

Chemical Principles

3. Electronic Structures and Properties of Atom

Review - A particle confined in a box

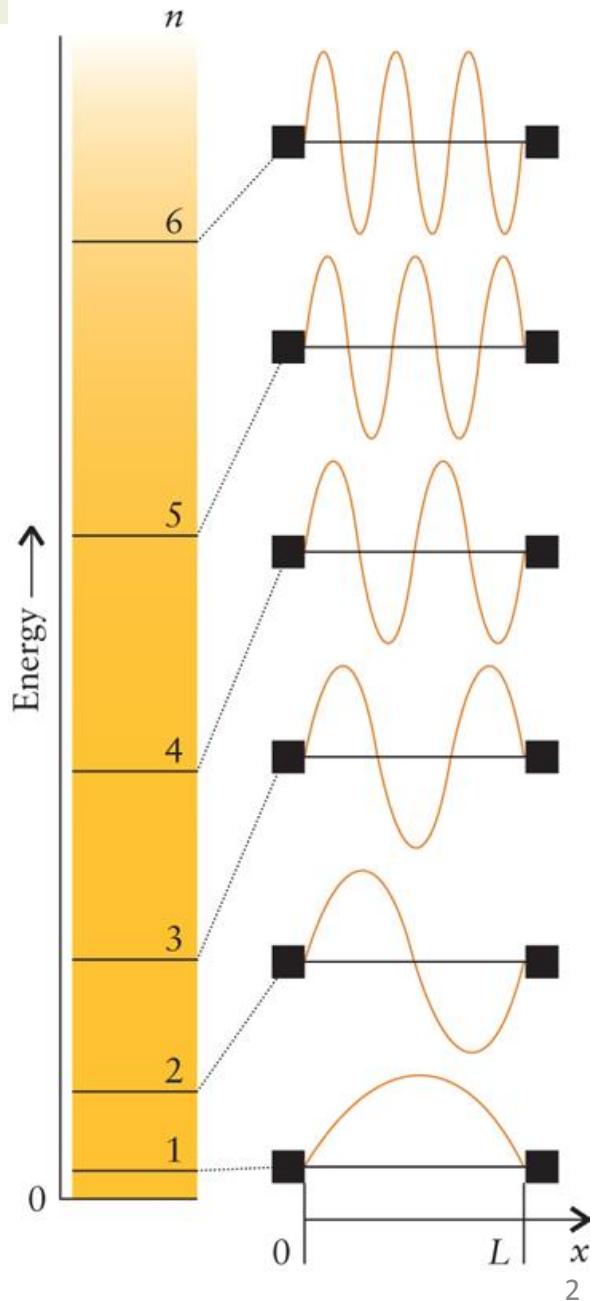
We have seen in one-dimension the wave function and energy are:

$$E_n = \frac{n^2 h^2}{8mL^2}$$

$$\psi_n(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right) \quad n = 1, 2, \dots$$

Both depend on the quantum number ($n = 1, 2, 3, \dots$), which is required because the wave function must be zero at boundaries ($x=0$ and $x=L$)

There are $(n-1)$ nodes in the wave function. The more nodes, the higher energy.

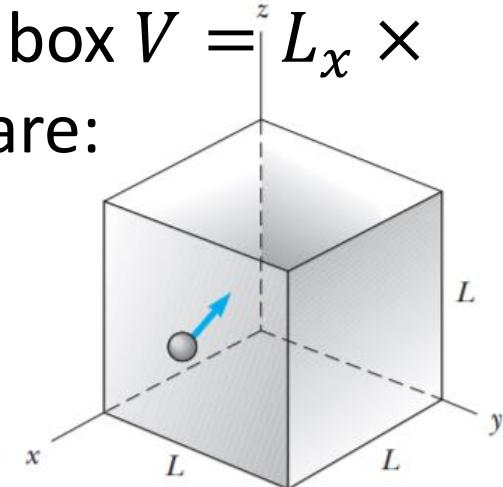


Review - A particle confined in a box

- For three-dimension box, the volume of box $V = L_x \times L_y \times L_z$, the energy and wave-function are:

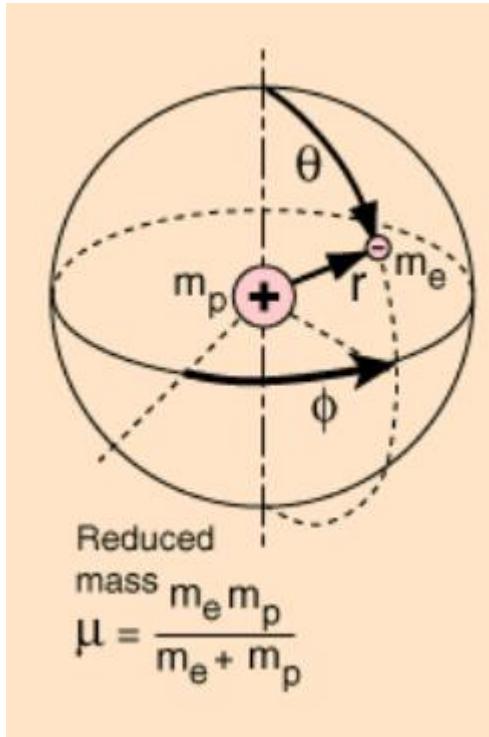
$$E_{n_x, n_y, n_z} = \frac{h^2}{8m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$$

$$\psi(r) = \sqrt{\frac{8}{V}} \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right) \sin\left(\frac{n_z \pi z}{L_z}\right)$$



- There are three quantum numbers, n_x , n_y , and n_z . The wave-function and energy depend on the three quantum numbers
- Different wave-functions (states) may have the same energy – **degeneracy**. For example, $(n_x, n_y, n_z) = (2,1,1)$, $(1,2,1)$, $(1,1,2)$ have the same energy for a particle in cubic box ($L_x = L_y = L_z$), but distribute differently in the space.

Solution for Hydrogen Atom



spherical coordinate

The only potential is between the electron and nuclear along the radial,

$$U(r) = \frac{-e^2}{4\pi\epsilon_0 r}$$

It is best to use the spherical coordinate system in which the Schrödinger equation becomes

$$\frac{-\hbar^2}{2\mu} \frac{1}{r^2 \sin\theta} \left[\sin\theta \frac{\partial}{\partial r} \left(r^2 \frac{\partial\Psi}{\partial r} \right) + \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial\Psi}{\partial\theta} \right) + \frac{1}{\sin\theta} \frac{\partial^2\Psi}{\partial\phi^2} \right] + U(r)\Psi(r,\theta,\phi) = E\Psi(r,\theta,\phi)$$

Solution for Hydrogen Atom

The wave-function is in three variables, given in two terms: a radial term $R_{n,l}(r)$ and an angle term $Y_{l,m_l}(\theta, \phi)$. There are three quantum numbers (n, m, m_l) in the wave-function.

$$\psi_{n,l,m_l}(r, \theta, \phi) = NR_{n,l}(r)Y_{l,m_l}(\theta, \phi)$$

$$n = 1, 2, \dots$$

$$l = 0, 1, 2, \dots, n - 1$$

$$m_l = l, l - 1, \dots, -l$$

The energy is

$$E_n = \frac{-me^4}{8\epsilon_0^2 h^2} \frac{1}{n^2} = \frac{-13.6eV}{n^2} \quad n = 1, 2, 3, \dots$$

Which depends on one quantum number ($n = 1, 2, 3 \dots$) only.

Solution for Hydrogen Atom - Energy

The energy matches the hydrogen spectra, and the **Rydberg** constant is obtained:

$$\nu_{ij} = \mathcal{R} \left(\frac{1}{n_i^2} - \frac{1}{n_j^2} \right)$$

As the energy levels are given by

$$E_n = \frac{-me^4}{8\epsilon_0^2 h^2} \frac{1}{n^2} = \frac{-13.6eV}{n^2} \quad n = 1, 2, 3, \dots$$

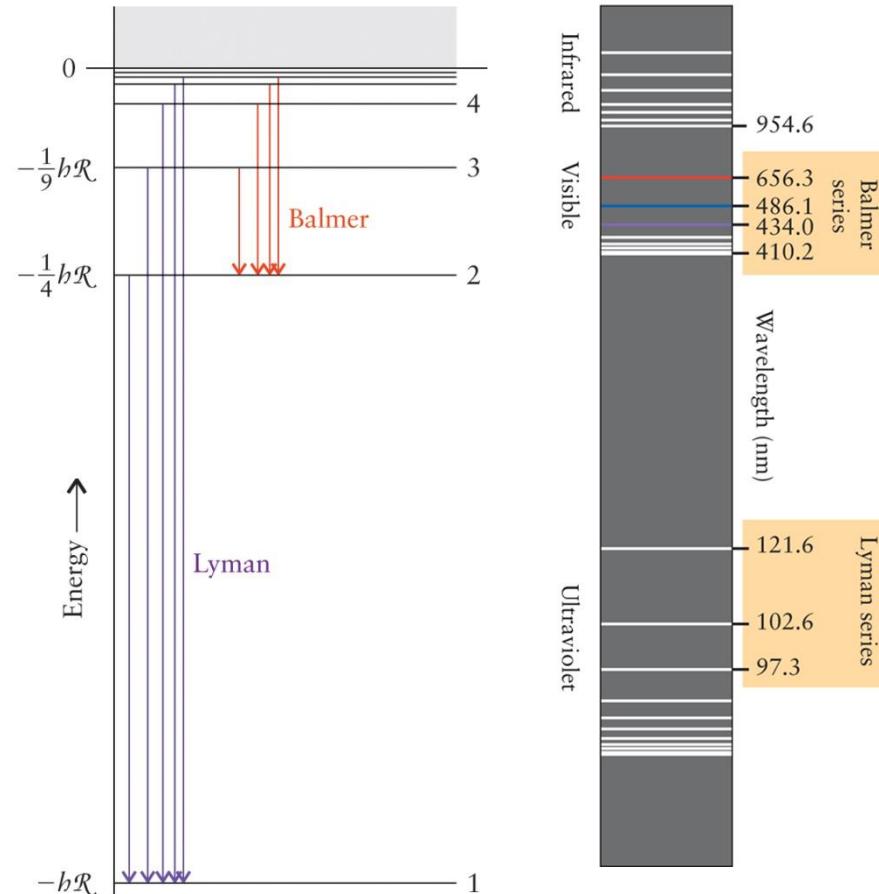


FIGURE 2.1 The permitted energy levels of a hydrogen atom as calculated from Eq. 2. The levels are labeled with the quantum number n , which ranges from 1 (for the lowest state) to infinity (for the separated proton and electron).

Solution for Hydrogen Atom - functions

The radial and angle terms are associated with the three quantum numbers.

TABLE 2.1 Hydrogenlike Wavefunctions* (Atomic Orbitals), $\psi = RY$

(a) Radial wavefunctions			(b) Angular wavefunctions		
n	l	$R_{nl}(r)$	l	$“m_l”^\dagger$	$Y_{lm_l}(\theta, \phi)$
1	0	$2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$	0	0	$\left(\frac{1}{4\pi}\right)^{1/2}$
2	0	$\frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2 - \frac{Zr}{a_0}\right)e^{-Zr/2a_0}$	1	x	$\left(\frac{3}{4\pi}\right)^{1/2} \sin \theta \cos \phi$
2	1	$\frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)e^{-Zr/2a_0}$	1	y	$\left(\frac{3}{4\pi}\right)^{1/2} \sin \theta \sin \phi$
3	0	$\frac{2}{9\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2}\left(3 - \frac{2Zr}{a_0} + \frac{2Z^2r^2}{9a_0^2}\right)e^{-Zr/3a_0}$	1	z	$\left(\frac{3}{4\pi}\right)^{1/2} \cos \theta$
3	1	$\frac{2}{9\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2 - \frac{Zr}{3a_0}\right)e^{-Zr/3a_0}$	2	xy	$\left(\frac{15}{16\pi}\right)^{1/2} \sin^2 \theta \sin 2\phi$
3	2	$\frac{4}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}$	2	yz	$\left(\frac{15}{4\pi}\right)^{1/2} \cos \theta \sin \theta \sin \phi$
			2	zx	$\left(\frac{15}{4\pi}\right)^{1/2} \cos \theta \sin \theta \cos \phi$
			2	$x^2 - y^2$	$\left(\frac{15}{16\pi}\right)^{1/2} \sin^2 \theta \cos 2\phi$
			2	z^2	$\left(\frac{5}{16\pi}\right)^{1/2} (3 \cos^2 \theta - 1)$

*Note: In each case, $a_0 = \epsilon_0 h^2 / \pi m_e e^2$, or close to 52.9 pm; for hydrogen itself, $Z = 1$.

†In all cases except $m_l = 0$, the orbitals are sums and differences of orbitals with specific values of m_l .

The quantum numbers

The three quantum numbers:

- $n = 1, 2, 3\dots$ is called **principle QN**. It represents a **shell**, denoted by the value.
- $l = 0, 1, \dots (n-1)$ is called **orbital angular momentum QN**. It represents a **subshell**, denoted by **s, p, d, f...**
- $m_l = (-l, -(l-1), \dots, 0, \dots (l-1), l$ is called **magnetic QN**. It represents an **orbital** in different orientation (e.g. p_x, p_y, p_z).

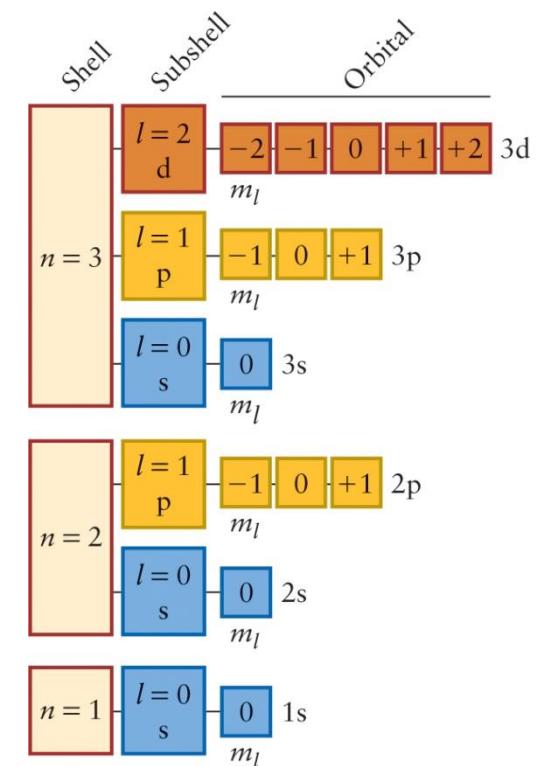


FIGURE 2.3 A summary of the arrangement of shells, subshells, and orbitals in an atom and the corresponding quantum numbers. Note that the quantum number m_l is an alternative label for the individual orbitals: in chemistry, it is more common to use x, y , and z instead, as shown in Figs. 2.9 through 2.11.

The wave-function of 1s

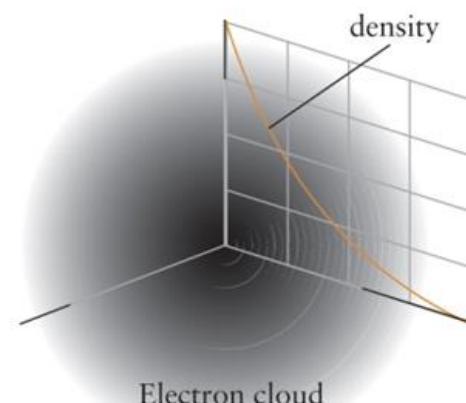
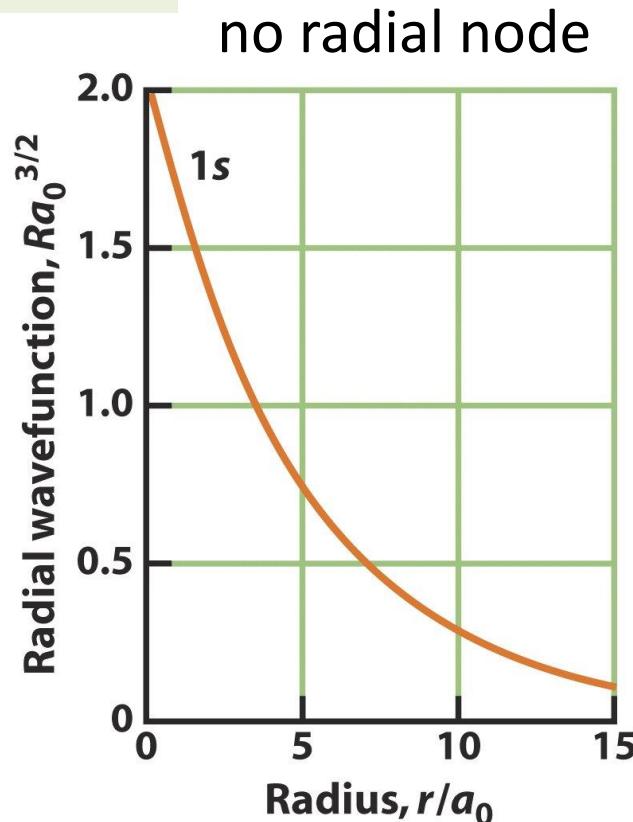
When $n = 1$ and $l = 0$, the radial function is

$$2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$$

We can draw it along the radial in Bohr length.

