Welcome to
APS104S – Introduction to Materials & Chemistry

Lecture 2

January 6, 2016

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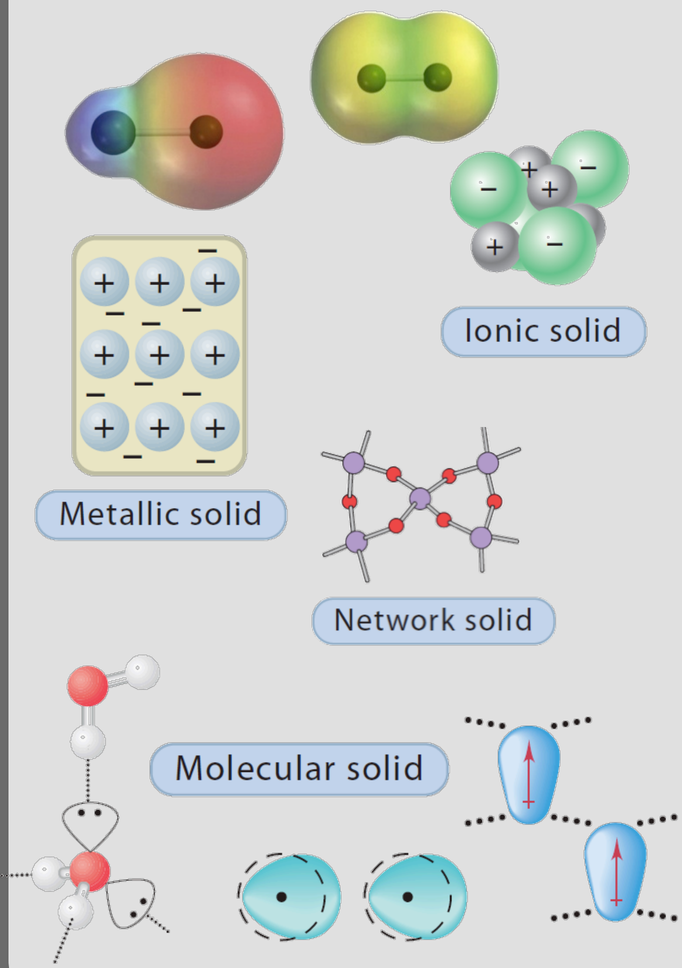
Atomic Structure & Bonding

CHAPTER 2_C



topics:

atomic models

electronic structure & quantum mechanics

quantum numbers

bonding forces and energies

primary interatomic bonds

secondary bonding

Subjects we will study today

- Atomic models (Bohr model; wave mechanical model)
- Quantum numbers
- Orbitals
- Aufbau principle
- Electronic structure

Atomic models

Evolution of atomic models

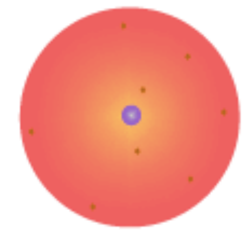
1803

Dalton proposes the indivisible unit of an element is the atom.

1904

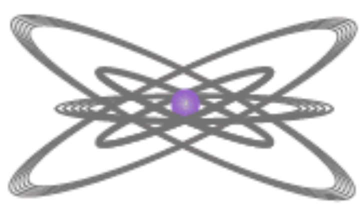
Thomson discovers electrons, believed to reside within a sphere of uniform positive charge (the "plum pudding" model).

1911



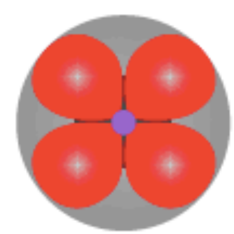
Rutherford demonstrates the existence of a positively charged nucleus that contains nearly all the mass of an atom.

1913



Bohr proposes fixed circular orbits around the nucleus for electrons.

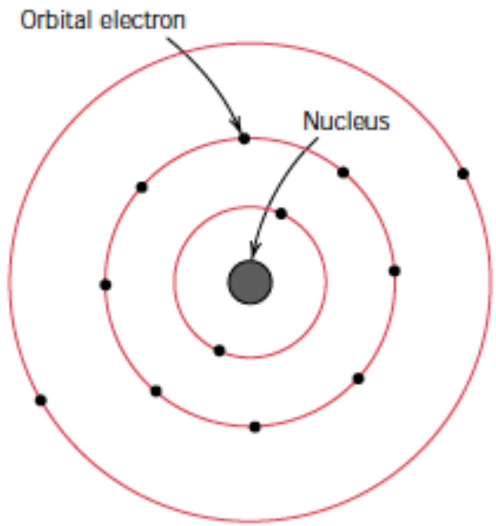
1926



In the current model of the atom, electrons occupy regions of space (orbitals) around the nucleus determined by their energies.

Source: MIT open cource ware

Bohr's model (1913)

