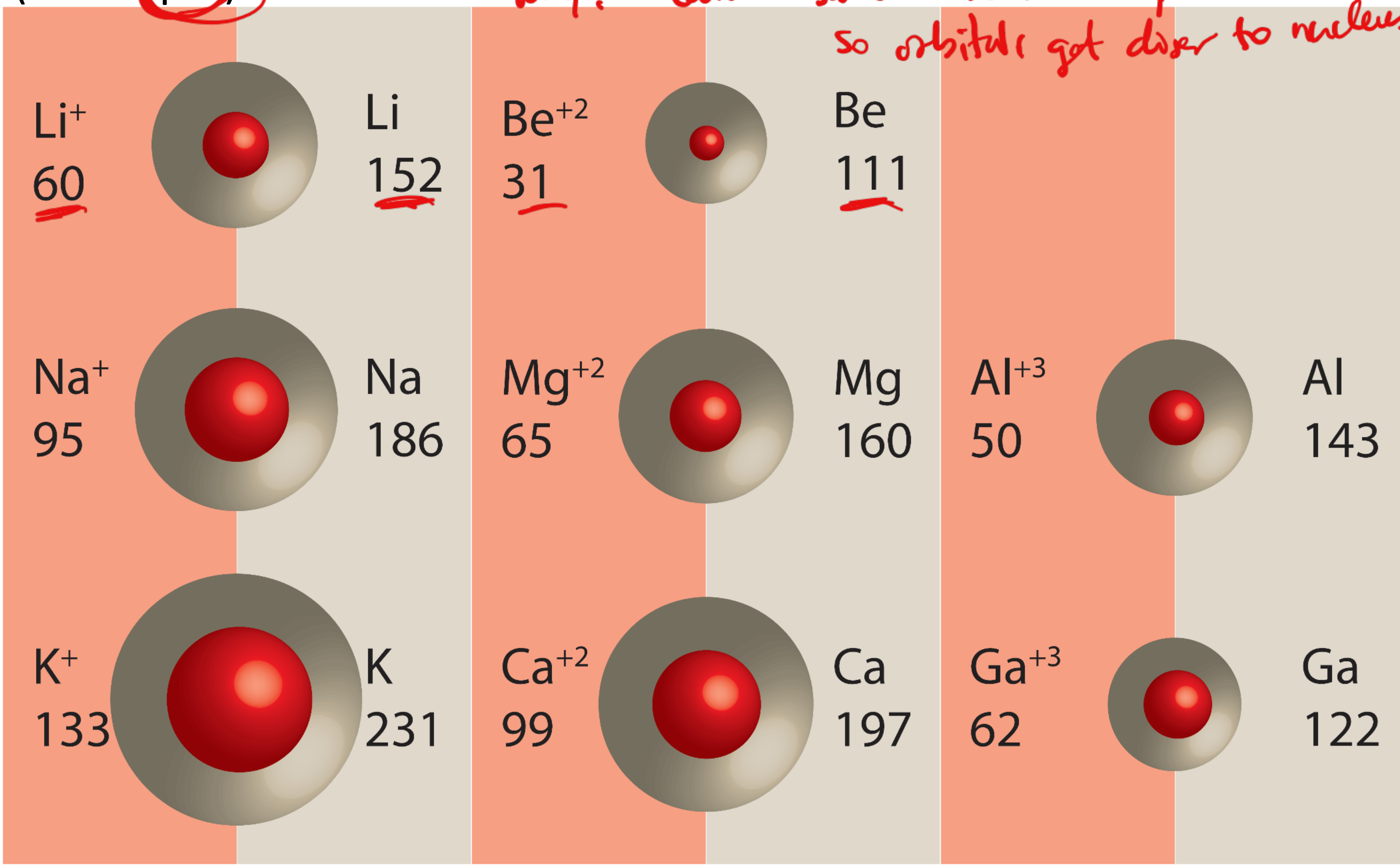
- the H-H bond distance in H_2 is 0.74 Å
- the Si-H bond distance in SiH_4 is 1.46 Å

Remember 1 Å = 1 x 10^{-10} m

Cationic radii

For a given atom, its cation is always smaller than the neutral species.
(size in pm)

