

## Quantum numbers, electronic structure

### Electronic Structure of Atoms :

- I. Quantum numbers
  - I.1. Principle quantum number ( $n$ )
  - I.2. Azimuthal quantum number ( $l$ )
  - I.3. Magnetic Quantum Number ( $m$ )
  - I.4. Spin Quantum Number ( $s$ )
- II. Electronic configuration principles
  - II.1. Aufbau principle
  - II.2. Pauli's exclusion principle
  - II.3. Hund's Rule of maximum multiplicity
- III. Electronic configurations of Elements.

### I. Quantum numbers

Each orbital in an atom is specified by a set of three quantum numbers ( $n, l, m$ ) and each electron is designated by a set of four quantum numbers ( $n, l, m$  and  $s$ ).

#### I.1. Principle quantum number ( $n$ )

It was proposed by *Bohr's* and denoted by ' $n$ '.

#### Introduction to the Bohr Model

Niels Bohr was a Danish physicist who made a fundamental contribution to our understanding of atomic structure and quantum mechanics. He made the first successful attempt at modeling the hydrogen atom by assuming that the electron executes orbital motion about the proton (i.e., the nucleus). It came into existence with the modification of Rutherford's model of an atom. Rutherford's model introduced the nuclear model of an atom, in which he explained that a nucleus (positively charged) is surrounded by negatively charged electrons.

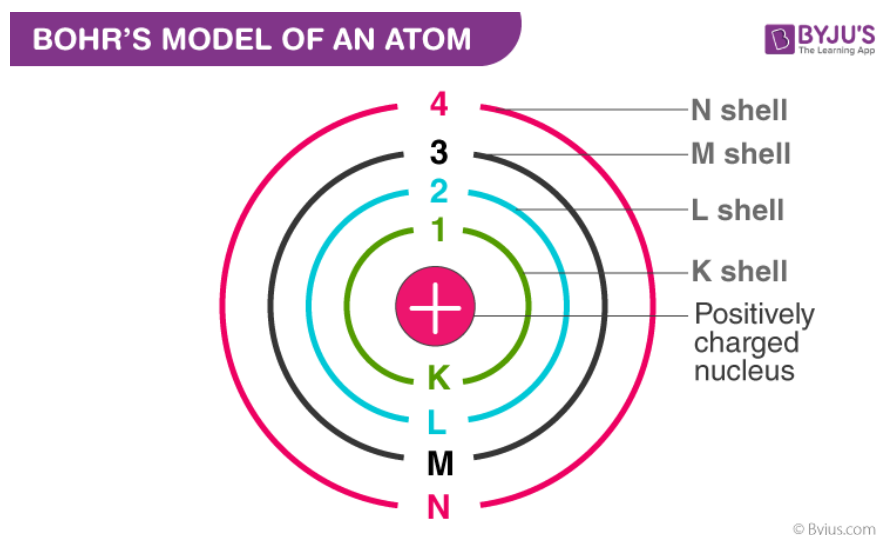
Bohr theory modified the atomic structure model by explaining that electrons move in fixed orbitals (shells) and not anywhere in between and he also explained that each orbit (shell) has a fixed energy. Rutherford explained the nucleus of an atom and Bohr modified that model into electrons and their energy levels.

#### Postulates of Bohr's Model of an Atom

- In an atom, electrons (negatively charged) revolve around the positively charged nucleus in a definite circular path called orbits or shells.

- Each orbit or shell has a fixed energy and these circular orbits are known as orbital shells.
- The energy levels are represented by an integer ( $n=1, 2, 3\dots$ ) known as the quantum number or Bhor's number. This range of quantum number starts from nucleus side with  $n=1$  having the lowest energy level. The orbits  $n=1, 2, 3, 4\dots$  are assigned as K, L, M, N.... shells and when an electron attains the lowest energy level, it is said to be in the ground state.
- The electrons in an atom move from a lower energy level to a higher energy level by gaining the required energy and an electron moves from a higher energy level to lower energy level by losing energy.