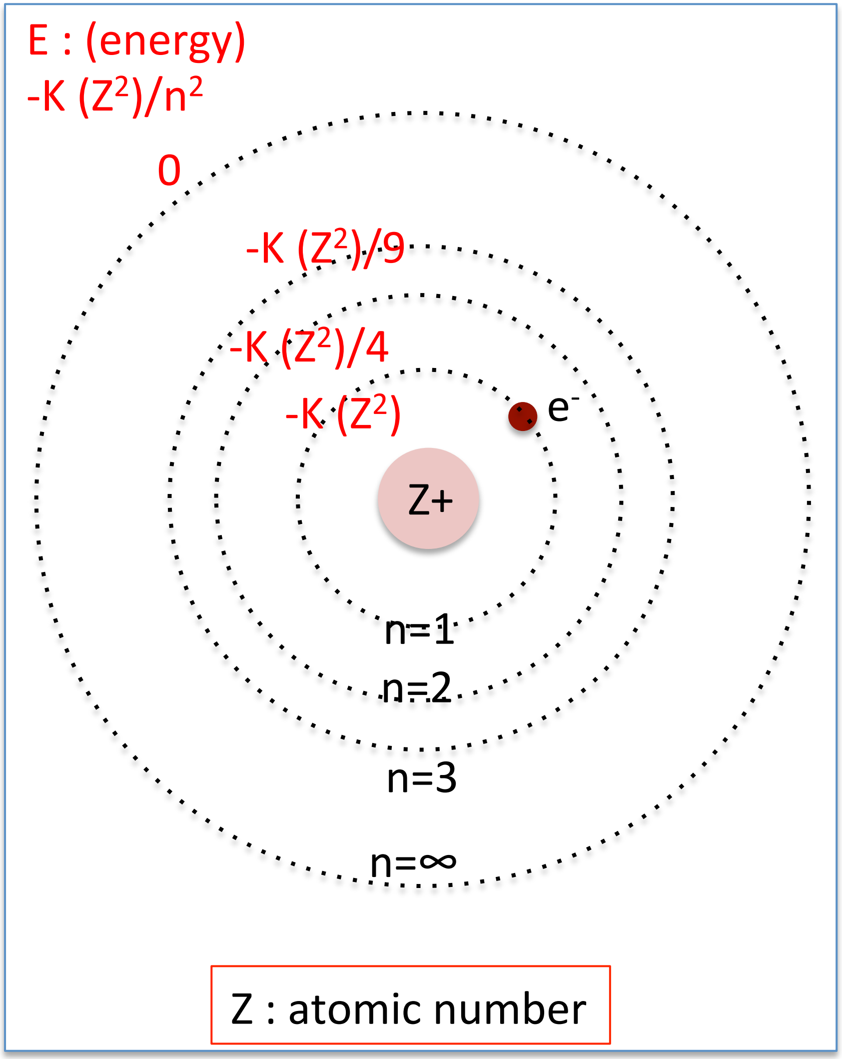


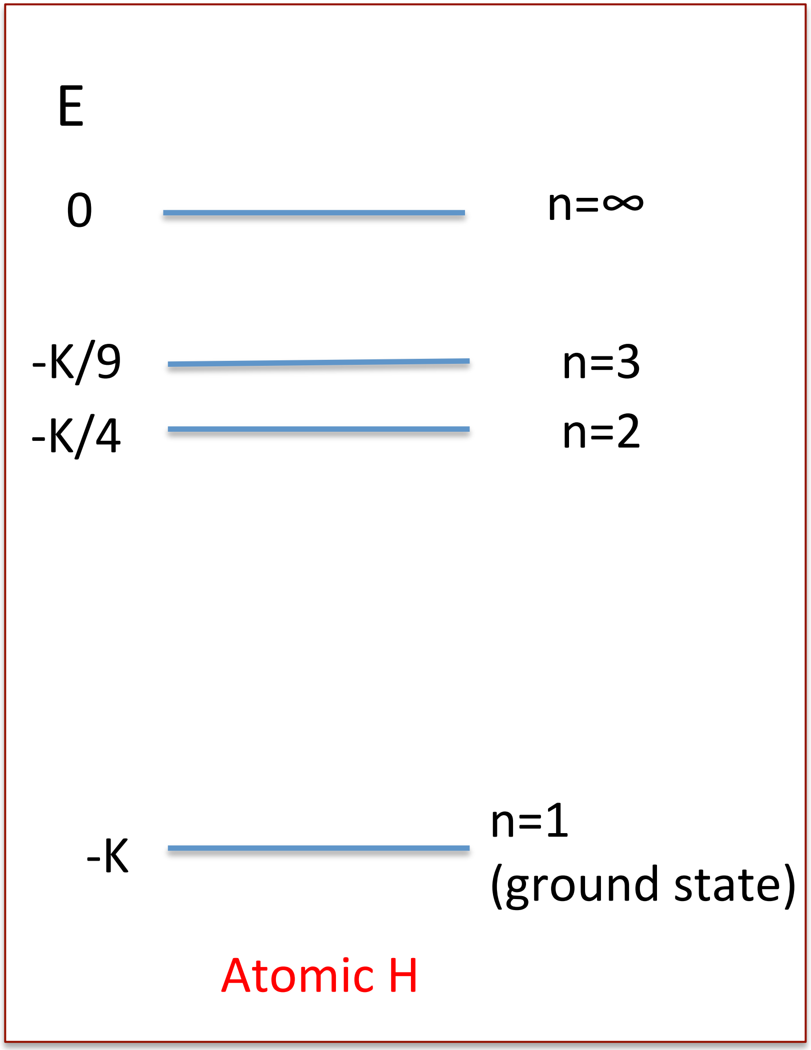
He developed a quantitative model for the atom –
called **Planetary Model**.
(e^- orbiting the positive nucleus in a circular orbit)

Central ideas:

- Nucleus is dense & electrons that are only allowed in certain circular **orbits**.
- Electrons undergo changes in energy only by moving between energy levels.
- Energy of electrons and the radii of orbitals are **quantized** (function of **n**).

Bohr's model (1913)





About Niels Bohr

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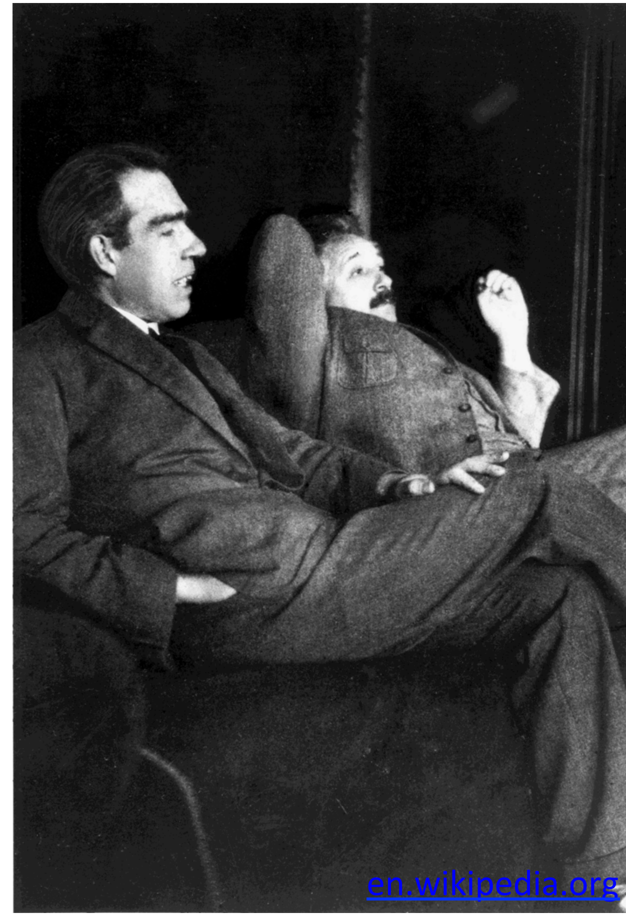


en.wikipedia.org

Niels Bohr with Albert Einstein (December 1925)

Plate 31 Royal visit to Carlsberg on May 22, 1957. From left to right, Queen Elizabeth, the Duke of Edinburgh, Niels Bohr, Crown Princess (later Queen) Margrethe, Mrs Bohr, King Fredrik IX. (Niels Bohr Archive.)

