

Readings for today: Section 1.12 – Orbital Energies (of many-electron atoms), Section 1.13 – The Building-Up Principle. (Same sections in 5th and 4th ed.)

Read for Lecture #8: Section 1.14 – Electronic Structure and the Periodic Table, Section 1.15, 1.16, 1.17, 1.18, and 1.20 – The Periodicity of Atomic Properties. (Same sections in 5th and 4th ed.)

Topics: Multi-Electron Atoms

I. Wavefunctions and Binding Energies for Multi-electron Atoms

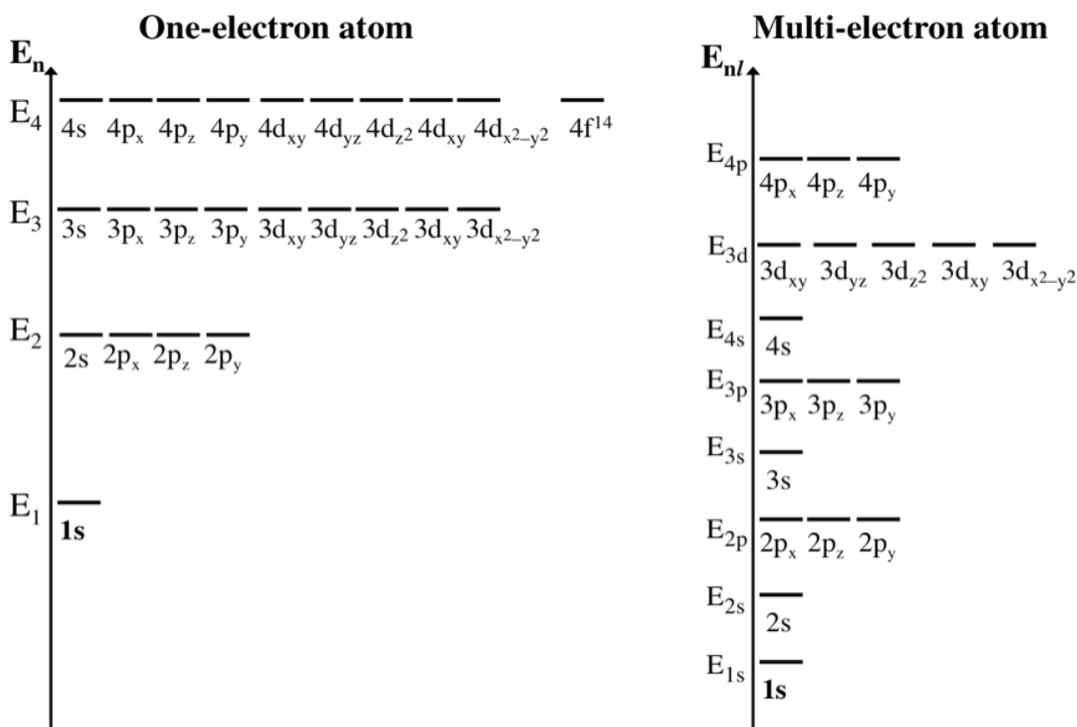
II. Electron Configurations

I. WAVEFUNCTIONS AND BINDING ENERGIES FOR MULTIELECTRON ATOMS

The Schrödinger equation correctly describes the electronic structure for all atoms.

Multi-electron orbitals are **similar in shape** and have the same **nodal structure** as corresponding hydrogen one-electron orbitals.

However, there are important differences in thinking about multi-electron binding energies! All orbitals in a multi-electron atom are lower in energy (_____) than the corresponding orbital in a hydrogen atom.



The lower energy results in multi-electron atoms results from a higher Z --- a stronger pull from the nucleus.

The principal quantum number, n , is no longer the sole determining factor for the orbital energies of multi-electron atoms. **Binding energy now depends on _____ and _____.**

▪

$$E_n = -IE_n = -\frac{Z^2 R_H}{n^2} \quad E_{n,l} = -IE_{n,l} = -\frac{(Z_{\text{eff}}^{n,l})^2 R_H}{n^2}$$

For _____-electron atoms For _____-electron atoms

Where Z_{eff} is the effective charge experienced by the electron in the n,l

state. Z_{eff} _____ the same as Z for the nucleus.

Z_{eff} differs from Z because of _____.