Since $l = 0$, the angle term is a constant

$$Y_{lm_l}(\theta, \phi) = \left(\frac{1}{4\pi}\right)^{1/2}$$

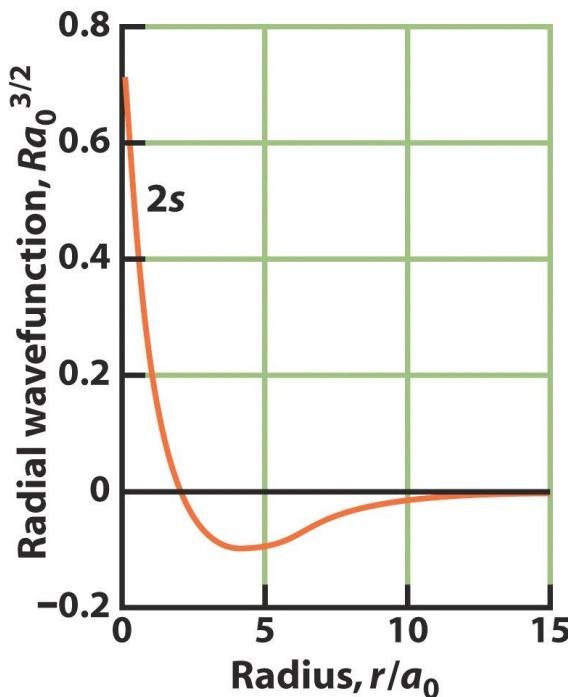


The wave-function of 2s and 3s

$n = 2, l = 0$

1 radial node

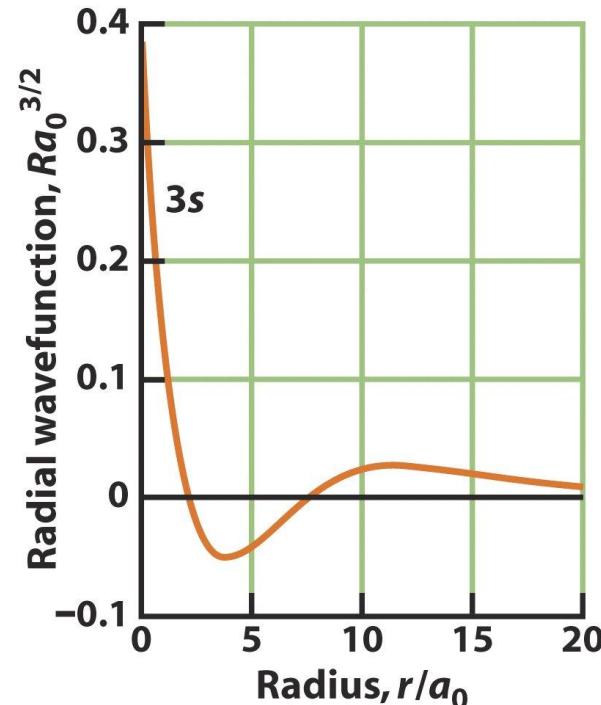
$$\frac{1}{2\sqrt{2}} \left(\frac{Z}{a_0}\right)^{3/2} \left(2 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0}$$



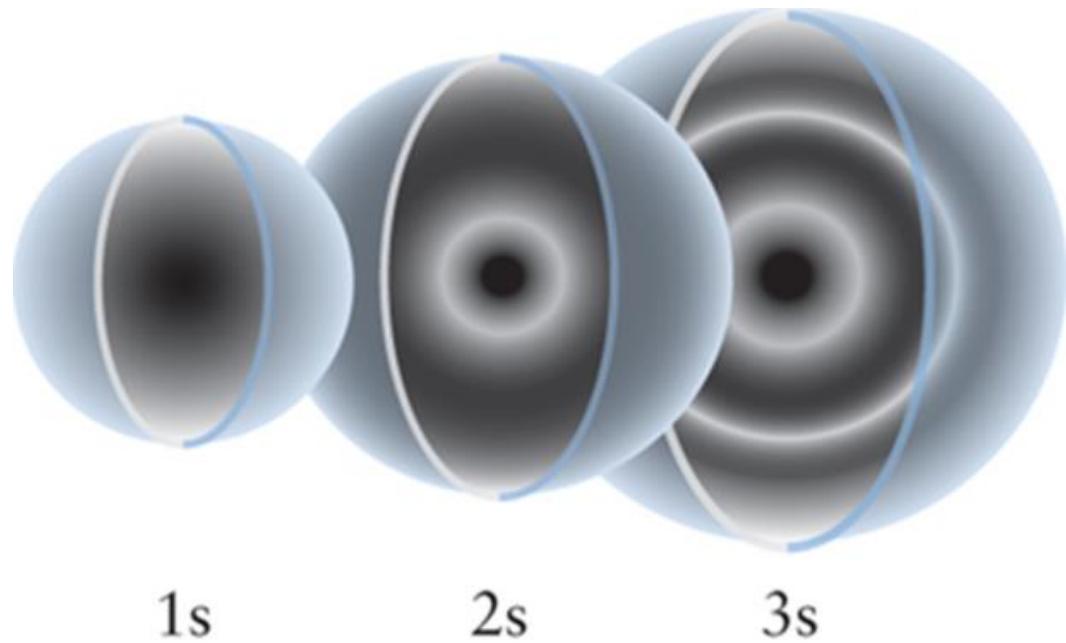
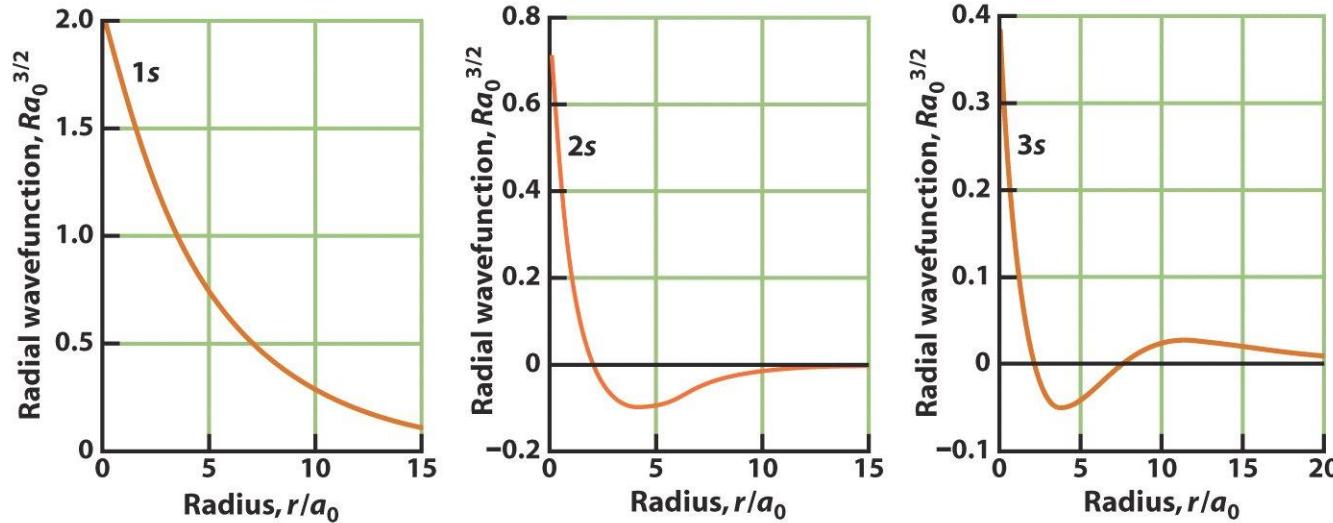
$n = 3, l = 0$

2 radial nodes

$$\frac{2}{9\sqrt{3}} \left(\frac{Z}{a_0}\right)^{3/2} \left(3 - \frac{2Zr}{a_0} + \frac{2Z^2r^2}{9a_0^2}\right) e^{-Zr/3a_0}$$



Comparison of 1s, 2s, and 3s



The p -orbitals

As $l = 1$, the angle function has three terms depending on m_l

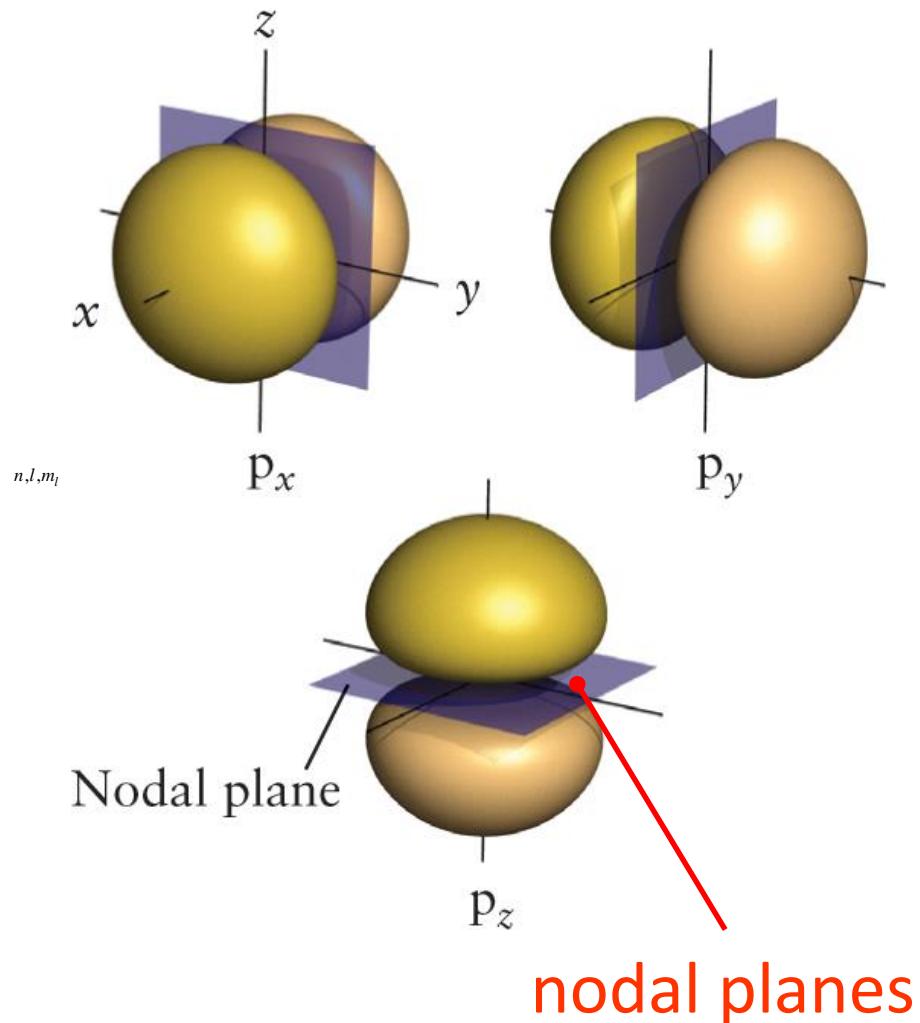
$$\left(\frac{3}{4\pi}\right)^{1/2} \sin \theta \cos \phi$$

$$\left(\frac{3}{4\pi}\right)^{1/2} \sin \theta \sin \phi$$

$$\left(\frac{3}{4\pi}\right)^{1/2} \cos \theta$$

The labels “x”, “y”, and “z” denote m_l values (+1, 0, -1).

There is a nodal plane on each function.



The radial part of p -orbitals

As $l = 1$, the principle QN can be 2, 3, ...

$n=2, l=1$, the radial function has no node:

$$2 \quad 1 \quad \frac{1}{2\sqrt{6}} \left(\frac{Z}{a_0} \right)^{3/2} \left(\frac{Zr}{a_0} \right) e^{-Zr/2a_0}$$

$n=3, l=1$, the radial function has one node:

$$3 \quad 1 \quad \frac{2}{9\sqrt{6}} \left(\frac{Z}{a_0} \right)^{3/2} \left(2 - \frac{Zr}{3a_0} \right) e^{-Zr/3a_0}$$

One less node than the s-orbital

The complete function of 2p_z

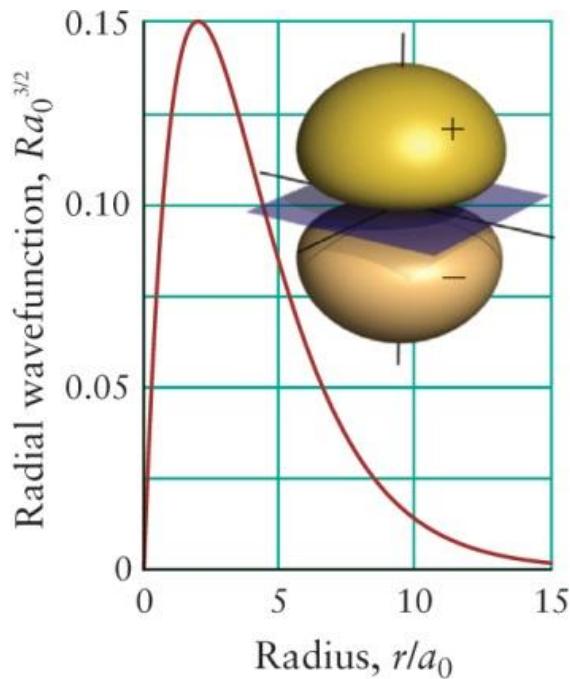
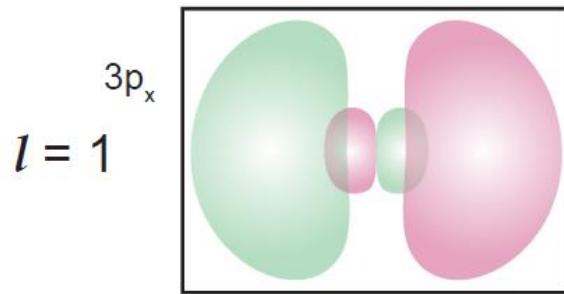
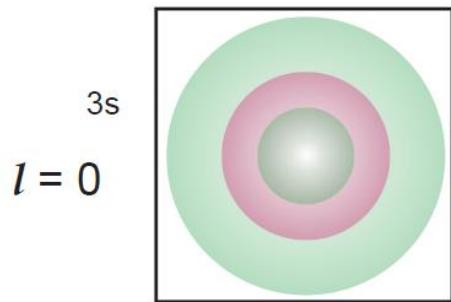


FIGURE 2.8 The boundary surface and the radial variation of a 2p-orbital along the (vertical) z-axis. All p-orbitals have boundary surfaces with similar shapes, including one nodal plane. Note that the orbital has opposite signs (as depicted by the different colors) on each side of the nodal plane.

$$\frac{1}{2\sqrt{6}} \left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right) e^{-Zr/2a_0} \left(\frac{3}{4\pi}\right)^{1/2} \cos \theta$$

- It has one planar node
- There is no node inside of the “ball”

Comparison of 3s and 3p_x



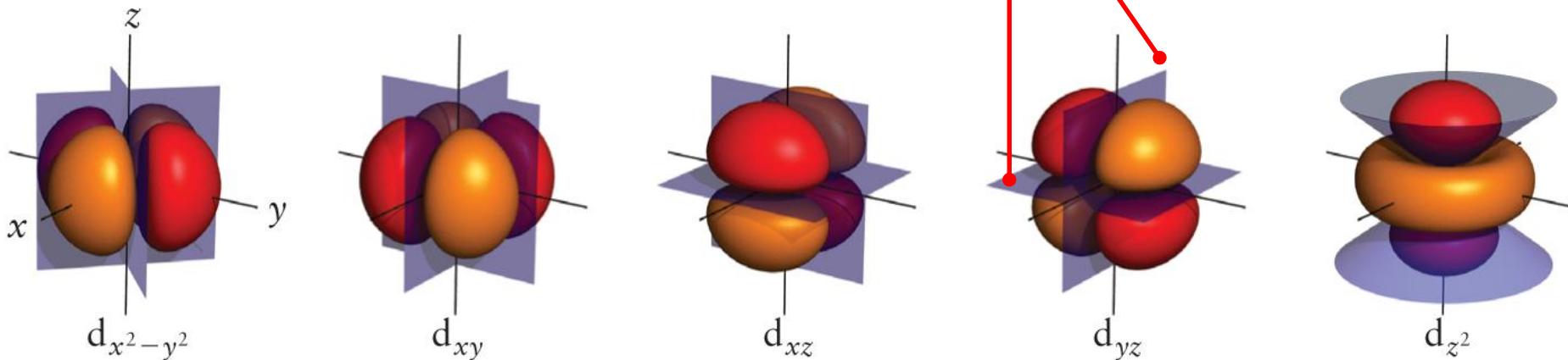
3s has two radial nodes

2px has one planar node and one radial node

The d-orbitals

$n = 3, 4, \dots; l = 2$

$ml = +2, +1, 0, -1, -2$; five d-orbitals



Be careful that the radial term has one-less node than that of the p-orbitals, for example, 3d has no radial node.

3

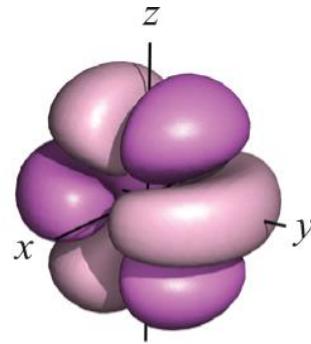
2

$$\frac{4}{81\sqrt{30}} \left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}$$

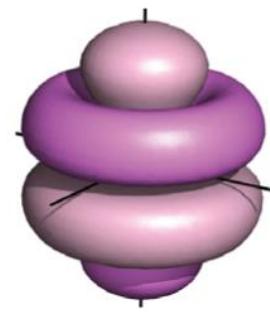
The f-orbitals

$n = 4, 5, \dots; l = 3$

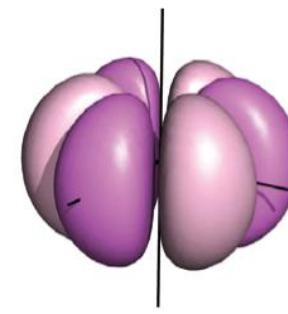
$ml = +3, +2, +1, 0, -1, -2, -3$; seven orbitals



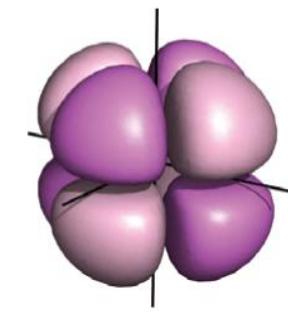
$f_{5yz^2-yr^2}$



$f_{5z^3-3zr^2}$

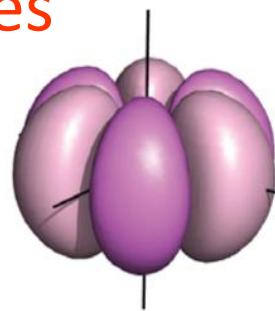


$f_{x^3-3xy^2}$

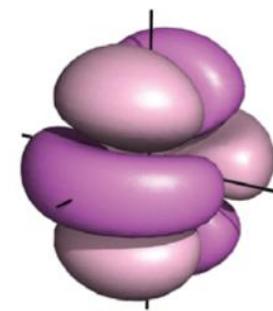


$f_{zx^2-zy^2}$

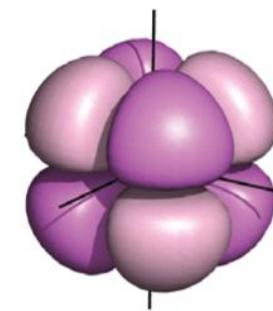
3 nodal planes



$f_{y^3-3yx^2}$



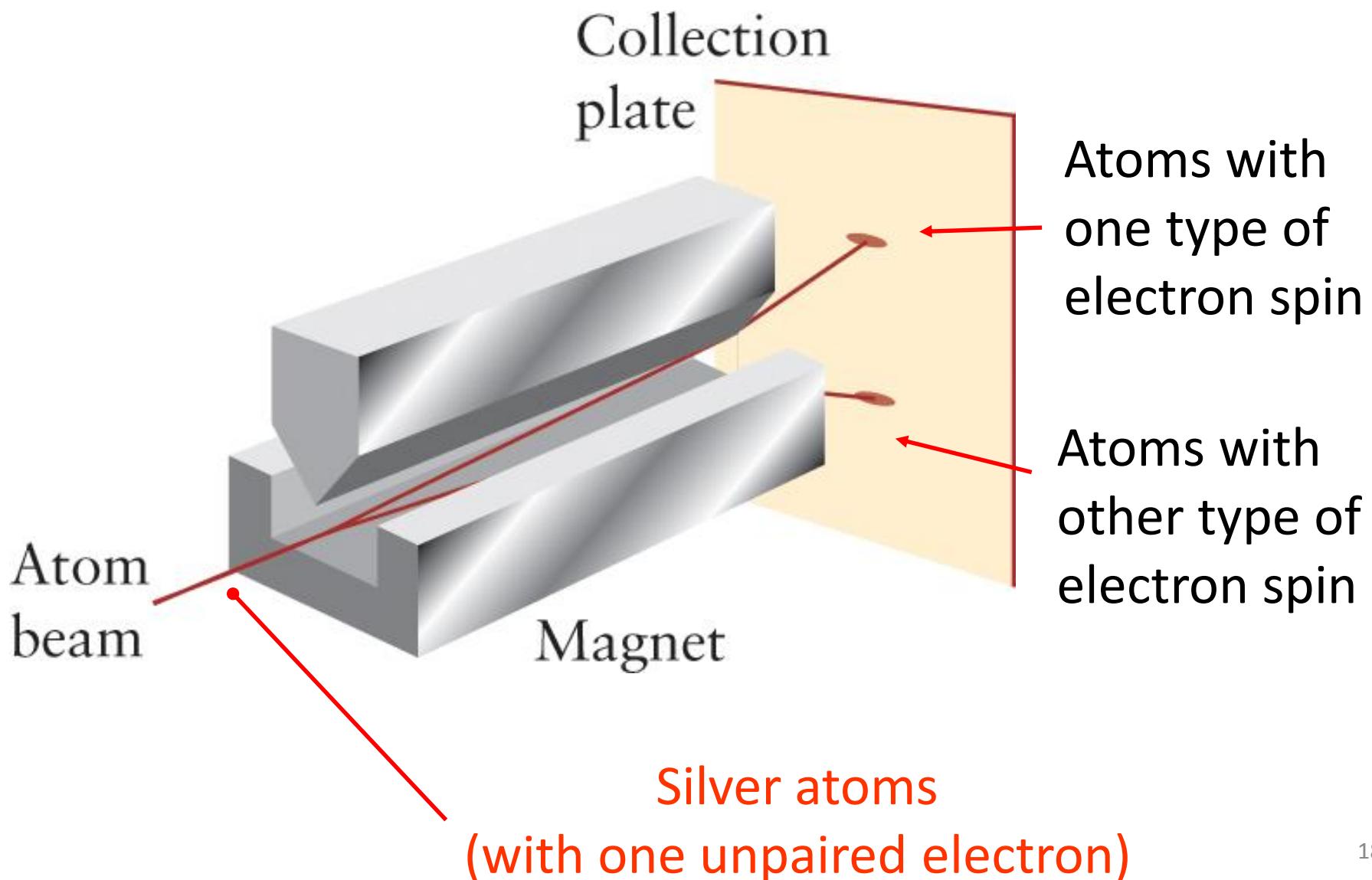
$f_{5xz^2-xr^2}$



f_{xyz}

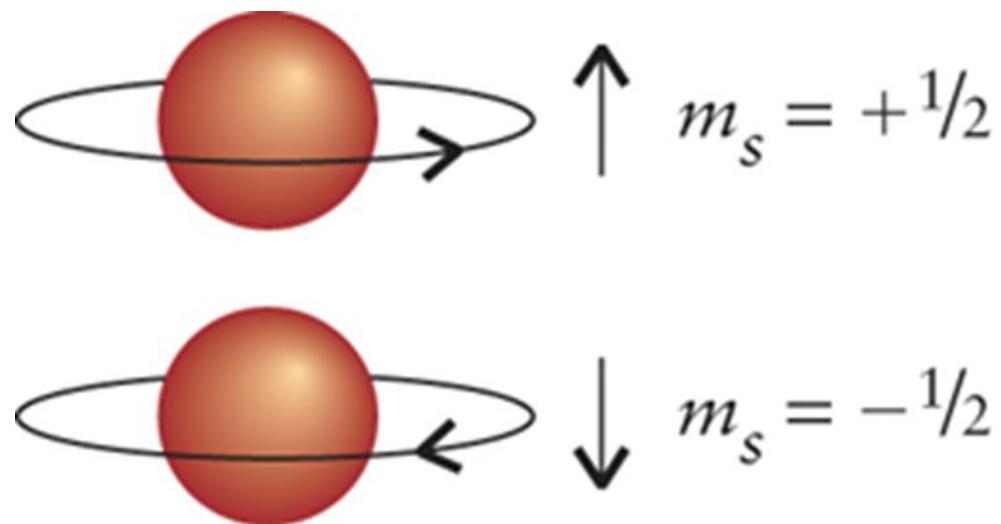
4f has no radial node

Stern and Gerlach Experiment: Electron Spin



Spin States of an Electron

Spin magnetic quantum number (m_s) has two possible values:



Spin interaction

Parallel spins

Higher energy



Paired spins

Lower energy



Complete wave function

$$\Psi_{n,l,m_l}(r, \theta, \phi) = NR_{n,l}(r)Y_{l,m_l}(\theta, \phi)\eta(m_s)$$

$$n = 1, 2, \dots$$

$$l = 0, 1, 2, \dots, n - 1$$

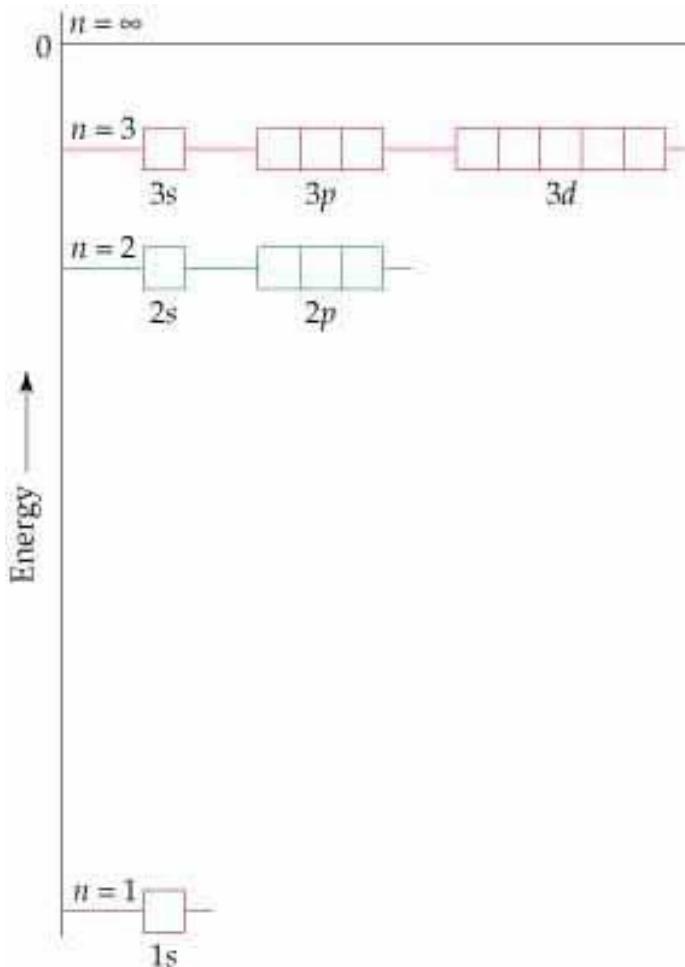
$$m_l = l, l - 1, \dots, -l$$

$$m_s = \frac{1}{2}, -\frac{1}{2}$$

TABLE 1.3 Quantum Numbers for Electrons in Atoms

Name	Symbol	Values	Specifies	Indicates
principal	n	1, 2, ...	shell	size
orbital angular momentum*	l	0, 1, ..., $n - 1$	subshell: $l = 0, 1, 2, 3, 4, \dots$ s, p, d, f, g, \dots	shape
magnetic	m_l	$l, l - 1, \dots, -l$	orbitals of subshell	orientation
spin magnetic	m_s	$+\frac{1}{2}, -\frac{1}{2}$	spin state	spin direction

Energy levels – hydrogen

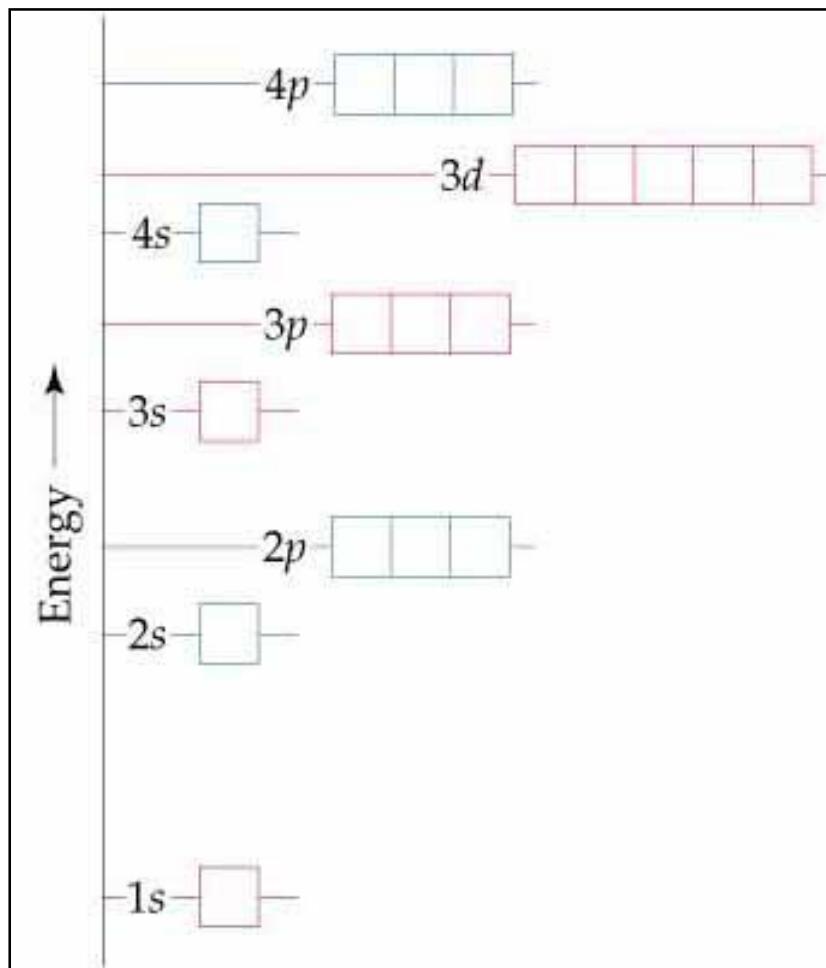


Energy only depends on principle quantum number n

Degeneracy – multiple states share the same energy

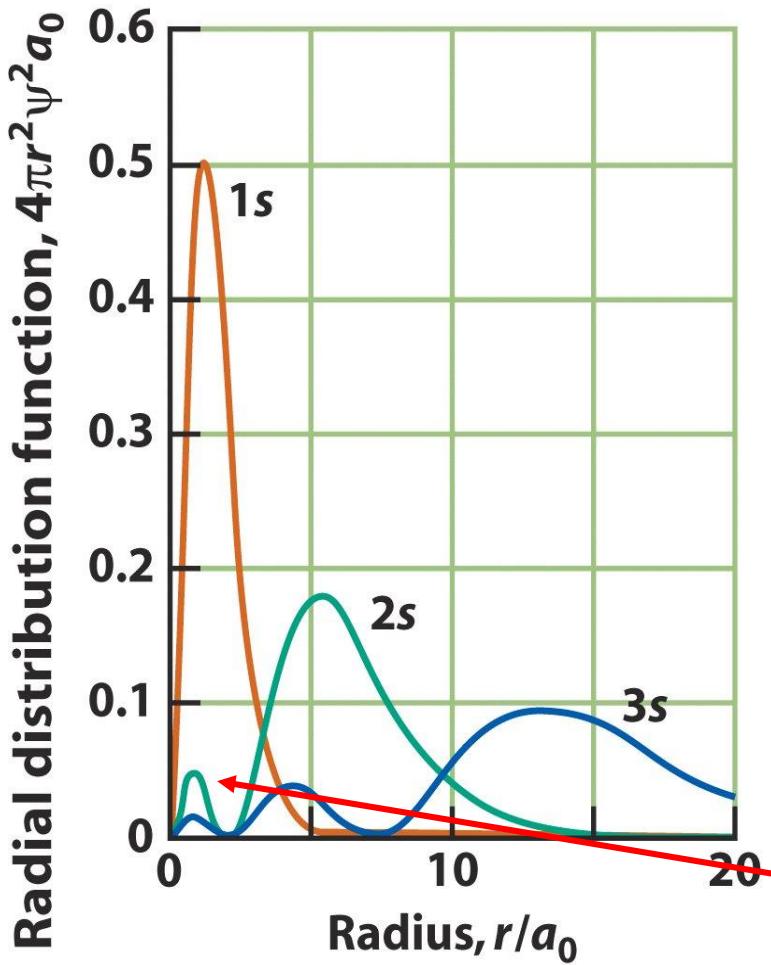
There is only one electron, there is no electron-electron interaction

Energy levels of multi-electron atoms



- Due to electron-electron interactions, the **degeneracy is broken**.
- Due to penetration and shielding effect, the energy order is
 $s < p < d < f$
- The s orbital can be so penetrated that the **4s** orbital is lower in energy than 3d

The probability of finding the electron in distance r/a_0



- The probability of finding the electron in radial distance r/a_0 including contribution from angles.
- For s orbital, it can be calculated by surface area

$$4\pi r^2 \psi_{n,l,m_l}^2$$

- The inner peaks are near the nucleus, lowering energy significantly.

The penetration and Shielding effect

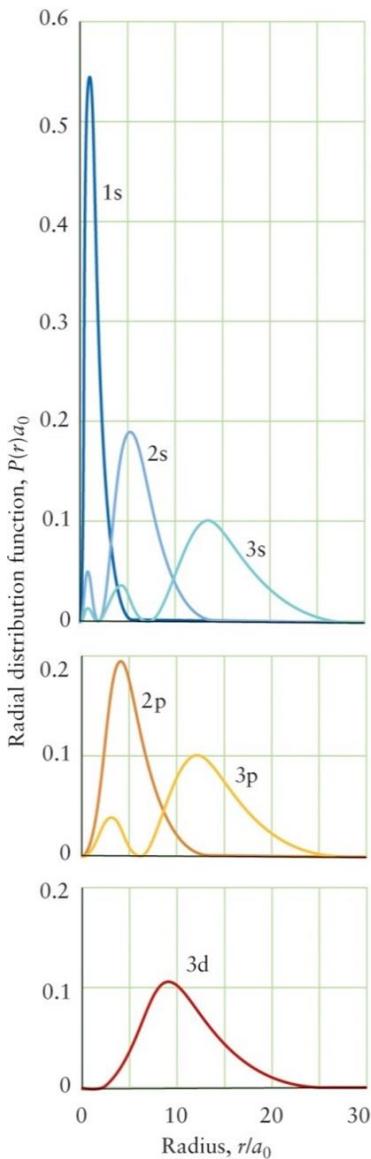


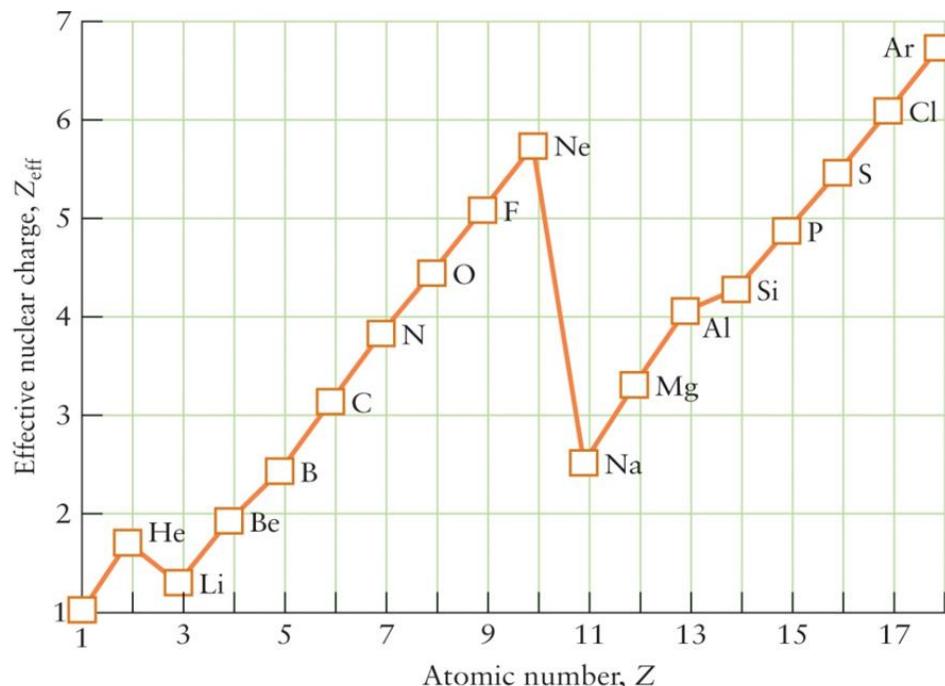
FIGURE 2.15 The radial distribution functions for s-, p-, and d-orbitals in the first three shells of a hydrogen atom. Note that the probability maxima for orbitals of the same shell are close to each other; however, note also that an electron in an *ns*-orbital has a higher probability of being found close to the nucleus than does an electron in an *np*-orbital or an *nd*-orbital.

- Comparing 2s and 2p, or 3s, 3p, 3d,
- s-orbital penetrates to inner shell, closer to nucleus than the p-orbital.
- p-orbital penetrates to inner shell, closer to nucleus than the d-orbital
- The **effective nuclear charge Z^{eff}** is reduced for the outmost orbitals.

Effective nuclear charge

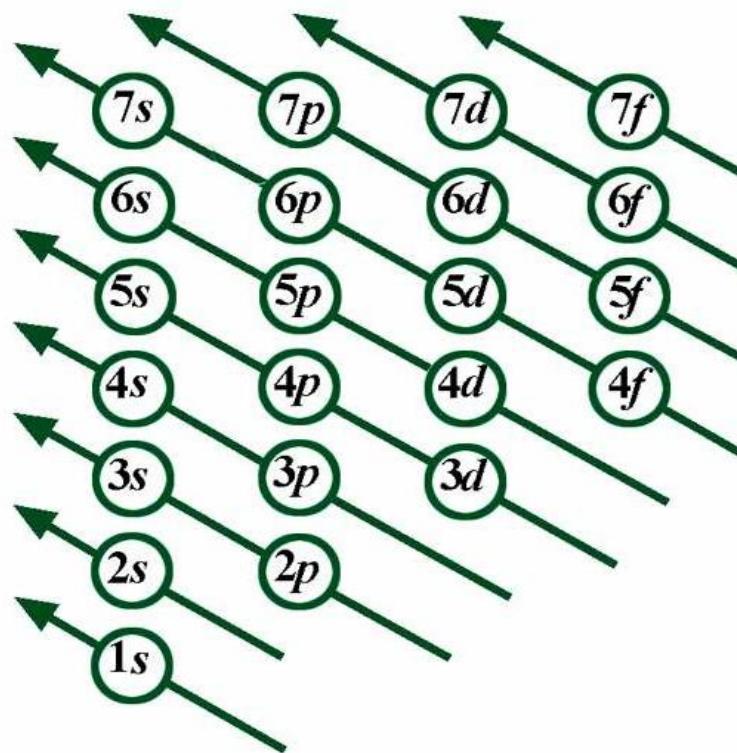
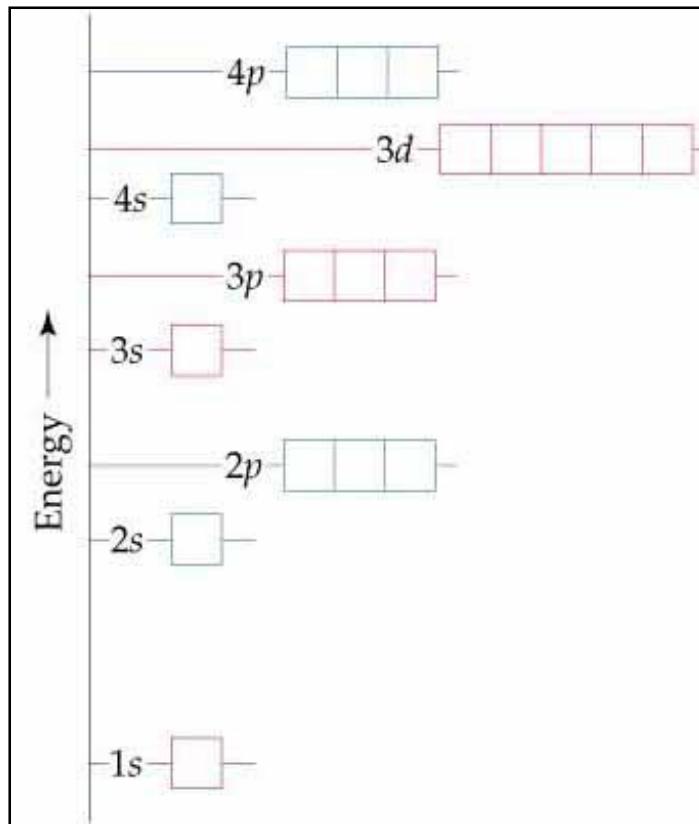
- Is the charge that affects the outmost valence electrons ;
- Because of the interaction among electrons, the effective charge is always lower than the atomic number Z.
- In one period, the effective charge increases.

FIGURE 2.19 The variation of the effective nuclear charge for the outermost valence electron with atomic number. Notice that the effective nuclear charge increases from left to right across a period but drops when the outer electrons occupy a new shell. (The effective nuclear charge is actually Z_{eff} , but Z_{eff} itself is commonly referred to as the charge.)



Orbitals in Many Electron Atoms

This qualitative energy-level diagram is useful for high periods



Building-up rules

Aufbau principle – electron occupies the lowest energy orbital first

Pauli exclusion principle – each orbital may be occupied by two electrons at most. In the case of double occupation, the electron spins are paired.

