# Trends

## in the

# Periodic Table

Reading: Gray: (2-2) to (2-4) and (2-9)
OGN: (3.1), (15.8) and (15.9)

# Now We Can Understand

- **Arrangement of the Periodic Table of Elements**
- **Trends in Atomic Size**
- **Trends in Ionization Energy**
- **Trends in Electron Affinity**
- **Trends in Electronegativity**
- **Various Types of Chemical Bonds**
- **Combining Ratios of Oxides and Hydrides**
- **Shapes of Molecules**

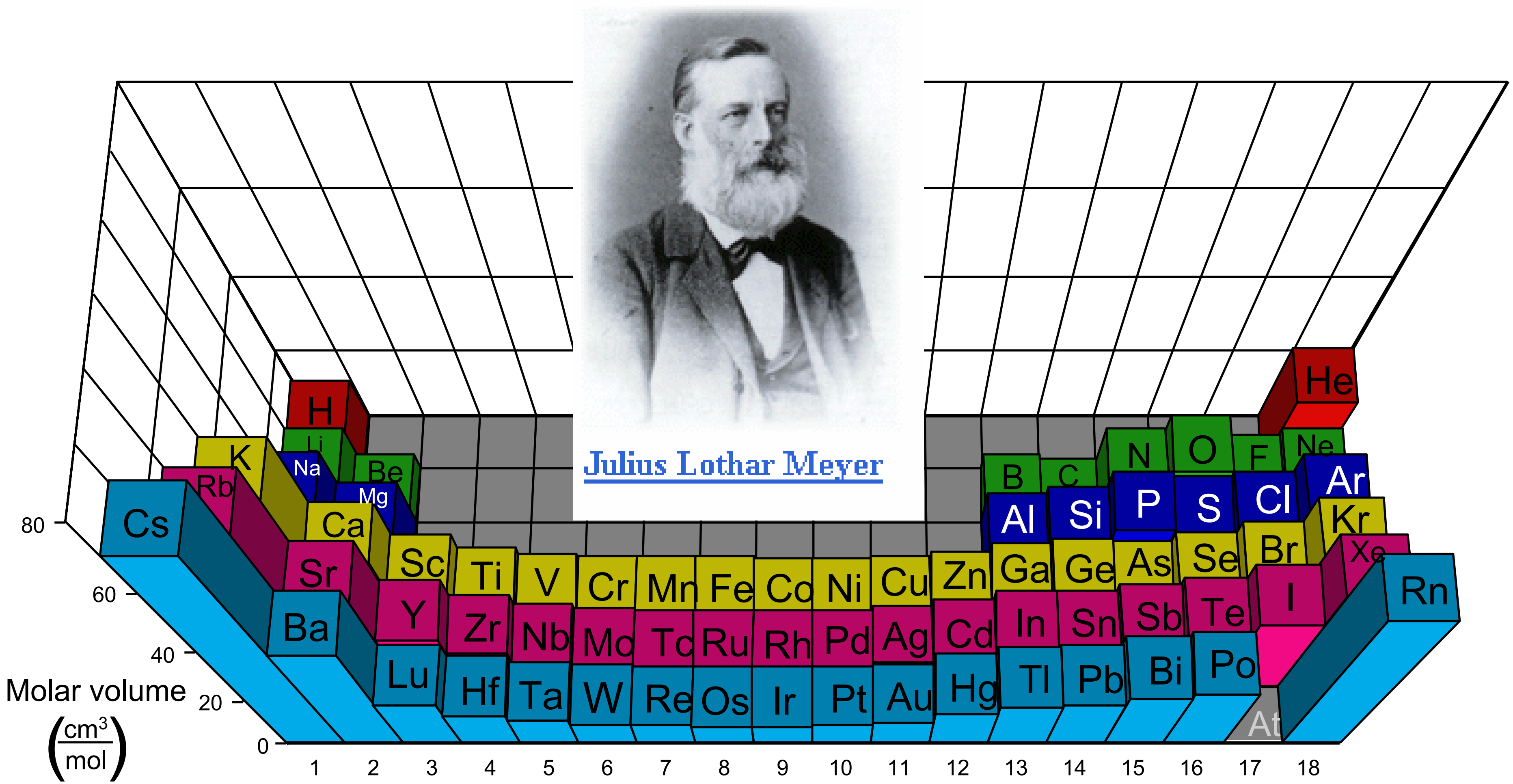
# Dmitri Mendeleev

St. Petersburg University

Invented the periodic table in 1869. Also in that year, he published his book, "Principles of Chemistry." His book compared the atomic weights and the properties of elements that were not known back then.

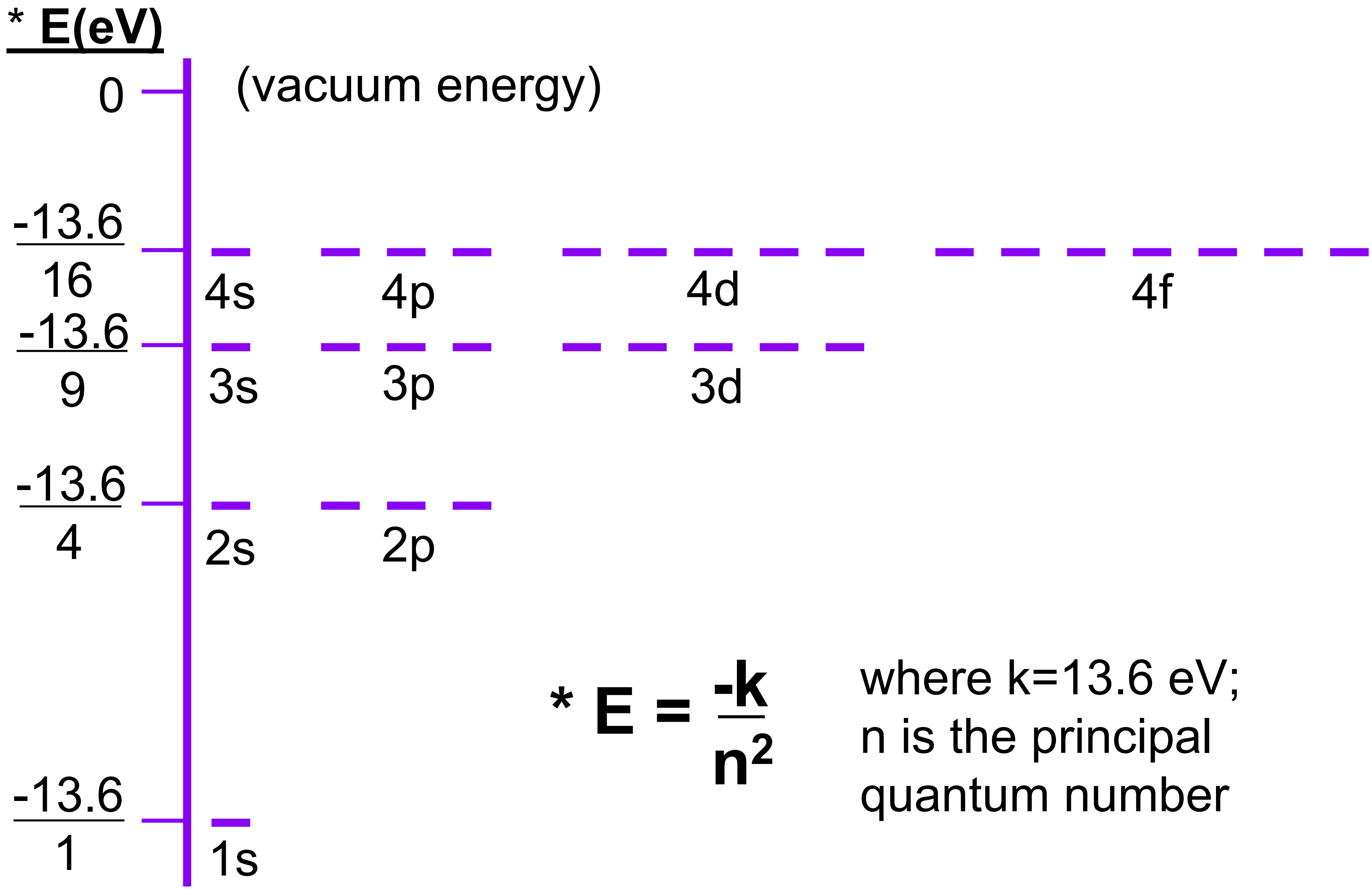
1906: One vote away from winning a Nobel Prize
Died in 1907

# Solid-State Molar Volumes (3D)




**In 1875, Lothar Meyer deduces a periodic trend**

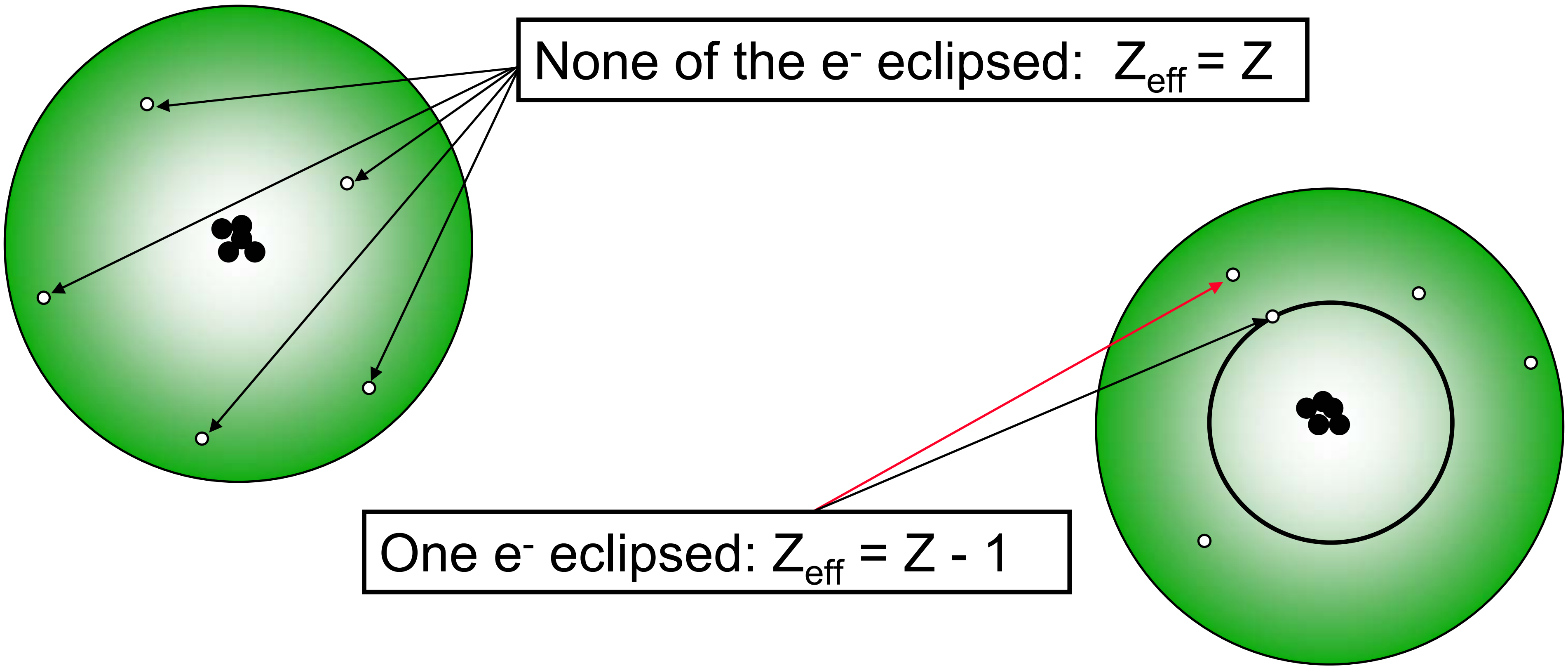
# Energy of One Electron in a H atom




$$* \; E = \frac{-k}{n^2}$$

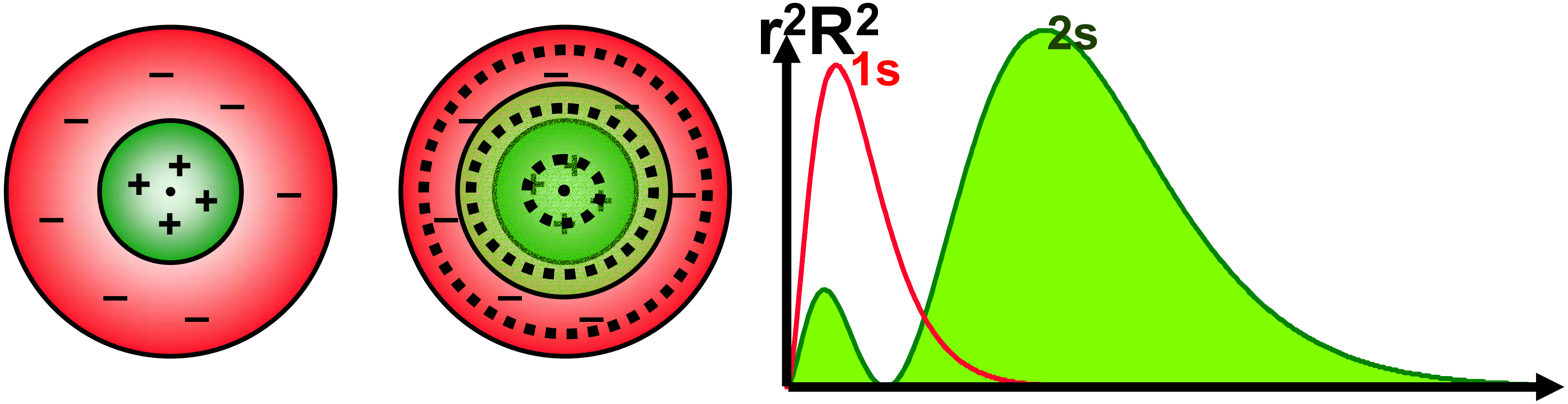
where k=13.6 eV;
n is the principal
quantum number