SHIELDING and Z_{eff}

To illustrate the effect of shielding, consider the two **extreme** shielding situations possible for the He atom ($Z = 2$).

Extreme CASE A for He: **Extreme** shielding



He nucleus (charge = _____)

Electron #2 maximally shields electron #1 from the (+) charge of the He nucleus

Electron #1 experiences a force on average of $Z_{\text{eff}} = \underline{\hspace{2cm}}$, not $Z_{\text{eff}} = +2e$.

$$E_{e\text{-}\#1} = \underline{\hspace{2cm}}_{e\text{-}\#1} = -\frac{(Z_{\text{eff}})^2 R_H}{n^2} = \underline{\hspace{2cm}} = \underline{\hspace{2cm}} \text{ J}$$

The energy of electron #1 is that of an electron in an H (1-electron) atom.

Extreme CASE B for He: No shielding



He nucleus (charge = +2e)

Electron #2 doesn't participate in shielding electron #1 from the He nucleus
 Electron #1 experiences a force on average of $Z_{\text{eff}} = \underline{\hspace{2cm}}$.

$$E_{e\text{-}\#1} = - IE_{e\text{-}\#1} = - \frac{(Z_{\text{eff}})^2 R_{\text{H}}}{n^2} = \underline{\hspace{2cm}} = \underline{\hspace{2cm}} \text{ J}$$

The energy of electron #1 is that of an electron in a $\underline{\hspace{2cm}}$ (1-electron) ion.

Extreme case A:	$Z_{\text{eff}} = 1,$	$IE_{\text{He}} = 2.18 \times 10^{-18} \text{ J}$	$\underline{\hspace{2cm}}$ shielding
Extreme case B:	$Z_{\text{eff}} = 2,$	$IE_{\text{He}} = 8.72 \times 10^{-18} \text{ J}$	$\underline{\hspace{2cm}}$ shielding
Experimentally determined		$IE_{\text{He}} = 3.94 \times 10^{-18} \text{ J}$	

So the reality is somewhere between total shielding and no shielding.

We can calculate the Z_{eff} from the experimentally determined IE:

$$IE = \frac{(Z_{\text{eff}})^2 R_{\text{H}}}{n^2}$$

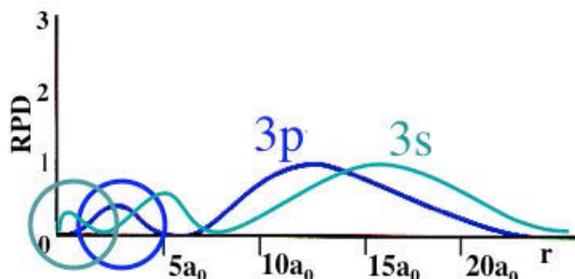
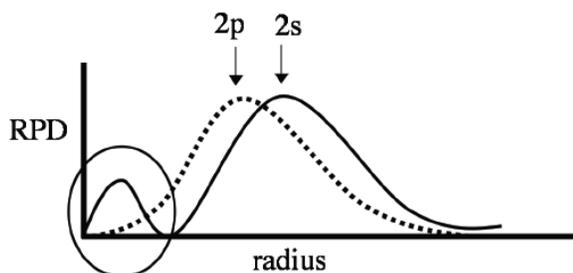
$$R_{\text{H}} = 2.180 \times 10^{-18} \text{ J}$$

For an IE_{He} of $3.94 \times 10^{-18} \text{ J}$, $Z_{\text{eff}} = \underline{\hspace{2cm}}$

between $\underline{\hspace{1cm}}$ ($\underline{\hspace{1cm}}$ shielding) and $\underline{\hspace{1cm}}$ ($\underline{\hspace{1cm}}$ shielding).

Why is $E_{2s} < E_{2p}$ and $E_{3s} < E_{3p} < E_{3d}$?

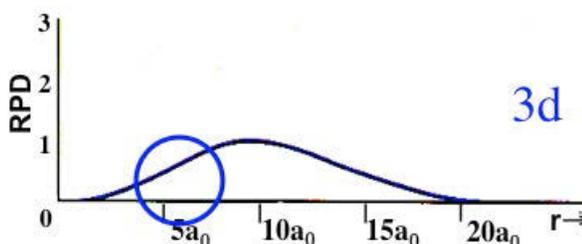
For a given n state (shell), electrons in orbitals with lower values of l _____ closer to the nucleus (even though r_{mp} decreases with increasing l !).