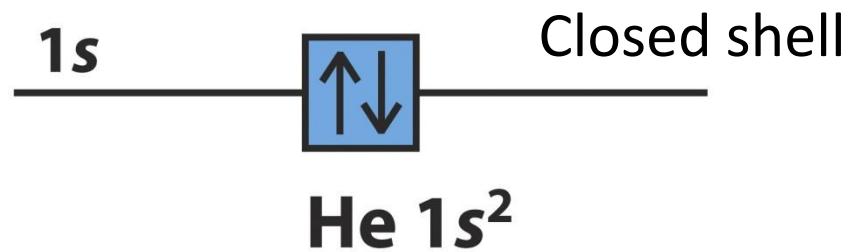
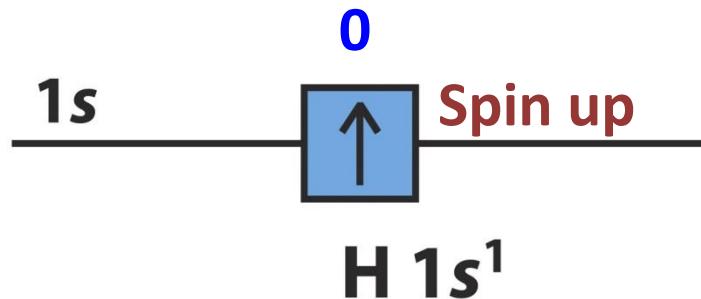
Hund rule – in degeneracy sub-shell, electrons occupy different subshells in parallel spin states, instead of occupying the same sub-shell with paired spins.

Electron configuration of Atom

Quantum Mechanics gave us a new way to view atoms

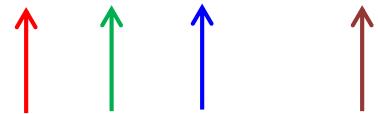
- Shells, subshells, orbitals and spins;
Together we call electron configuration;
- Atom properties radii, ionization energy, and electron affinity are described by its configuration.

Electron configurations and four quantum numbers



$1s$ electron (n, l, m_l, m_s)

- $1, 0, 0, (+\frac{1}{2} \text{ or } -\frac{1}{2})$

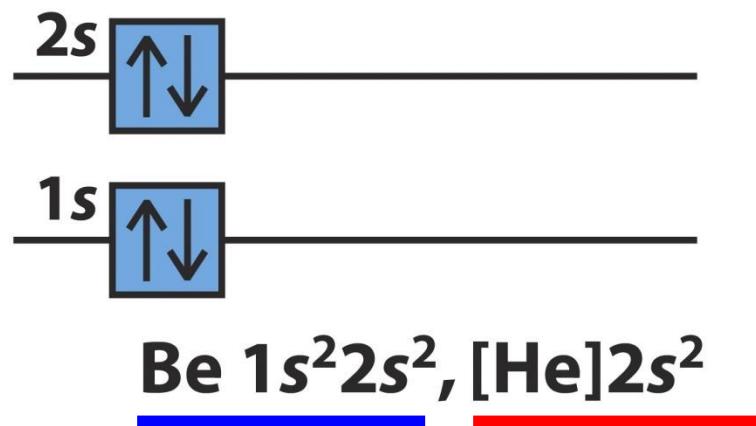
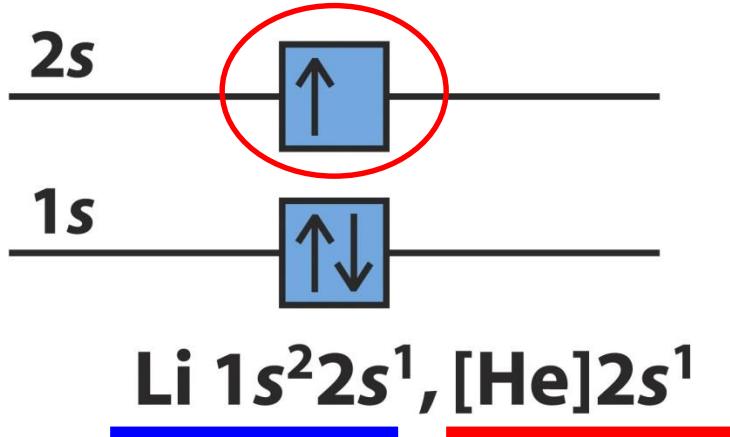


(n, l, m_l, m_s)

$1s$ electrons (n, l, m_l, m_s)

- $1, 0, 0, +\frac{1}{2}$
- $1, 0, 0, -\frac{1}{2}$

Electron Configurations – Li, Be



1s electrons (n, l, m_l, m_s)

- 1, 0, 0, $+\frac{1}{2}$
- 1, 0, 0, $-\frac{1}{2}$

2s electron*

- 2, 0, 0, $+\frac{1}{2}$

1s electrons (n, l, m_l, m_s)

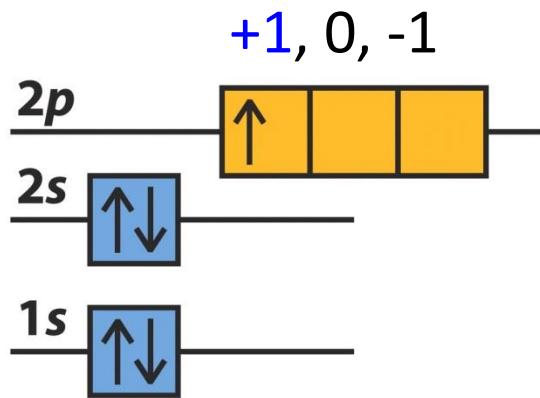
- 1, 0, 0, $+\frac{1}{2}$
- 1, 0, 0, $-\frac{1}{2}$

2s electrons

- 2, 0, 0, $+\frac{1}{2}$
- 2, 0, 0, $-\frac{1}{2}$

Electron Configurations – B, C

Hund's Rule



B $1s^2 2s^2 2p^1$, [He] $2s^2 2p^1$

1s electrons (n, l, m_l, m_s)

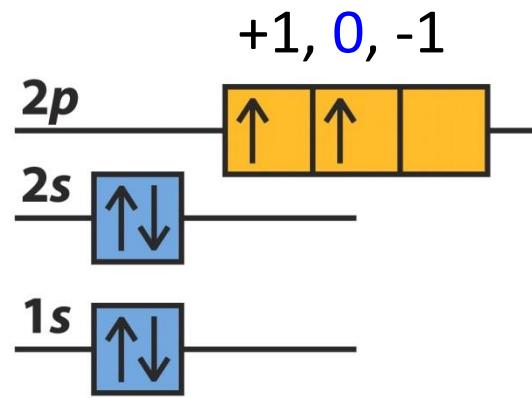
- $1, 0, 0, +\frac{1}{2}$
 - $1, 0, 0, -\frac{1}{2}$

2s electrons

- $2, 0, 0, +\frac{1}{2}$
 - $2, 0, 0, -\frac{1}{2}$

2p electron*

- 2, 1, +1, +½



C $1s^2 2s^2 2p^2$, [He] $2s^2 2p^2$

1s electrons (n, l, m_l, m_s)

- $1, 0, 0, +\frac{1}{2}$
 - $1, 0, 0, -\frac{1}{2}$

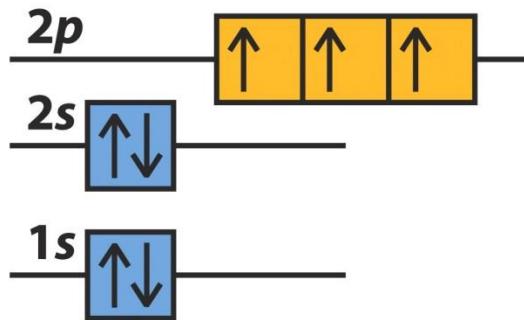
2s electrons

- $2, 0, 0, +\frac{1}{2}$
 - $2, 0, 0, -\frac{1}{2}$

2p electrons*

- 2, 1, +1, $\frac{1}{2}$
 - 2, 1, 0, $\frac{1}{2}$

Electron Configurations: N and O

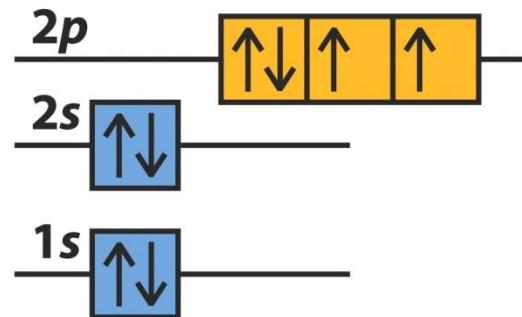


He core (n, l, m_l, m_s)

- 1, 0, 0, $+\frac{1}{2}$
- 1, 0, 0, $-\frac{1}{2}$
- 2, 0, 0, $+\frac{1}{2}$
- 2, 0, 0, $-\frac{1}{2}$

2p electrons*

- 2, 1, +1, $+\frac{1}{2}$
- 2, 1, 0, $+\frac{1}{2}$
- 2, 1, -1, $+\frac{1}{2}$



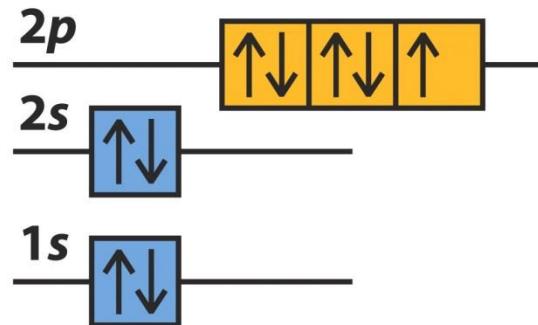
He core (n, l, m_l, m_s)

- 1, 0, 0, $+\frac{1}{2}$
- 1, 0, 0, $-\frac{1}{2}$
- 2, 0, 0, $+\frac{1}{2}$
- 2, 0, 0, $-\frac{1}{2}$

2p electrons*

- 2, 1, +1, $+\frac{1}{2}$
- 2, 1, 0, $+\frac{1}{2}$
- 2, 1, -1, $+\frac{1}{2}$
- 2, 1, +1, $-\frac{1}{2}$

Electron Configurations: F and Ne



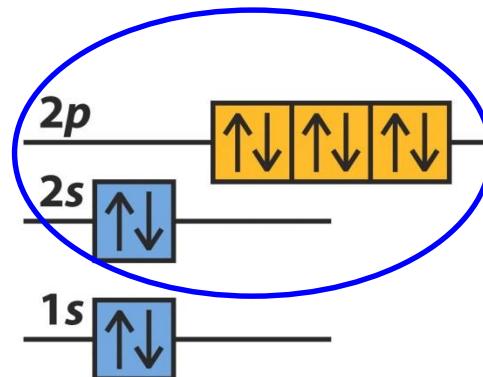
F $1s^2 2s^2 2p^5$, [He] $2s^2 2p^5$

He core (n, l, m_l, m_s)

2p electrons*

- 2, 1, +1, +½
- 2, 1, +1, -½
- 2, 1, 0, +½
- 2, 1, 0, -½
- 2, 1, -1, +½

Filled or closed shell



Ne $1s^2 2s^2 2p^6$, [He] $2s^2 2p^6$

He core (n, l, m_l, m_s)

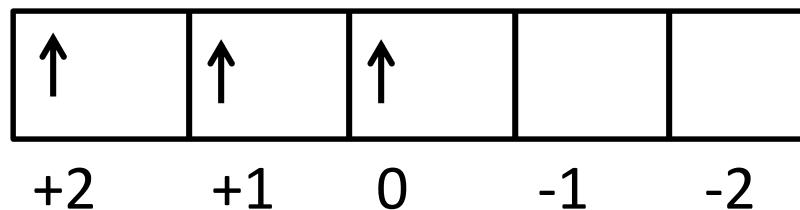
2p electrons

- 2, 1, +1, +½
- 2, 1, +1, -½
- 2, 1, 0, +½
- 2, 1, 0, -½
- 2, 1, -1, +½
- 2, 1, -1, -½

V (Z=23)

Electron configuration

Orbital box diagram $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$

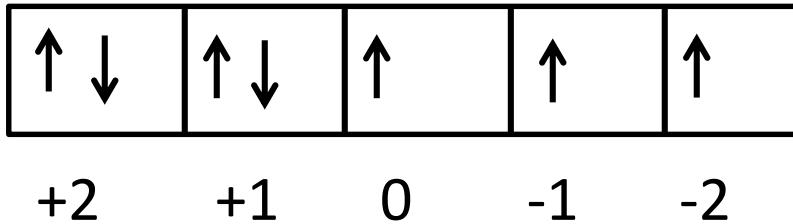


Co Z=27

Electron configuration

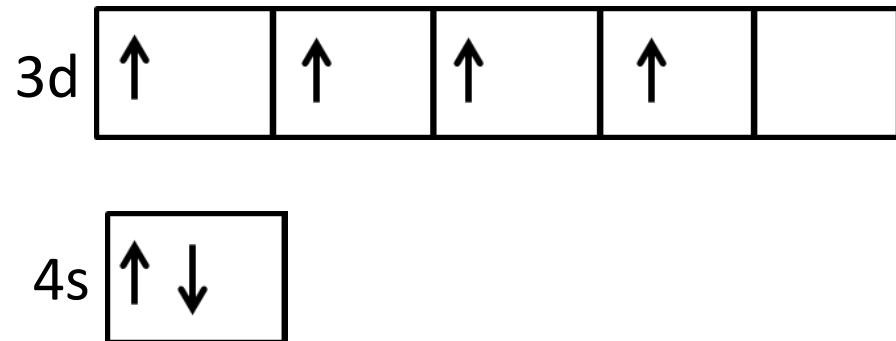
$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$

Orbital box diagram

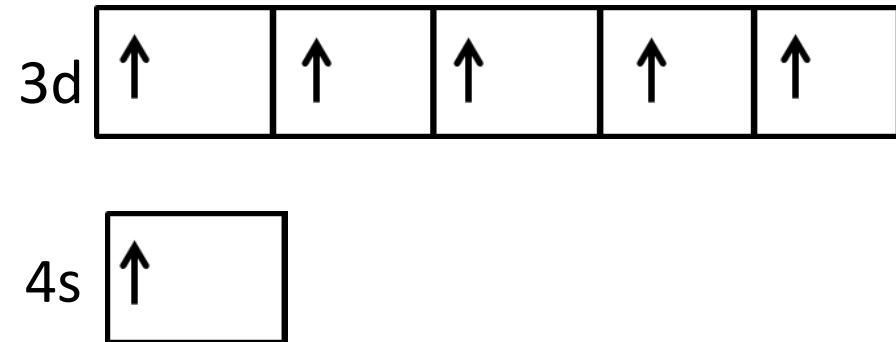


Cr Z=24

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



Observed $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$

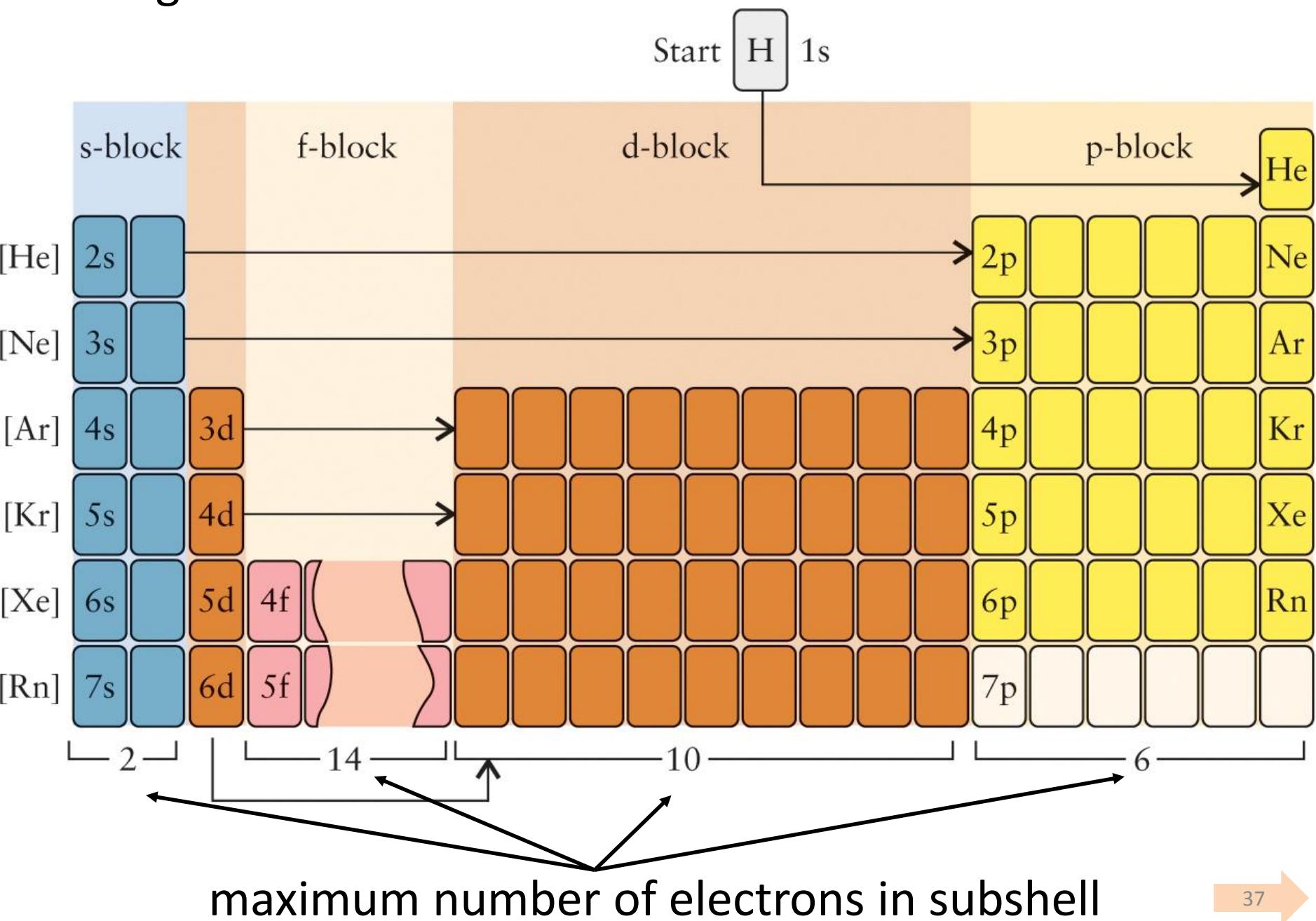


Half-filled or filled subshell stabilizes the electrons

A similar re-arrangement occurs with Cu (Z=29)

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$

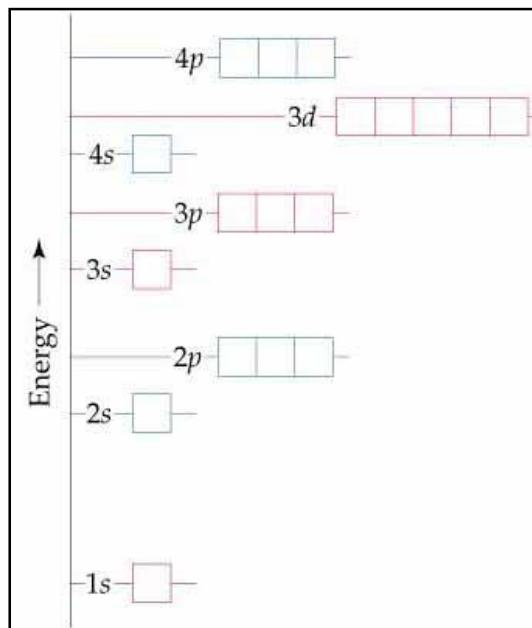
Filling order for orbitals



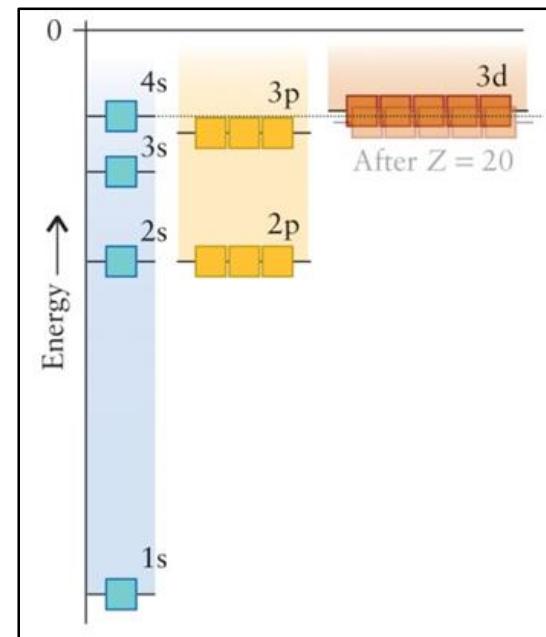
Electron configurations

Orbital energy decreases up on occupation

- The electron-electron interaction is rather complicated.
- As the occupancy increases, orbital energy level decreases, why?
- After $Z=20$, the 3d-orbital starts to be occupied, then the 3d is lower in energy than 4s.
- The consequence is that when electron is removed (ionization), **the 4s orbital** (the highest energy level) is removed first.