# Multiple-Electron Atoms

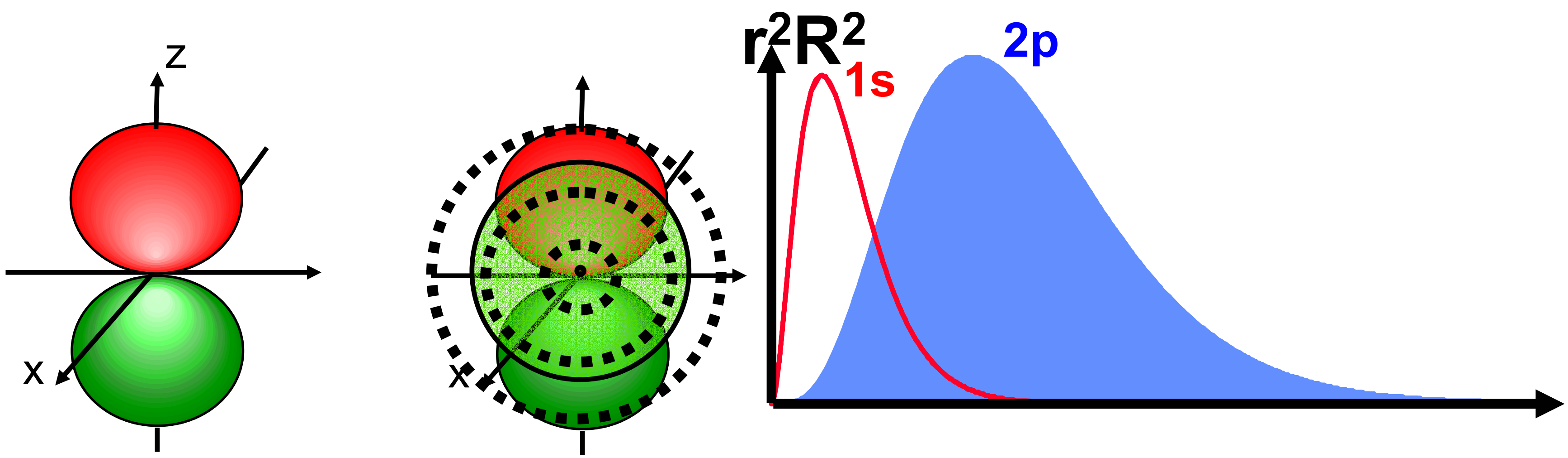



**On Average, $Z_{eff} < Z$**

**How Much Less $Z_{eff} < Z$ Determines Atomic Properties**

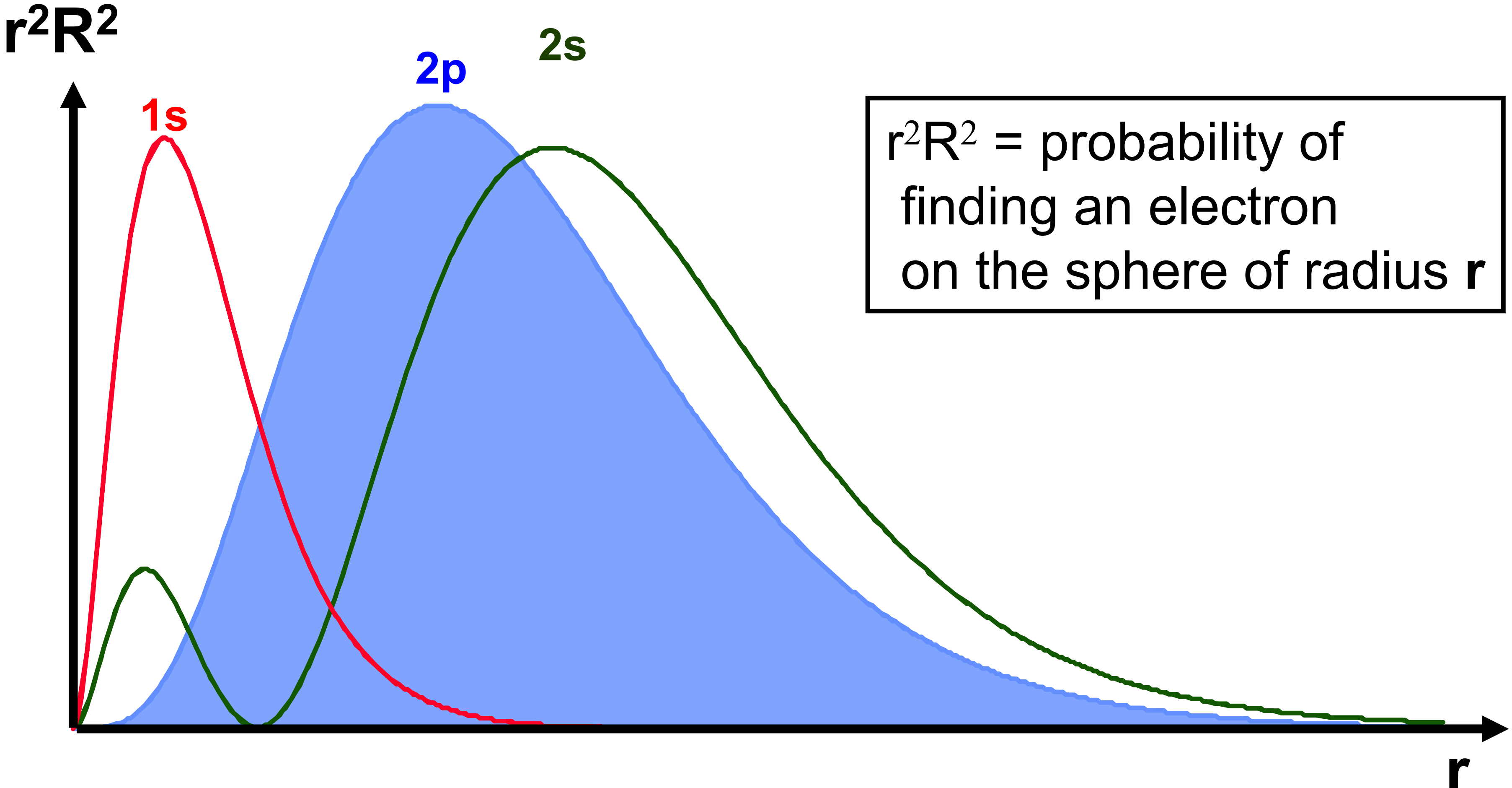


r²R²
1s
2s

z
x
x
r²R²
1s
2p

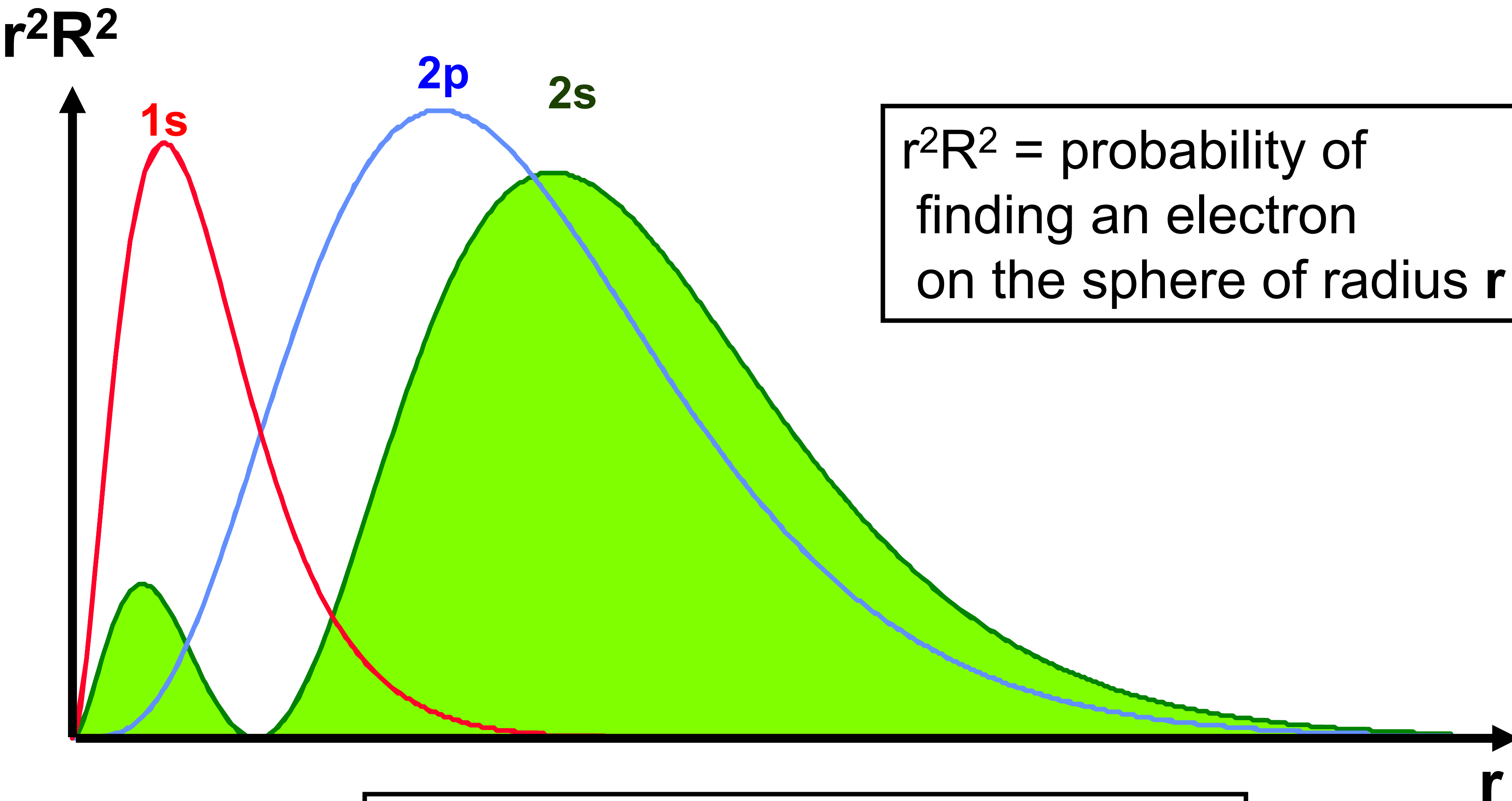
# Shielding




$r^2R^2$ = probability of finding an electron on the sphere of radius **r**

An electron in the **2p** orbital penetrates somewhat into the **1s** orbital

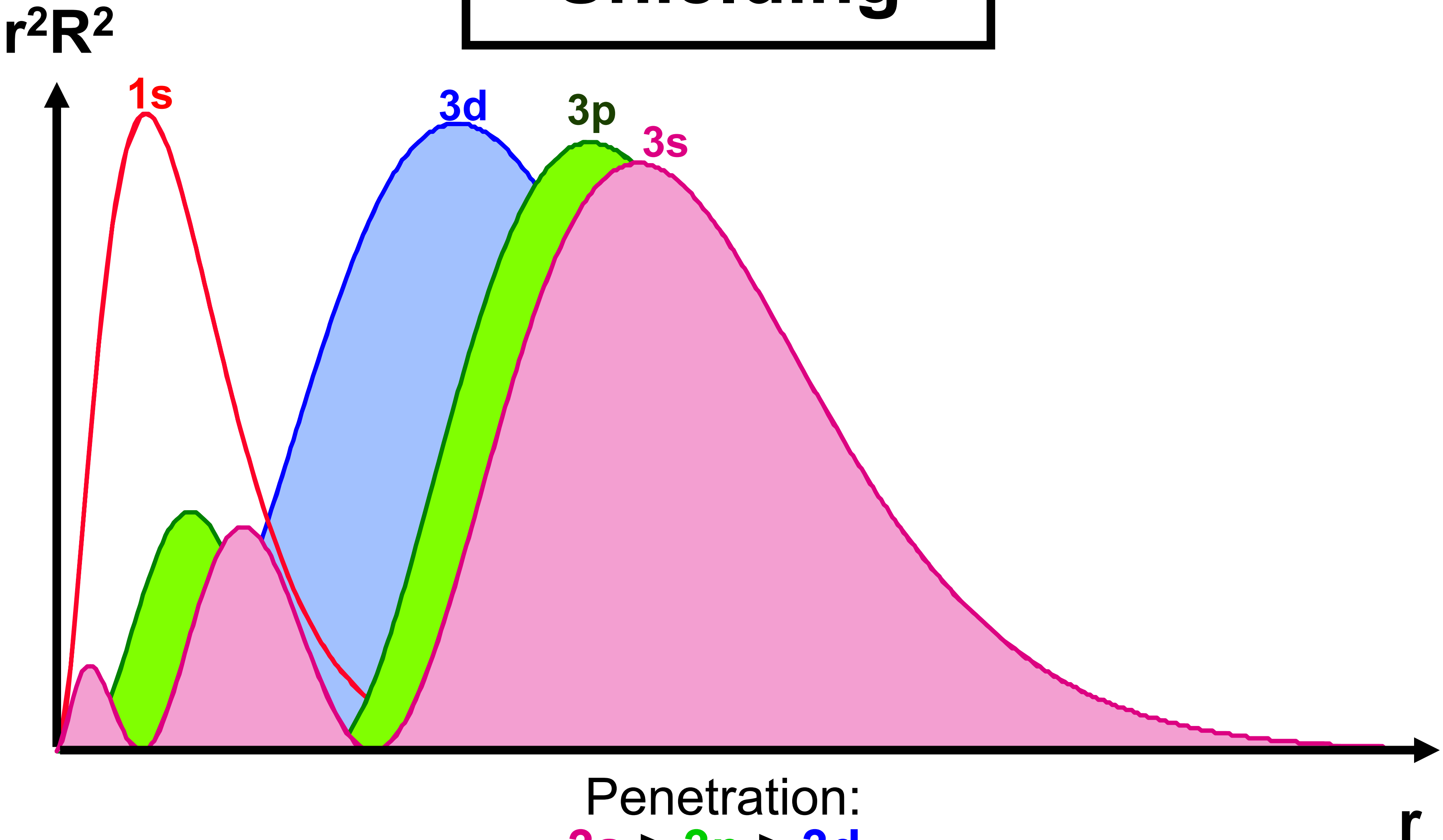
# Shielding




$r^2R^2$ = probability of finding an electron on the sphere of radius **r**

But a **2s** electron penetrates the **1s** orbital **better** than a **2p** electron

# Shielding

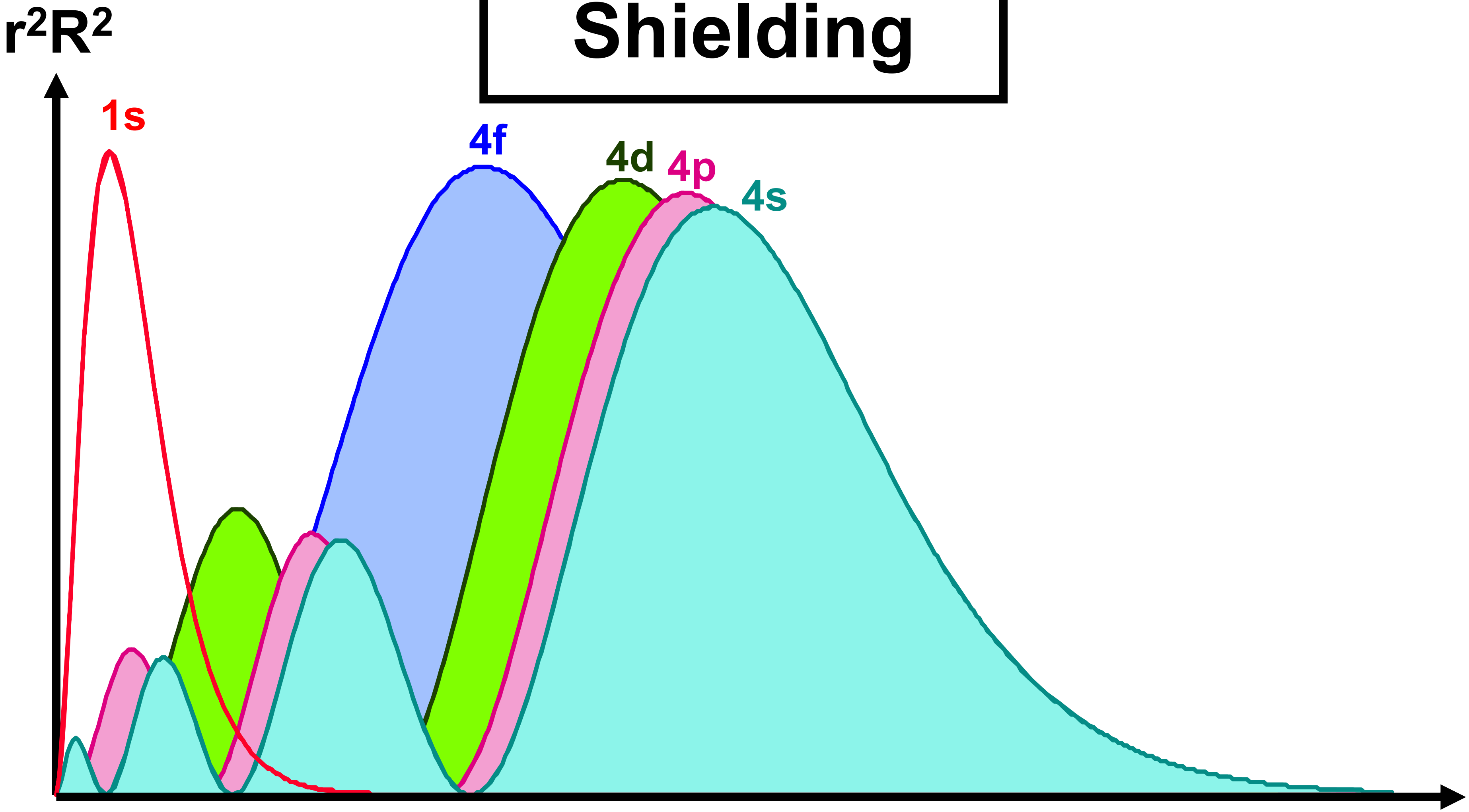



Penetration:

**3s > 3p > 3d**

A **3s** electron penetrates the 1s orbital **better** than a **3p** electron

# Shielding

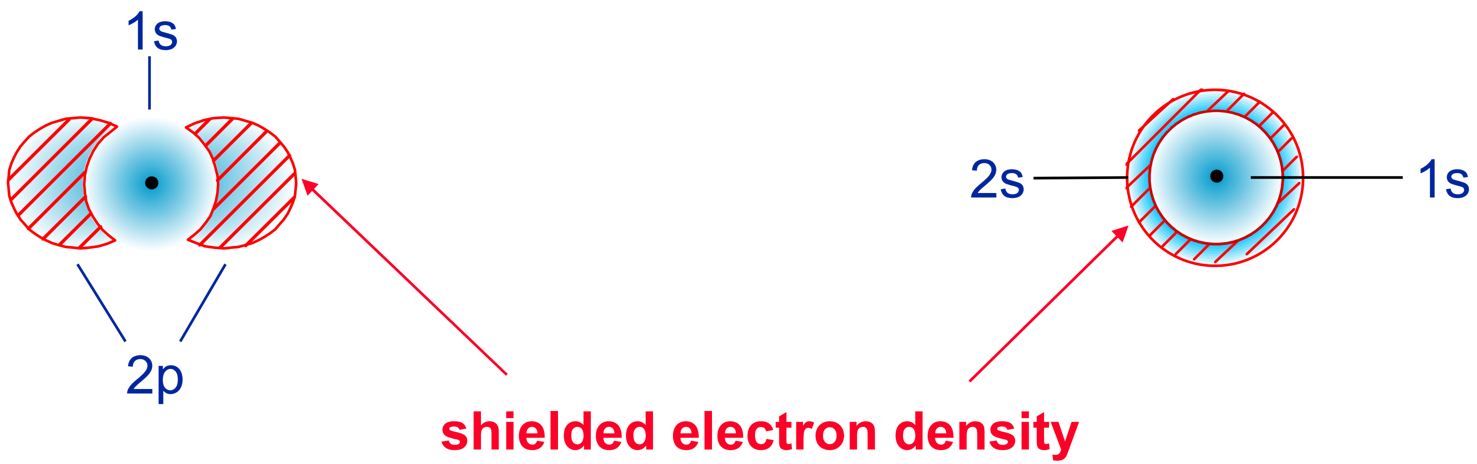



Penetration:

**4s > 4p > 4d > 4f**

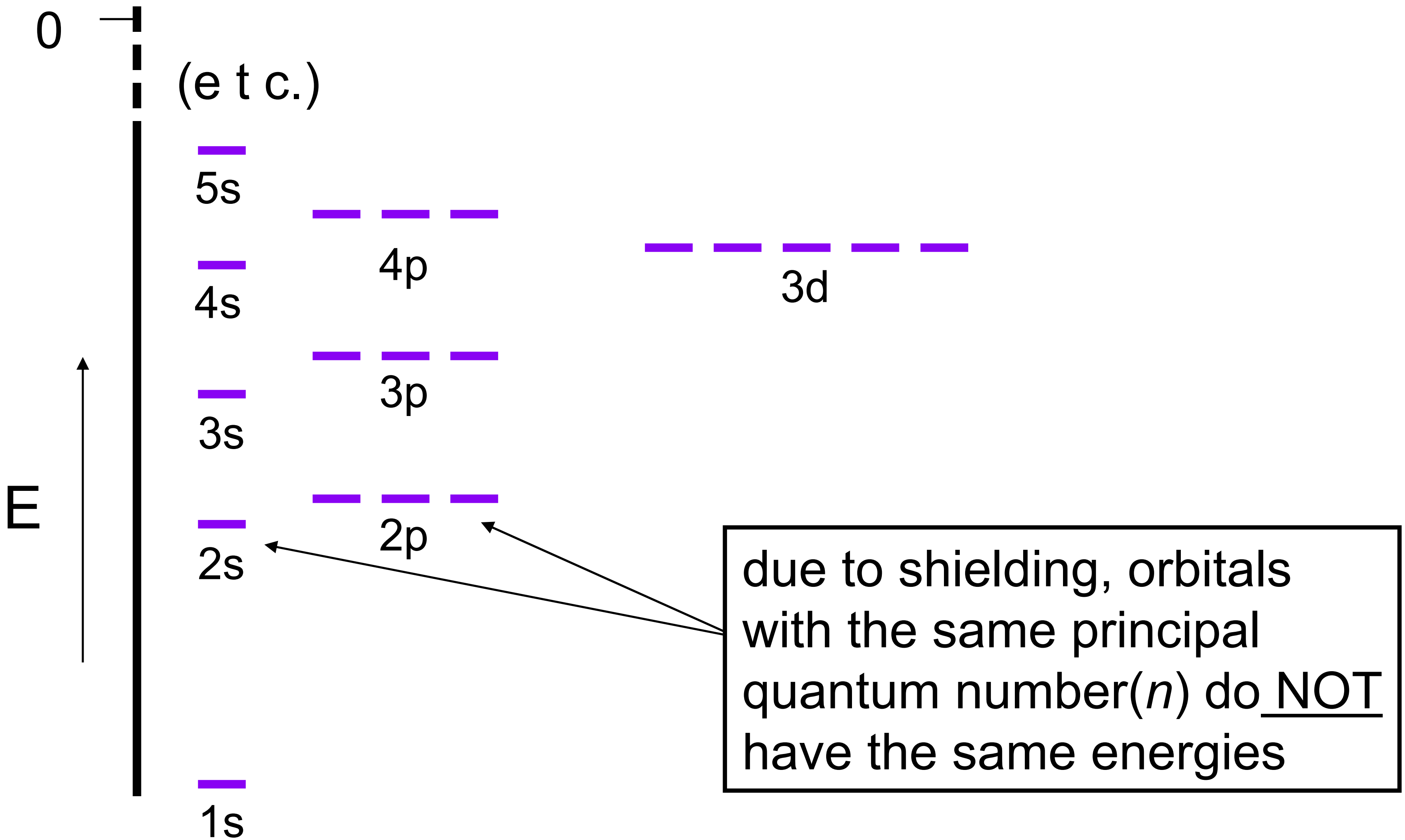
A **4s** electron penetrates the 1s orbital **better** than a **4p** electron

# Another View of 2s vs 2p Shielding

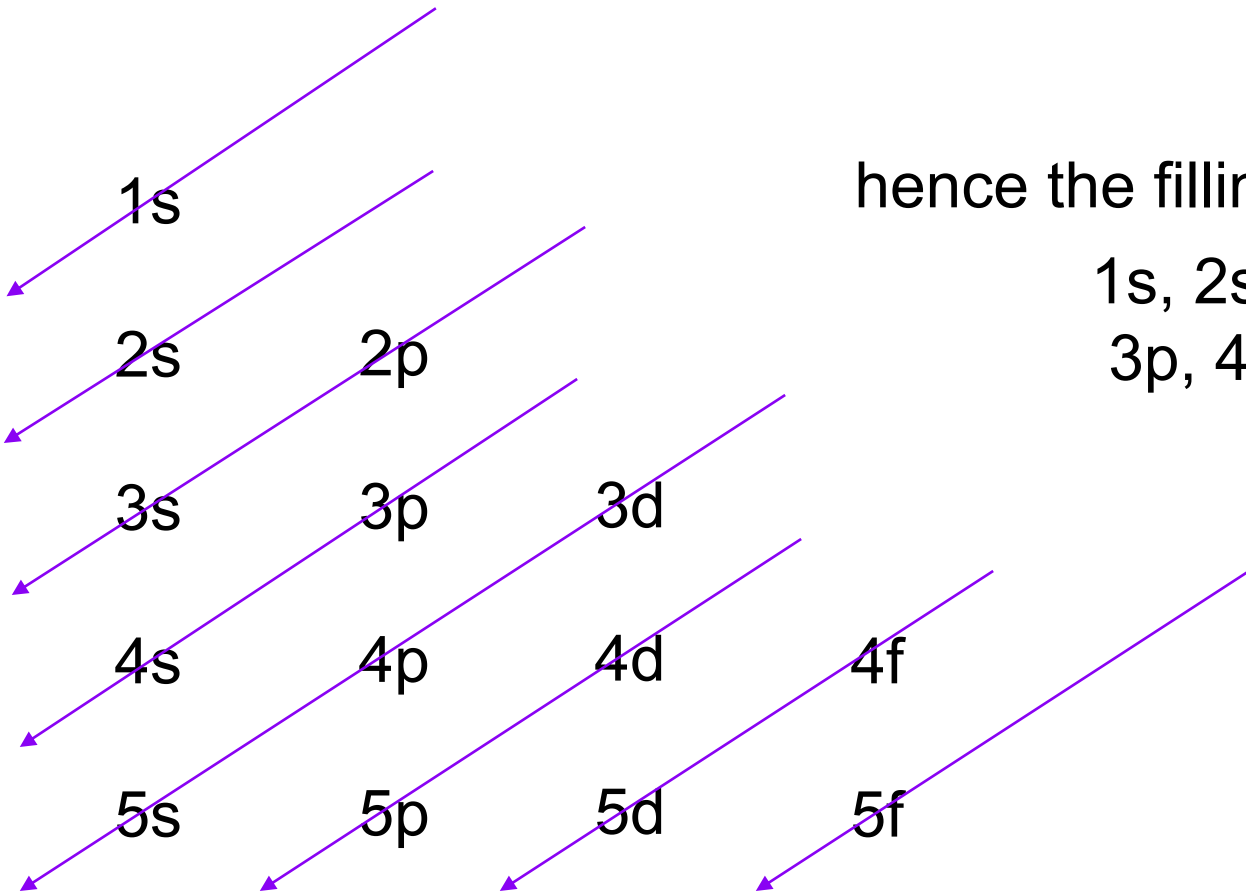



2s Penetrates More into 1s Than Does 2p
2s is Therefore **Lower in E** Than 2p

# Energy of Multi-Electron Atoms



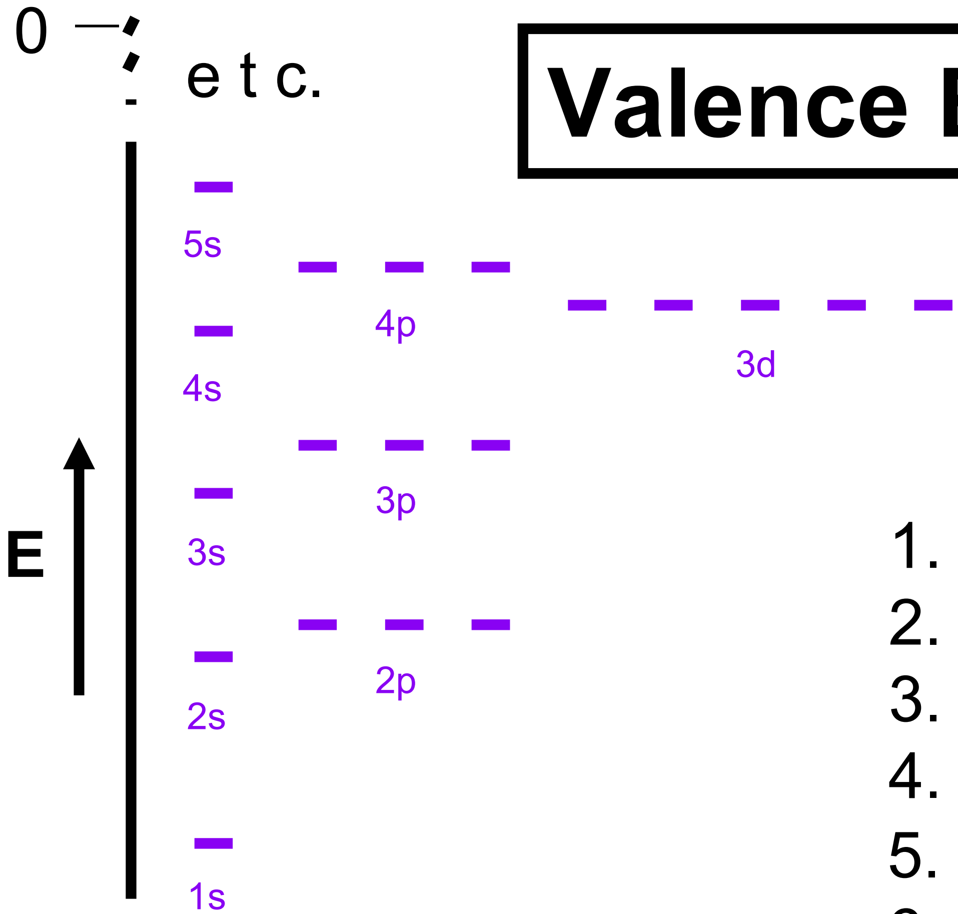
# Mnemonic for Filling Order




hence the filling order is:

1s, 2s, 2p, 3s,
3p, 4s, 3d, etc.