More advanced model

Wave-mechanical model

Wave-mechanical model

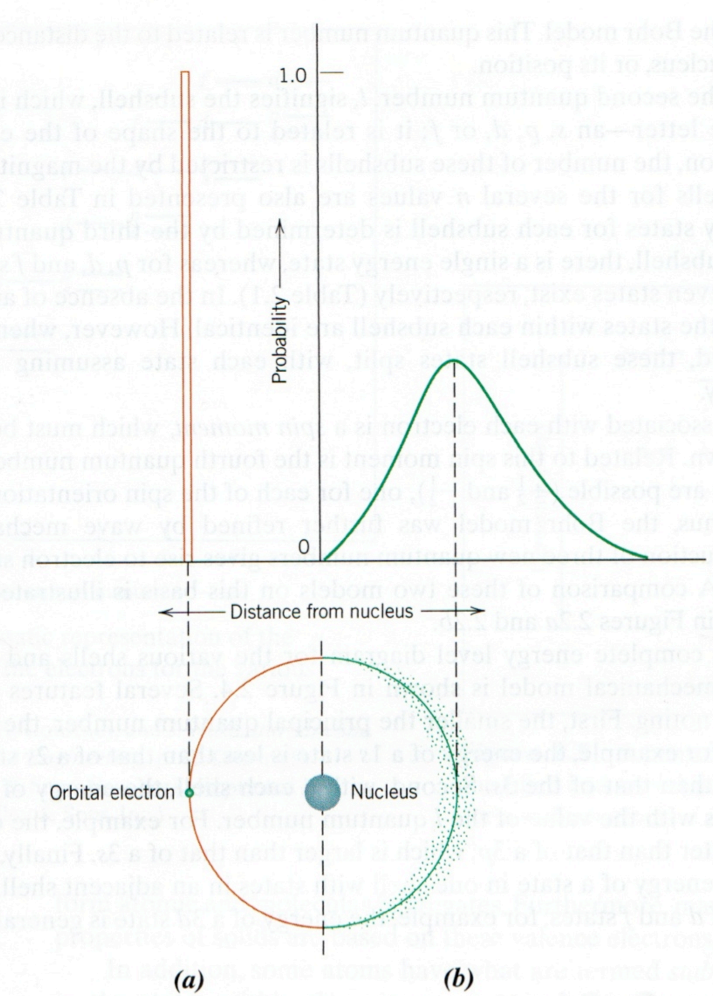
There are some limitations with the Bohr model

The model to address this:

wave-mechanical model

- electron exhibit both wavelike and particle-like properties

- Its position is not a discrete orbit, but the probability of an electron being at various locations around the nucleus

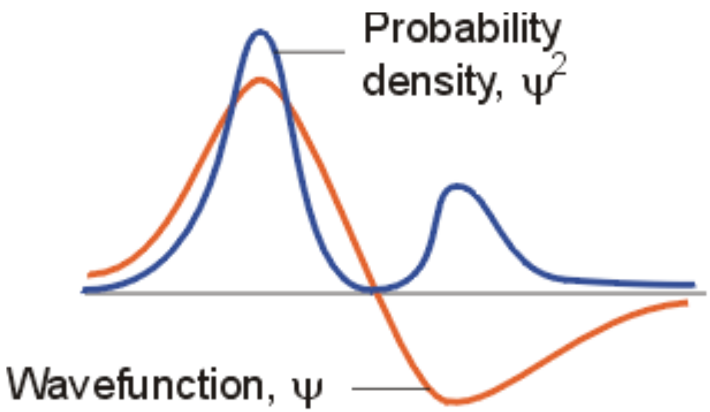


Source: Callister Book

Some clarifications about orbitals

- **Question:** could you locate the precise position of the electron? A German physicist, **Werner Heisenberg**, answered **"no"** in what he called the **uncertainty principle.**
- We can never know both the **momentum and position** of an electron in an atom. Therefore, Heisenberg said that we shouldn't view electrons as moving in well-defined orbits about the nucleus!
- With Heisenberg's uncertainty principle in mind, an Austrian physicist named **Erwin Schrodinger** derived a set of equations or **wave functions** **(Ψ)** in 1926 for electrons.
- According to Schrodinger, electrons confined in their orbits would set up standing waves and **you could describe only the probability (Ψ^2) of where an electron could be**.
- The distributions of these probabilities formed regions of space about the nucleus were called **orbitals**. Orbitals could be described as **electron density cloud**.
- The densest area of the cloud is where you have the greatest probability of finding the electron and the least dense area is where you have the lowest probability of finding the electron.

Schrödinger's quantum mechanical model of the atom



ORBITAL : the region of space within which an electron is found.

- Ψ (wave function) does NOT describe the exact location of the electron.
- Ψ^2 is proportional to the probability of finding an e^- at a given point.

3 Quantum Numbers are needed to describe an **orbital**.

4 Quantum Numbers are needed to define the state of an **electron**.

Quantum numbers & Orbital shapes

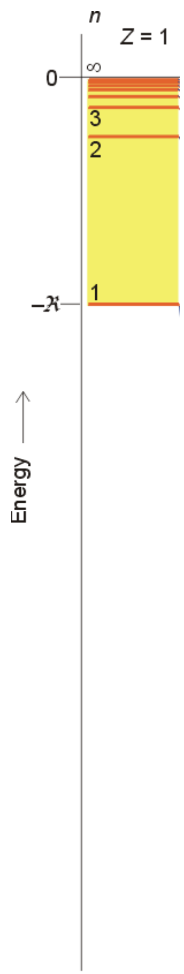
Quantum numbers

- In wave mechanics, four quantum numbers are needed to characterize each e^- in an atom
- Shells → principle quantum number (n=1,2,3,4,5) indicated as (K,L,M,N,O)
- Sub-shells "angular quantum number" → l (0,.., n-1) (orbital shape)
- Magnetic quantum number: m_l ($-l$,..,l) (the number of energy states for each sub-shell) (px,py,pz → -1,0,+1)
- Spin quantum number (m_s) (+1/2, -1/2)

$$E = E\,(n, l, m_l, m_s)$$

Principle quantum number, n

Principle quantum number ***(n)*** *determines the* *size (distance of the electron from the nucleus)* *and the* *energy of the atomic orbital.*



H (Z = 1)

Allowed Values: *n* = 1, 2, 3, …

- *As n increases, the number of allowed orbitals and their size increases.*
- *The increased size allows the* ***electrons to reside further from the nucleus.***
- *As the electron moves away from the nucleus, its energy increases, therefore n also indicates the energy of electrons.*

Angular momentum quantum number - *l*

- The orbitals belonging to each **shell** are classified into **sub-shells** distinguished by a quantum number *l*.
- The **angular momentum quantum number** defines the three dimensional **shape** of the orbitals found within a particular shell.