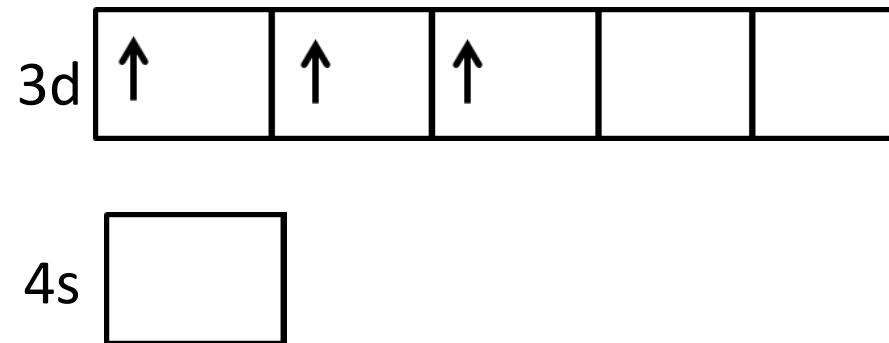
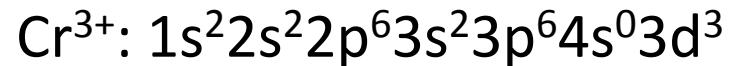
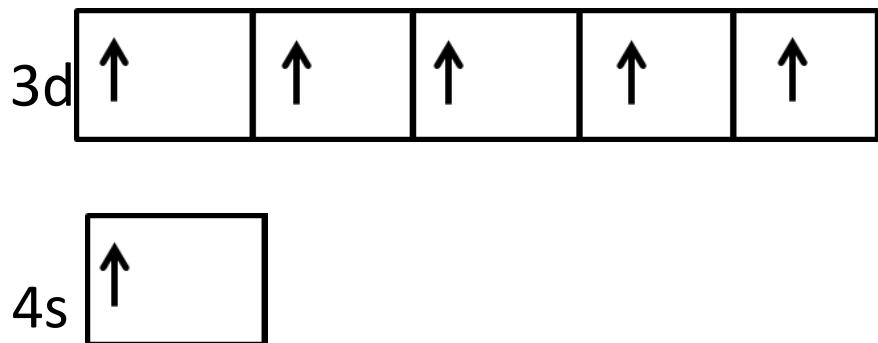
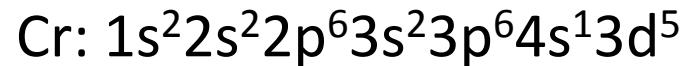
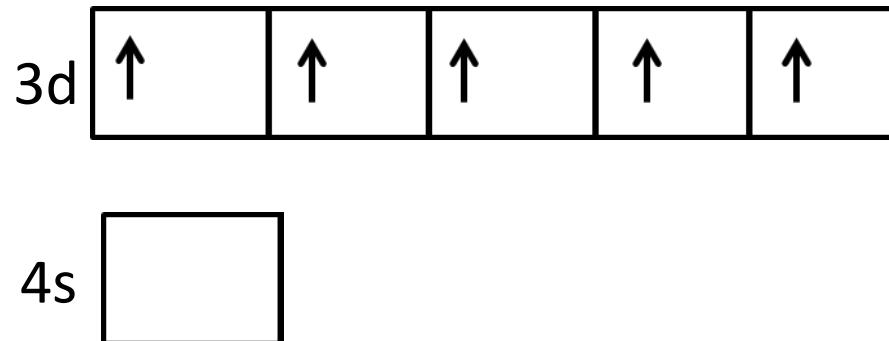
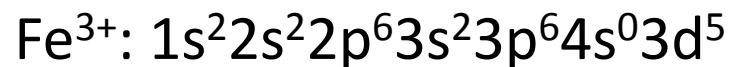
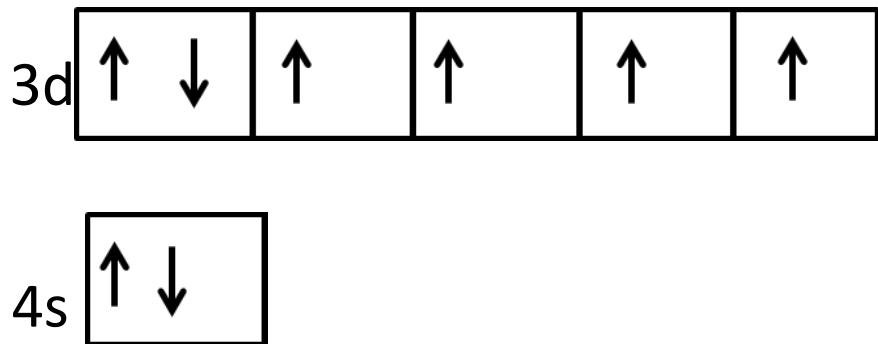


After $Z=20$



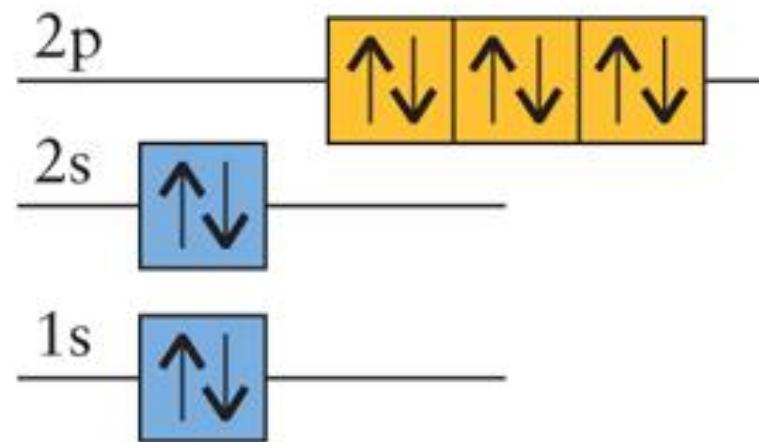
Fe³⁺ and Cr³⁺

Transition metals always lose electrons from their 4s-orbital first



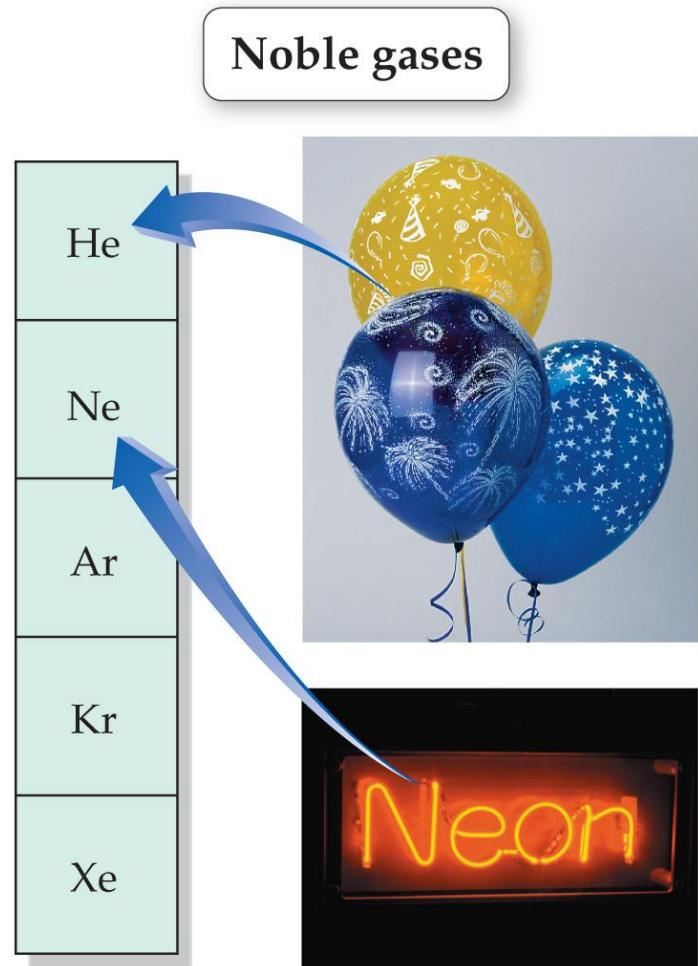
Filled Shells

Filled shell is very stable. That is when atoms get a filled shell they tend to stop reacting.



10 Ne $1s^2 2s^2 2p^6$, [He] $2s^2 2p^6$

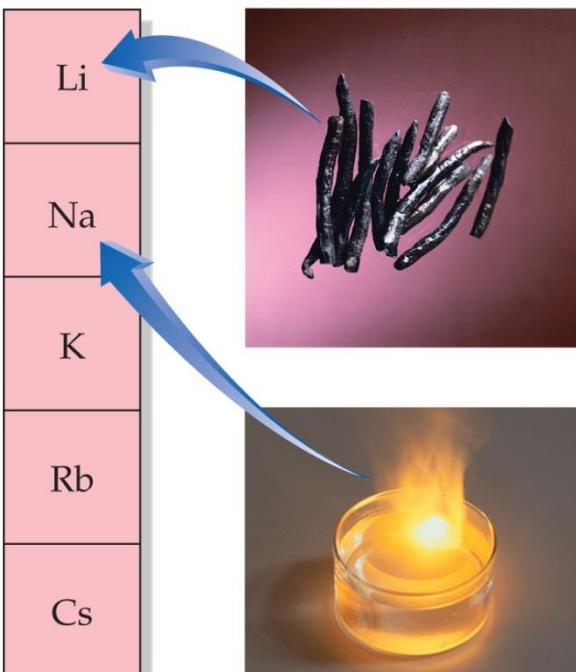
Noble Gas Electron Configuration



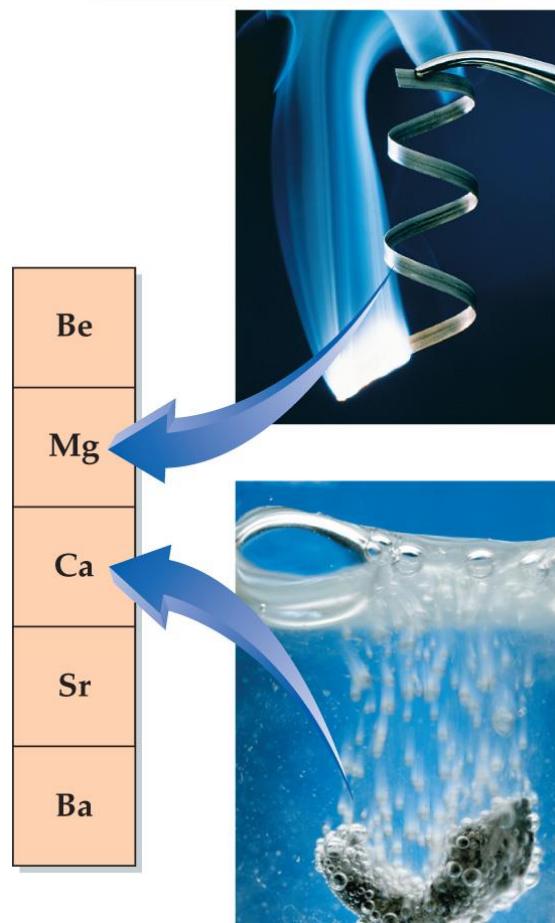
Elements in Group 1-17 are all reactive.

Atoms gain and lose to get a Noble Gas Electron Config.

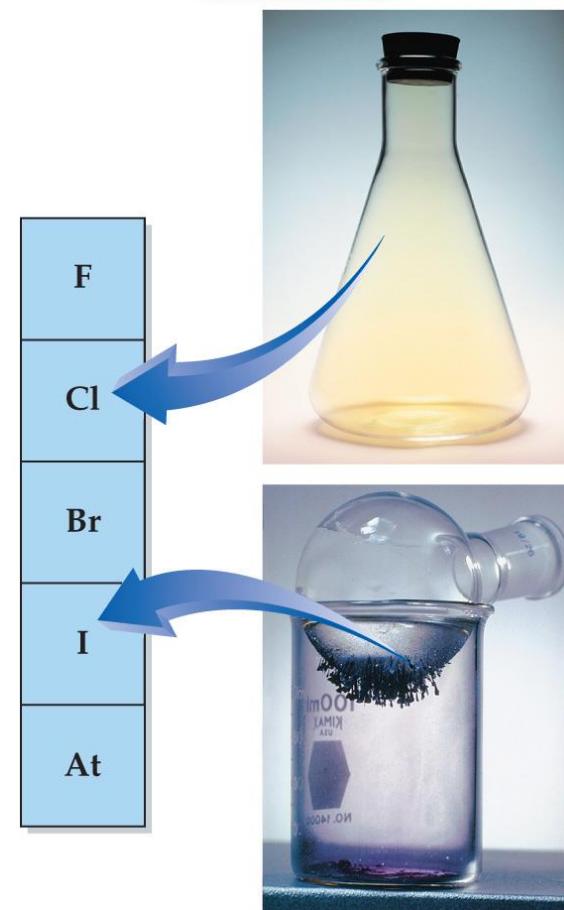
Alkali metals



Alkaline earth metals



Halogens



Ions are stabilized by forming filled shells

The following cations and anions have filled shells (like Noble Gases).

1	1A	2	2A	13	14	15	16	17	18	8A
Li ⁺	Be ²⁺							O ²⁻	F ⁻	
Na ⁺	Mg ²⁺							S ²⁻	Cl ⁻	
K ⁺	Ca ²⁺							Ga ³⁺	Se ²⁻	Br ⁻
Rb ⁺	Sr ²⁺							In ³⁺	Te ²⁻	I ⁻
Cs ⁺	Ba ²⁺									
Transition metals form cations with various charges										

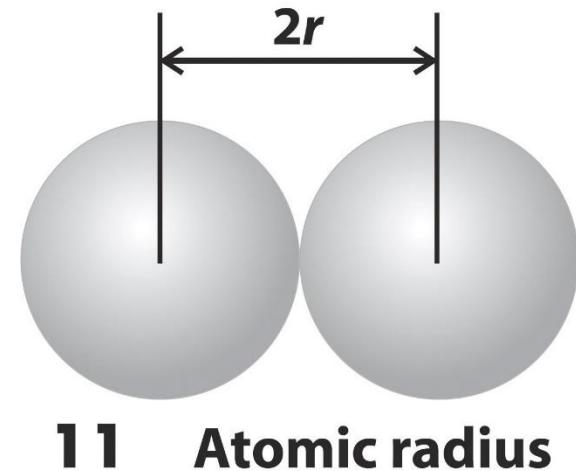
Two Inherent Properties in Atoms

Two most direct factors that influence physical properties such as:

- Atomic radius
- Stable cations or anions.
- Metal characteristics

are:

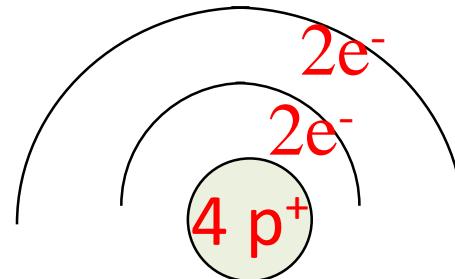
1. Number of valence shells
2. Effective nuclear charge



$$1 \text{ pm} = 10^{-12} \text{ m} = 100 \text{ \AA}$$

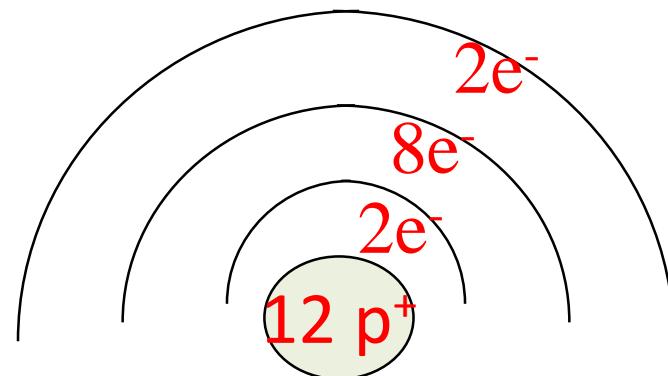
Adding more valence shells increases an atoms radii

Be 2 valance shells



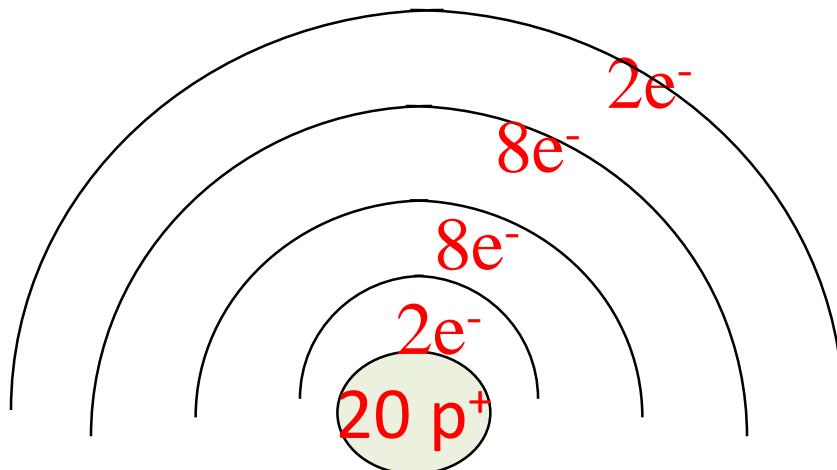
105 pm

Mg 3 valance shells



150 pm

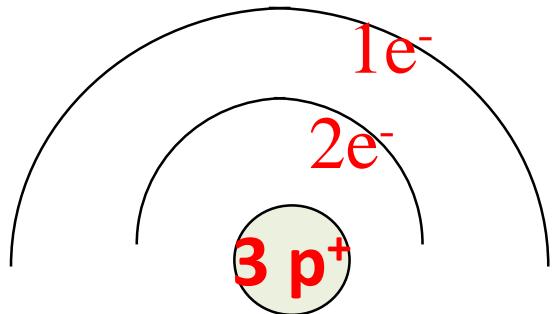
Ca 4 valance shells



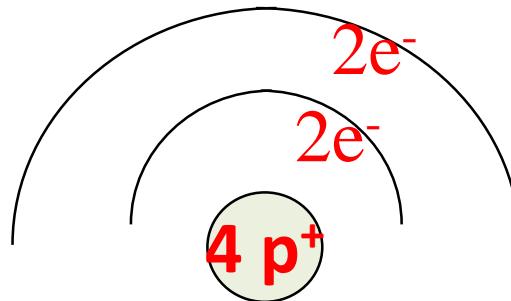
180 pm

Effective nuclear charge reduces the atomic size:

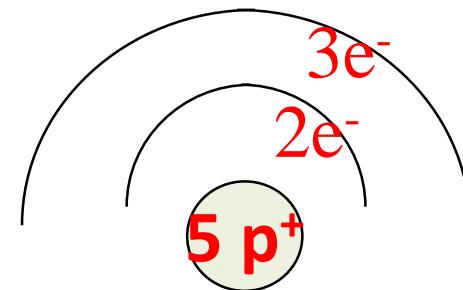
increasing effective charge pulling electrons inward