# Valence Electrons

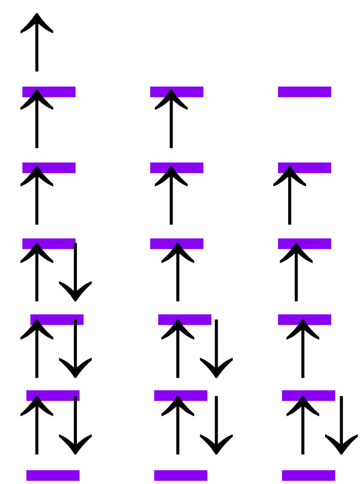



element
shell
electrons in shell
valence electrons
(underlined)

1. **H** $\underline{(1s)^1}$
2. **He** $\underline{(1s)^2}$
3. **Li** $(1s)^2\underline{(2s)^1}$
4. **Be** $(1s)^2\underline{(2s)^2}$
5. **B** $(1s)^2\underline{(2s)^2(2p)^1}$
6. **C** $(1s)^2\underline{(2s)^2(2p)^2}$
7. **N** $(1s)^2\underline{(2s)^2(2p)^3}$
8. **O** $(1s)^2\underline{(2s)^2(2p)^4}$
9. **F** $(1s)^2\underline{(2s)^2(2p)^5}$
10. **Ne** $(1s)^2\underline{(2s)^2(2p)^6}$

e t c.

**2p- orbital**

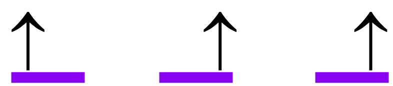


**Valence Electrons:**
electrons in the outermost shell (in other words, the set of electrons with highest principal quantum number)

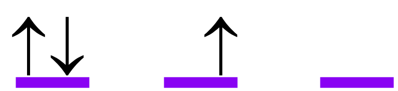
# Orbital Filling Energies

Example:

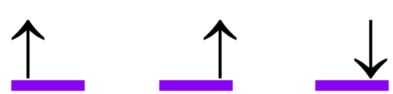
lowest energy for 3 electrons in **p** orbital



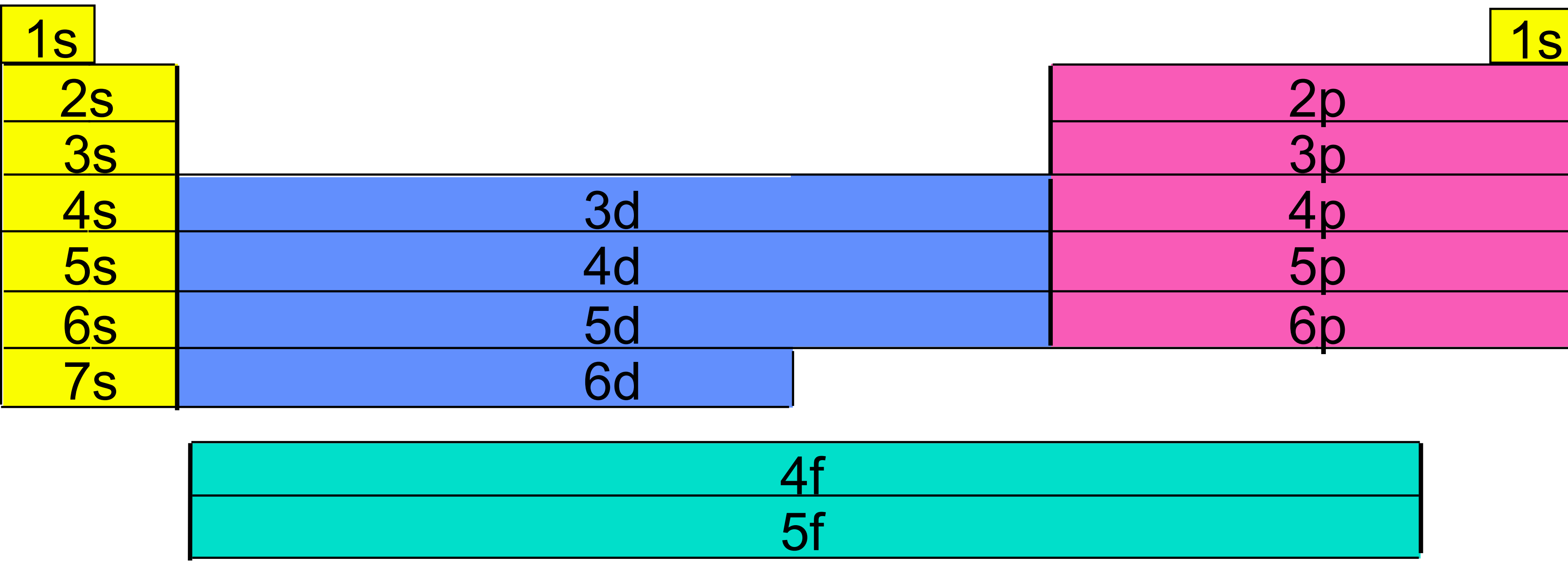
energy increases when a second electron is put in same orbital



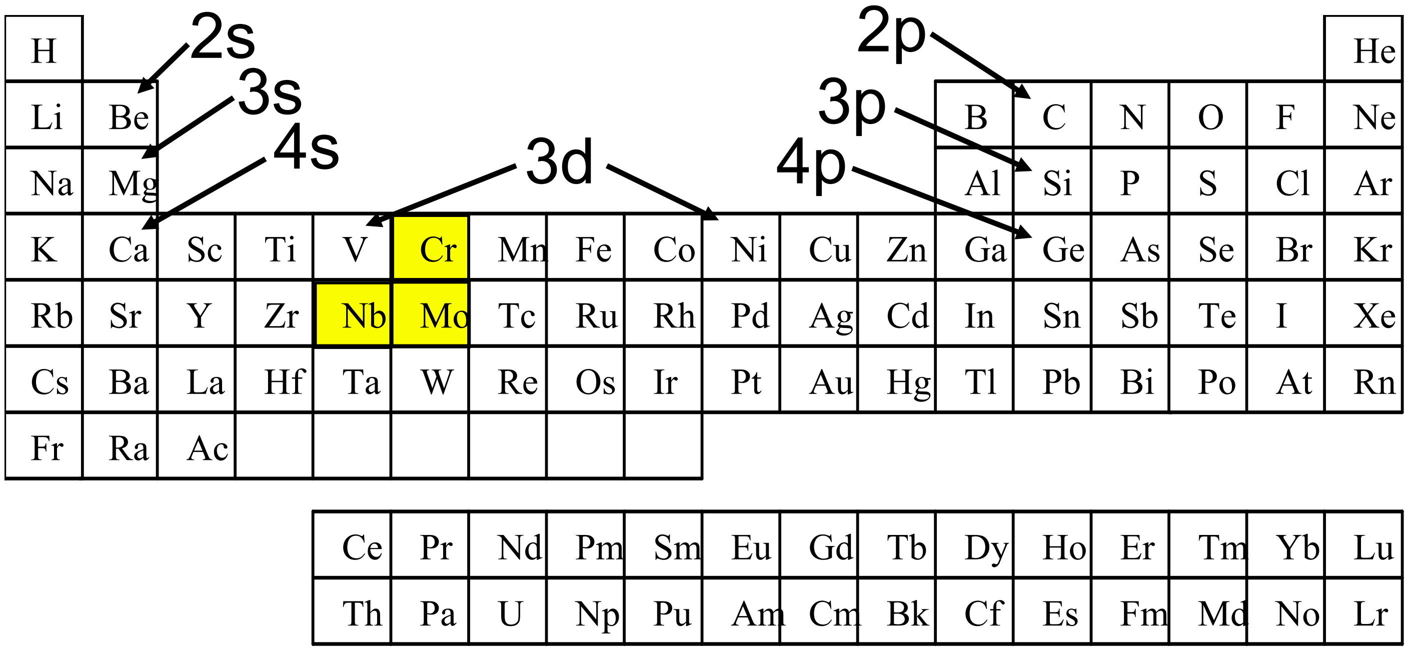
energy also increases when spins are mixed in orbitals



# Organization of Periodic Chart



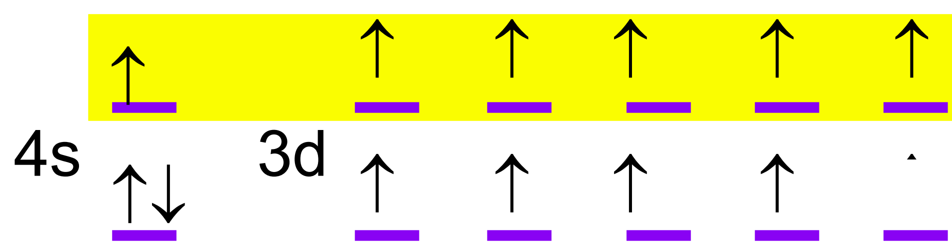
# Exceptions to Filling Order



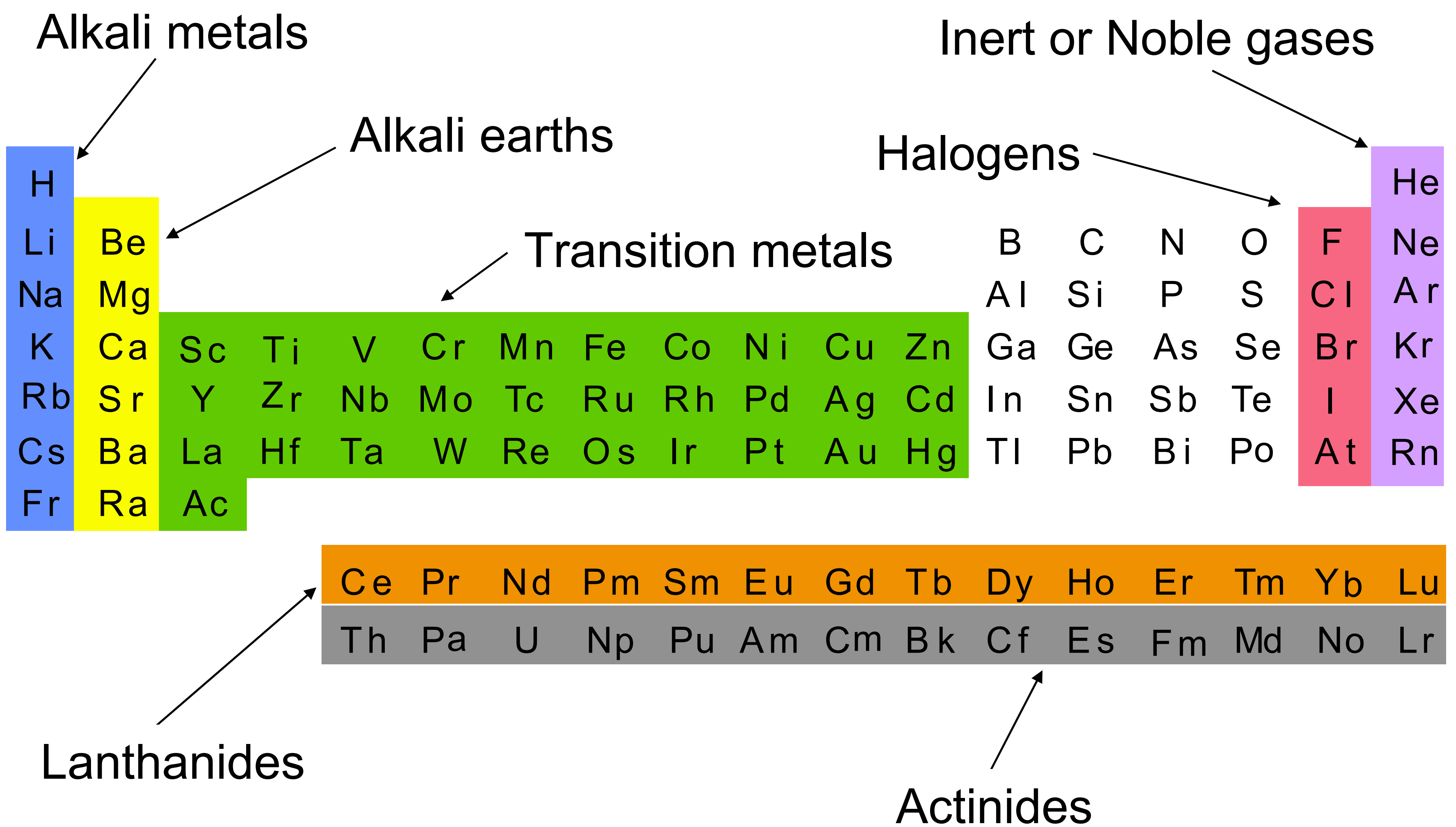

23. **V** $(4s)^2(3d)^3$
24. **Cr** $(4s)^1(3d)^5$
25. **Mn** $(4s)^2(3d)^5$

40. **Zr** $(5s)^2(4d)^2$
41. **Nb** $(5s)^1(4d)^4$
42. **Mo** $(5s)^1(4d)^5$

Exceptions occur because electrons don’t like to pair up in orbitals; so the highlighted atoms have lower energy.