Note : Bohr's theory satisfactorily explains the spectra of species having one electron, viz. hydrogen atom, etc.  ${}^2\text{He}^+$ ,  ${}^3\text{Li}^{2+}$



Principale quantum number, determines :

- the average distance between electron and nucleus (radius) :

Each orbit has a radius associated with it. According to Bohr, radius of orbit in which electron moves is :

$$r_n = \frac{n^2}{Z} * a_0$$

Where,  $n$  = Orbit number,  $Z$  = Atomic number of element,  $a_0 = r_1 = 0.529 \text{ nm}$  ( radius of first orbit)

- The energy of the electron in an orbit where electron is present :

Each orbit has an energy associated with it. Calculation of energy of electron in Bohr's orbit

$$E_n = \frac{Z^2}{n^2} * E_1$$

When  $n=1$  :  $E_n = E_1 = -13.6 \text{ eV}$  ( $1 \text{ eV} = 1.6 \times 10^{-19} \text{ joule}$ )

➤ **The velocity :**

In each orbit, electron has a velocity associated with it. Calculation of velocity of electron

$$v_n = \frac{Z}{n} * v_1$$

Absorption and emission

Quantisation of energy of electron

1. *In ground state*: No energy emission. In ground state energy of atom is minimum and for 1<sup>st</sup> orbit of H-atom,  $n=1$ ,  $E_1 = -13.6 \text{ eV}$
2. *In excited state*: Energy levels greater than  $n = 1$  are excited state. i.e. for H-atom are excited state  $n = 1, 2, 3, 4, \dots$ . For H-atom first excitation state is  $n=2$ .
3. *Excitation potential*: Energy required to excite electron from ground state to any excited state.

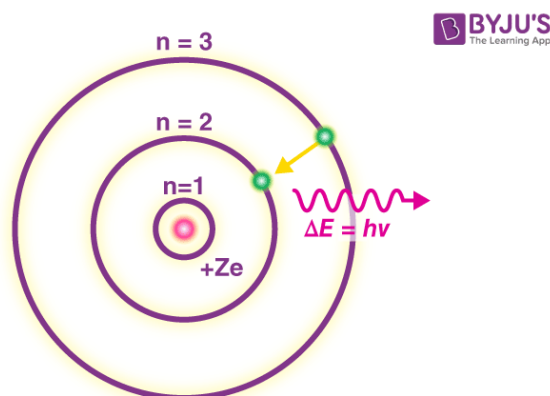
Ground state  $\longrightarrow$  Excited state

That :  $\Delta E = |E_f - E_i|$

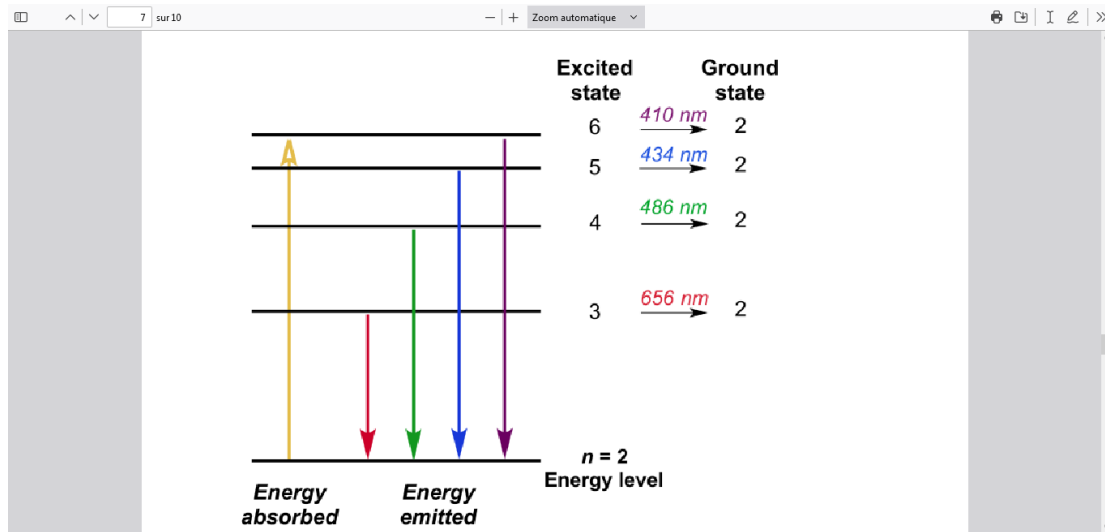
1<sup>st</sup> excitation potential =  $|E_2 - E_1| = |-3.4 - (-13.6)| = 10.2 \text{ eV}$ .

2<sup>nd</sup> excitation potential =  $|E_3 - E_1| = |-1.5 - (-13.6)| = 12.1 \text{ eV}$

4. *Ionisation energy* : The minimum energy required to relieve the electron from the binding of nucleus.