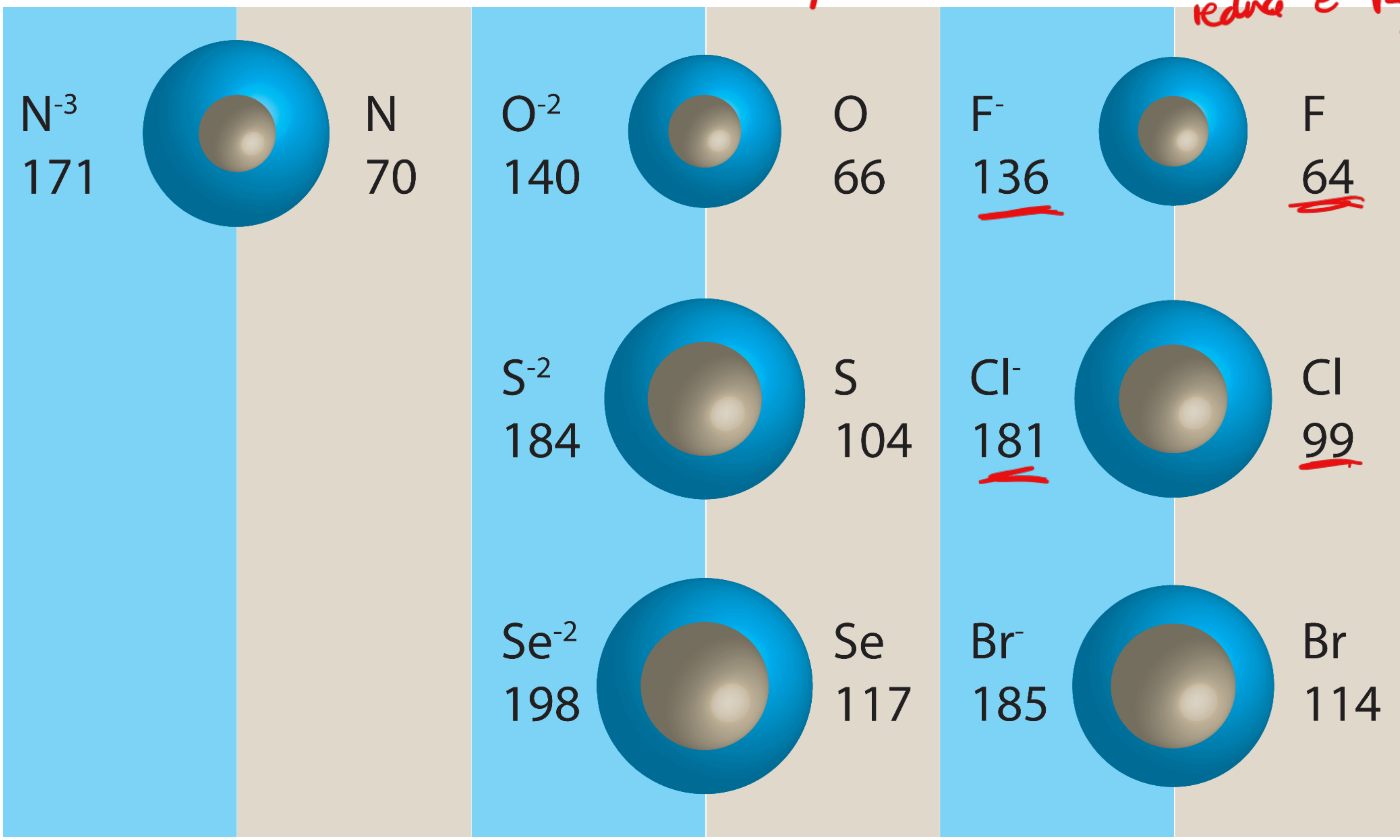
why? cation - same Z less e^- repulsion
so orbitals get closer to nucleus



Anionic radii

For a given atom, its anion is always larger than the neutral species.
(size in pm)

same Z but more e^- repulsion so orbitals swell to reduce e^- repulsion



Isoelectronic species

Atoms and ions with the same number of electrons are said to be *isoelectronic*. In a set of isoelectronic species, the most negative species has the largest radius.

same | e^- config (same # e^-'s)

18e^- | 18e^- | 18e^-

K^+ | Ar | Cl^-

Z=19 | Z=18 | Z=17

Increasing Atomic or Ionic Radius ← due to less attraction to nucleus

Z ↓

Clicker Question

Which of the following isoelectronic species is expected to have the largest radius?

a. O^{2-}
b. N^{3-}
c. Na^{+}
d. F^{-}

Effective nuclear charge (Z_{eff})

Coulomb's Law

$$E \propto \frac{q^{(+)}q^{(-)}}{r}$$

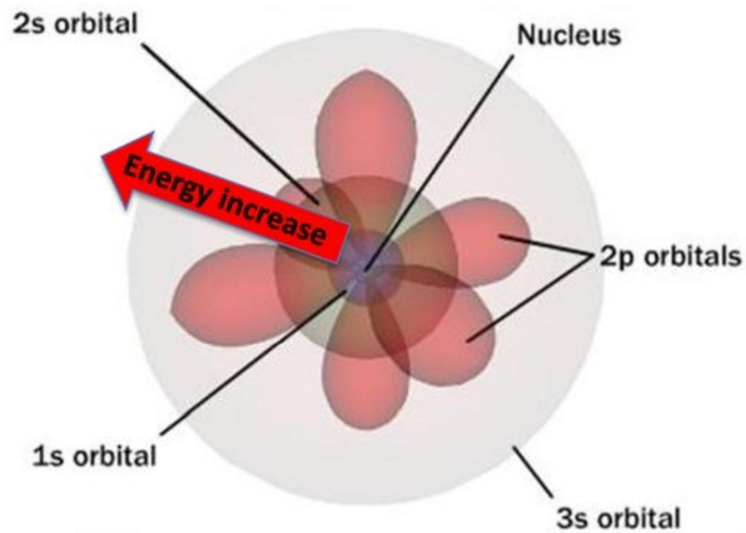
Idea: core e^- screen + charge So the valence e^- "feel" less $\rightarrow Z_{eff}$

Core electrons are close to the nucleus and effectively screen some of its positive charge from valence electrons further away. Valence electrons also partially screen each other from the nuclear charge. Thus, a valence electron "feels" an effective nuclear charge (Z_{eff}) that is less than the actual nuclear charge Z.