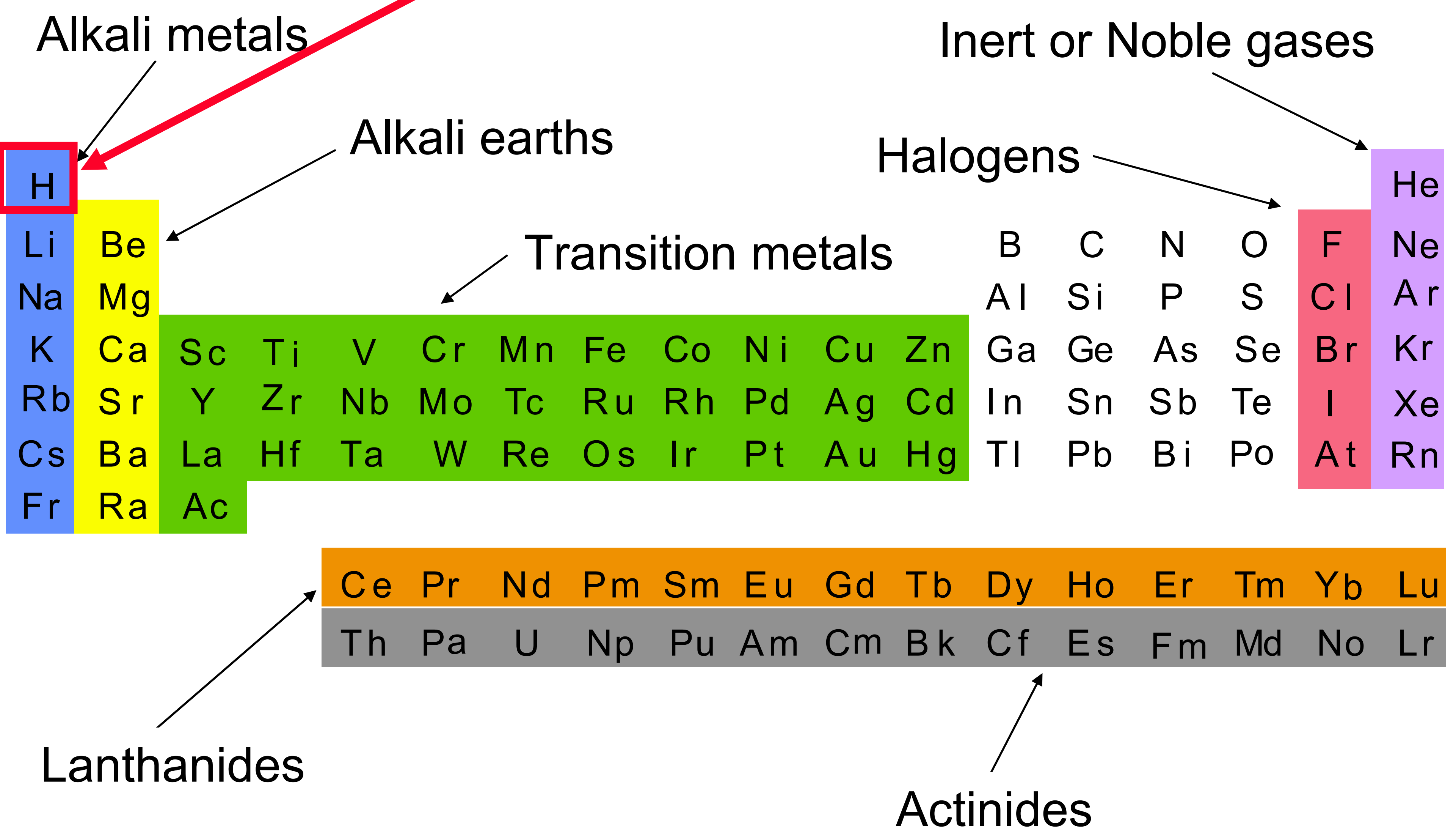


# Element Groups

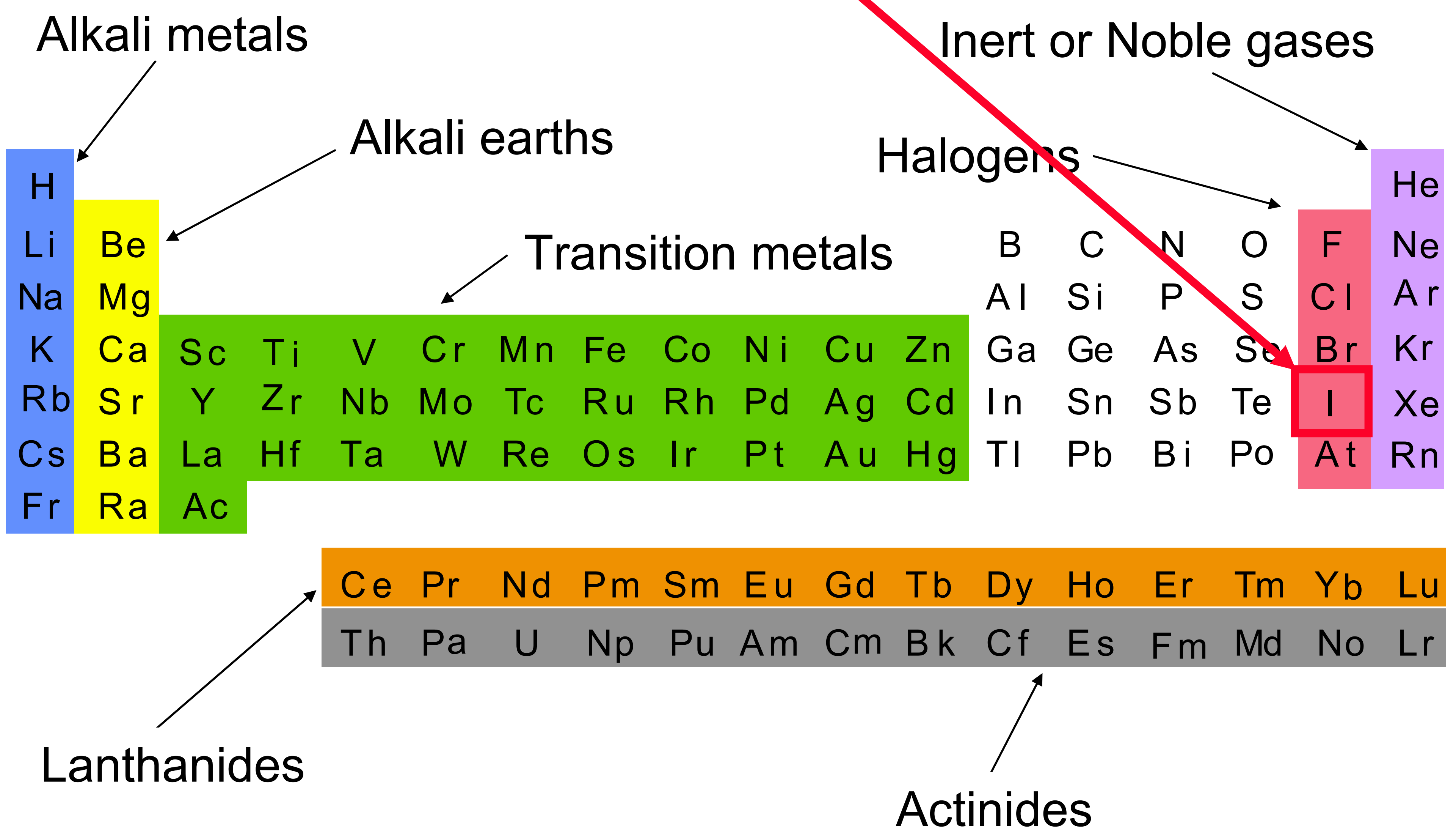


**Hydrogen:**

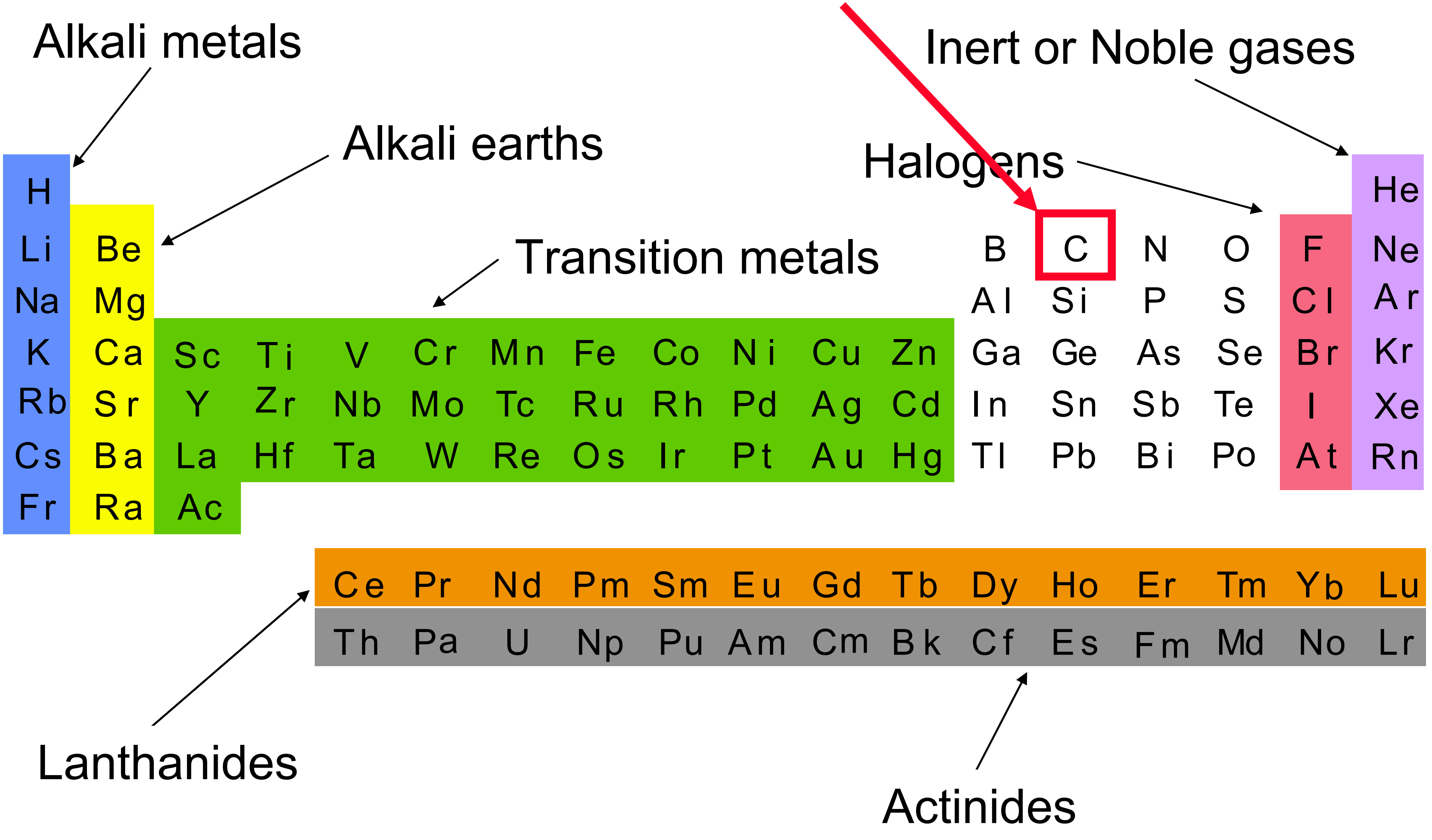
**From Greek: Hydro-genes: “Water forming”**

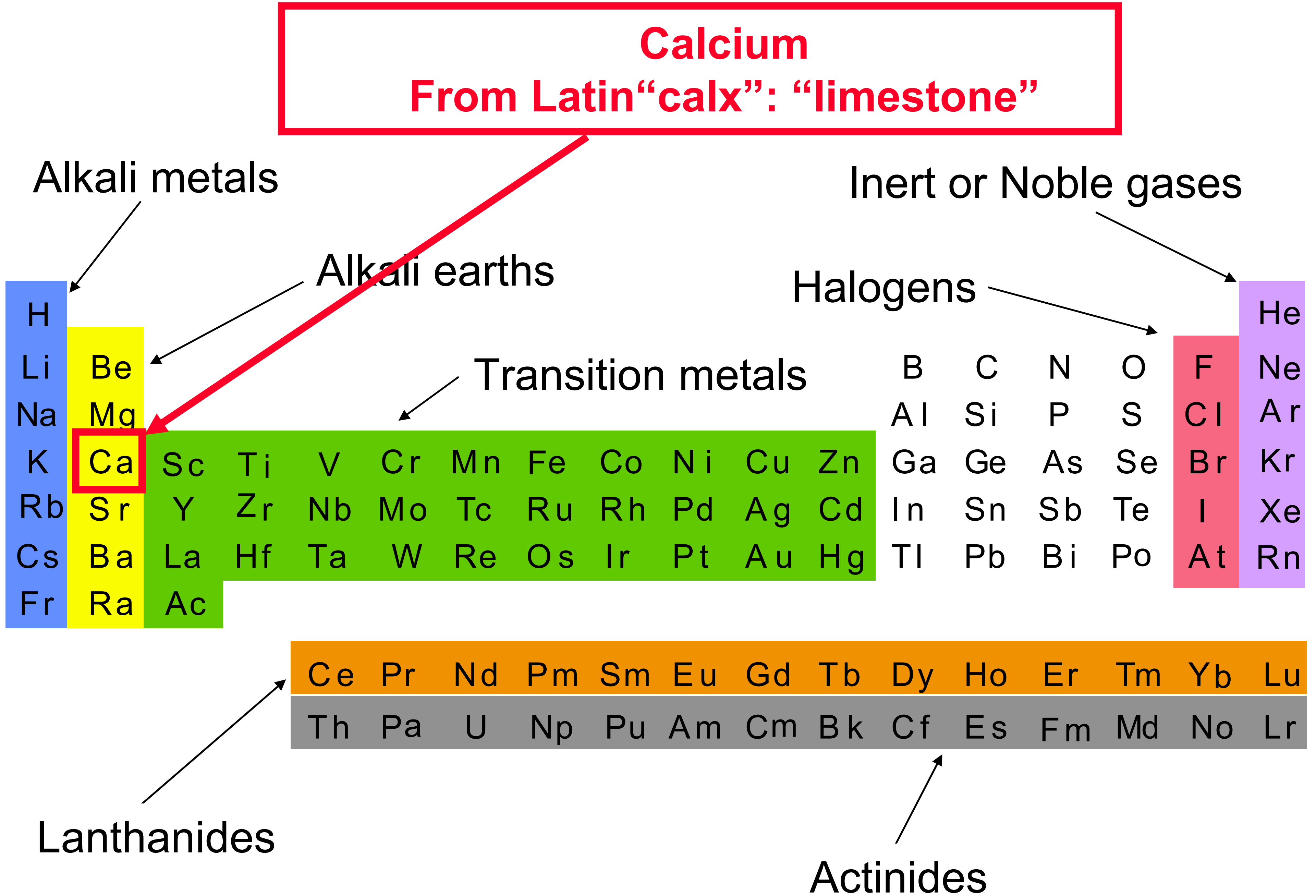


**Iodine: violet crystals**
**From Greek “iodes”: “violet”**



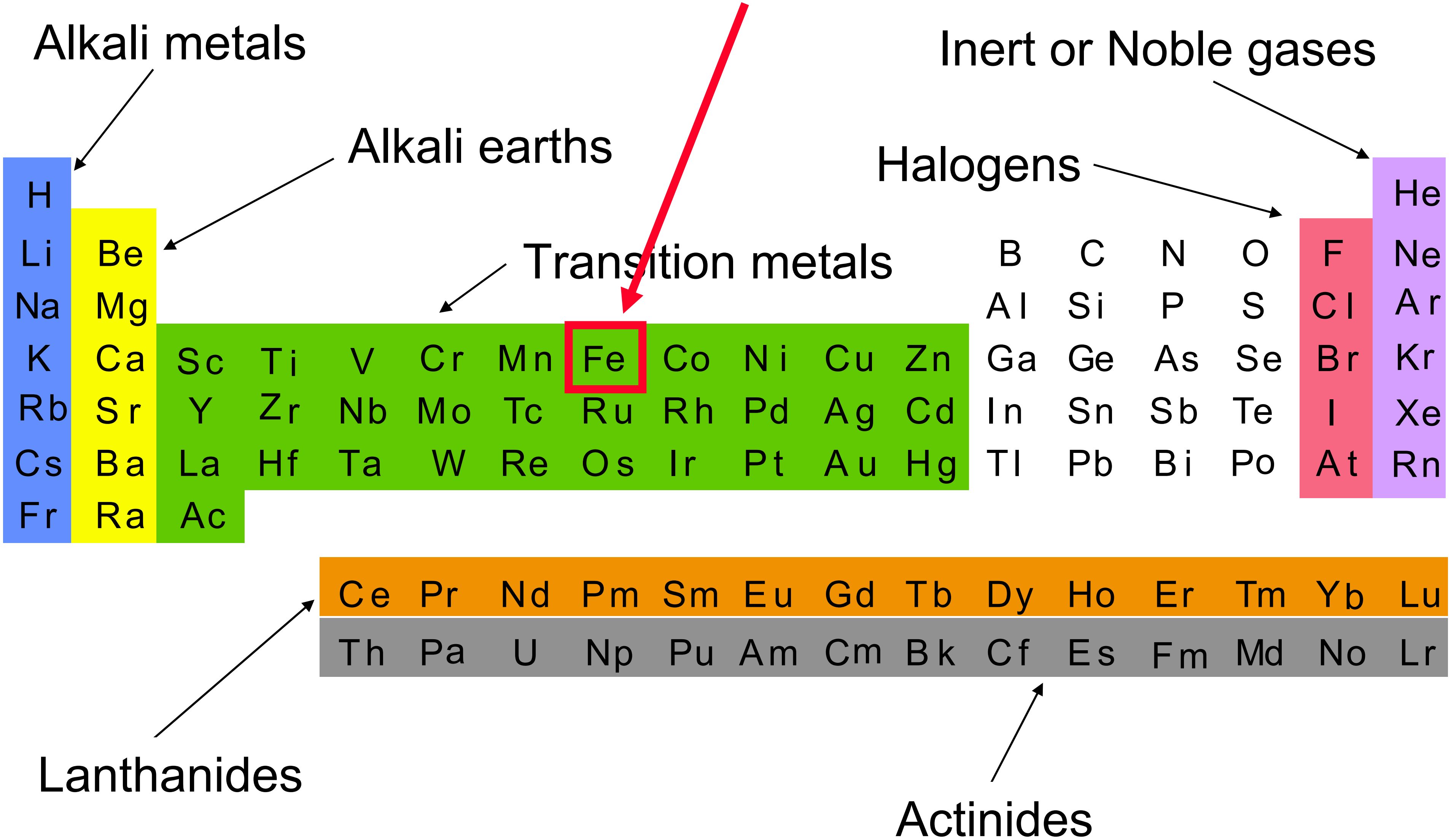
# Carbon
# From Latin“carbo”: “charcoal”




Calcium
From Latin“calx”: “limestone”
Alkali metals
Inert or Noble gases
Alkali earths
Halogens
Transition metals
H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl Ar
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
Fr Ra Ac
Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr
Lanthanides
Actinides