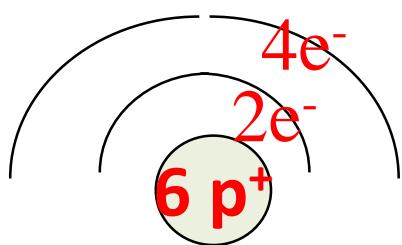
Li (145 pm)



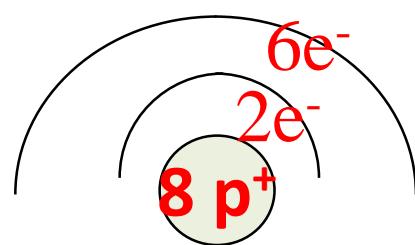
Be (105 pm)



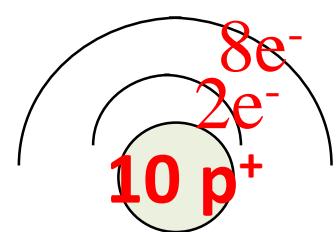
B (85 pm)



C (70 pm)



O (60 pm)

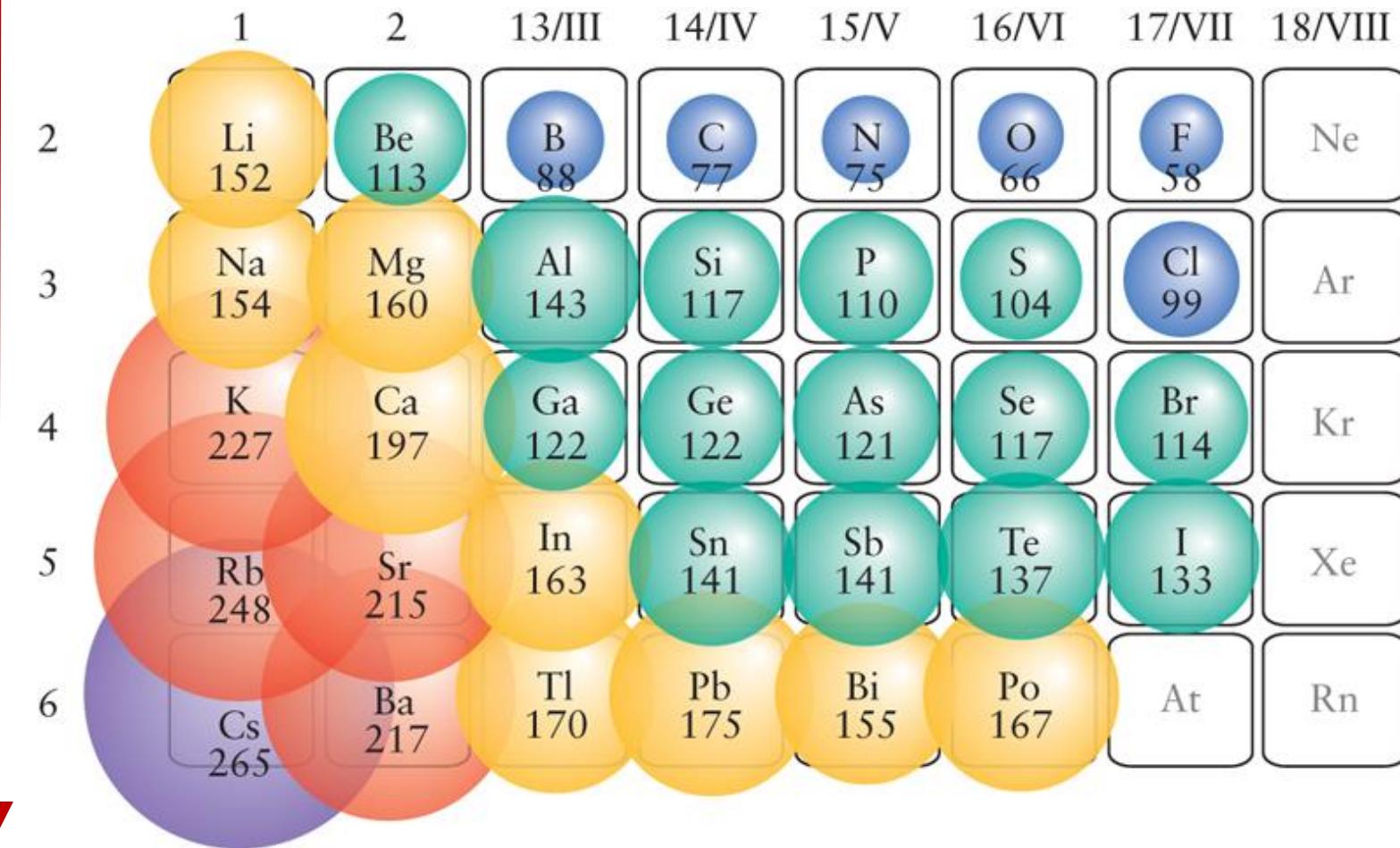


Ne (58 pm)

Periodic Trend: Atomic Radius

increases down a group
↑Valence Shells

decreases across a period
↑Effective Nuclear Force



Atomic Radii

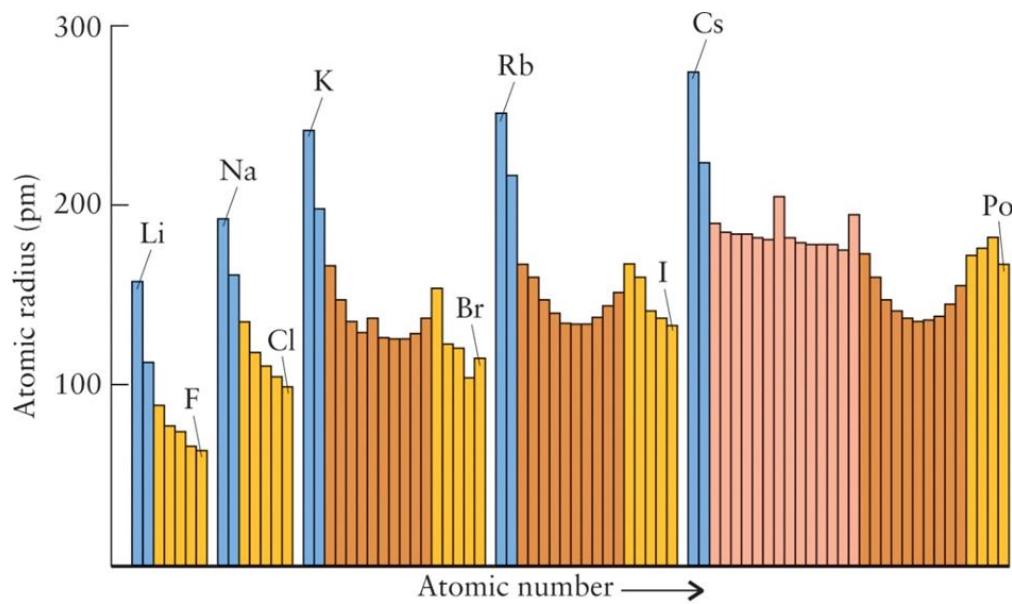


FIGURE 2.21 The periodic variation in the atomic radii of the elements. The decrease across a period can be explained in terms of the effect of increasing effective nuclear charge, the increase down a group by the occupation of shells with increasing principal quantum number.

Rank the atoms from Largest to Smallest and Why?

S, I, Na, Al, Cl, Cs

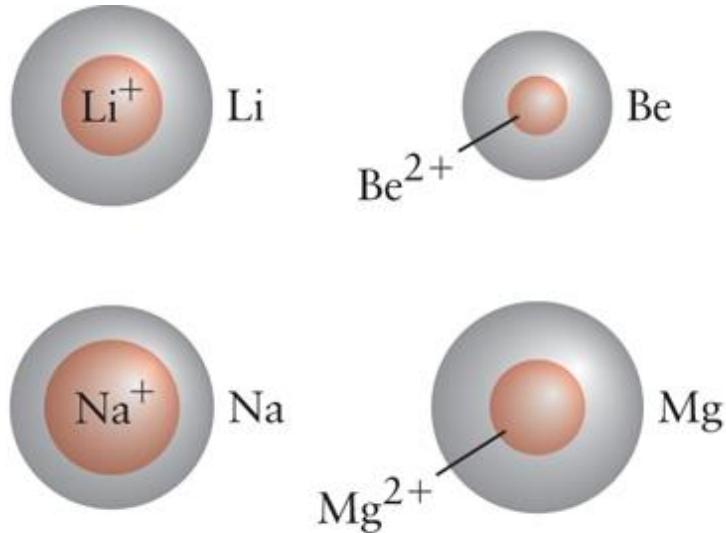
Group 1 2 14 15 16 17

Period

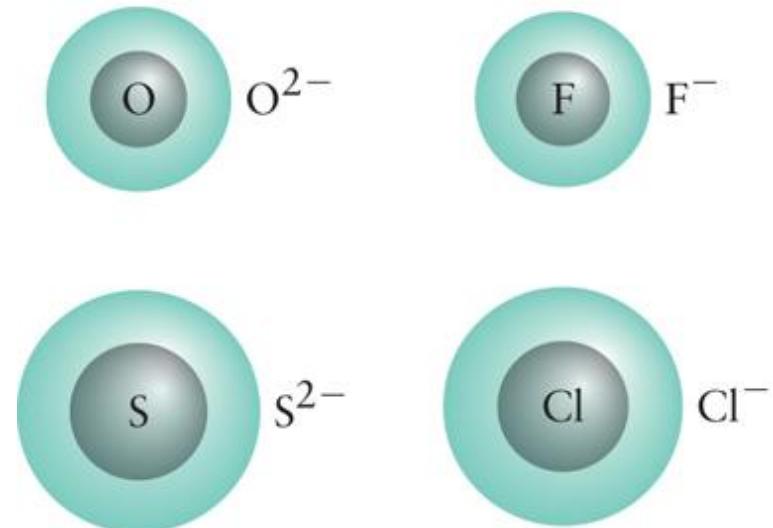
Li lithium 6.94 2s ¹	Be beryllium 9.01 2s ²																	
Na sodium 22.99 3s ¹	Mg magnesium 24.31 3s ²																	
K potassium 39.10 4s ¹	Ca calcium 40.08 4s ²	Sc scandium 44.96 3d ¹ 4s ²	Ti titanium 47.87 3d ² 4s ²	V vanadium 50.94 3d ³ 4s ²	Cr chromium 52.00 3d ⁵ 4s ¹	Mn manganese 54.94 3d ⁵ 4s ²	Fe iron 55.84 3d ⁶ 4s ²	Co cobalt 58.93 3d ⁷ 4s ²	Ni nickel 58.69 3d ⁸ 4s ²	Cu copper 63.55 3d ¹⁰ 4s ¹	Zn zinc 65.41 3d ¹⁰ 4s ²	Ga gallium 69.72 4s ² 4p ¹	Ge germanium 72.64 4s ² 4p ²	As arsenic 74.92 4s ² 4p ³	Se selenium 78.96 4s ² 4p ⁴	Br bromine 79.90 4s ² 4p ⁵	Kr krypton 83.80 3s ² 4p ⁶	
Rb rubidium 85.47 5s ¹	Sr strontium 87.62 5s ²	Y yttrium 88.91 4d ¹ 5s ²	Zr zirconium 91.22 4d ² 5s ²	Nb niobium 92.91 4d ⁴ 5s ¹	Mo molybdenum 95.94 4d ⁵ 5s ¹	Tc technetium (98) 4d ⁵ 5s ²	Ru ruthenium 101.07 4d ⁷ 5s ¹	Rh rhodium 102.90 4d ⁸ 5s ¹	Pd palladium 106.42 4d ¹⁰	Ag silver 107.87 4d ¹⁰ 5s ¹	Cd cadmium 112.41 4d ¹⁰ 5s ²	In indium 114.82 5s ² 5p ¹	Sn tin 118.71 5s ² 5p ²	Sb antimony 121.76 5s ² 5p ³	Te tellurium 127.60 5s ² 5p ⁴	I iodine 126.90 5s ² 5p ⁵	Xe xenon 131.29 5s ² 5p ⁶	
Cs cesium 132.91 6s ¹	Ba barium 137.33 6s ²	La lanthanum 138.91 5d ¹ 6s ²	Hf hafnium 178.49 5d ² 6s ²	Ta tantalum 180.95 5d ³ 6s ²	W tungsten 183.84 5d ⁴ 6s ²	Re rhenium 186.21 5d ⁵ 6s ²	Os osmium 190.23 5d ⁶ 6s ²	Ir iridium 192.22 5d ⁷ 6s ²	Pt platinum 195.08 5d ⁹ 6s ¹	Au gold 196.97 5d ¹⁰ 6s ¹	Hg mercury 200.59 5d ¹⁰ 6s ²	Tl thallium 204.38 6s ² 6p ¹	Pb lead 207.2 6s ² 6p ²	Bi bismuth 208.98 6s ² 6p ³	Po polonium (209) 6s ² 6p ⁴	At astatine (210) 6s ² 6p ⁵	Rn radon (222) 6s ² 6p ⁶	
Fr francium (223) 7s ¹	Ra radium (226) 7s ²	Ac actinium (227) 6d ¹ 7s ²	Rf rutherfordium (261) 6d ² 7s ²	Db dubnium (262) 6d ³ 7s ²	Sg seaborgium (266) 6d ⁴ 7s ²	Bh bohrium (264) 6d ⁵ 7s ²	Hs hassium (267) 6d ⁶ 7s ²	Mt meitnerium (268) 6d ⁷ 7s ²	Ds darmstadtium (271) 6d ⁸ 7s ²	Rg roentgenium (272) 6d ¹⁰ 7s ¹	Cn copernicium (285) 6d ¹⁰ 7s ²	Fl florovium (289) 7s ² 7p ²	113	114	115	Lv livermorium (293) 7s ² 7p ⁴	117	118
Lanthanoids (lanthanides)		6	Ce cerium 140.12 4f ¹ 5d ¹ 6s ²	Pr praseodymium 140.91 4f ¹ 6s ²	Nd neodymium 144.24 4f ² 6s ²	Pm promethium (145) 4f ⁵ 6s ²	Sm samarium 150.36 4f ⁷ 6s ²	Eu europium 151.96 4f ⁷ 5d ¹ 6s ²	Gd gadolinium 157.25 4f ⁹ 6s ²	Tb terbium 158.93 4f ¹⁰ 6s ²	Dy dysprosium 162.50 4f ¹¹ 6s ²	Ho holmium 164.93 4f ¹² 6s ²	Er erbium 167.26 4f ¹³ 6s ²	Tm thulium 168.93 4f ¹⁴ 6s ²	Yb ytterbium 173.04 4f ¹⁴ 6s ²	Lu lutetium 174.97 5d ¹ 6s ²		
Actinoids (actinides)		7	Th thorium 232.04 6d ² 7s ²	Pa protactinium 231.04 5f ² 6d ¹ 7s ²	U uranium 238.03 5f ³ 6d ¹ 7s ²	Np neptunium (237) 5f ⁵ 6d ¹ 7s ²	Pu plutonium (244) 5f ⁷ 7s ²	Am americium (243) 5f ⁷ 7s ²	Cm curium (247) 5f ⁷ 6d ¹ 7s ²	Bk berkelium (247) 5f ⁹ 7s ²	Cf californium (251) 5f ¹⁰ 7s ²	Es einsteinium (252) 5f ¹¹ 7s ²	Fm fermium (257) 5f ¹² 7s ²	Md mendelevium (258) 5f ¹³ 7s ²	No nobelium (259) 5f ¹⁴ 7s ²	Lr lawrencium (261) 5f ¹⁴ 7s ²		

Ion Sizes

atom → cation
radius **decreases**



atom → anion
radius **increases**



Removing electrons:
1. Lose of a shell;
2. Higher “+Z” in
nucleus draws e⁻
in.

More electrons weakens +Z
nuclear electrostatic
attraction and at the same
time an increase in e⁻ to e⁻
repulsions.

Ion Sizes

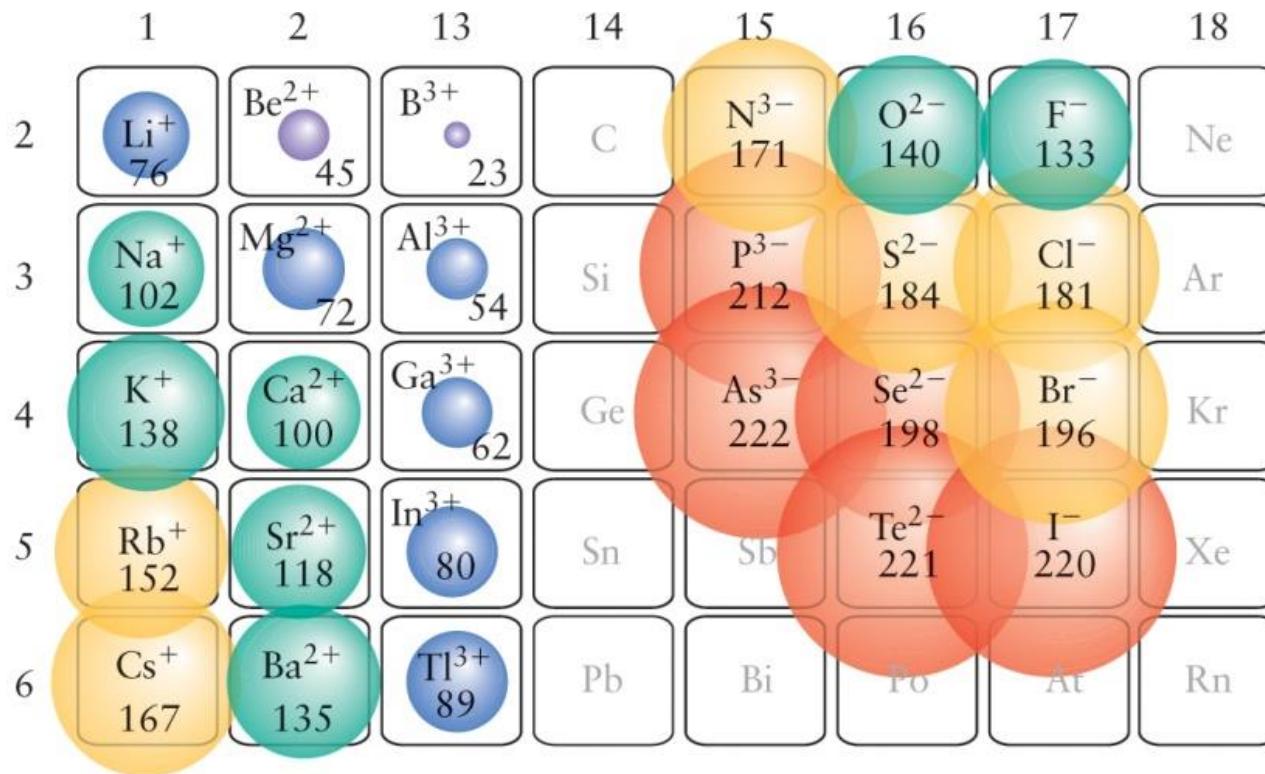


FIGURE 2.22 The ionic radii (in picometers) of the ions of the main-group elements. Note that cations are typically smaller than their parent atoms, whereas anions are larger—in some cases, very much larger.

Rank the following from smallest to largest: S^{2-} , Cl^- , K^+ , Ca^{2+} , Ga^{3+} .

- A. $Cl^- > S^{2-} > K^+ > Ca^{2+} > Ga^{3+}$
- B. $S^{2-} > Cl^- > Ga^{3+} > Ca^{2+} > K^+$
- C. $Ga^{3+} > Ca^{2+} > K^+ > S^{2-} > Cl^-$
- D. $Ga^{3+} > Ca^{2+} > K^+ > Cl^- > S^{2-}$

Periodic Table of the Elements

The periodic table displays the following information for each element:

- Atomic Number:** The element's position in the table.
- Element Name:** The name of the element.
- Symbol:** The one- or two-letter symbol for the element.
- Atomic Weight:** The molar mass of the element.
- Electron Configuration:** The arrangement of electrons in the atom, shown in brackets with superscripts indicating the number of electrons in each orbital.