Note: Z_{eff} is a theoretically calculated property.

Shell Structure of Atoms

Orbitals become larger as the energy level increases



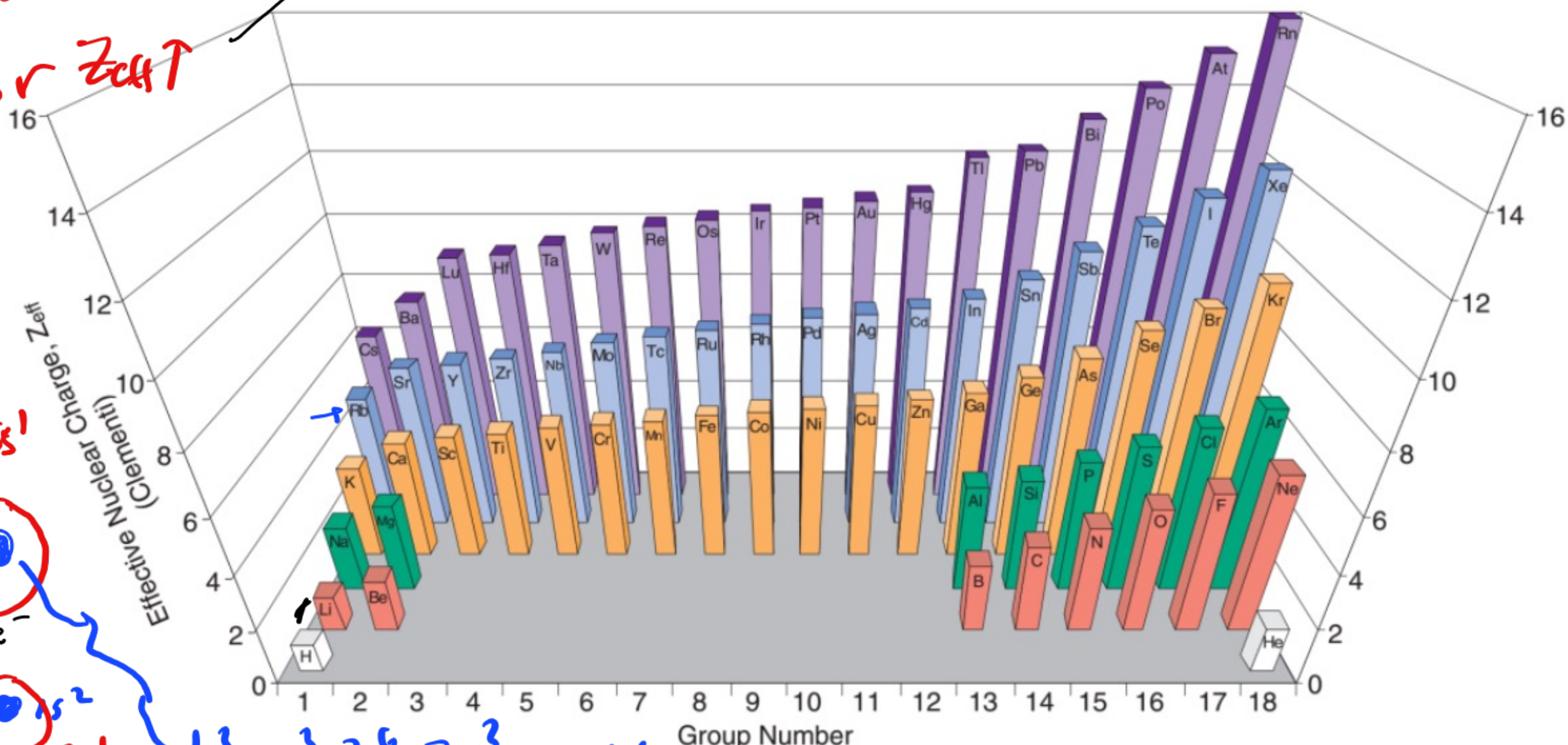
- **Electrons filling order : 1s, 2s 2p, 3s**
- **Orbitals** arranged in order of **increasing energy: 1s, 2s 2p, 3s**
- **Orbitals** arranged in **increasing size: (smallest) 1s <2s <2p < 3s (largest)**

Effective nuclear charge (Z_{eff})

t to b Z_{eff} ↑

l to r Z_{eff} ↑

core is fixed, as is screening so Z_{eff} ↑ as Z ↑.



$5s^1$

Rb:

$Z=37$

core $36e^-$

Li: $1s^2$ $2s^1$

$Z=3$

core $2e^-$

$1s^2, 2s^2, 2p^6, 3s^2 \cdots 4p^6$

↑ the p,d orbitals screen less efficiently than the s so screening ↓ as you go t to b and Z_{eff} ↑