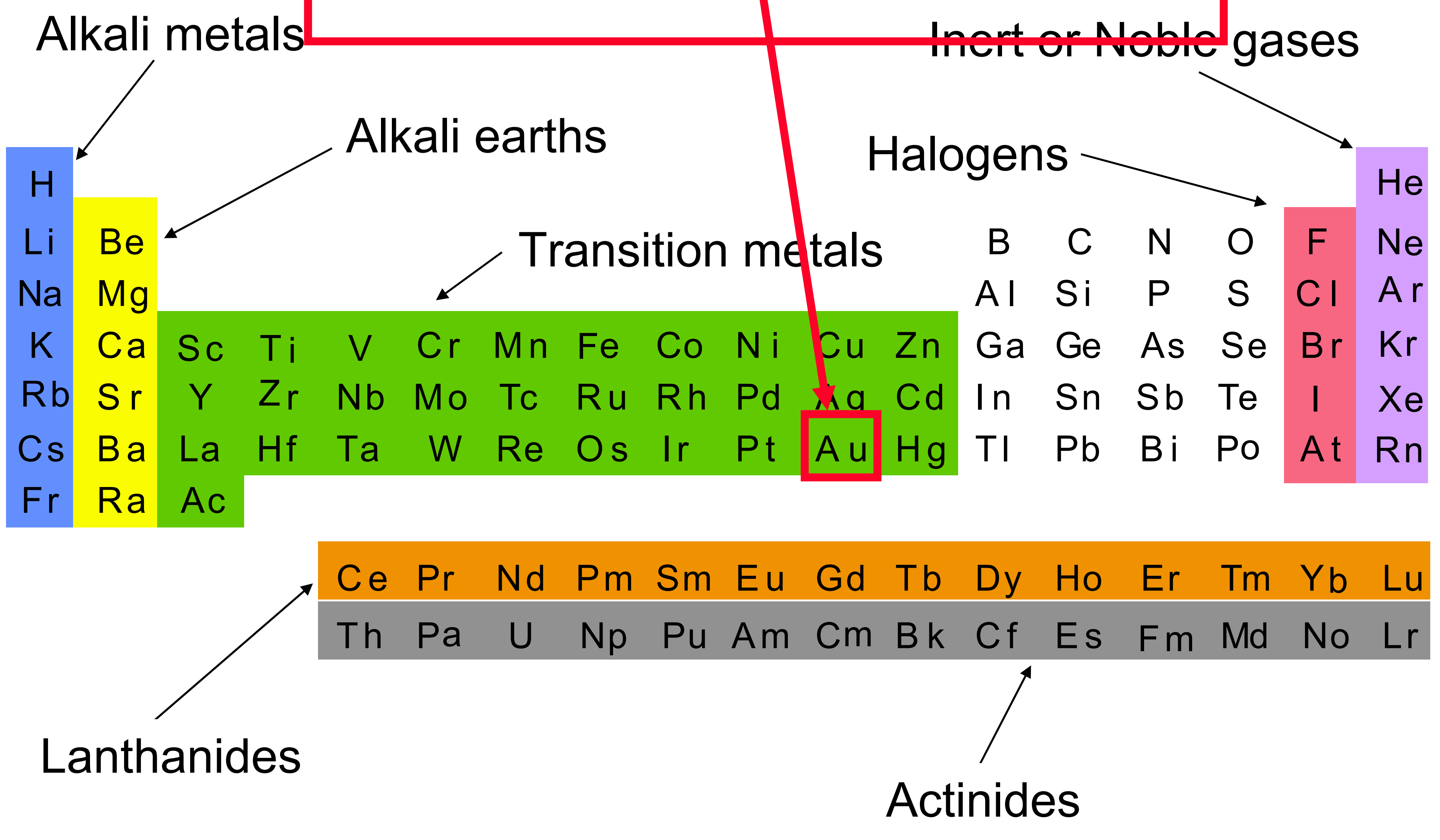
**Iron: Fe**

**From Latin“iron”: “ferrum”**



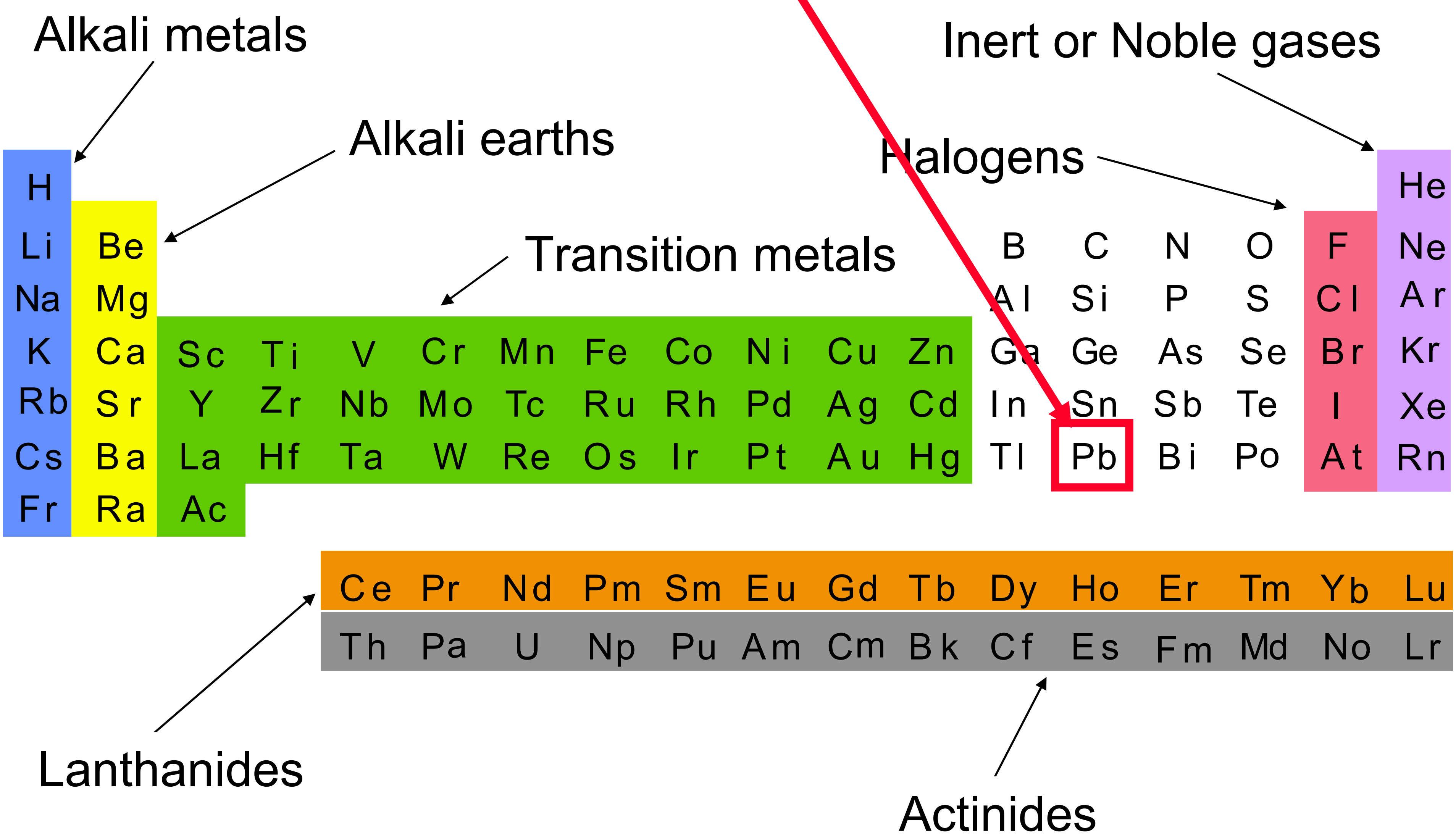
**Gold: Au**

**From Latin“aurum”: “shining dawn”**



**Lead: Pb**

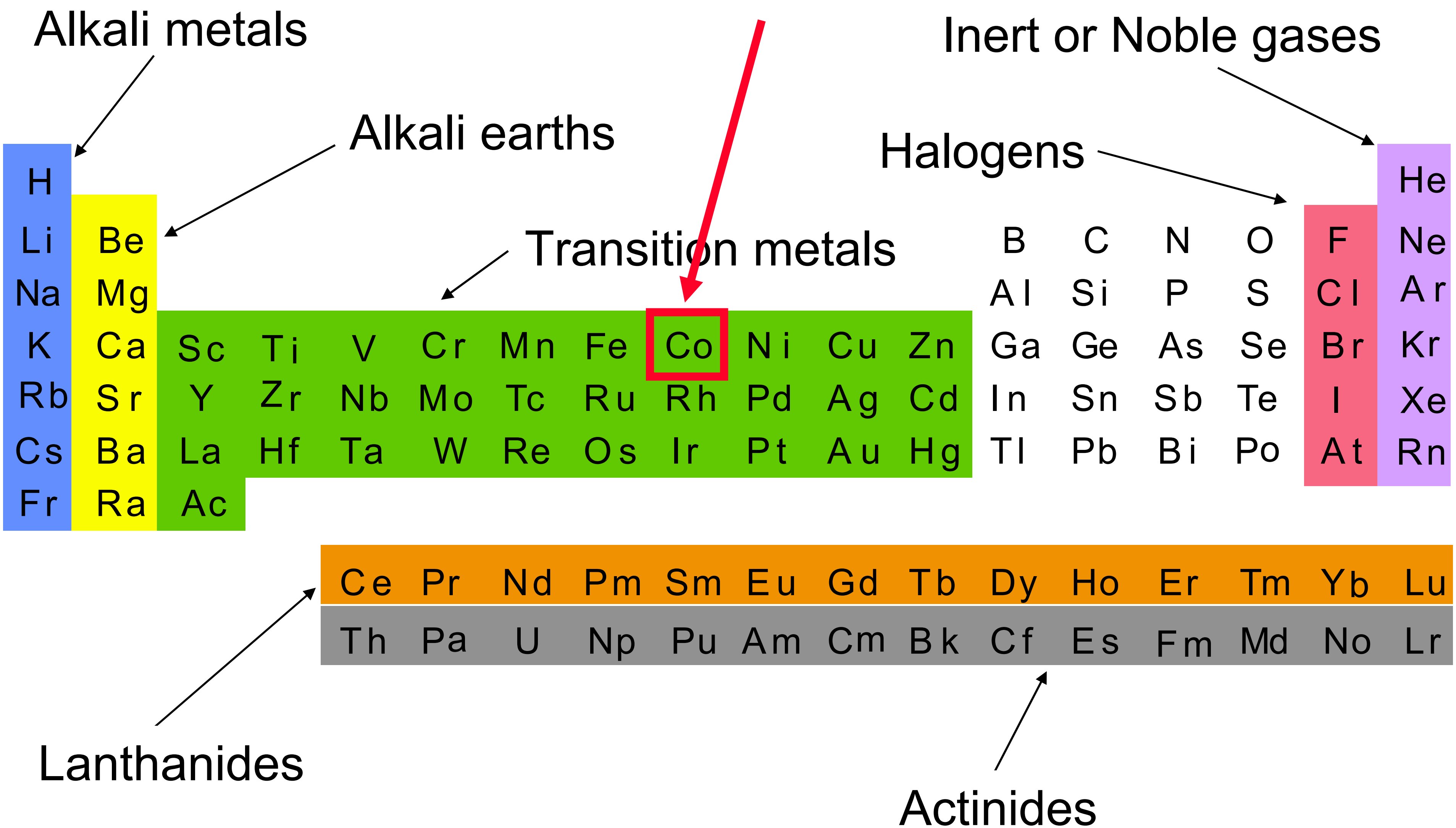
**From Latin“plumbum”: “heavy”**



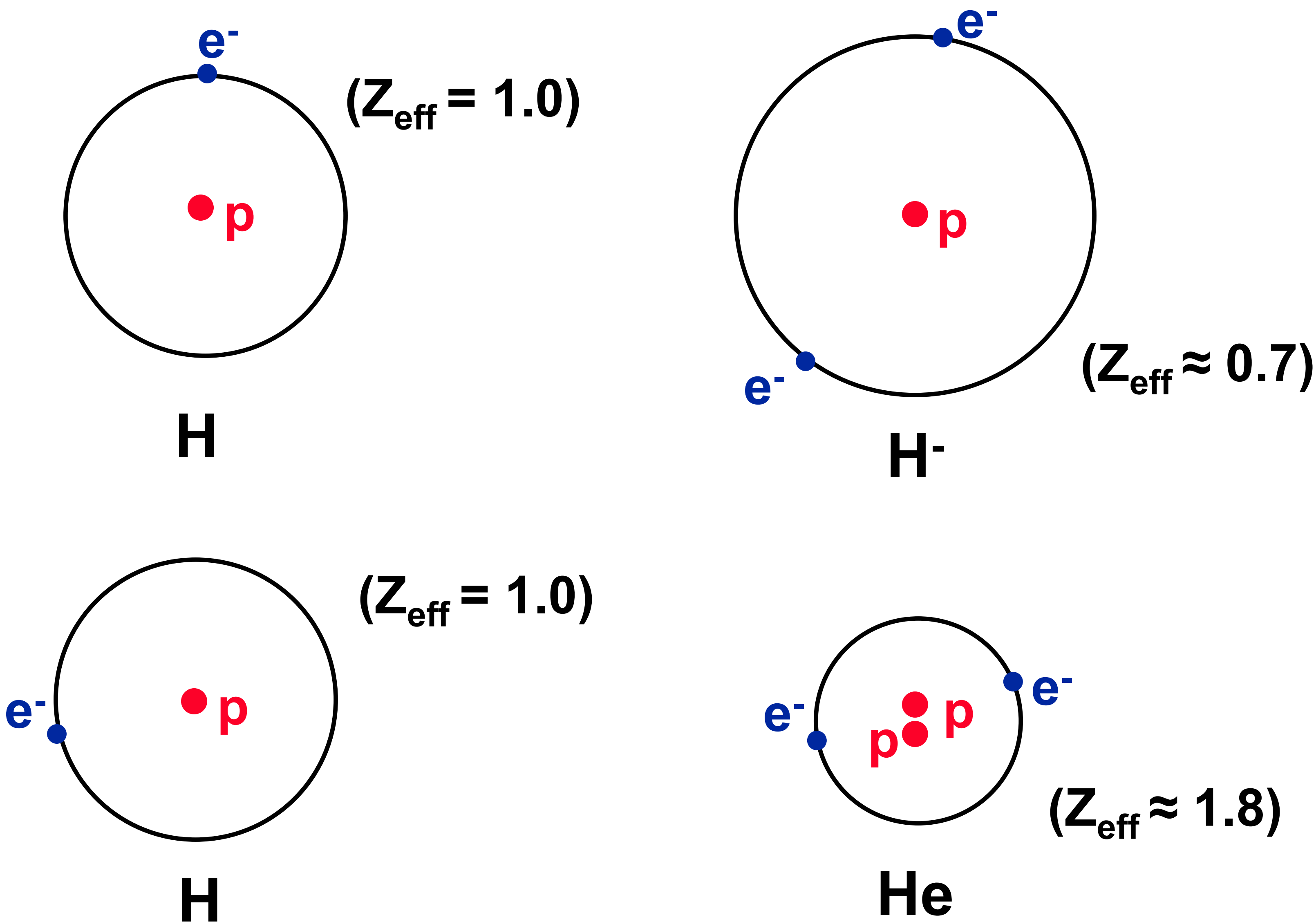
**Cobalt: Co**

**From German"kobold": "goblin or evil spirits"**

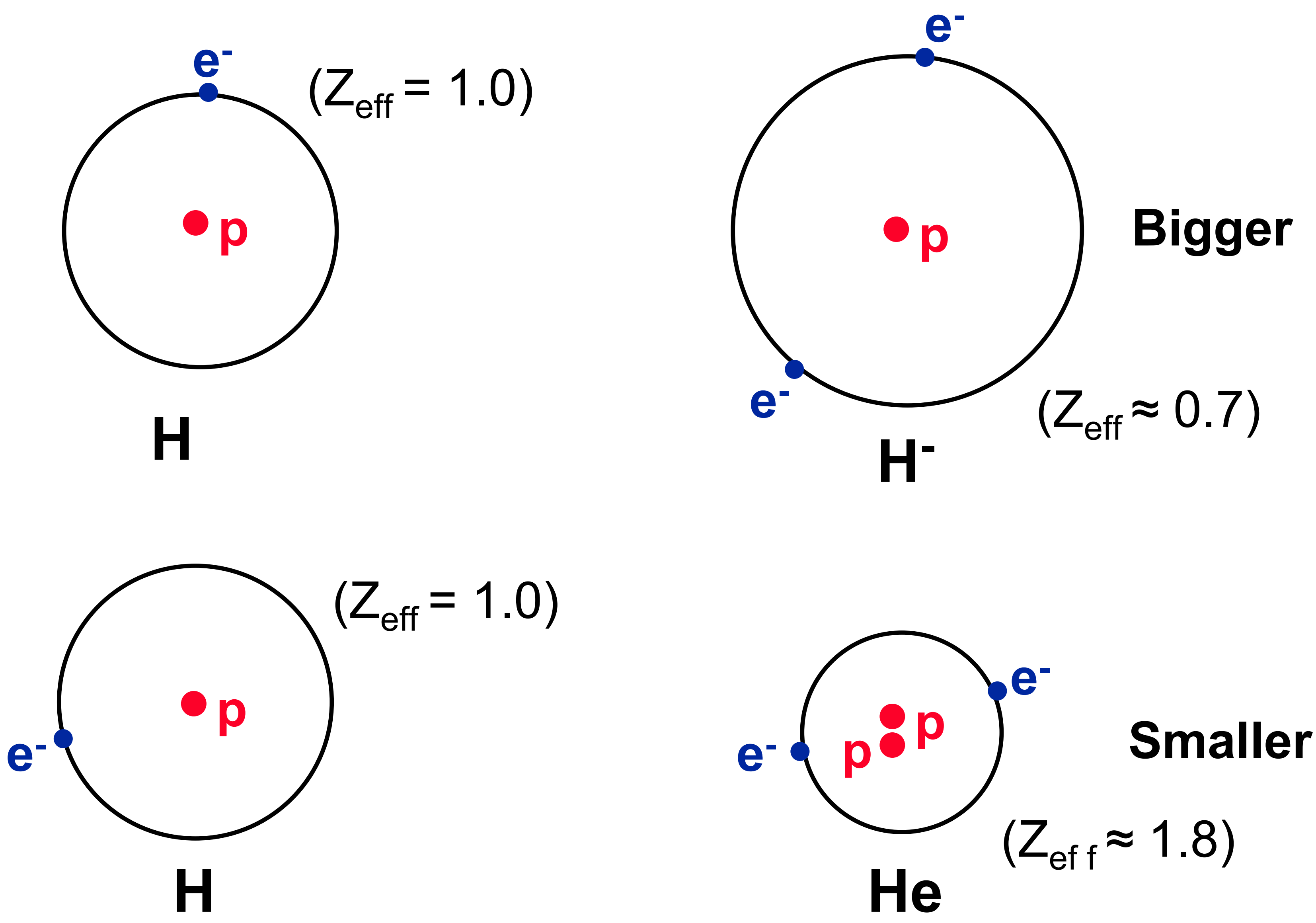
**Unwanted metal in what were thought to be copper ores**



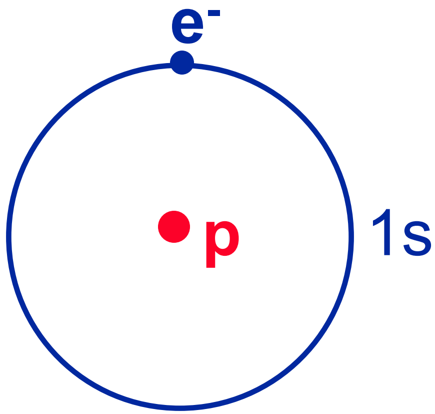
# Effective Nuclear Charge



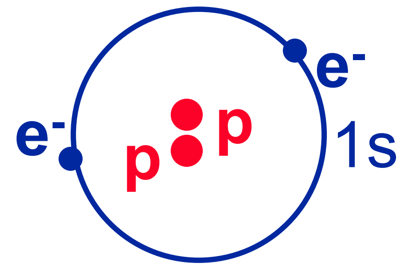
# Atomic Size and Ionization Energy



# Trends in $Z_{eff}$

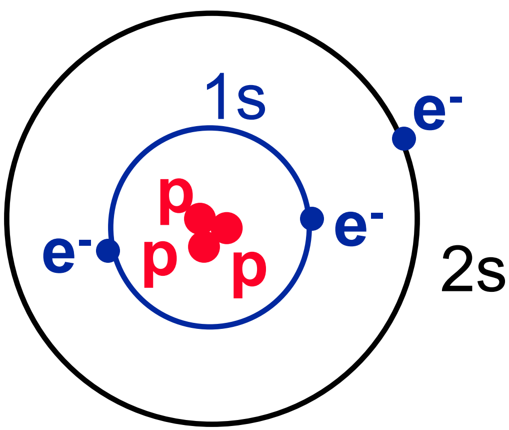



H ($Z_{eff}$ =1.0)



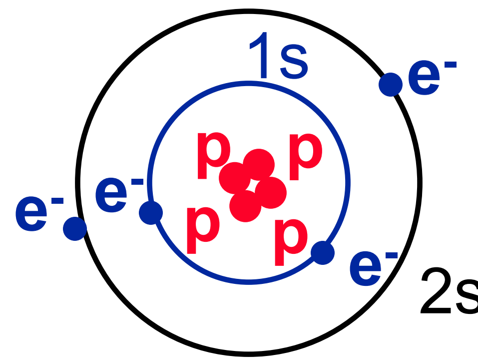

Smaller

He ($Z_{eff}$ ≈1.8)




Bigger

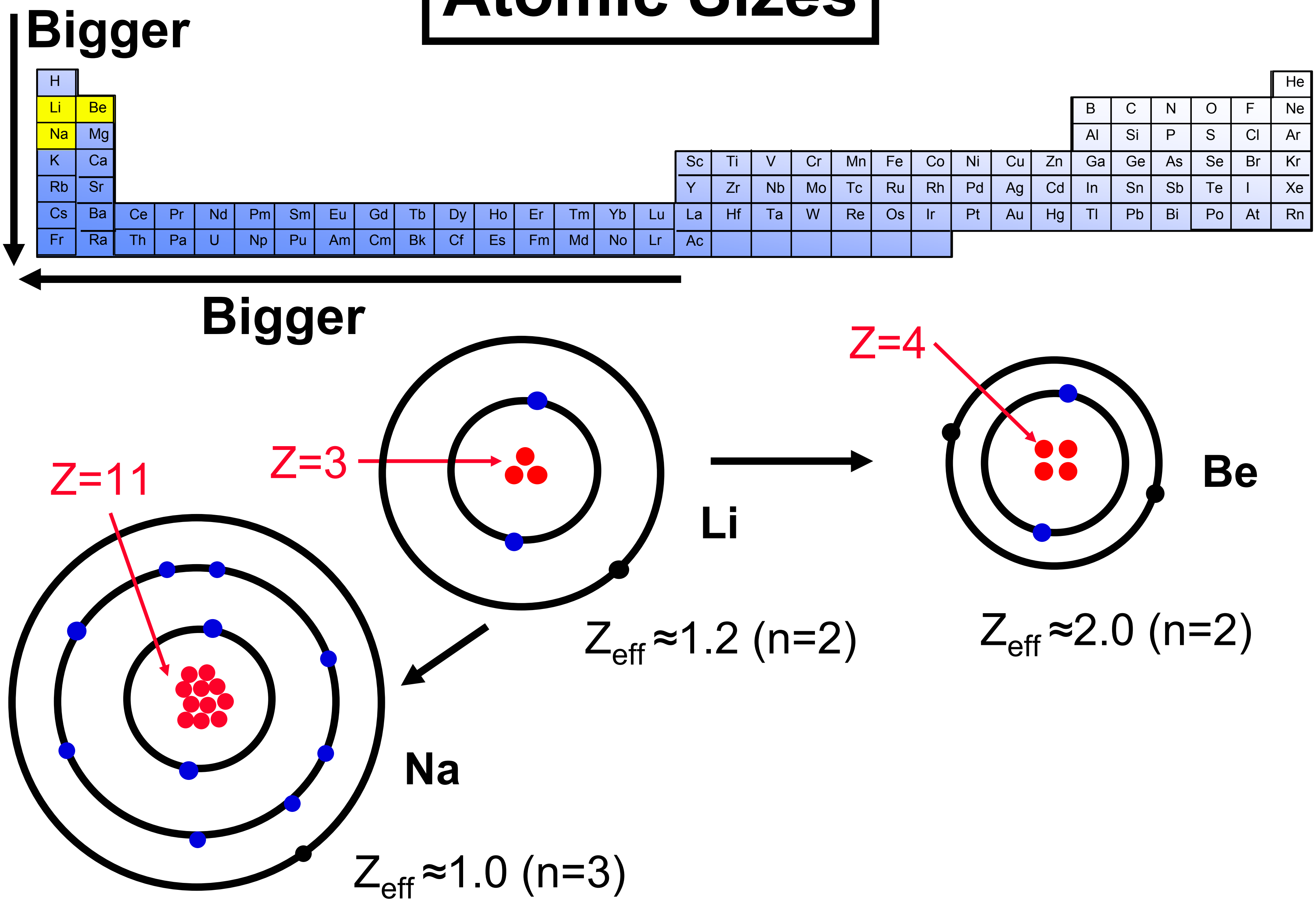
Li ($Z_{eff}$ ≈1.2 in n=2)



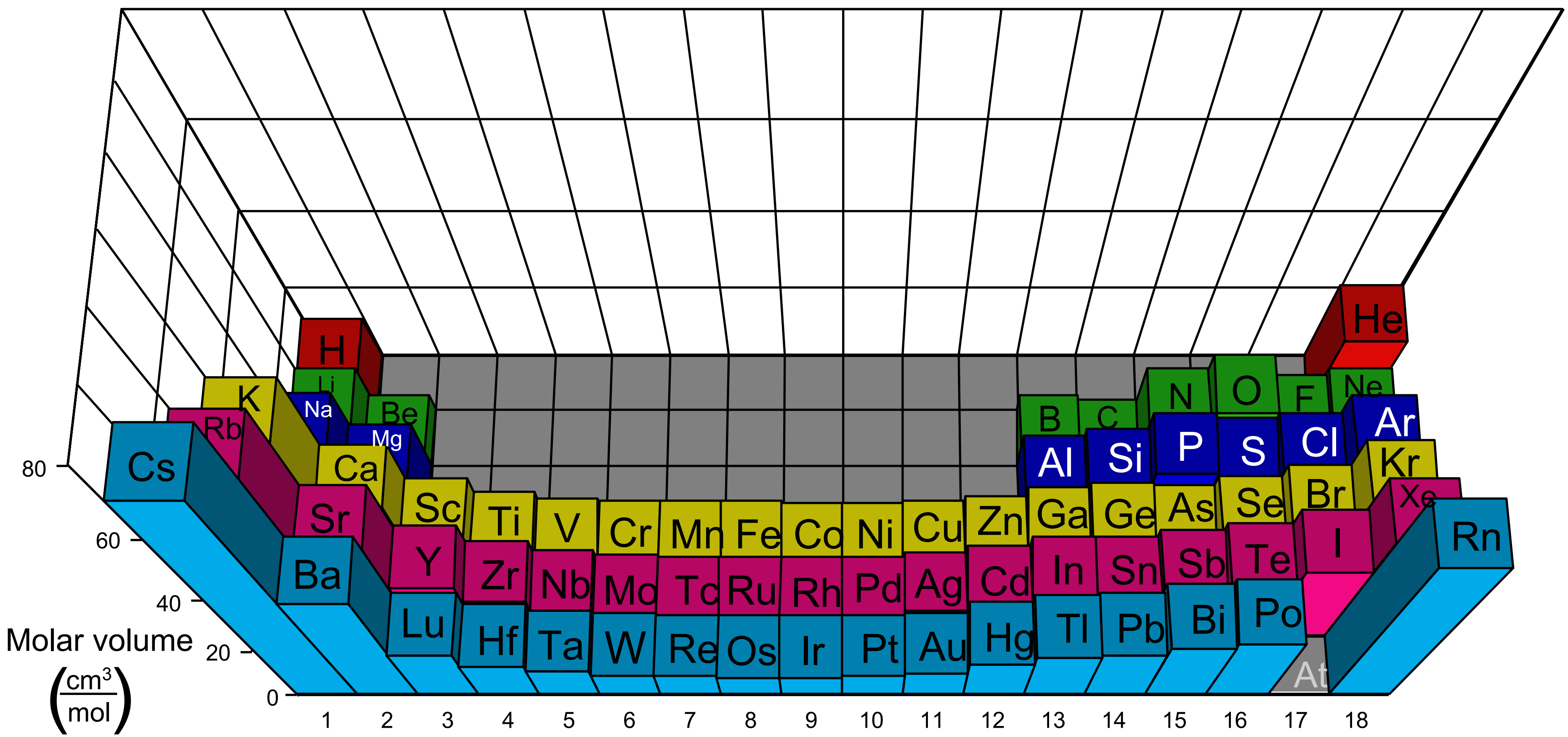

Smaller Again

Be ($Z_{eff}$ ≈2.0 in n=2)