Allowed Values: $l = 0, 1, 2, 3, \ldots n-1$

Quantum Number *l*	0	1	2	3	4
Sub-shell Notation	s	p	d	f	g

Increasing Energy →

Example: $n = 3$ $l = 0, 1, 2$

shell *subshells*

3s 3p 3d orbitals

Magnetic quantum number - m_l

A **subshell** with quantum number ***l*** consists of **2*l* + 1** individual orbitals.

The **magnetic quantum number**, m_l, distinguishes orbitals of a given ***n*** and ***l*** by their **orientation in space**.

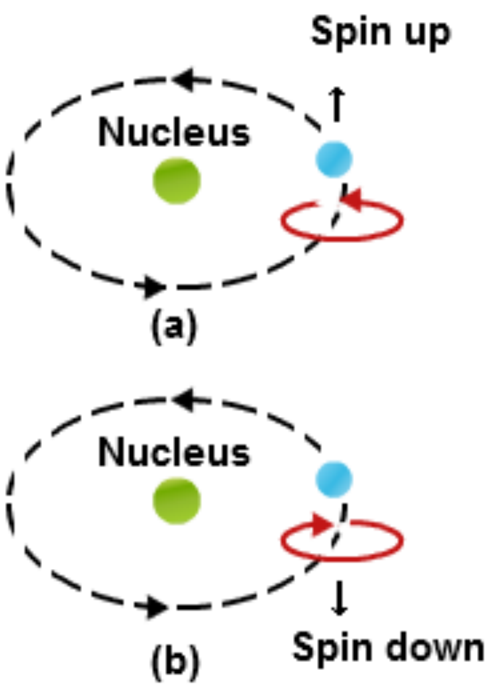
Allowed Values: $m_l = -l,\ldots,+l$

Example: **for a 3 p orbital (n = 3, l=1)** $m_l = -1, 0, 1$

p_x, p_y, p_z

Spin quantum number - m_s

- While revolving in an orbit, electron spins too.
- Proposed that electron spins either up or down – (4^{th} quantum number (s) = electron spin)



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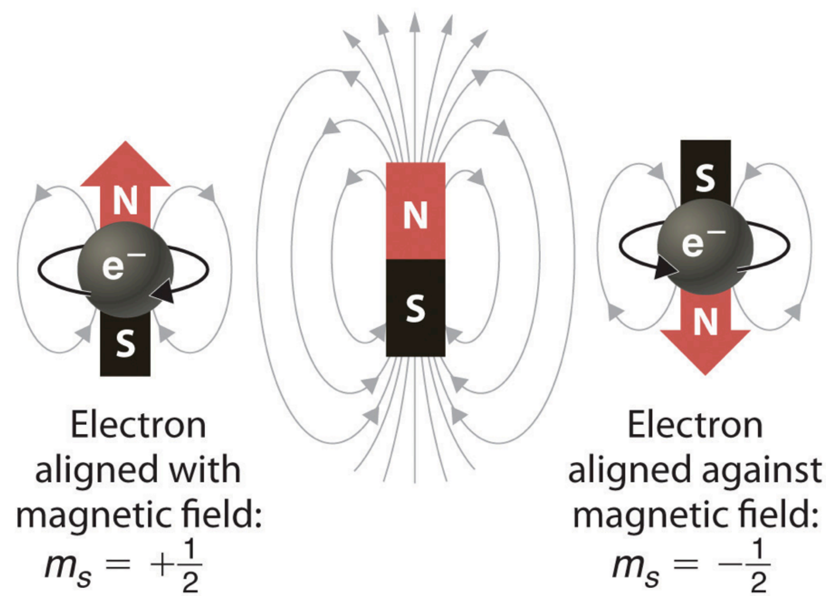
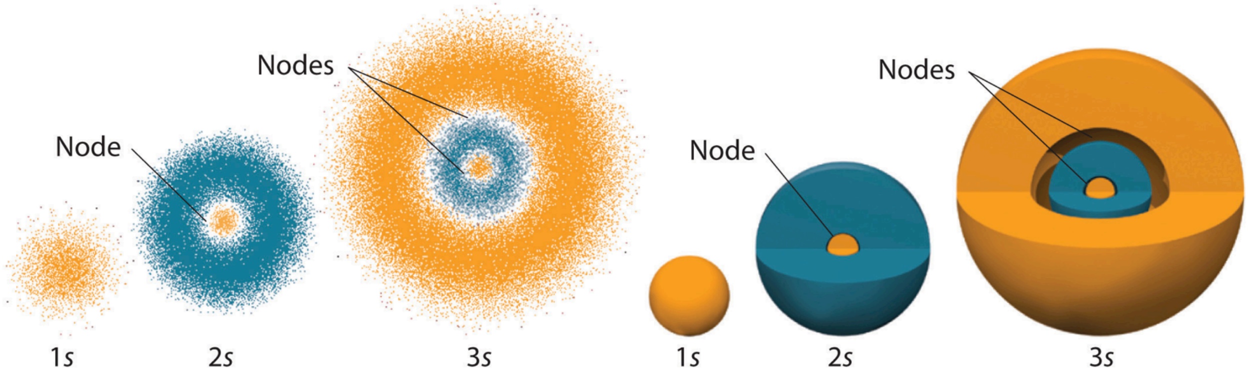


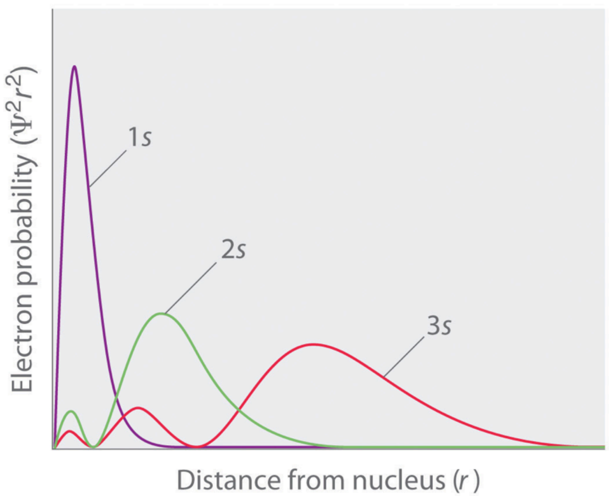
Source of photos: Averill & Eldredge book