When an atom absorbs a quantum of energy, it is said to be in an excited state relative to its normal (ground) state. When an excited atom returns to the ground state, it emits light.



The emission or absorption of electromagnetic radiation can occur only in conjunction with a transition between two stationary states. The frequency of the emitted or absorbed radiation is proportional to the difference in energy of the two stationary states (1 and 2):

$$E = |E_f - E_i| = h\nu$$

where  $h$  is Planck's constant ( $h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$ ).

Emission of a quantum of light occurs when the atom is in an excited state quantum number  $n=n_f$  and decays to a lower energy state (quantum number  $n=n_i$ )

$$h\nu = |E_f - E_i|$$

where,  $\nu$  is the frequency of the emitted light quantum (photon). Because

$$\nu = c/\lambda$$

we have

$$1/\lambda = \nu/c = (E_f - E_i)/hc = Z^2 E_0/hc \left| \frac{1}{n_f^2} - \frac{1}{n_i^2} \right| = R_H \left| \frac{1}{n_f^2} - \frac{1}{n_i^2} \right|$$

$R_H$ : is called the Rydberg constant

So :

$$\nu = Z^2 c R_H \left| \frac{1}{n_f^2} - \frac{1}{n_i^2} \right|$$

$$\Delta E = h\nu = |E_f - E_i| = Z^2 h c R_H \left| \frac{1}{n_f^2} - \frac{1}{n_i^2} \right|$$

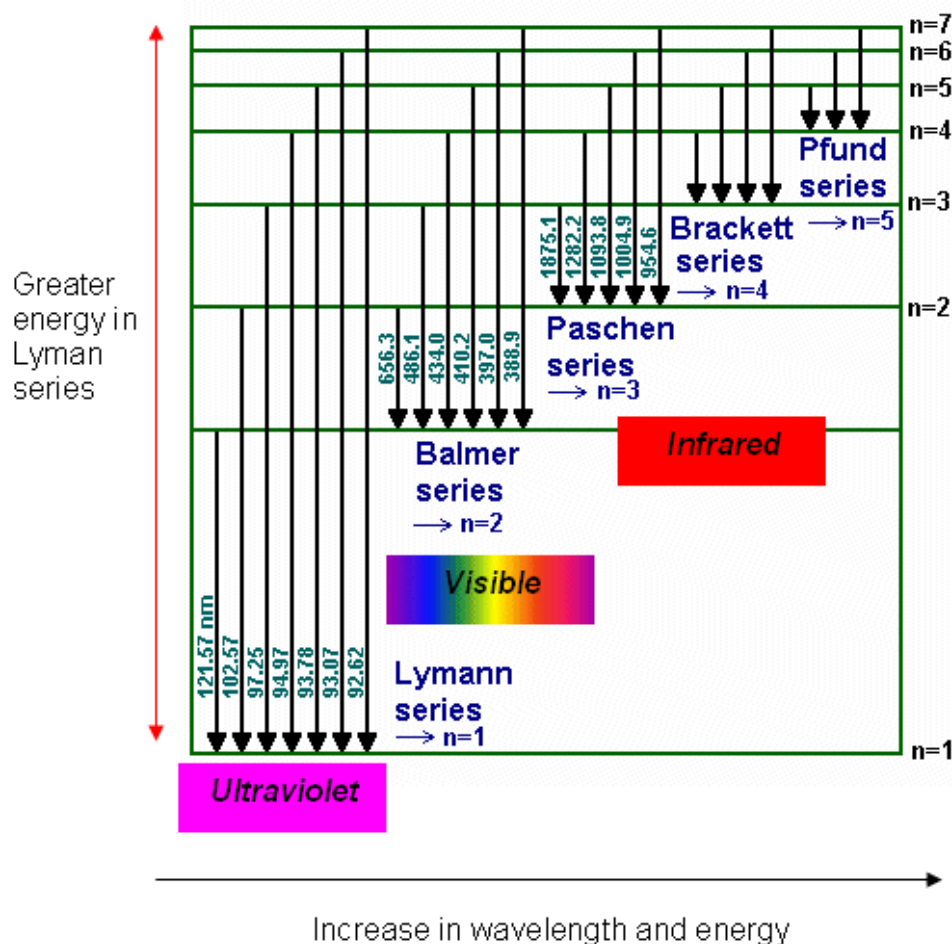
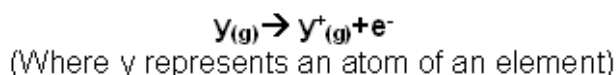
Spectral evidence for quantisation (Explanation for hydrogen spectrum on the basis of bohr atomic model) :