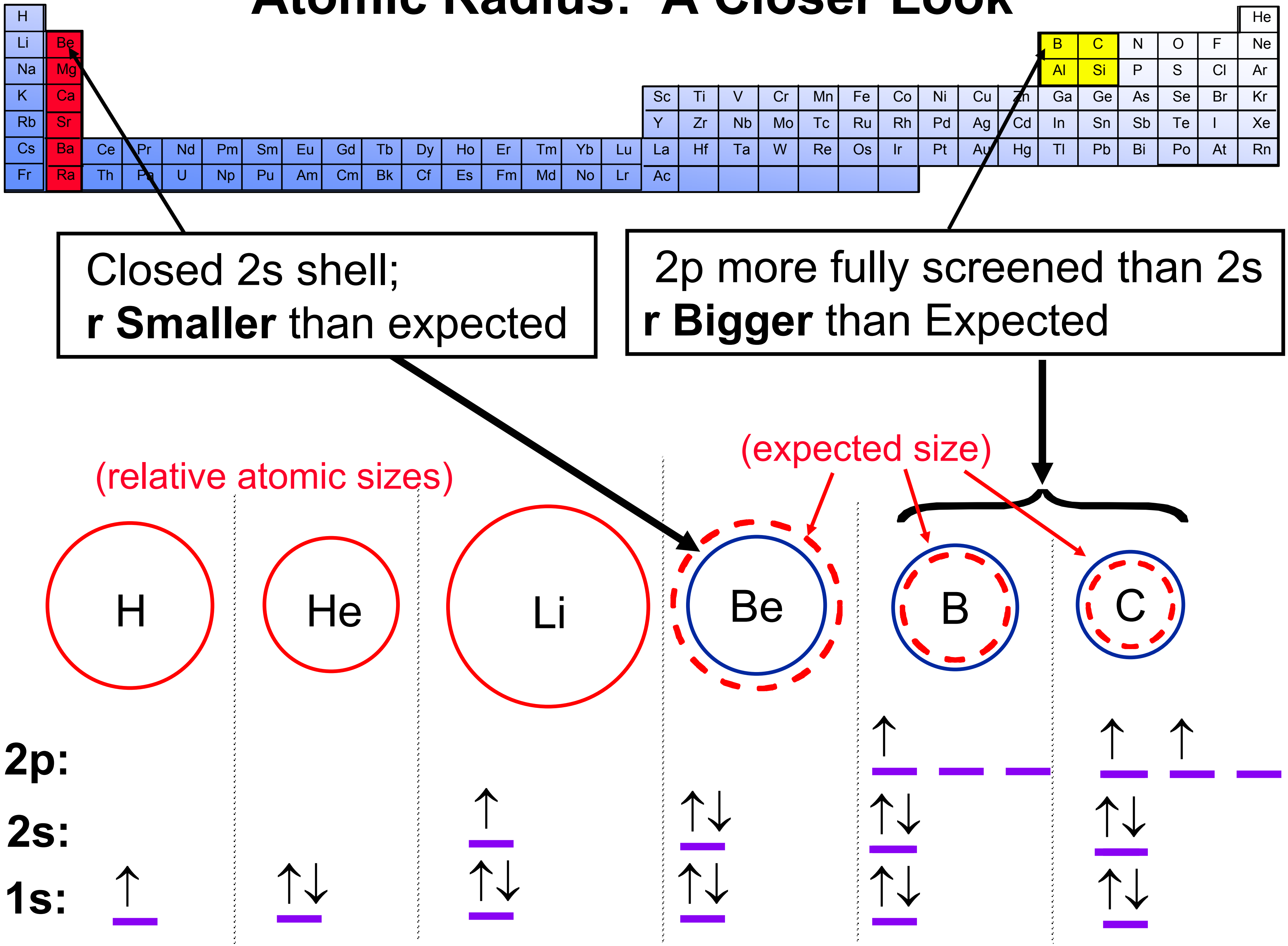
# Atomic Sizes



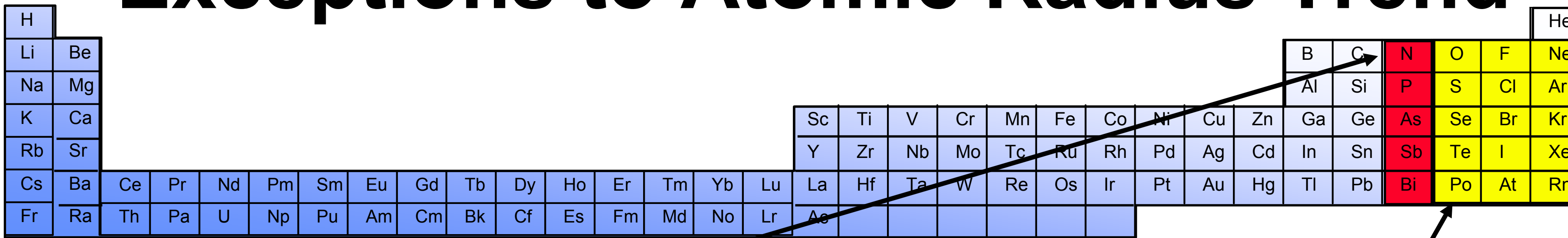
# Solid-State Molar Volumes (3D)