Orbital shapes – *s* orbital



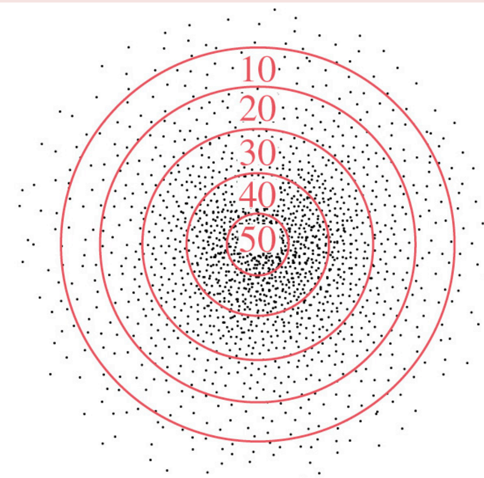
(a) Electron probability **(b) Contour probability**

l = 0
m = 0



(c) Radial probability

Dartboard: 1s Orbital Analogy

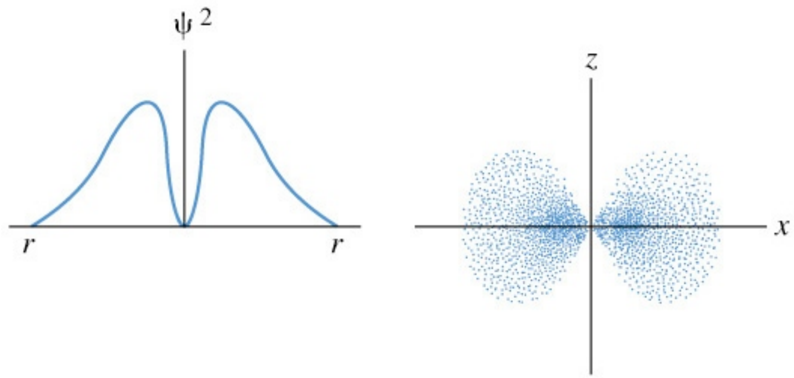


Orbital: For illustration, it is taken to be a **boundary surface** enclosing the **volume** where an electron spends most of the time (**95%**).

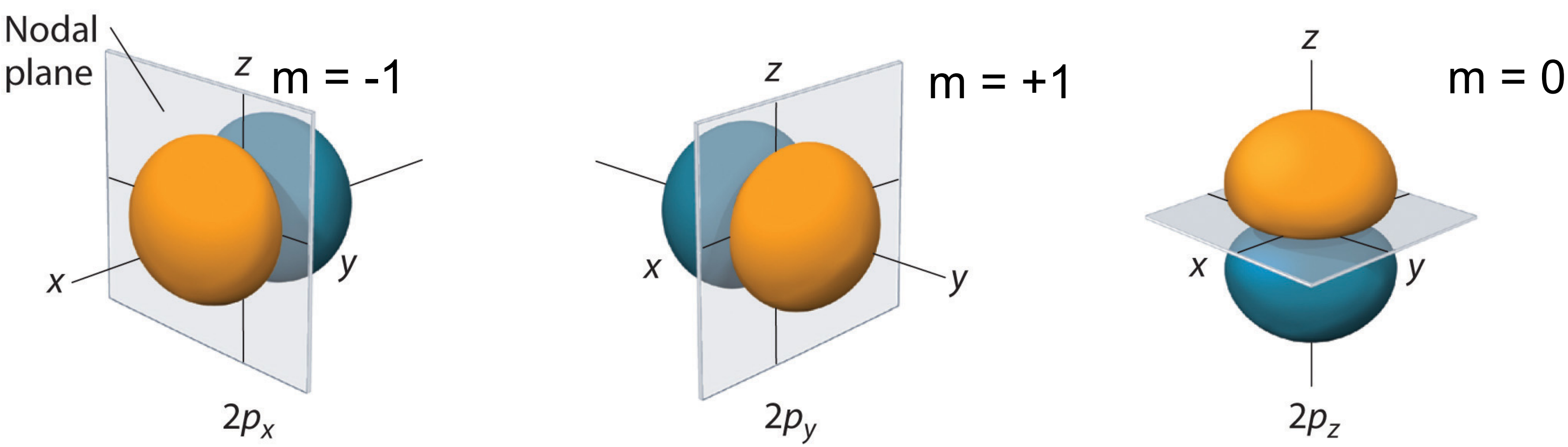
Source of photos: Averill & Eldredge book

Orbital shapes – *p* orbital

l = 1



The Three Equivalent 2p Orbitals of the Hydrogen Atom



The ***p* orbitals** are **dumbbell shaped** with their electron density concentrated **in identical lobes** residing on opposite sides of a **nodal plane**.