1. The light absorbed or emitted as a result of an electron changing orbits produces characteristic absorption or emission spectra which can be recorded on the photographic plates as a series of lines, the optical spectrum of hydrogen consists of several series of lines called Lyman, Balmer, Paschen, Brackett, Pfund and Humphrey. These spectral series were named by the name of scientist who discovered them.
2. To evaluate wavelength of various H-lines Ritz introduced the following expression,

$$U = Z^2 c R_H \left| \frac{1}{n_f^2} - \frac{1}{n_i^2} \right|$$

$R_H$  : Rydberg's constant. It's theoretical value =  $1.09737 \times 10^7 \text{ m}^{-1}$

3. Although H- atom consists only one electron yet it's spectra consist of many spectral lines as shown in fig.
4. If an electron from  $n$ th excited state comes to various energy states, the maximum spectral lines obtained will be  $(n(n-1))/2$  ;  $n$ = principal quantum number.
5. Thus, at least for the hydrogen atom, the Bohr Theory accurately describes the origin of atomic spectral lines.



Limitations of Bohr's Model of an Atom :

- Bohr's model of an atom failed to explain the Zeeman Effect (effect of magnetic field on the spectra of atoms).
- It also failed to explain the Stark effect (effect of electric field on the spectra of atoms).
- It violates the Heisenberg Uncertainty Principle.
- It could not explain the spectra obtained from larger atoms.

I.2. Azimuthal quantum number ( $l$ ) :

- Azimuthal quantum number is also known as angular quantum number. Proposed by *Sommerfeld* and denoted by ' $l$ '.

Within the shells, electrons are further grouped into subshells of four different types, identified as s, p, d, and f in order of increasing energy. The first shell ( $n=1$ ) has only

an s subshell; the second shell ( $n = 2$ ) has an s and a p subshell; the third shell has s, p, and d subshells, and the fourth has s, p, d and f subshells. The number of subshells is equal to the shell number. A specific subshell is symbolized by writing the number of the shell, followed by the letter for the subshell.

Of which : for  $n \leq 4$  :  $l = [0, n-1]$ .

Example :

$n = 1 ; l = 0$	1s
$n = 2 ; l = 0, 1$	2s, 2p
$n = 3 ; l = 0, 1, 2$	3s, 3p, 3d
$n = 4 ; l = 0, 1, 2, 3$	4s, 4p, 4d, 4f

Note : For a given value of 'n' the total value of 'l' is always equal to the value of 'n'.

The maximum number of electrons in subshell )  $2(2l+1)$

s- subshell	→ 2 electrons	d- subshell	→ 10 electrons
p- subshell	→ 6 electrons	f- subshell	→ 14 electrons

### I.3. Magnetic quantum number ( $m$ )

- It was proposed by *Zeeman* and denoted by 'm'.
- It gives the number of permitted orientation of subshells.
- The value of  $m$  varies from  $-l$  to  $+l$  through zero.
- It tells about the splitting of spectral lines in the magnetic field i.e. this quantum number proved the Zeeman effect.
- For a given value of 'n' the total value of 'm' is equal to 2 n.
- For a given value of 'l' the total value of 'm' is equal to  $(2l+1)$ .
- *Degenerate orbitals* : Orbitals having the same energy are known as degenerate orbitals. e.g. for p subshell  $p_x p_y p_z$
- The number of degenerate orbitals of s subshell =0.

Shell number:	1	2	3	4
Subshell designation:	s	s , p	s , p , d	s , p , d , f
Number of orbitals:	1	1 , 3	1 , 3 , 5	1 , 3 , 5 , 7

© 2013 Pearson Education, Inc.

### I.1.4. Spin quantum numbers ( $s$ )

- It was proposed by *Goldshmidt & Ulen Back* and denoted by the symbol of 's'.
- The value of « s » is  $1/2$ , and  $-1/2$  which signifies the spin or rotation or direction of electron on its axis during movement.

- The spin may be clockwise or anticlockwise.