Legend:

- Metal (Blue)
- Metalloid (Green)
- Nonmetal (Orange)

Highlighted Groups:

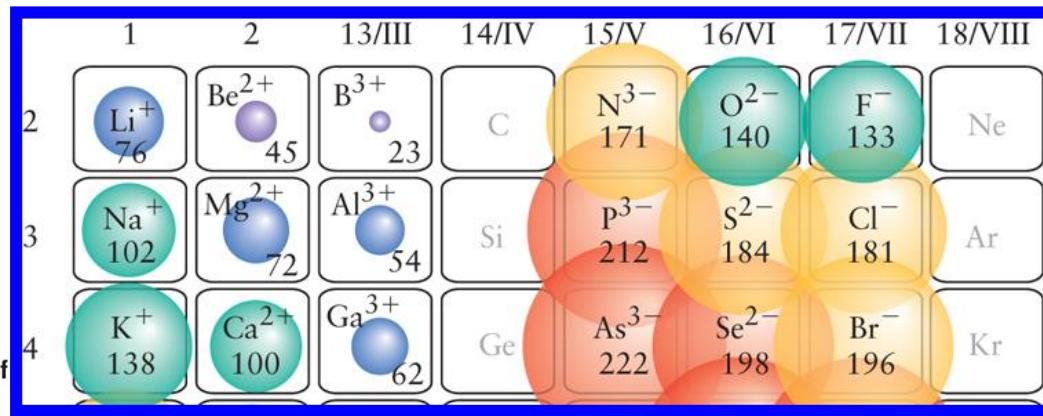
- Group 13:** Aluminum (Al), Gallium (Ga), Indium (In).
- Group 17:** Chlorine (Cl), Bromine (Br), Iodine (I).

Clicker Question: 8 of 10

Rank the following from smallest to largest: S^{2-} , Cl^- , K^+ , Ca^{2+} , Ga^{3+} .

- A. $Cl^- > S^{2-} > K^+ > Ca^{2+} > Ga^{3+}$
- B. $S^{2-} > Cl^- > Ga^{3+} > Ca^{2+} > K^+$
- C. $Ga^{3+} > Ca^{2+} > K^+ > S^{2-} > Cl^-$
- D. $Ga^{3+} > Ca^{2+} > K^+ > Cl^- > S^{2-}$

Periodic Table of



Group	1	2		13/III	14/IV	15/V	16/VI	17/VII	18/VIII								
Period	Li lithium 6.94 $2s^1$	Be beryllium 9.01 $2s^2$		Li+ 76	Be^{2+} 45	B^{3+} 23	C	N^{3-} 171	O^{2-} 140	F^{-} 133							
2	Na sodium 22.99 $3s^1$	Mg magnesium 24.31 $3s^2$		Na+ 102	Mg^{2+} 72	Al^{3+} 54	Si	P^{3-} 212	S^{2-} 184	Cl^{-} 181							
3	K potassium 39.10 $4s^1$	Ca calcium 40.08 $4s^2$	Sc scandium 44.96 $3d^14s^2$	Ti titanium 47.87 $3d^24s^2$	V vanadium 50.94 $3d^34s^2$	Cr chromium 52.00 $3d^54s^1$	Mn manganese 54.94 $3d^64s^2$	Fe iron 55.84 $3d^64s^2$	Co cobalt 58.93 $3d^74s^2$	Ni nickel 58.69 $3d^84s^2$							
4	Rb rubidium 85.47 $5s^1$	Sr strontium 87.62 $5s^2$	Y yttrium 88.91 $4d^15s^2$	Zr zirconium 91.22 $4d^25s^2$	Nb niobium 92.91 $4d^45s^1$	Mo molybdenum 95.94 $4d^55s^1$	Tc technetium (98) $4d^55s^1$	Ru ruthenium 101.07 $4d^75s^1$	Rh rhodium 102.90 $4d^85s^1$	Pd palladium 106.42 $4d^{10}5s^1$	Ag silver 107.87 $4d^{10}5s^1$						
5	Cs cesium 132.91 $6s^1$	Ba barium 137.33 $6s^2$	La lanthanum 138.91 $5d^16s^2$	Hf hafnium 178.49 $5d^46s^2$	Ta tantalum 180.95 $5d^56s^2$	W tungsten 183.84 $5d^66s^2$	Re rhenium 186.21 $5d^76s^2$	Os osmium 190.23 $5d^86s^2$	Ir iridium 192.22 $5d^96s^2$	Pt platinum 195.08 $5d^{10}6s^1$	Au gold 196.97 $5d^{10}6s^1$						
6	Fr francium (223) $7s^1$	Ra radium (226) $7s^2$	Ac actinium (227) $6d^17s^2$	Rf rutherfordium (261) $6d^27s^2$	Db dubnium (262) $6d^37s^2$	Sg seaborgium (266) $6d^47s^2$	Bh bohrium (264) $6d^57s^2$	Hs meitnerium (267) $6d^67s^2$	Mt mendelevium (268) $6d^{10}7s^2$	Ds darmstadtium (271) $6d^{10}7s^2$	Rg roentgenium (272) $6d^{10}7s^1$						
7	Lanthanoids (lanthanides)			Ce cerium 140.12 $4f^15d^6s^2$	Pr praseodymium 140.91 $4f^26s^2$	Nd neodymium 144.24 $4f^36s^2$	Pm promethium (145) $4f^46s^2$	Sm samarium 150.16 $4f^56s^2$	Eu europium 151.96 $4f^66s^2$	Gd gadolinium 157.25 $4f^75d^16s^2$	Tb terbium 158.93 $4f^86s^2$	Dy dysprosium 162.50 $4f^{10}6s^2$	Ho holmium 164.93 $4f^{11}6s^2$	Er erbium 167.26 $4f^{12}6s^2$	Tm thulium 168.93 $4f^{13}6s^2$	Yb ytterbium 173.04 $5d^16s^2$	Lu lutetium 174.97 $5d^26s^2$
	Actinoids (actinides)			Th thorium 232.04 $6d^37s^2$	Pa protactinium 231.04 $5f^66d^17s^2$	U uranium 238.03 $5f^66d^17s^2$	Np neptunium (237) $5f^67s^2$	Pu plutonium (244) $5f^77s^2$	Am americium (243) $5f^77s^2$	Cm curium (247) $5f^86d^17s^2$	Bk berkelium (251) $5f^97s^2$	Cf californium (257) $5f^{10}7s^2$	Es einsteiniun (259) $5f^{11}7s^2$	Fm fermium (261) $5f^{12}7s^2$	Md mendelevium (262) $5f^{13}7s^2$	No nobelium (265) $5f^{14}7s^2$	Lr lawrencium (267) $6d^17s^2$

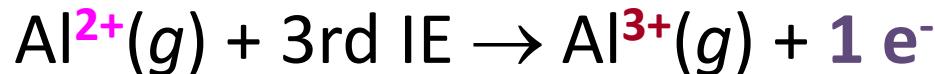
Clicker Answer: 8 of 10

Ionization Energy

1. Valence shells
2. Effective nuclear charge

Minimum energy needed to **remove an electron** from an atom.

- Valence electron easiest to remove.
- $M(g) + \text{1st IE} \rightarrow M^{1+}(g) + \mathbf{1 e^-}$
- $M^{1+}(g) + \text{2nd IE} \rightarrow M^{2+}(g) + \mathbf{1 e^-}$



Trends in Ionization Energy

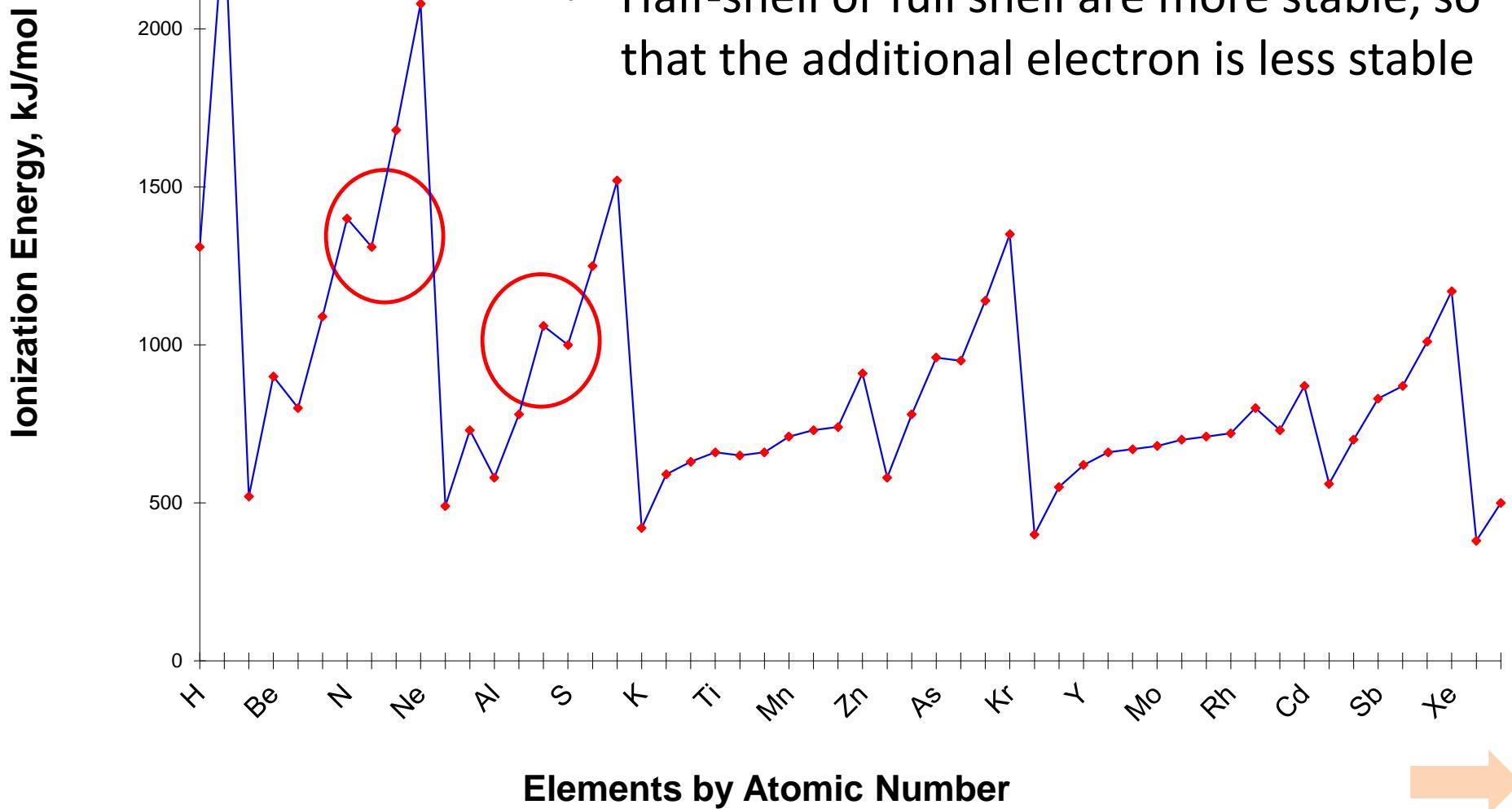
Increasing effective nuclear charge

Valence shells

		Increasing effective nuclear charge														
		H 1310														He 2370
	2	Li 519	Be 900	B 799	C 1090	N 1400	O 1310	F 1680	Ne 2080							
	3	Na 494	Mg 736	Al 577	Si 786	P 1011	S 1000	Cl 1255	Ar 1520							
	4	K 418	Ca 590	Ga 577	Ge 784	As 947	Se 941	Br 1140	Kr 1350							
	5	Rb 402	Sr 548	In 556	Sn 707	Sb 834	Te 870	I 1008	Xe 1170							
	6	Cs 376	Ba 502	Tl 590	Pb 716	Bi 703	Po 812	At 1037	Rn 1036							

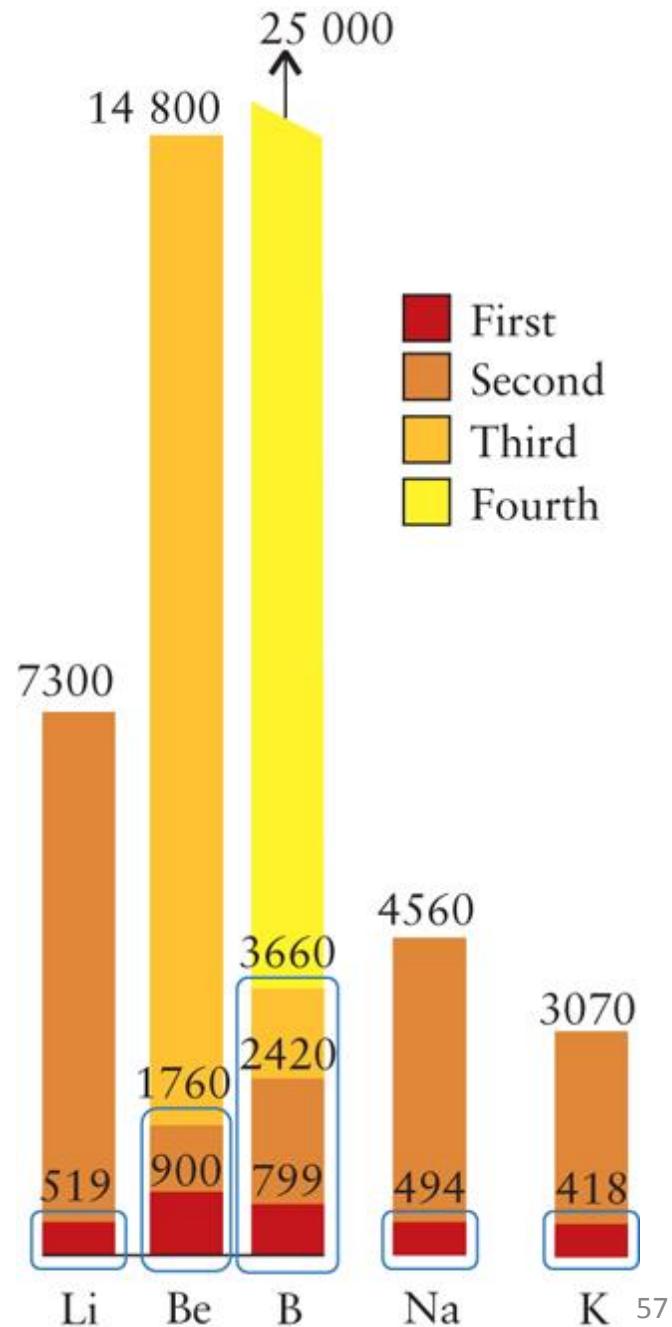
Ionization Energy of Elements 1-56

- IE decrease as shells are increased
- At each shell, the IE increase as effective charge increase
- Half-shell or full shell are more stable, so that the additional electron is less stable



Multiple Ionizations

- It is increasingly more difficult to remove additional electron;
- Removing an electron from an **inner shell** (core) require even **higher energies**.



Periodic Trend: Electron Affinity



$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$

Negative values: energy is required to add an electron

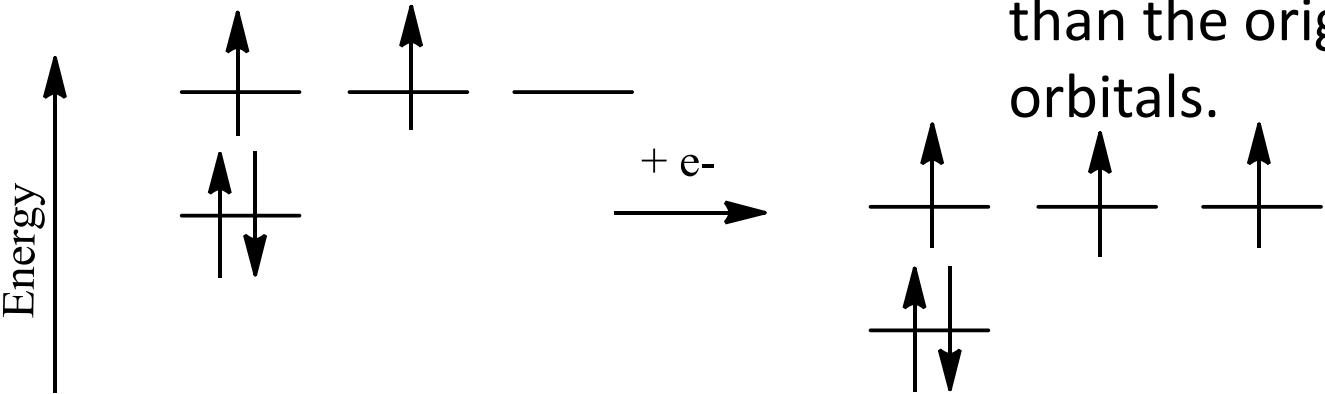
Positive values: energy released or favorable.

			H +73	18/VIII							
				He <0							
1	2	13/III	14/IV	15/V	16/VI	17/VII					
Li +60	Be ≤ 0	B +27	C +122	N -7	O +141 -844	F +328	Ne <0				
Na +53	Mg ≤ 0	Al +43	Si +134	P +72	S +200, -532	Cl +349	Ar <0				
K +48	Ca +2	Ga +29	Ge +116	As +78	Se +195	Br +325	Kr <0				
Rb +47	Sr +5	In +29	Sn +116	Sb +103	Te +190	I +295	Xe <0				
Cs +46	Ba +14	Tl +19	Pb +35	Bi +91	Po +174	At +270	Rn <0				

Why is Group 14 so favorable and Group 15 so unfavorable?

The overall effect is that half-filled shells are more stable in partially filled shells

Group 14 Valence Shells, i.e. carbon

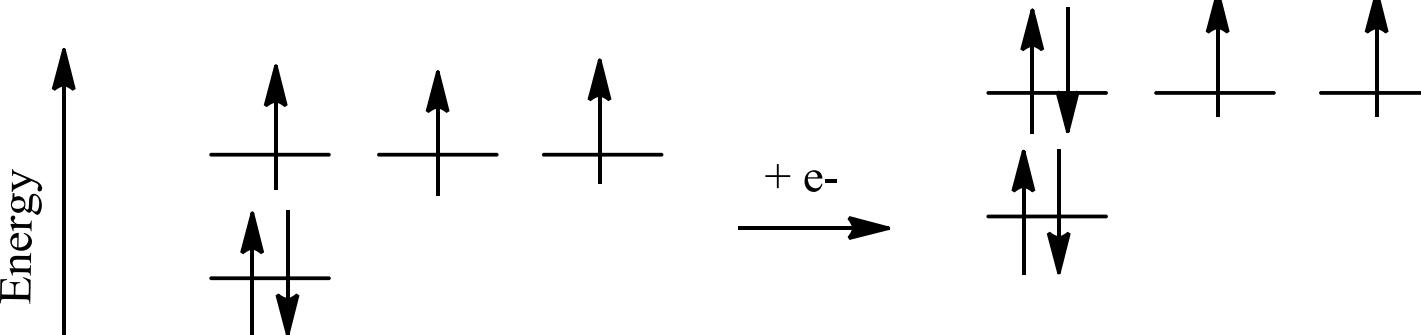


when carbon gains an electron, the orbitals are lower in energy than the original ground state orbitals.

Carbon +122 EA

Nitrogen -7 EA

Group 15 Valence Shells, i.e. nitrogen



when nitrogen gains an electron, the orbitals are higher in energy than the original ground state orbitals.