Source of photos: Averill & Eldredge book

Quantum numbers

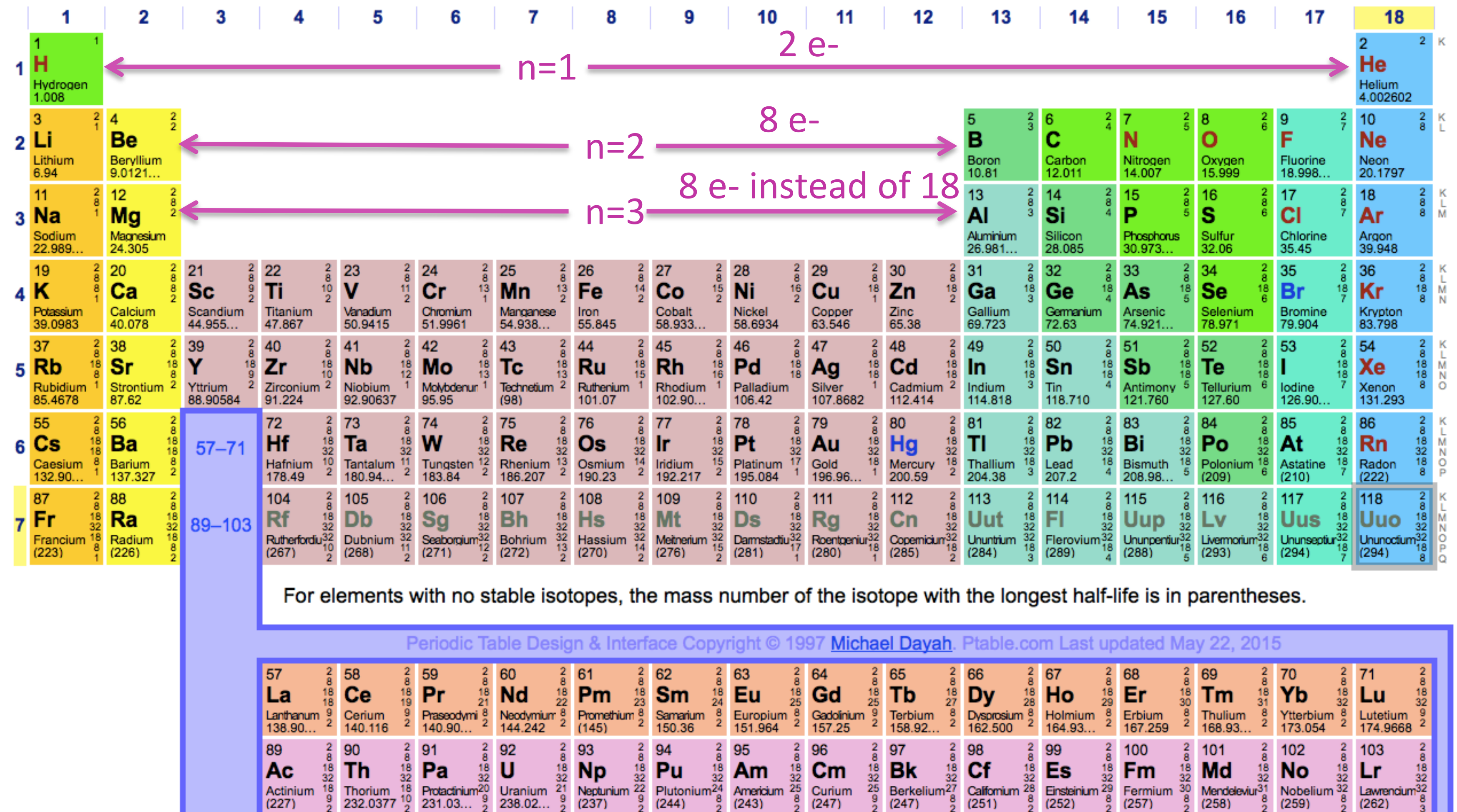
shell Sub-shell Number of orbitals

n	l	*Subshell Designation*	m_l	*Number of Orbitals in Subshell*	*Number of Orbitals in Shell*
1	0	1s	0	1	1
2	0	2s	0	1	4
	1	2p	-1, 0, 1	3	
3	0	3s	0	1	9
	1	3p	-1, 0, 1	3	
	2	3d	-2, -1, 0, 1, 2	5	
4	0	4s	0	1	16
	1	4p	-1, 0, 1	3	
	2	4d	-2, -1, 0, 1, 2	5	
	3	4f	-3, -2, -1, 0, 1, 2, 3	7	

Values of n, l, and m, through n = 4

Let's go to the periodic table and see if this reconciles

Electron filling in the periodic table



Discrepancy between populating electrons just in ascending quantum numbers

Source: http://www.ptable.com

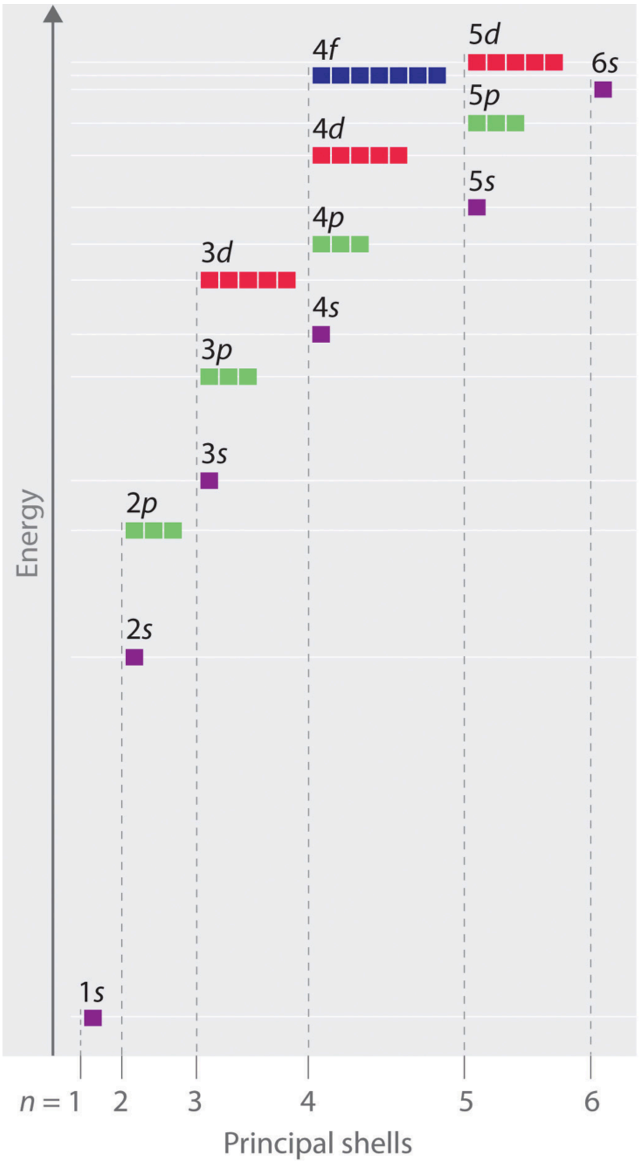
Electronic structure (Aufbau principle)

Modified energy-level diagram

Is drawn based on the Aufbau principle

(directs the electron filling sequence)

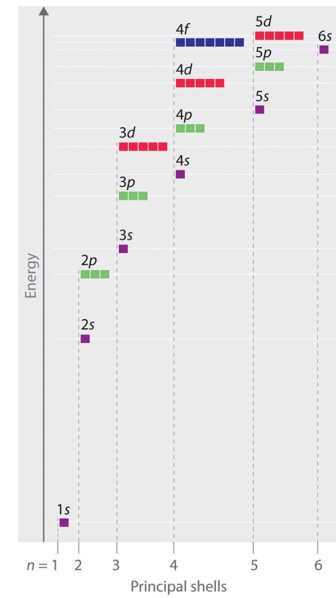
Aufbau is a German noun that means "construction". The Aufbau principle is sometimes called the **building-up principle.**