SHELL NUMBER:	1	2	3	4
Subshell designation:	<i>s</i>	<i>s , p</i>	<i>s , p , d</i>	<i>s , p , d , f</i>
Number of orbitals:	1	1 , 3	1 , 3 , 5	1 , 3 , 5 , 7
Number of electrons:	2	2 , 6	2 , 6 , 10	2 , 6 , 10 , 14
Total electron capacity:	2	8	18	32

© 2013 Pearson Education, Inc.

Determine the other quantum numbers associated with the principal quantum number value  $n=4$ .

Solution:

$$n=3 \Rightarrow \text{Shell : } N ; 0 \leq l \leq n - 1 \Rightarrow 0 \leq l \leq 3$$

$$\Rightarrow l=0 \text{ (Subshell : } s), l=1 \text{ (Subshell : } p), l=2 \text{ (Subshell : } d), l=3 \text{ (Subshell : } f)$$

$$-1 \leq m_l \leq +1 \Rightarrow -3 \leq m_l \leq +3$$

$$l=0 \Rightarrow -0 \leq m_l \leq +0 \Rightarrow \boxed{\phantom{0}}$$

$$l=1 \Rightarrow -1 \leq m_l \leq +1 \Rightarrow \boxed{\phantom{0}} \boxed{\phantom{0}} \boxed{\phantom{0}}$$

$$l=2 \Rightarrow -2 \leq m_l \leq +2 \Rightarrow \boxed{\phantom{0}} \boxed{\phantom{0}} \boxed{\phantom{0}} \boxed{\phantom{0}} \boxed{\phantom{0}}$$

$$l=3 \Rightarrow -3 \leq m_l \leq +3 \Rightarrow \boxed{\phantom{0}} \boxed{\phantom{0}} \boxed{\phantom{0}} \boxed{\phantom{0}} \boxed{\phantom{0}} \boxed{\phantom{0}} \boxed{\phantom{0}}$$

## II. Electronic configuration principles

The distribution of electrons in different orbitals of atom based on their energy level is known as electronic configuration of the atoms.

Filling up of orbitals in the ground state of atom is governed by the following rules:

### II.2. Aufbau principle

- Auf bau is a German word, meaning ‘building up’.
- According to this principle, “In the ground state, the atomic orbitals are filled in order of increasing energies i.e. in the ground state the electrons first occupy the lowest energy orbitals available”.



➤ In fact the energy of an orbital is determined by the quantum number  $n$  and  $l$  with the help of  $(n+l)$  rule or Bohr Bury rule. According to this rule :

(a) Lower the value of  $n + l$ , lower is the energy of the orbital and such an orbital will be filled up first.

(b) When two orbitals have same value of  $(n+l)$  the orbital having lower value of “ $n$ ” has lower energy and such an orbital will be filled up first .

Thus, order of filling up of orbitals is as follows:

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

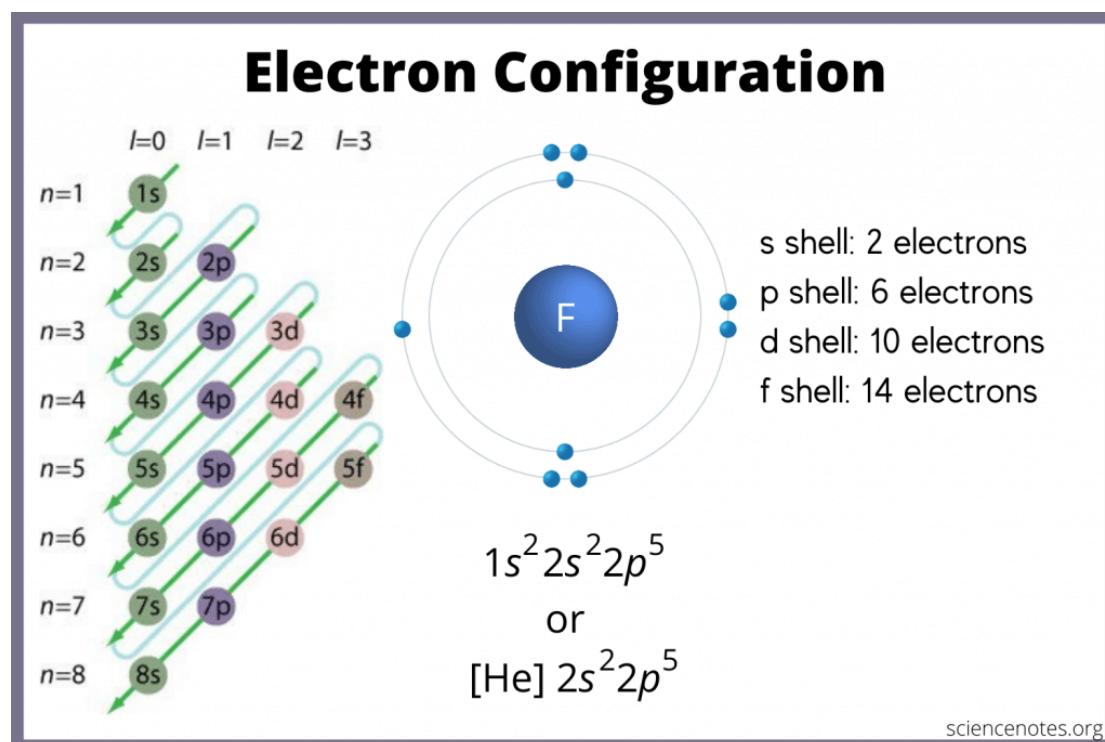
$1s(n=1, l=0) \Rightarrow (n+l=1), 2p(n=2, l=1) \Rightarrow (n+l=3).$