# Atomic Radius: A Closer Look

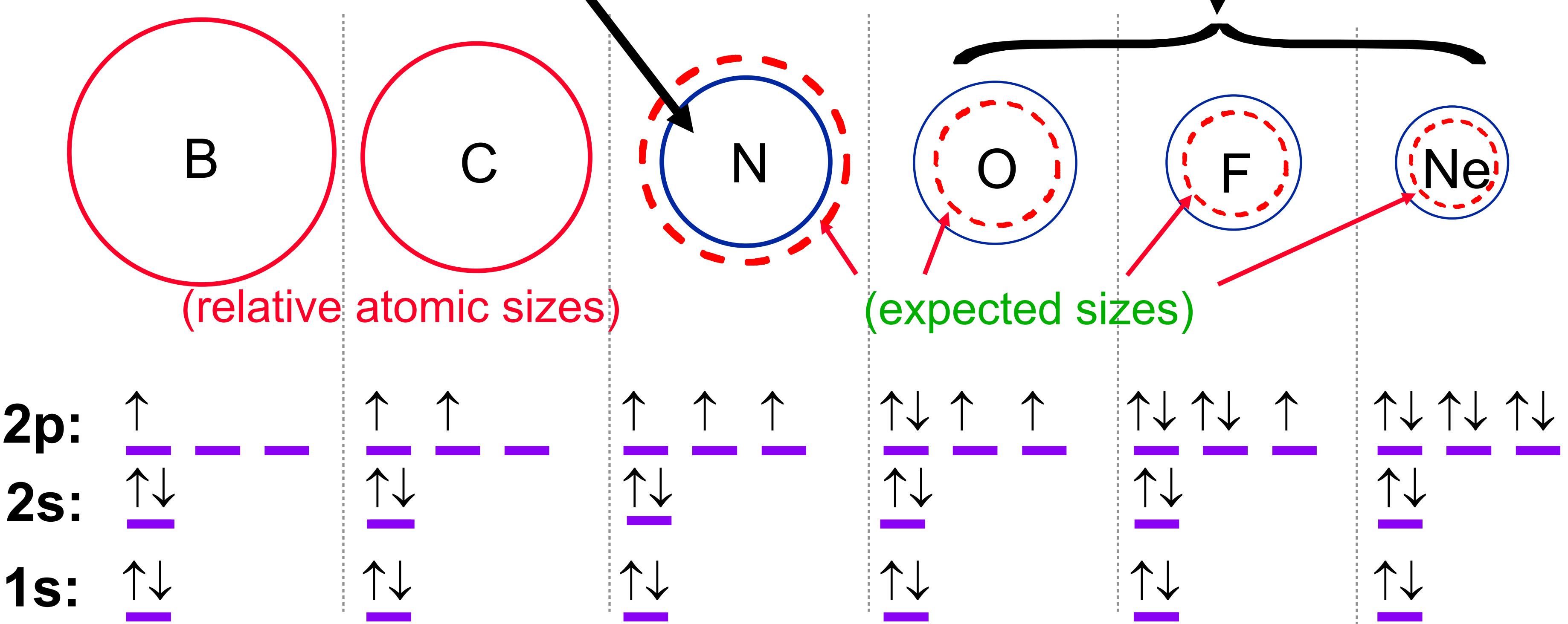


# Exceptions to Atomic Radius Trend

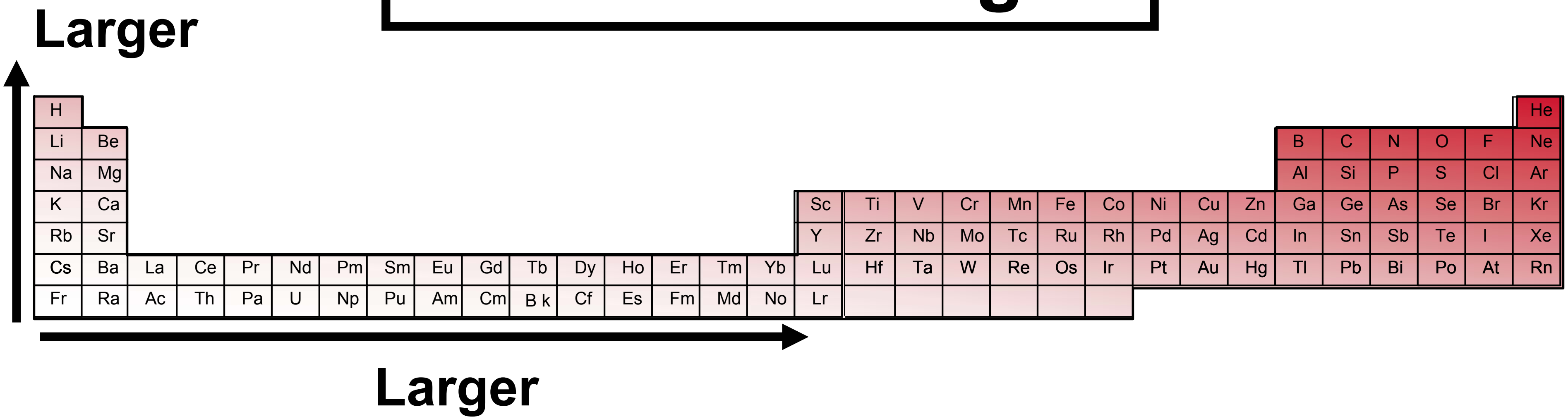


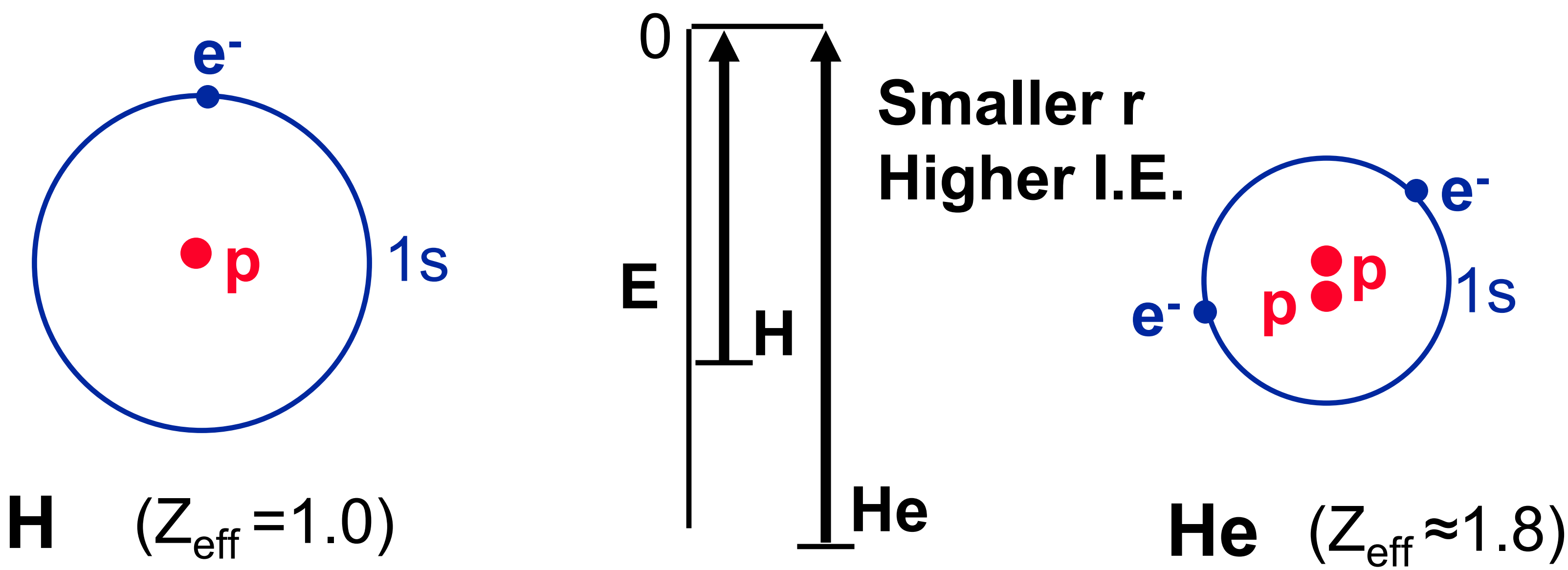

Half-filled p Shell
r **Smaller** Than Expected

Extra Repulsion in 2p set
r **Bigger** Than Expected



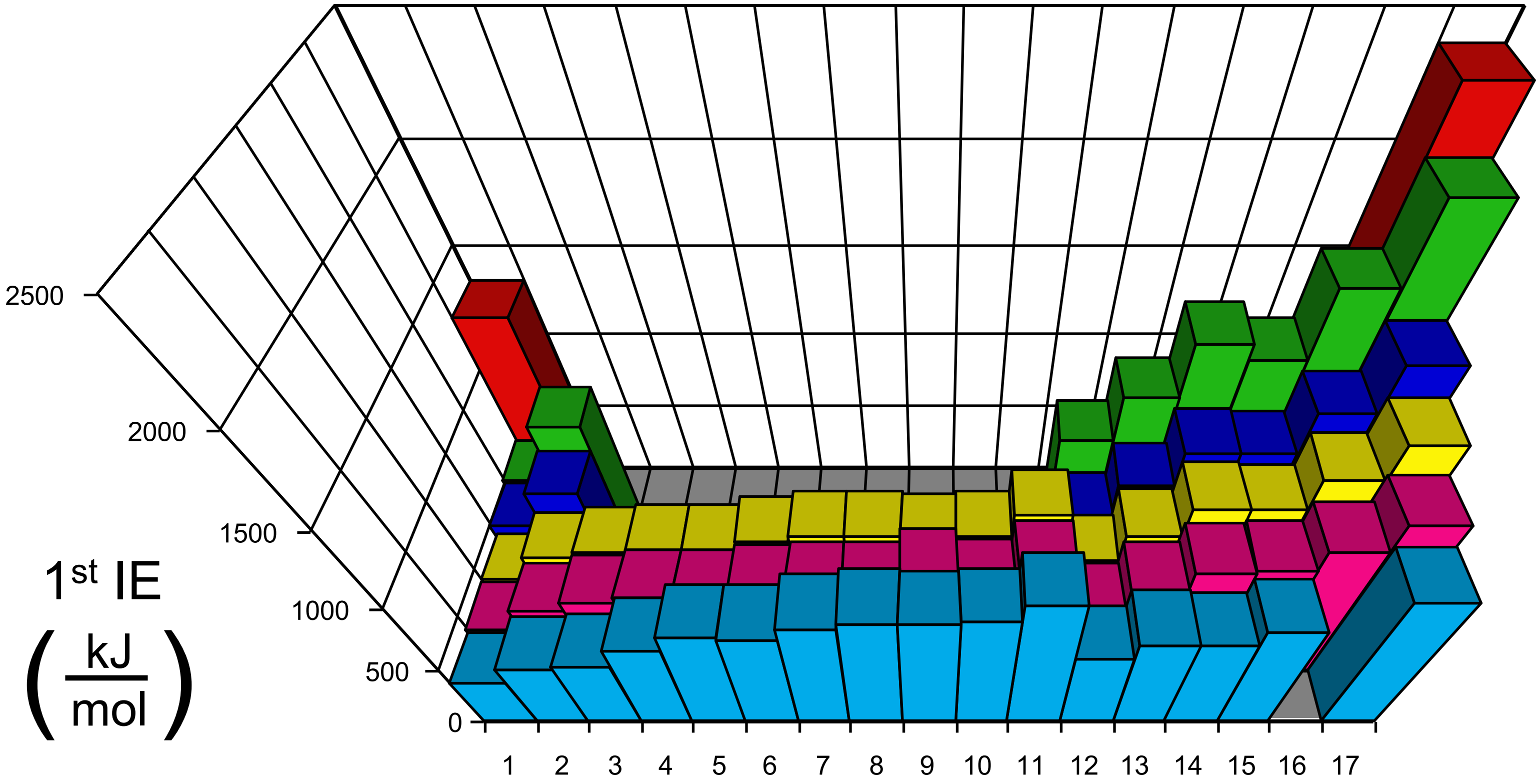
# Ionization Energies



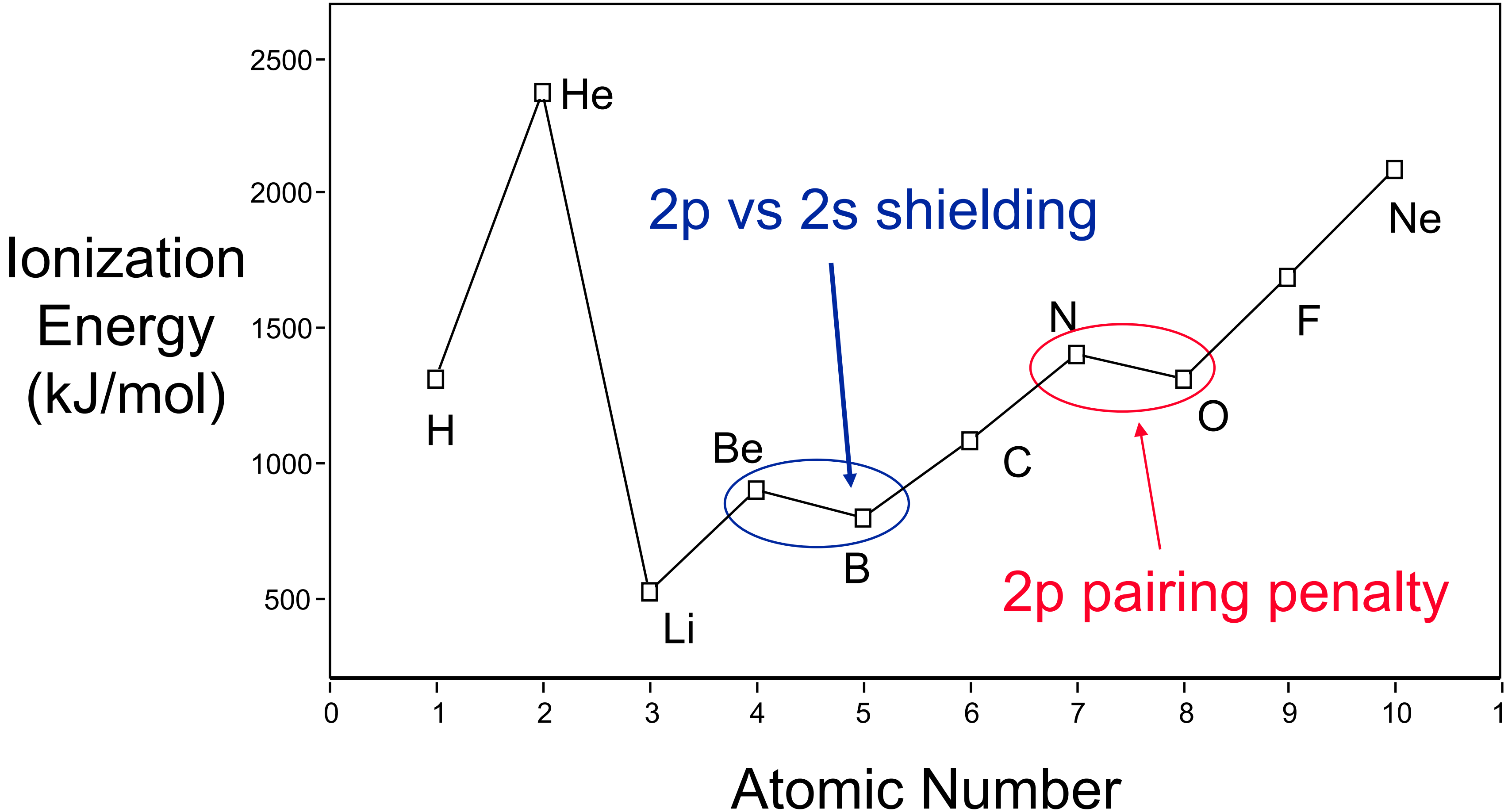




Smaller Atoms ➔ Harder to Remove Electrons

# First Ionization Energy ( 3D )

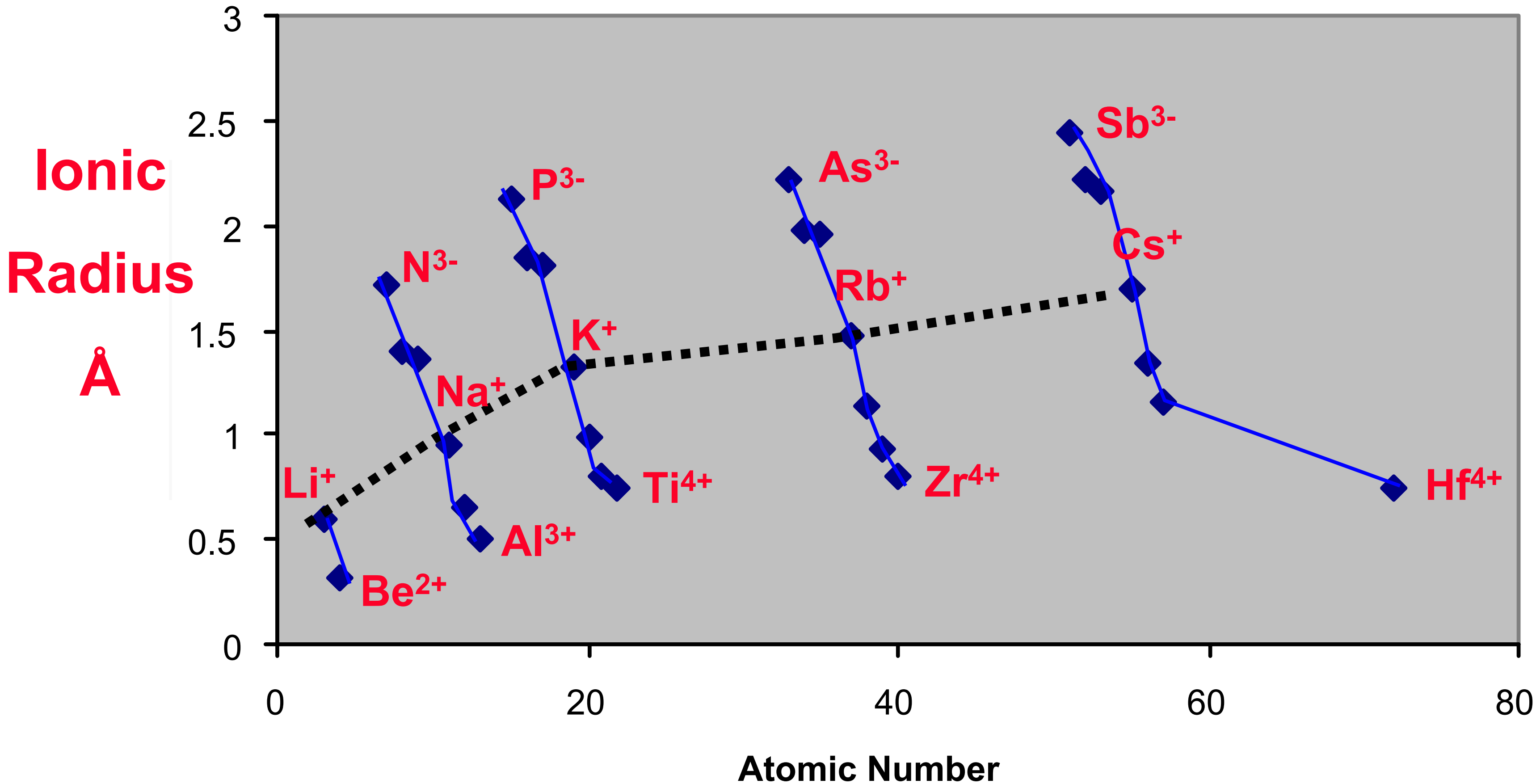


# Details of Ionization Energies




**Smaller r = Higher I.E.**

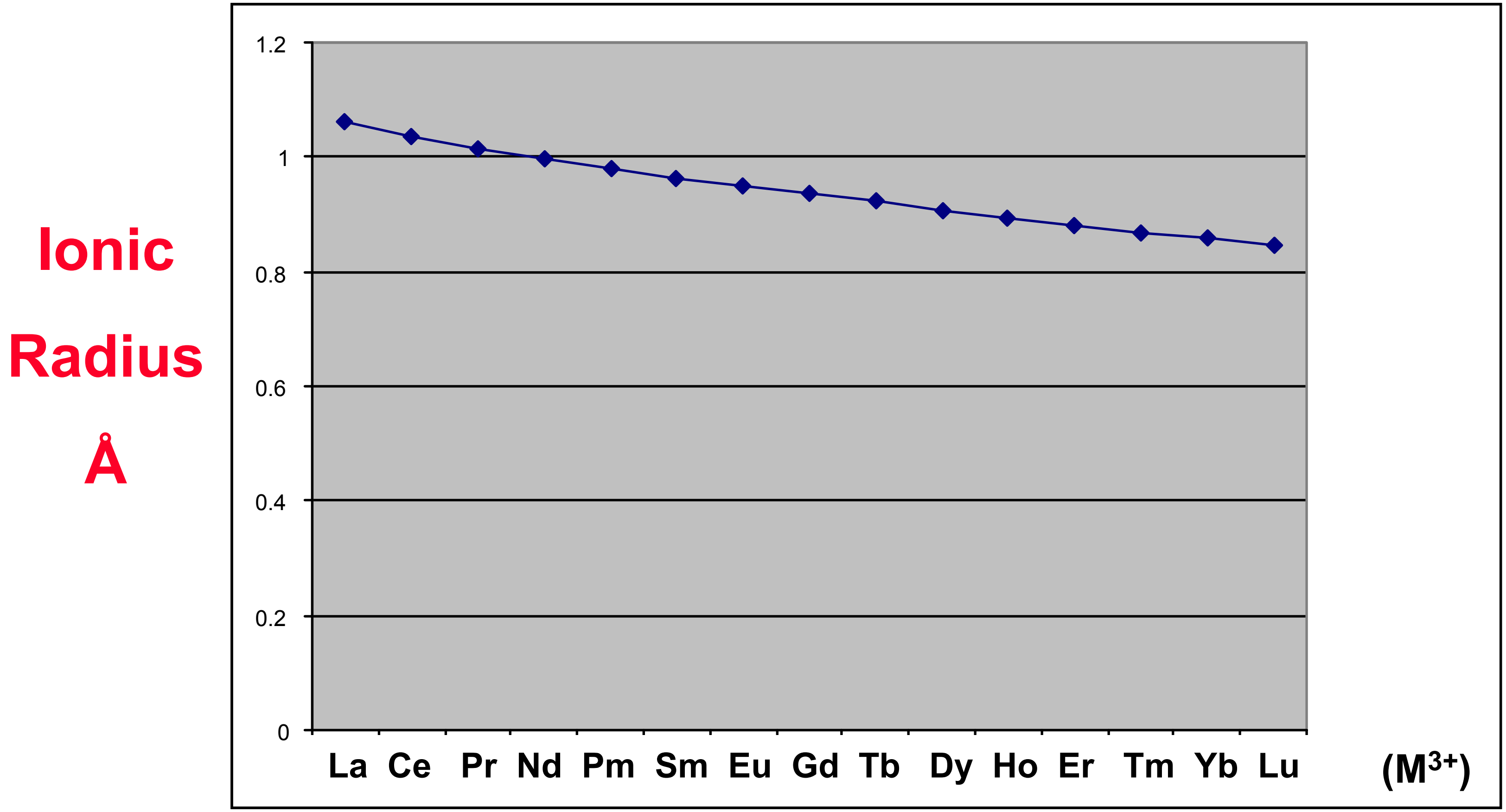
# Ionic Radii




**Radius decreases for isoelectronic atoms as Positive charge increases ( —— )**

**Discontinuity at $K^+$ due to d-orbitals (increased $Z_{eff}$)**

# Lanthanide Contraction

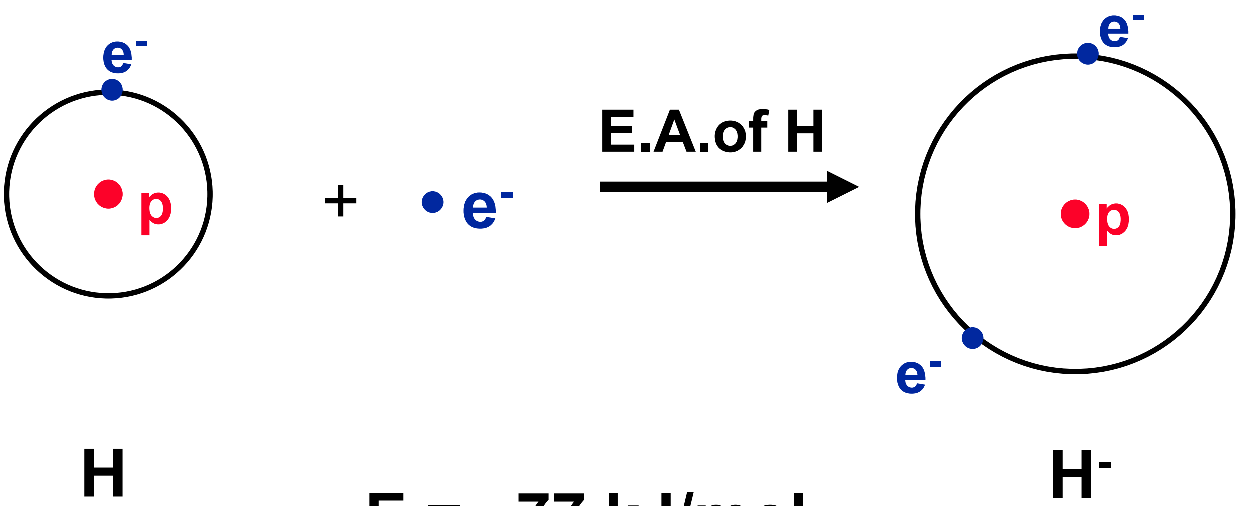



**All are $5s^2 5p^6 4f^{n-1}$**

**Responsible for many features of TM's that follow Lanthanides in periodic table**

# Electron Affinity

**Energy Released By Addition of an Electron to the Element**

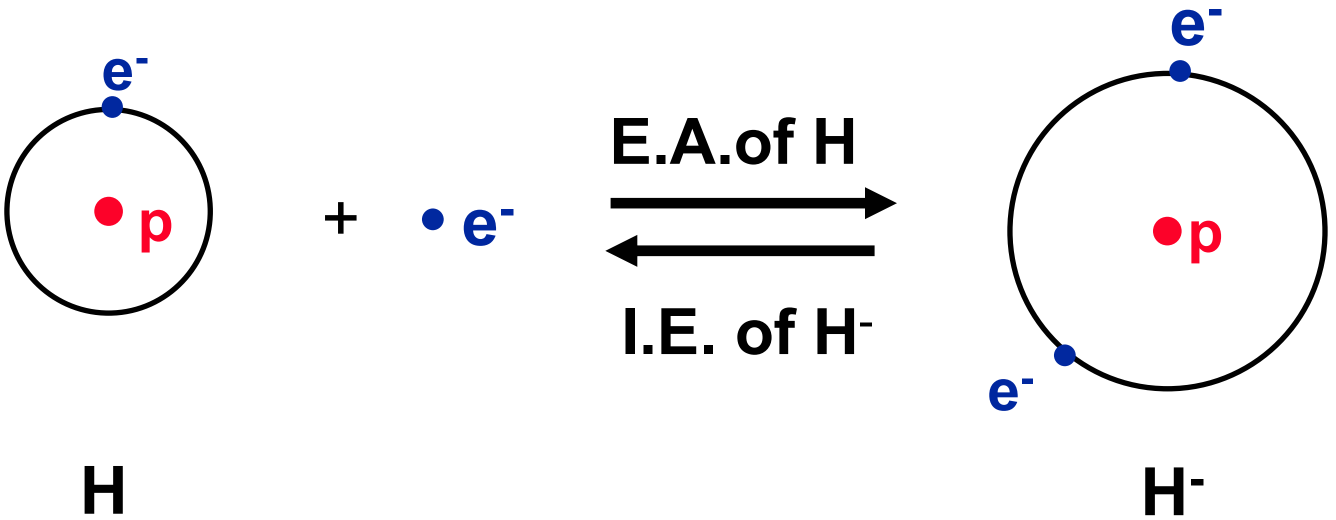



**E = –77 kJ/mol**

**E.A. = 77 kJ/mol**

By Definition, E.A is **Positive** when Energy is **Released**
(Opposite the thermodynamic definition!)

# Electron Affinity vs. Ionization Energy

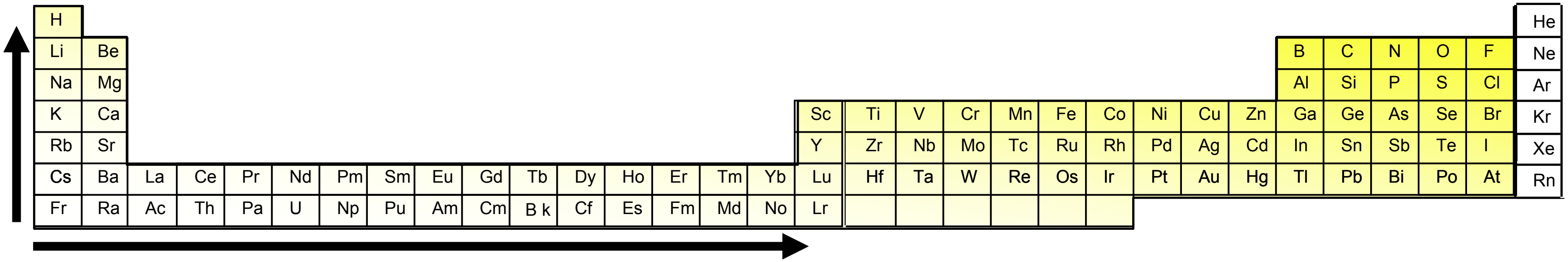



= (+) Electron Affinity of Element X

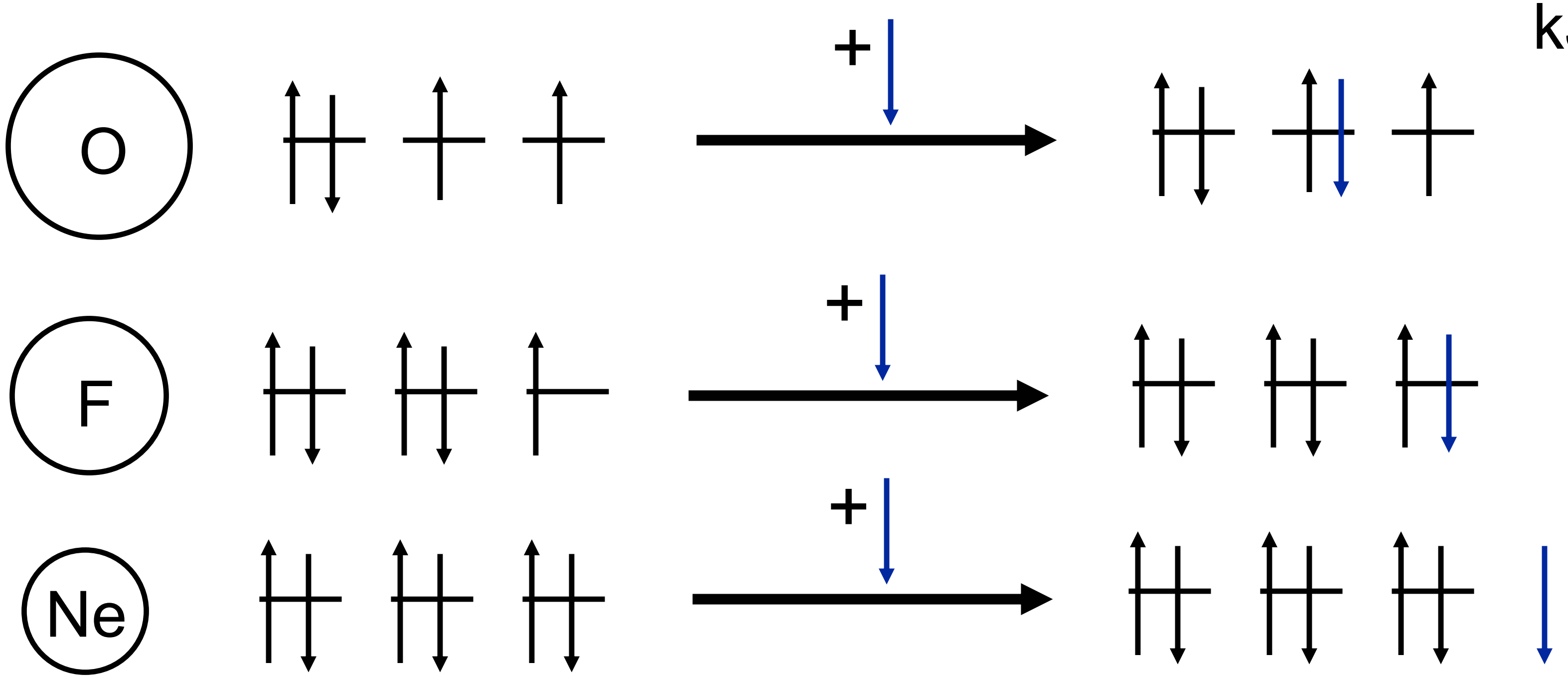
(+) Ionization Energy of Anion $X^-$

# Electron Affinity

Larger

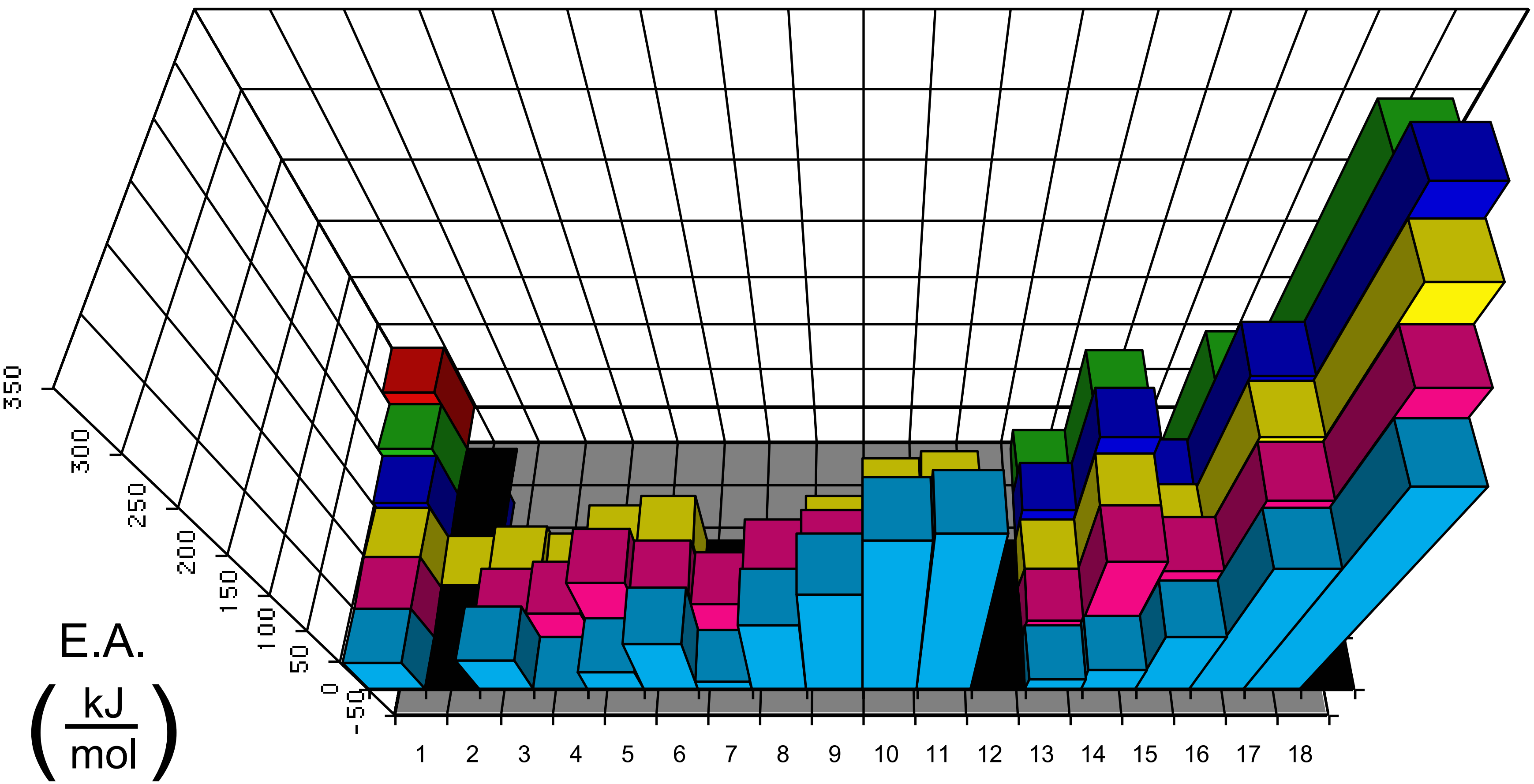



Larger




| | EA kJ/mol |
|---|---|
| O | 142 |
| F | 333 |
| Ne | -29 |

# Electron Affinity (3D)




Note: Black elements have negative EA’s

# Electron Affinity vs. Ionization Energy

## Electron Affinity

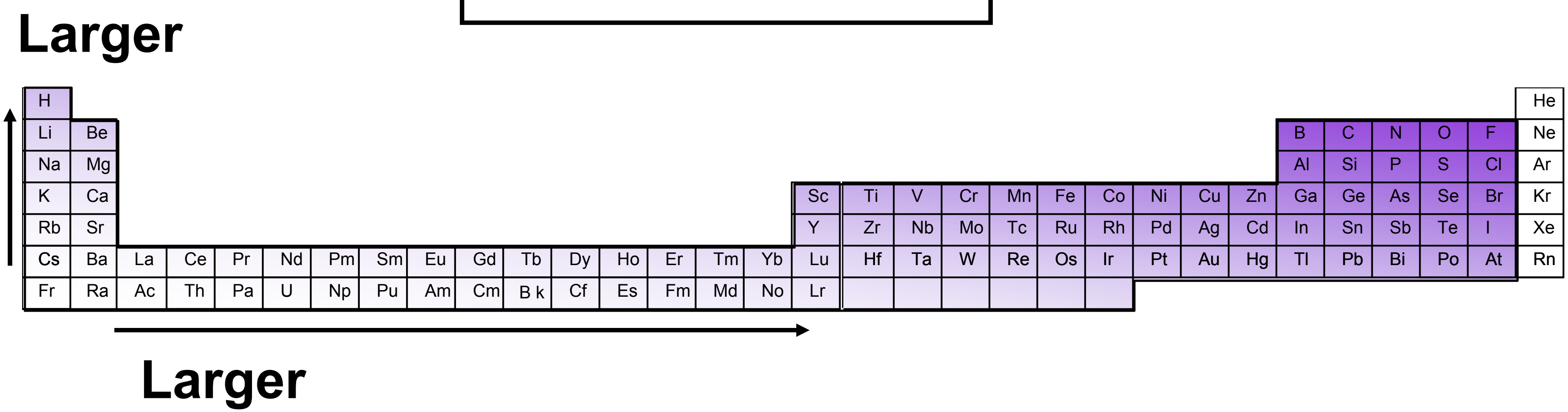
- Can be either + or - in sign
- No atom has a positive 2nd E.A.