Source of photos: Averill & Eldredge book

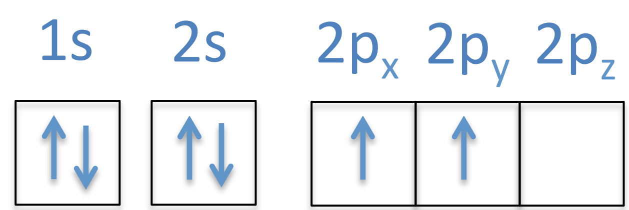
There are 3 parts to the Aufbau (construction) principle

- ***Pauli exclusion principle***: in any atom, each e^- has a unique set of 4 quantum numbers (n, l, m_l, m_s) (like SIN for each e^-).
- Electrons fill orbitals from lowest to highest energy.
- ***Hund's rule***: degeneracy: orbitals of equivalent energy strive for unpaired electron spins.



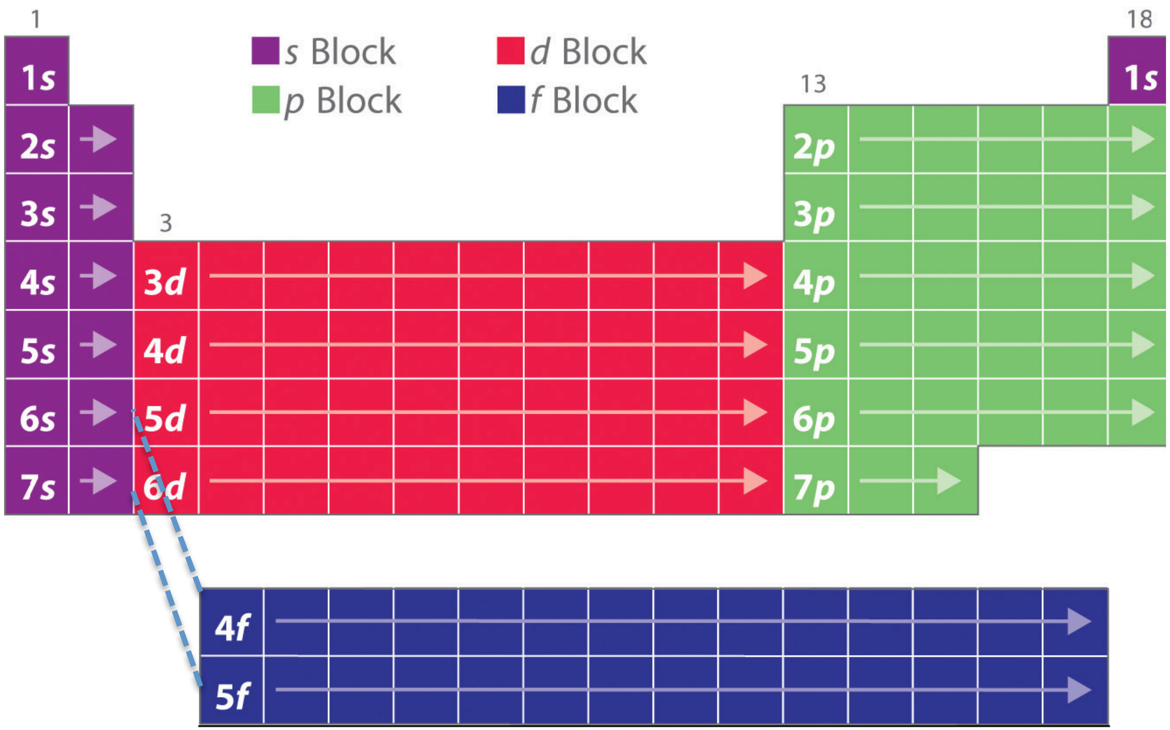
$_6C : 1s^2\ 2s^2\ 2p^2$

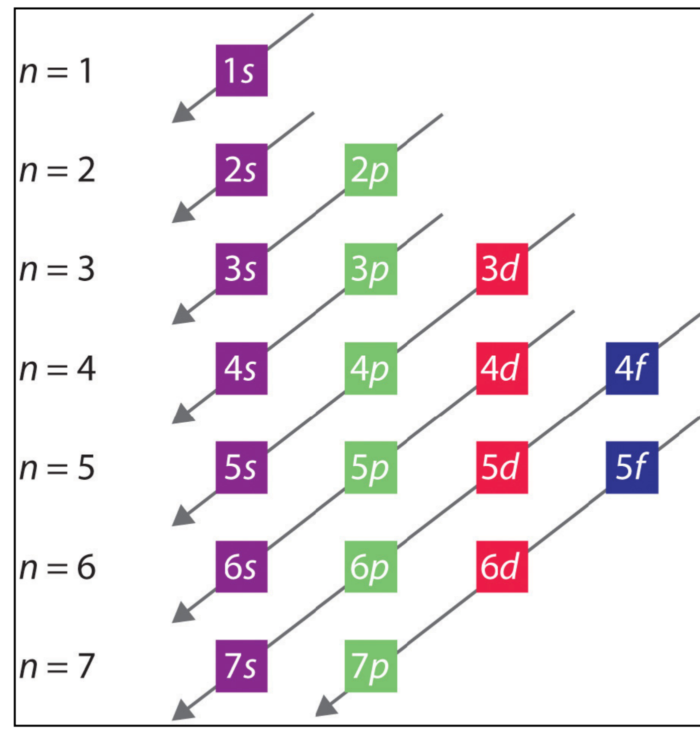
l = 0   l = 1



Box representation

Aufbau Principle - Predicting the Order in Which Orbitals are Filled in Multi-electron Atoms