This means (for the same n):

s -electrons are less shielded than p electrons. Thus $E_{2s} < E_{2p}$

p -electrons are less shielded than d -electrons. Thus $E_{3p} < E_{3d}$



Thus in a multi-electron atom, effects of penetration and shielding give rise to the order of energies of orbitals in a given shell of $s < p < d < f$.

II. ELECTRON CONFIGURATIONS

Electron configuration describes the electronic structure of an atom by specifying which orbitals are occupied. This notation is very useful, since electron structure dictates the chemical properties and reactivity of a given atom.

How do we determine the electron configuration of an atom?

AUFBAU PRINCIPLE

Fill energy states (which depend on ___ and ___) one electron at a time, starting with the lowest energy state and following:

1) The Pauli Exclusion Principle

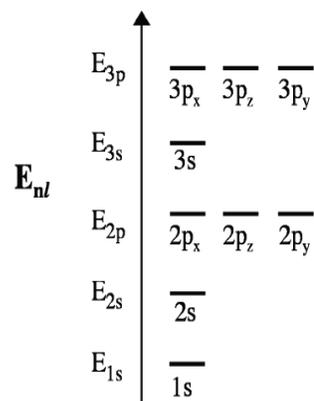
2) Hund's rule: when electrons are added to states of the same E , a single electron enters each state before a second electron enters any state. Spins remain _____ prior to adding a second electron to any state.

Let's try this for O ($Z = 8$).

Electron configuration: _____

(specifying m_l): _____

You need only provide m_l notation if specifically asked.

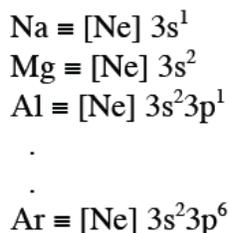
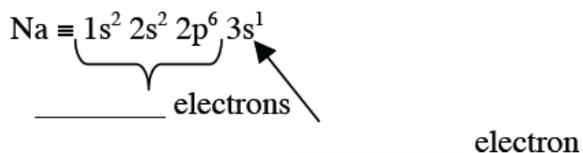


Electron configurations can be simplified by considering core versus valence electrons.

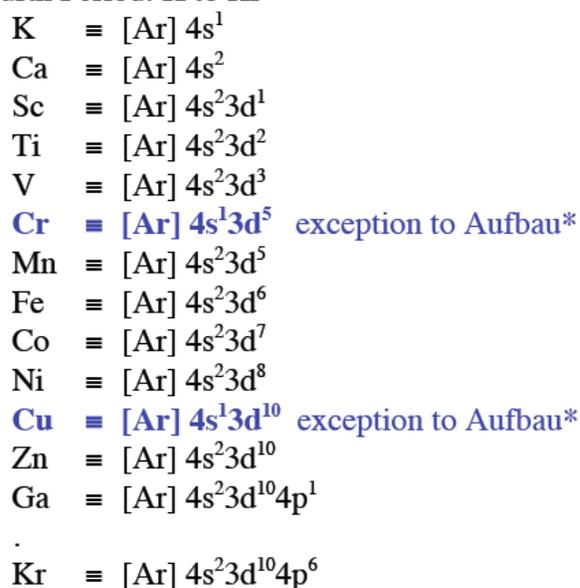
Core electrons: electrons in inner shells making up a noble gas configuration.

Valence electrons: electrons in the outer most shell. Valence electrons are the exciting ones. In general, only the valence electrons participate in chemical reactions.

Third Period: Na to Ar



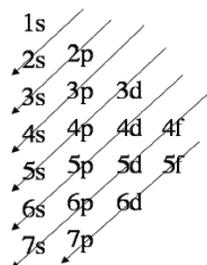
Fourth Period: K to Kr



* Exceptions to the Aufbau principle: filled (____) and half-filled (____) d-orbitals have lower energy than simple theory predicts.

Fifth Period: Rb to Xe. Mo and Ag are counterpart anomalies to Cr and Cu in 4th period.

Additional anomalies and other effects are difficult to predict.