## Ionization Energy

- Always Positive
- 2nd I.E.s are always > 1st I.E.'s

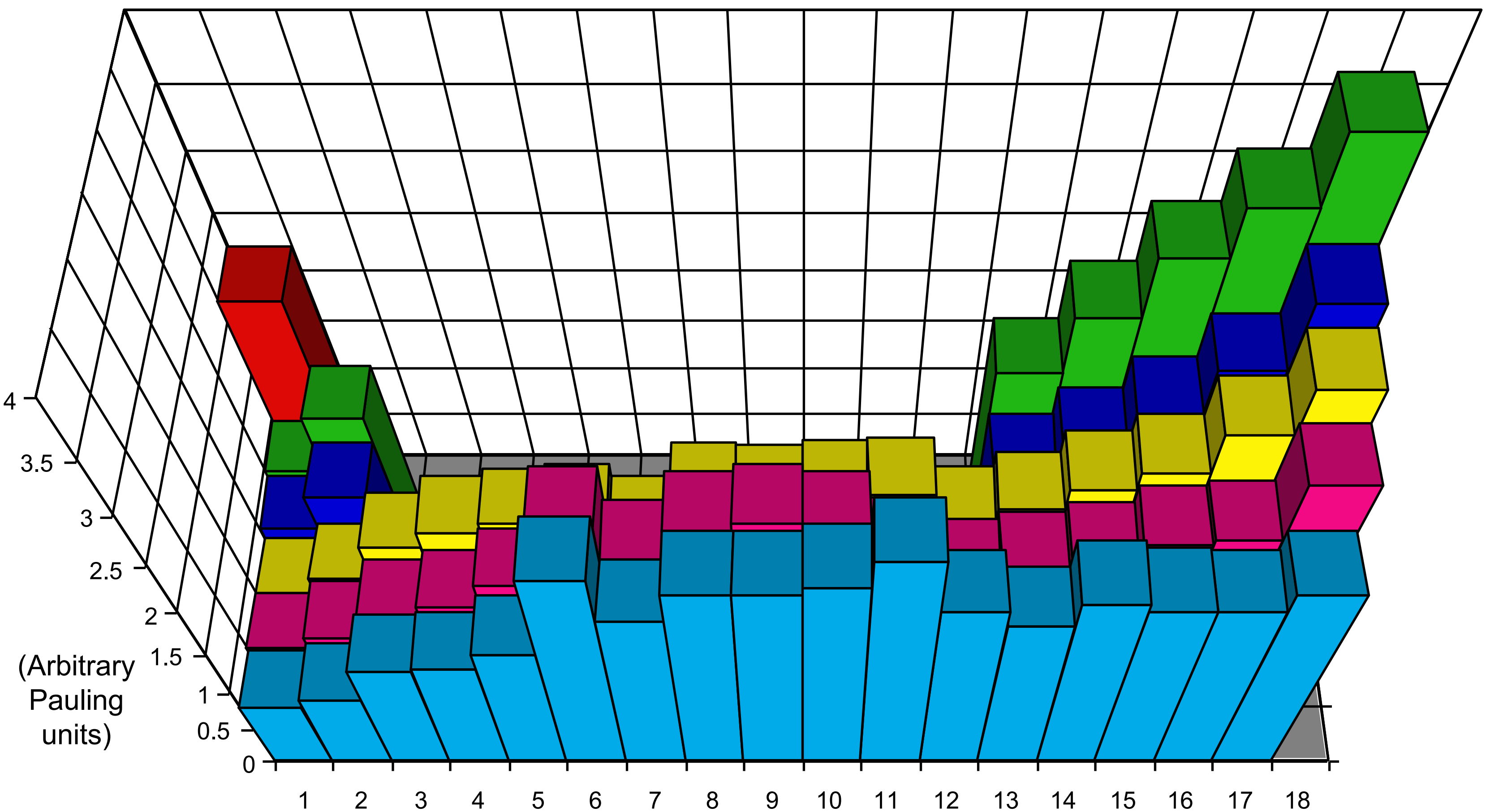
# Electronegativity

$$EN = \frac{\text{I.E.} + \text{E.A.}}{2}$$




**Electronegativity Generally Follows I.E. Trend**

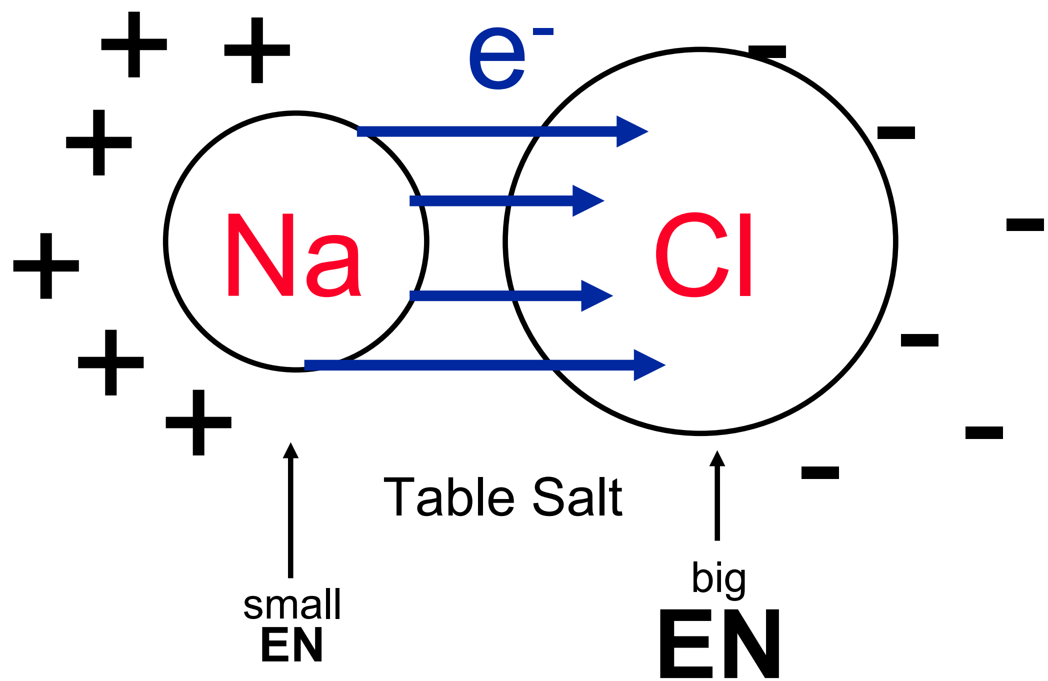
# Electronegativity ( 3D )



# Electronegativity, I.E., and E.A.

- In a bond, the distribution of electrons is determined by how much each atom pulls on its own as well as the other atom's electrons. So electronegativity = I.E. + E.A.

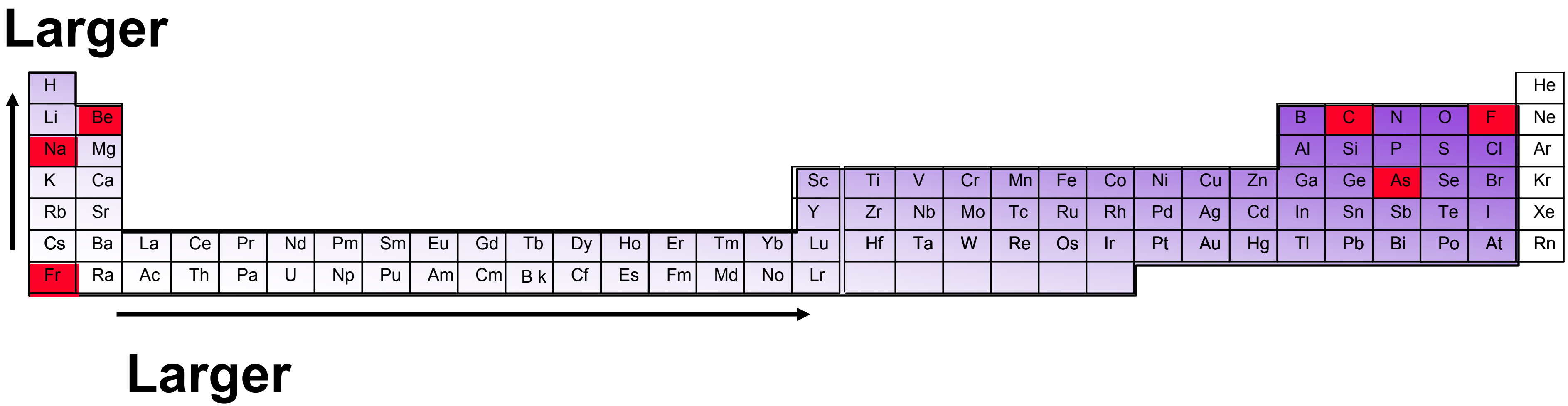
**Example:**




- Na has low E.A. and I.E.
- Cl has high E.A. and I.E.
- Electronegativity = (I.E. + E.A.)/2

**Cl is more electronegative than Na.**

# Some Representative Electronegativities




Electronegativities:

| | |
|---|---|
| Be = 1.6 | C = 2.6 |
| Na = 0.9 | As = 2.2 |
| Fr = 0.7 | F = 4.0 |

- Fluorine has the highest electronegativity, Francium has the lowest E.N.

# Types of Chemical Bonds

## Ionic Bonding

$Na\bullet + Cl\bullet \longrightarrow [Na]^+ \; [:Cl]^-$

Na has Low I.E., low E.A. ➡ Lower EN; loses $e^-$

Cl has High I.E., high E.A. ➡ Higher EN; gains $e^-$

$Li\bullet + H\bullet \longrightarrow [Li]^+ \; [:H]^-$

Li has Low I.E., low E.A. ➡ Lower EN; loses $e^-$

H has High I.E., high E.A. ➡ Higher EN; gains $e^-$

# Types of Chemical Bonds

## Covalent Bonding

$Cl\cdot + Cl\cdot \longrightarrow Cl:Cl = Cl—Cl$

$H\cdot + Br\cdot \longrightarrow H:Br = H—Br$

Electrons Shared ≈ Equally

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**Hydrogen Bonding**: $Cl—H\cdots OH_2$

**Van der Waals Bonding**: $Ar\cdots HCl$

# Now We Can Understand

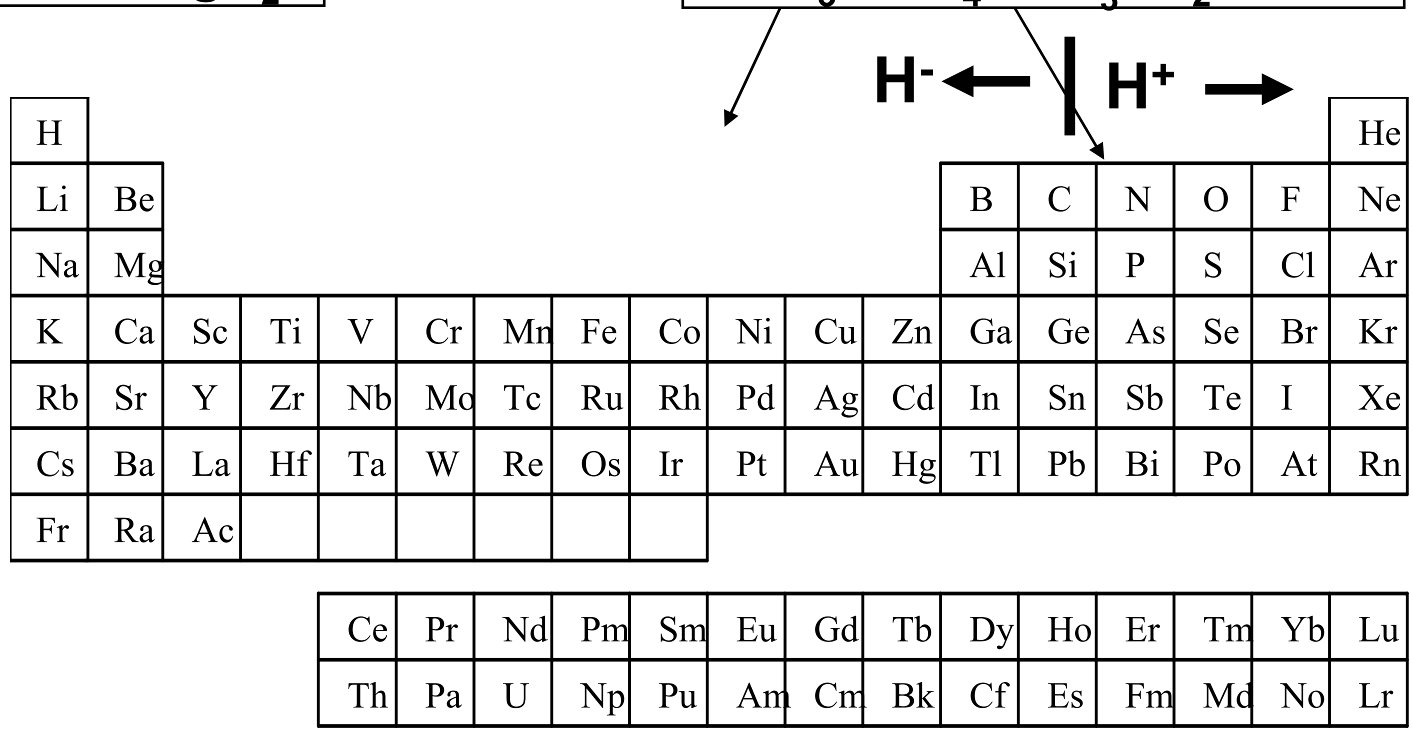
- Arrangement of the Periodic Table of Elements
- Trends in Atomic Size
- Trends in Ionization Energy
- Trends in Electron Affinity
- Trends in Electronegativity
- Various Types of Chemical Bonds
- Combining Ratios of Oxides and Hydrides
- Shapes of Molecules

# Periodic Trends in Bonding

## Stoichiometry of Binary Hydrides

| | |
|---|---|
| LiH | $BeH_2$ |
| NaH | $MgH_2$ |

| | | | | |
|---|---|---|---|---|
| $BH_3$ | $CH_4$ | $NH_3$ | $H_2O$ | HF |
| $AlH_3$ | $SiH_4$ | $PH_3$ | $H_2S$ | HCl |



# Periodic Trends in Bonding

## Stoichiometry of Binary Oxides

$Li_2O$ $BeO$
$Na_2O$ $MgO$

$B_2O_3$ $CO_2$ $N_2O_5$ $O_2$ $OF_2$
$Al_2O_3$ $SiO_2$ $P_2O_5$ $SO_3$ $OCl_2$

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H | | | | | | | | | | | | | | | | | He |
| Li | Be | | | | | | | | | | | B | C | N | O | F | Ne |
| Na | Mg | | | | | | | | | | | Al | Si | P | S | Cl | Ar |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe |
| Cs | Ba | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn |
| Fr | Ra | Ac | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | | |
| | | | | Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |
| | | | | Th | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lr |

**$H_aX_b$ for Hydrides; $O_{a/2}X_b$ (Usually) for Oxides**

# H.M.S. Sheffield Falklands War of 1982

Al normally inert due to formation of tough surface coating of $Al_2O_3$

Al metal burns in air and if hot enough, will form $Al_2O_3$ continuously from $H_2O$

# Acid/Base Properties of Oxides

**Basic**

$Na_2O(s) + H_2O \longrightarrow 2\,Na^+(aq) + 2\,OH^-(aq)$

$BaO(s) + H_2O \longrightarrow Ba^{2+}(aq) + 2\,OH^-(aq)$

**Basic**

$MnO(s) + 2H^+ \longrightarrow Mn^{2+}(aq) + H_2O$

$NiO(s) + 2H^+ \longrightarrow Ni^{2+}(aq) + H_2O$

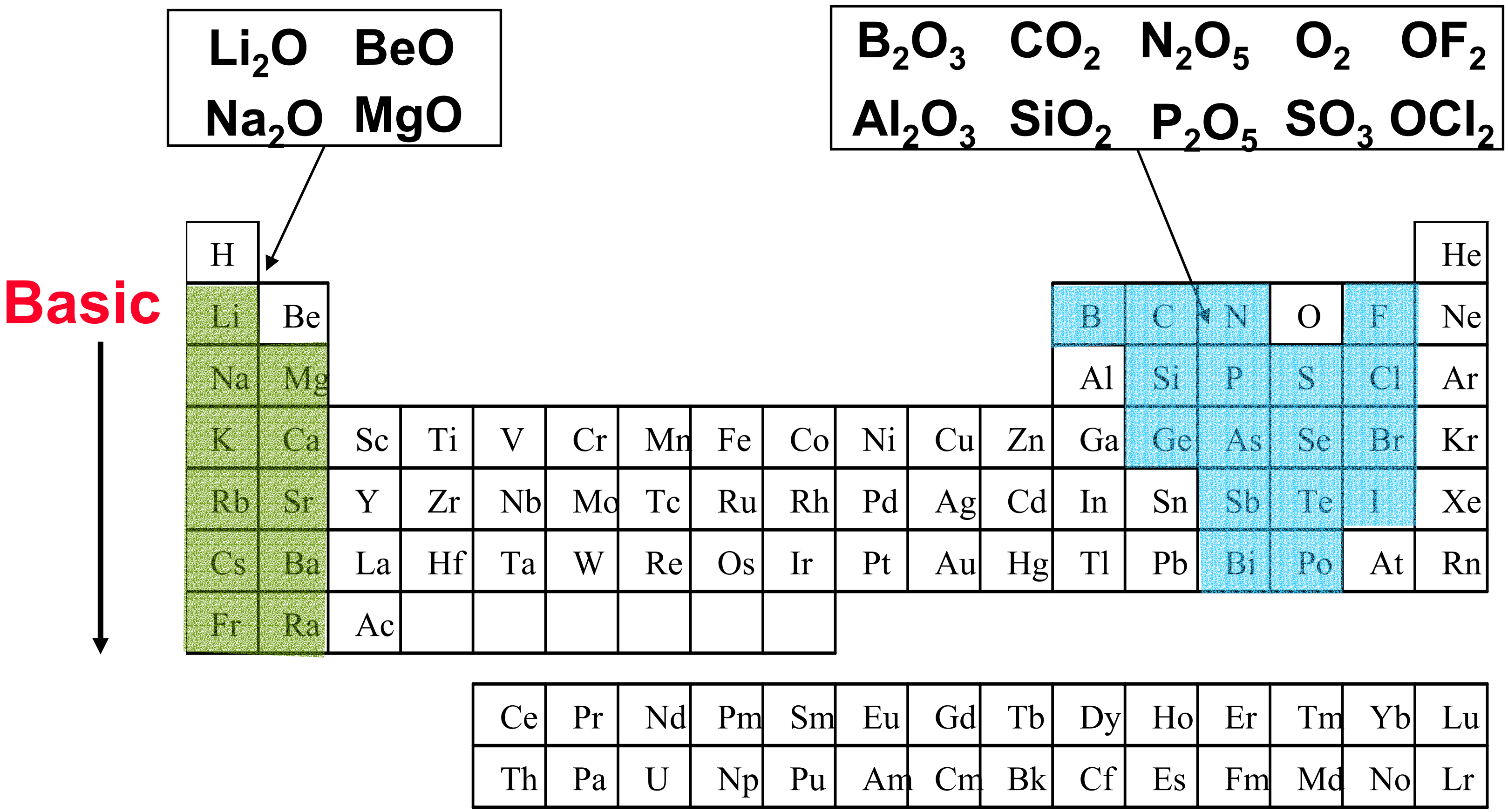
**Acidic**

$SO_3(s) + H_2O \longrightarrow H^+(aq) + HSO_4^-(aq)$

$P_4O_{10}(s) + 6H_2O \longrightarrow 4\,H^+(aq) + 4H_2O\ PO_3^-(aq)$

- Basic oxides have pushed too much electron density Onto O, and it loses it by reacting with $H_2O$ (liberating $OH^-$)
- Acidic oxides have less electron density than they can accomodate, and so grab more O from $H_2O$ (liberating $H^+$)

# Acid/Base Properties of Oxides




**Acidity increases going up and to right**

End

# Trends

## in the

# Periodic Table

Reading: Gray: (2-2) to (2-4) and (2-9)
OGN: (3.1), (15.8) and (15.9)