The Inert-pair effect

Group 13 to 15, common oxidation numbers differ by 2, because **two s-electrons are inert-pair.**

At low period, the s orbital is more stable due to the penetration, **so that Pb⁴⁺ is rare.**

In indium 114.82 $5s^25p^1$	Sn tin 118.71 $5s^25p^2$	Sb antimony 121.76 $5s^25p^3$
Tl thallium 204.38 $6s^26p^1$	Pb lead 207.2 $6s^26p^2$	Bi bismuth 208.98 $6s^26p^3$

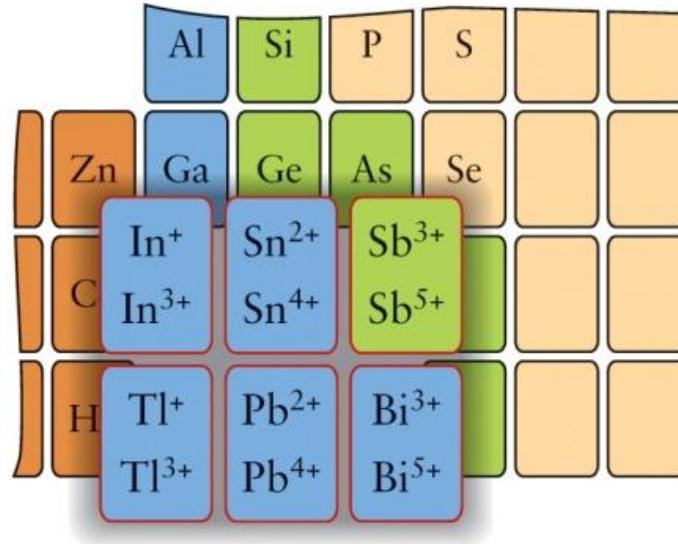


FIGURE 2.31 The typical ions formed by the heavy elements in Groups 13 through 15 show the influence of the inert pair—the tendency to form compounds in which the oxidation numbers differ by 2.

Metallic Character

Physical and Chemical properties

Metals:

Malleable (bend) and ductile (make a wire).

Shiny so reflect light (mirrors).

Electrical and thermal conduct.

Basic.

Lose electrons—**oxidized**.

Nonmetals:

Brittle.

Dull.

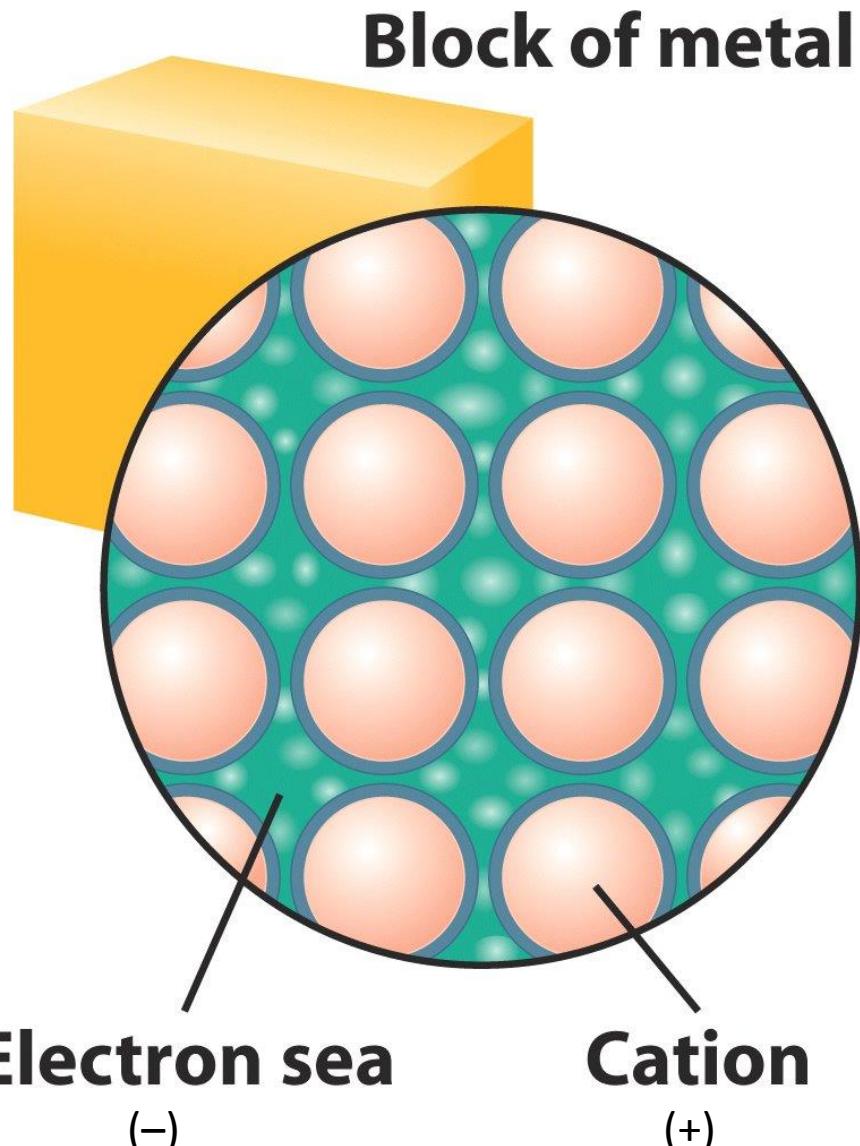
Electrical and thermal insulators.

Acidic.

Gain electrons—**reduced**.

Metallic Bonding

- Electrons are mobile as in the sea .
- This enables metals to conduct an electric current.
- Also accounts for their luster, and malleability- being deformed without shattering.
- The less bounded to nucleus, the more mobile electrons.



Trends in Metallic Character

Least
Metallic

Group	1	2
2	Li lithium 6.94 2s ¹	Be beryllium 9.01 2s ²
3	Na sodium 22.99 3s ¹	Mg magnesium 24.31 3s ²

Period 1	
H hydrogen 1.0079 1s ¹	

Period	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17			
2	Sc scandium 44.96 3d ¹ 4s ²	Ti titanium 47.87 3d ² 4s ²	V vanadium 50.94 3d ³ 4s ²	Cr chromium 52.00 3d ⁵ 4s ¹	Mn manganese 54.94 3d ⁵ 4s ²	Fe iron 55.84 3d ⁶ 4s ²	Co cobalt 58.93 3d ⁷ 4s ²	Ni nickel 58.69 3d ⁸ 4s ¹	Cu copper 63.55 3d ¹⁰ 4s ²	Zn zinc 65.41 3d ¹⁰ 4s ²	Ga gallium 69.72 4s ² 4p ¹	Ge germanium 72.64 4s ² 4p ²	As arsenic 74.92 4s ² 4p ³	Se selenium 78.96 4s ² 4p ⁴	Br bromine 79.90 4s ² 4p ⁵	Kr krypton 83.80 4s ² 4p ⁶		
3	Ca calcium 40.08 4s ²	Sc scandium 44.96 3d ¹ 4s ²	Ti titanium 47.87 3d ² 4s ²	V vanadium 50.94 3d ³ 4s ²	Cr chromium 52.00 3d ⁵ 4s ¹	Mn manganese 54.94 3d ⁵ 4s ²	Fe iron 55.84 3d ⁶ 4s ²	Co cobalt 58.93 3d ⁷ 4s ²	Ni nickel 58.69 3d ⁸ 4s ¹	Cu copper 63.55 3d ¹⁰ 4s ²	Zn zinc 65.41 3d ¹⁰ 4s ²	Ga gallium 69.72 4s ² 4p ¹	Ge germanium 72.64 4s ² 4p ²	As arsenic 74.92 4s ² 4p ³	Se selenium 78.96 4s ² 4p ⁴	Br bromine 79.90 4s ² 4p ⁵		
4	Rb rubidium 85.47 5s ¹	Sr strontium 87.62 5s ²	Y yttrium 88.91 4d ¹ 5s ²	Zr zirconium 91.22 4d ² 5s ²	Nb niobium 92.91 4d ⁴ 5s ¹	Mo molybdenum 95.94 4d ⁵ 5s ²	Tc technetium (98) 4d ⁵ 5s ²	Ru ruthenium 101.07 4d ⁷ 5s ¹	Pd rhodium 102.90 4d ⁸ 5s ¹	Rh palladium 106.42 4d ¹⁰	Ag silver 107.87 4d ¹⁰ 5s ²	Cd cadmium 112.41 4d ¹⁰ 5s ²	In indium 114.82 5s ² 5p ¹	Sn tin 118.71 5s ² 5p ²	Sb antimony 121.76 5s ² 5p ³	Te tellurium 127.60 5s ² 5p ⁴	I iodine 126.90 5s ² 5p ⁵	
5	Cs cesium 132.91 6s ¹	Ba barium 137.33 6s ²	La lanthanum 138.91 5d ¹ 6s ²	Hf hafnium 178.49 5d ² 6s ²	Ta tantalum 180.95 5d ³ 6s ²	W tungsten 183.84 5d ⁴ 6s ²	Rh rhenium 190.23 5d ⁵ 6s ²	Os osmium 192.22 5d ⁶ 6s ²	Ir iridium 195.08 5d ⁷ 6s ¹	Pt platinum 196.97 5d ¹⁰ 6s ¹	Au gold 199.59 5d ¹⁰ 6s ²	Hg mercury 204.38 6s ² 6p ¹	Tl thallium 207.2 6s ² 6p ²	Pb lead 207.2 6s ² 6p ³	Bi bismuth 208.98 6s ² 6p ⁴	At astatine (209) 6s ² 6p ⁵	Rn radon (210) 6s ² 6p ⁶	
6	Fr francium (223) 7s ¹	Ra radium (226) 7s ²	Ac actinium (227) 7s ²	Th thorium 232.04 6d ² 7s ²	Dy dysprosium 231.04 5f ² 6d ¹ 7s ²	Pr praseodymium 231.04 4f ³ 6s ²	Nd neodymium 238.03 5f ⁴ 6d ¹ 7s ²	Pm promethium (237) 5f ⁵ 6d ¹ 7s ²	Sm samarium (244) 5f ⁶ 7s ²	Eu europium (243) 5f ⁷ 6s ²	Gd gadolinium 151.96 4f ⁷ 6s ²	Tb terbium 157.25 4f ⁹ 5d ¹ 6s ²	Dy dysprosium 162.50 4f ¹⁰ 6s ²	Ho holmium 164.93 4f ¹¹ 6s ²	Er erbium 167.26 4f ¹² 6s ²	Tm thulium 168.93 4f ¹³ 6s ²	Yb ytterbium 173.04 4f ¹⁴ 6s ²	Lu lutetium 174.97 5d ¹ 6s ²
7	Lanthanoids (lanthanides)		Actinoids (actinides)		Ce cerium 140.12 4f ¹ 5d ¹ 6s ²	Pr praseodymium 140.91 4f ² 6s ²	Nd neodymium 144.24 4f ³ 6s ²	Pm promethium (145) 4f ⁶ 6s ²	Sm samarium 150.36 4f ⁷ 6s ²	Eu europium 151.96 4f ⁸ 6s ²	Gd gadolinium 157.25 4f ⁹ 5d ¹ 6s ²	Tb terbium 158.93 4f ¹⁰ 6s ²	Dy dysprosium 162.50 4f ¹¹ 6s ²	Ho holmium 164.93 4f ¹² 6s ²	Er erbium 167.26 4f ¹³ 6s ²	Tm thulium 168.93 4f ¹⁴ 6s ²	Yb ytterbium 173.04 4f ¹⁵ 6s ²	Lu lutetium 174.97 5d ¹ 6s ²

Most
Metallic

Diagonal Relationships

React with nitrogen
to form nitrides

React with acids and bases

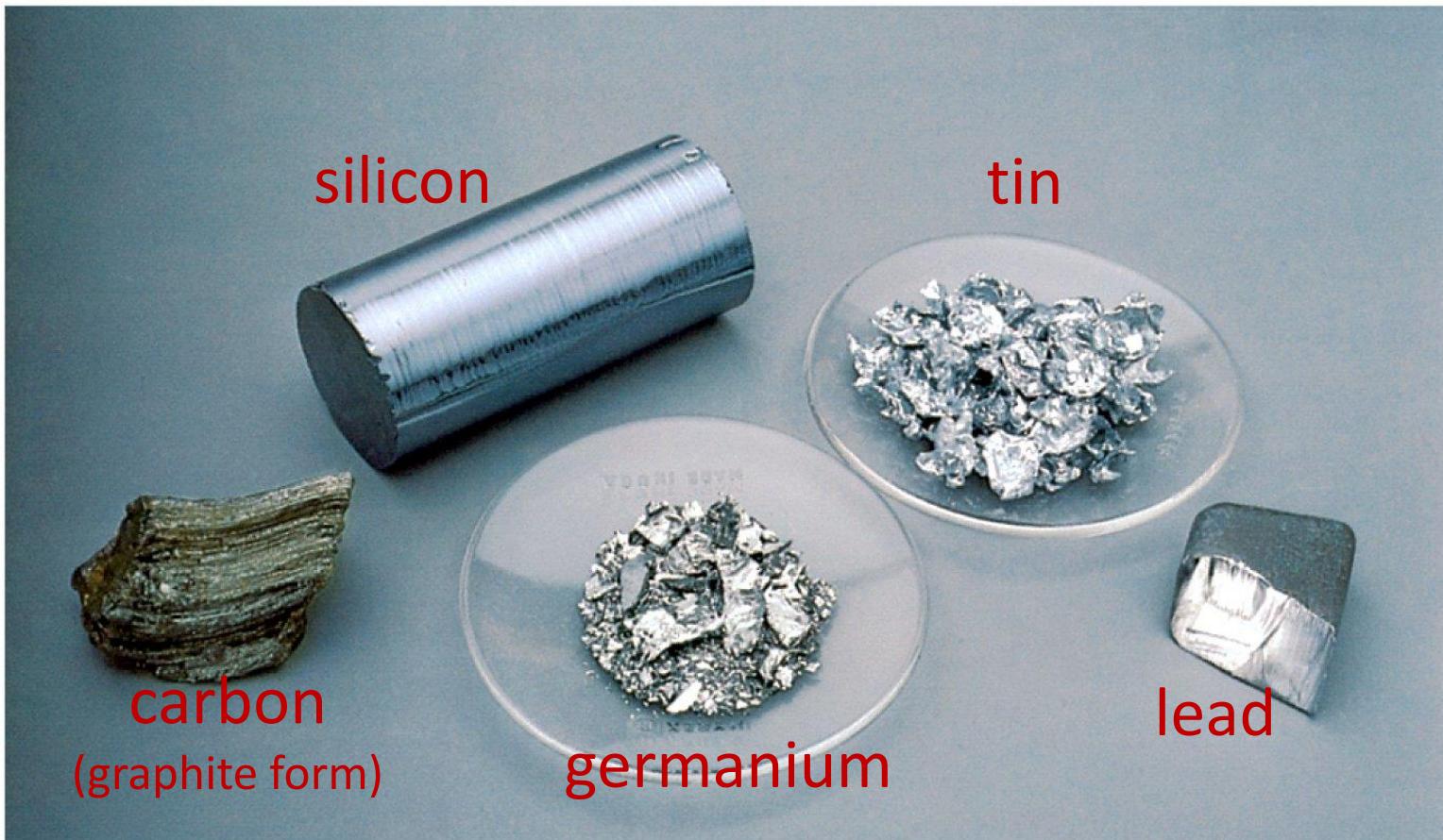


Brittle solids with high melting points

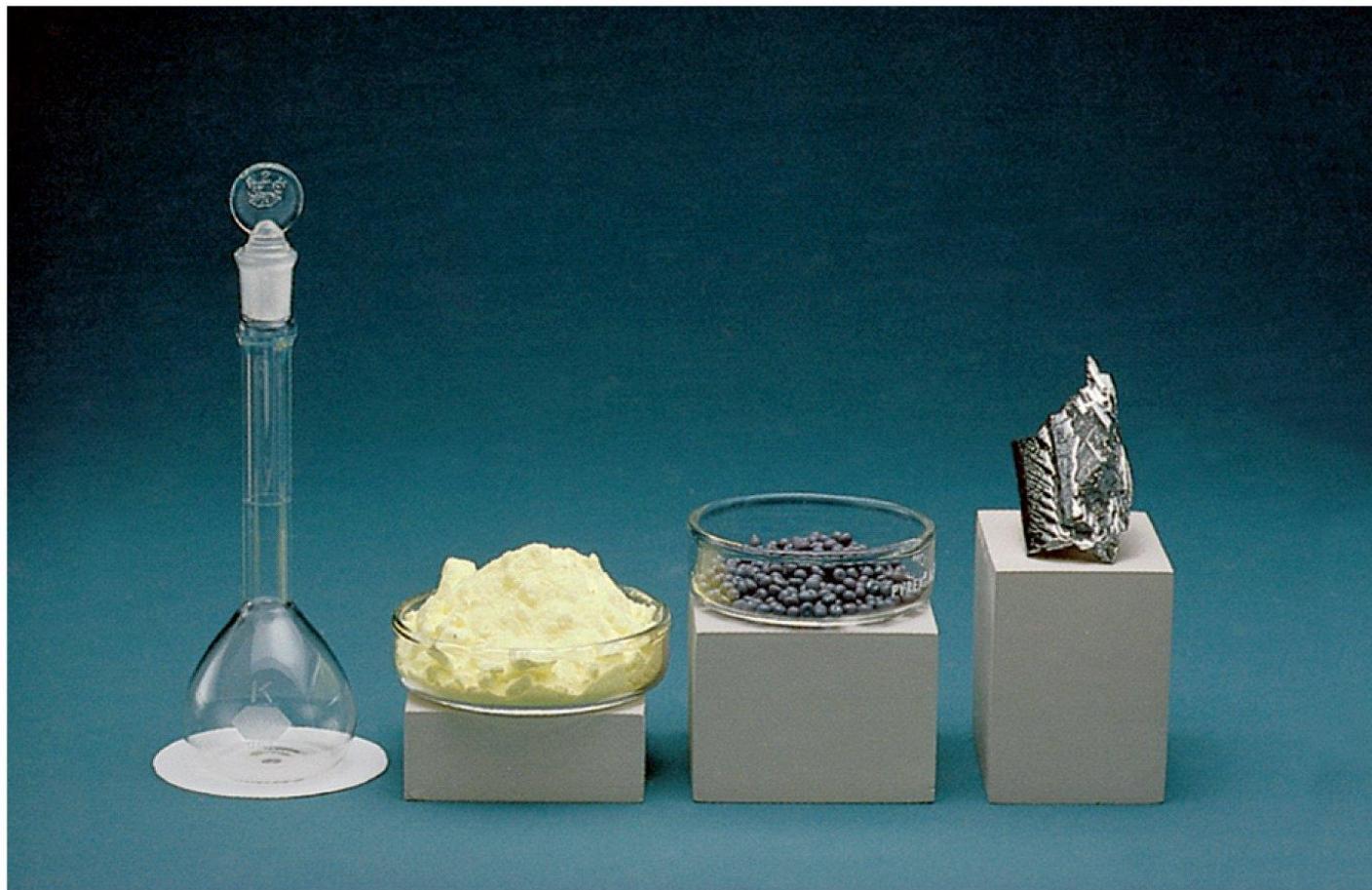
Group 14

Members become more metallic down the group.

- nonmetal (carbon)
- metalloids (silicon, germanium)
- metals (tin, lead)



Group 16 (chalcogens)



oxygen sulfur selenium tellurium
(nonmetal) (nonmetal) (metalloid) (metalloid)

General Properties of Element

S-block: low ionization potential, metallic, the heavier element, the more active

P-block: left and low, low ionization potential, metallic; right and upper, high electron affinity, non-metals

D-block: All metals, similar in properties because differences are in the inner shell (d-orbitals), they are transition series from s- to p- blocks, so called transition metals.

General Properties of Element

D-block: when a d-block atom loses electron, first loses its outmost s-electron.

D-block: d-electrons are similar in energy and a variable number can be lost. Variable oxidation states exist.

D-block: The variable number of d-electrons and similar properties make these elements common catalysts, and in various coordination chemicals.

Lanthanoids – useful in superconductor

Actinoids – all radioactive