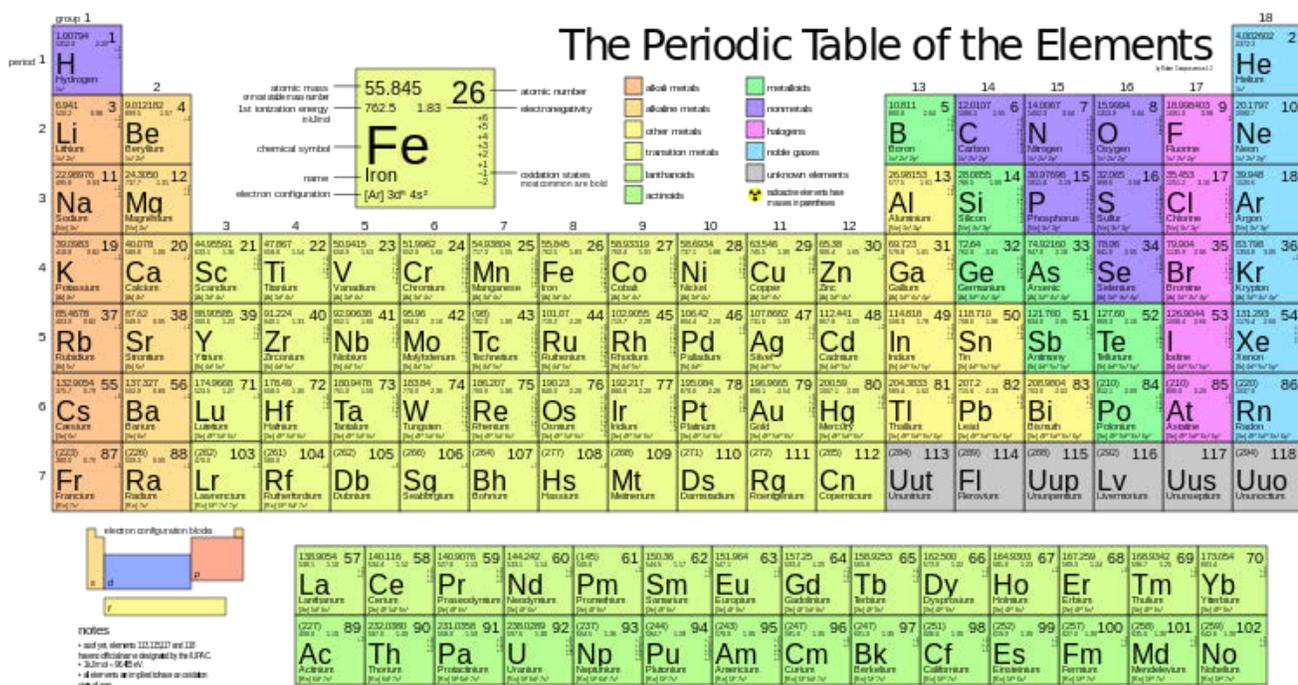


Mnemonic for electron configuration: diagonals

Using this chart, we can write out the correct order of orbitals with increasing energy from left to right:

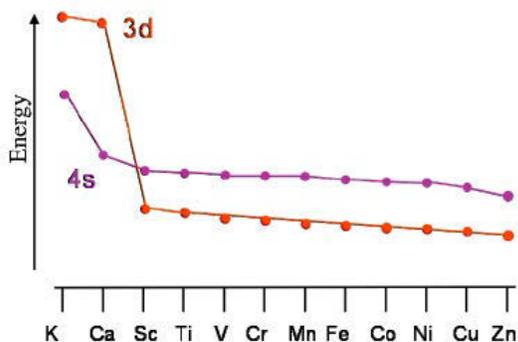
1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p

The periodic table can be used for writing electron configurations



Periodic Table of the Elements, by 2012rc, 2009. [Wikimedia Commons](https://commons.wikimedia.org/wiki/File:PeriodicTableOfElements-2012rc.png). License CC-BY.

ELECTRON CONFIGURATIONS OF IONS



- Electron configurations of ions are NOT ALWAYS the same as neutrals!!!

Once a **d orbital** is filled, the orbital energy **drops** to below the corresponding s orbital.

Consider Ti vs. Ti^{2+}

Ti = $[Ar]4s^23d^2$ (standard notation) but,

Ti = $[Ar] 3d^24s^2$ (based on energy levels) thus,

Ti^{2+} = $[Ar]$ _____ (electrons lost are from 4s)

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