Source: MIT open cource ware

Example 1

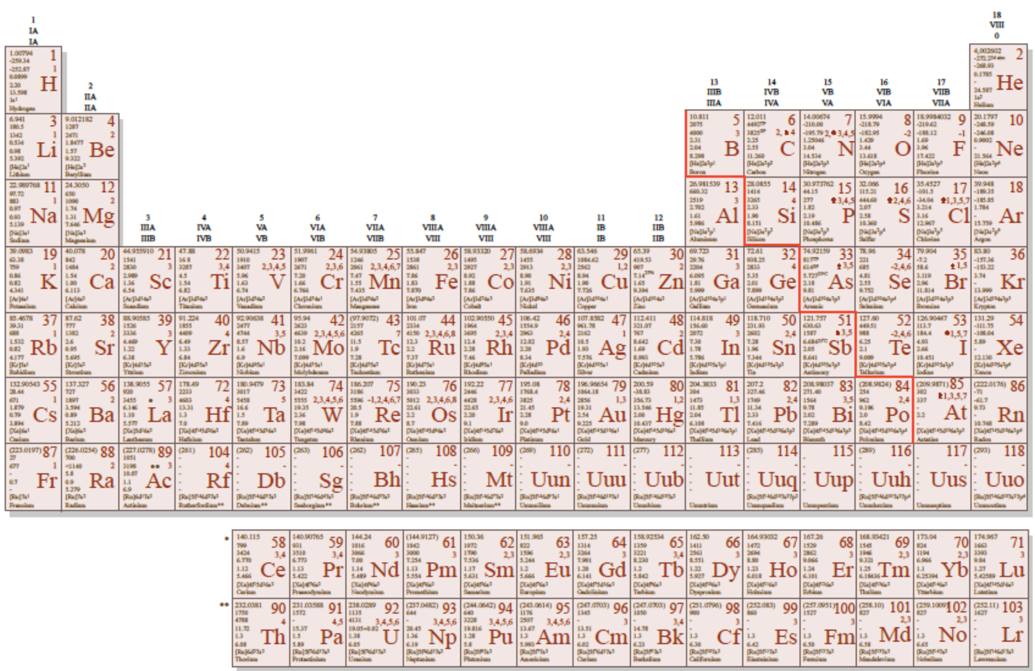
Write out the electron configuration for the following elements:

Boron (z=5): [He] $2s^2 2p^1$

Potassium (z=19): [Ar] $4s^1$

Chromium: [Ar]$3d^5 4s^1$

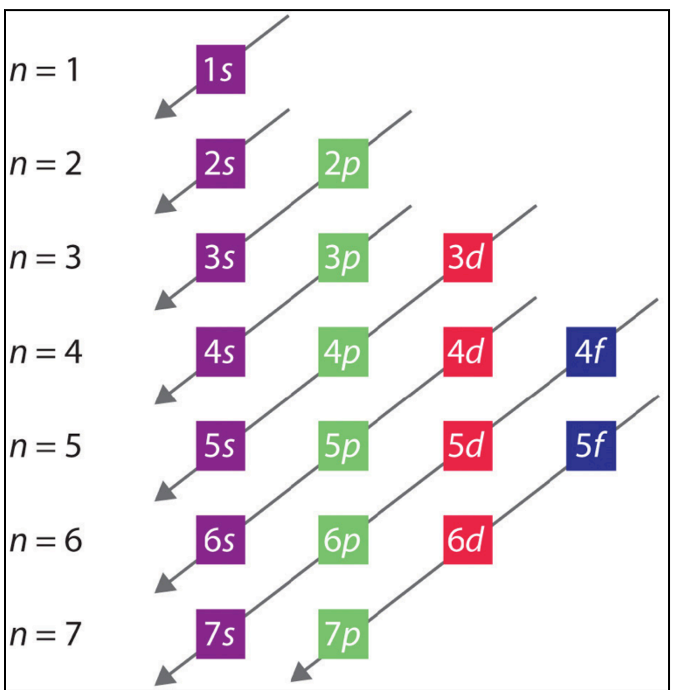
Copper: [Ar]$3d^{10} 4s^1$

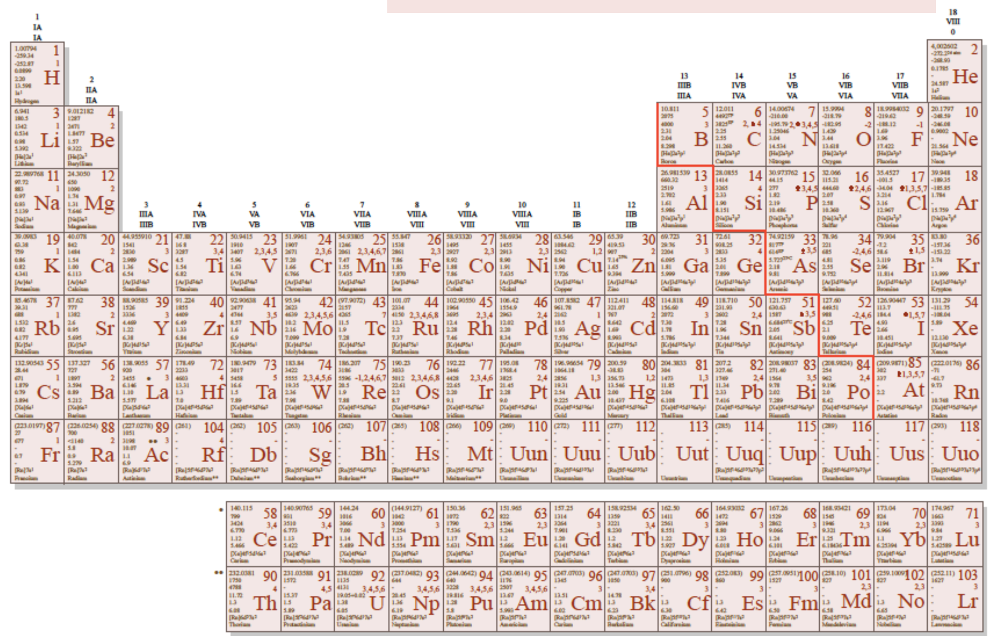


Example 2

- We have the electronic structure of two ions (A^{3+}:$3d^{10}$) and (B^{3+}:$3d^{5}$). Find their position and atomic number in the periodic table:
  - A: $3d^{10}\ 4s^2\ 4p^1$ → n=4; group 13 → $_{31}$Ga
  - B: $3d^6\ 4s^2$ → n=4; group 8 → $_{26}$Fe

Note: 4s orbital gets filled before 3d, and it looses electrons before 3d since it's on outer shell.





Example 3

How many orbitals and subshells are found within the principal shell n = 4? How do these orbital energies compare?

Shell "4" → subshell: 0, 1, 2, 3 → 4s, 4p, 4d, 4f

Number of orbitals: 1 (s) + 3 (p) + 5 (d) + 7 (f) = 16

Example 4

Identify the element with each ground state electron configuration.

- $[He]2s^22p^1$

Z= 2+2+1 = 5 → B

- $[Kr]5s^24d^{10}5p^4$

Z =

36 + 2 +10 +4 =

52 → Te