$1s$	$2s$	$2p$	$3s$	$3p$	$4s$	$4p$
$(n+l=1)$	$(n+l=2)$	$(n+l=3)$	$(n+l=3)$	$(n+l=4)$	$(n+l=4)$	$(n+l=5)$
$n=1$	$n=2$	$n=2$	$n=3$	$n=3$	$n=4$	$n=4$

### II.1.1. Energy rule (Klechkowski rule)

Thus, an important development has occurred because of the  $n+l$  rule. The energies of the various subshells are plotted along the vertical axis. The subshells are displaced left to right merely to avoid overcrowding. The order of increasing energy is as follows:

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



## II.2. Pauli's exclusion principle

- According to this principle, "No two electrons in an atom can have same set of all the four quantum numbers  $n$ ,  $l$ ,  $m$  and  $s$ ."
- In an atom any two electrons may have three quantum numbers identical but fourth quantum number must be different. If an orbital has two electrons they must be of opposite spin.
- Since this principle excludes certain possible combinations of quantum numbers for any two electrons in an atom, it was given the name exclusion principle. Its results are as follows :

(a) The maximum capacity of a main energy shell is equal to  $2n^2$  electron.

(b) The maximum capacity of a subshell is equal to  $2(2l+1)$  electron.

(c) Number of sub-shells in a main energy shell is equal to the value of  $n$ .

(d) Number of orbitals in a main energy shell is equal to  $n^2$

(e) One orbital cannot have more than two electrons.

- According to this principle an orbital can accommodate at the most two electrons with spins opposite



correct

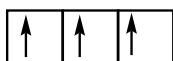


incorrect

## II.3. Hund's rule of maximum multiplicity

In the same subshell ( $p$ ,  $d$ , or  $f$ ) the electrons tend to fill the maximum of the quantum boxes with parallel spins (the electrons stay unpaired as much as possible).

- This rule provides the basis for filling up of degenerate orbitals of the same subshell.
- This implies that electron pairing begins with fourth, sixth and eighth electron in  $p$ ,  $d$  and  $f$  orbitals of the same subshell respectively.



correct

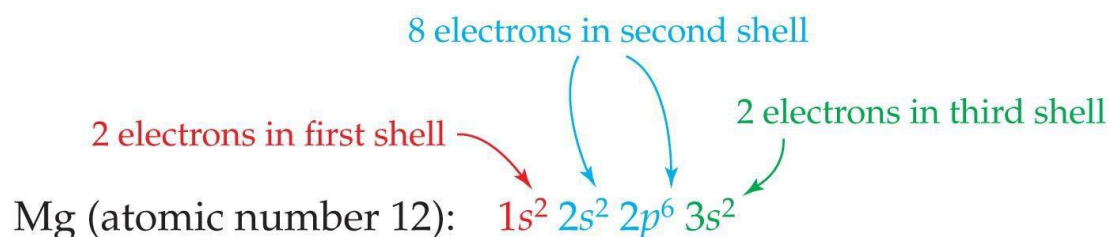


incorrect

## III. Electronic configurations (electronic structure) of elements.

The exact arrangement of electrons in the shells of the atom and the subshells is the electron configuration of the atom. While the electrons occupy the lowest available energy orbits where the total electrons = the atomic number.

The number of electrons in each subshell is indicated by a superscript.

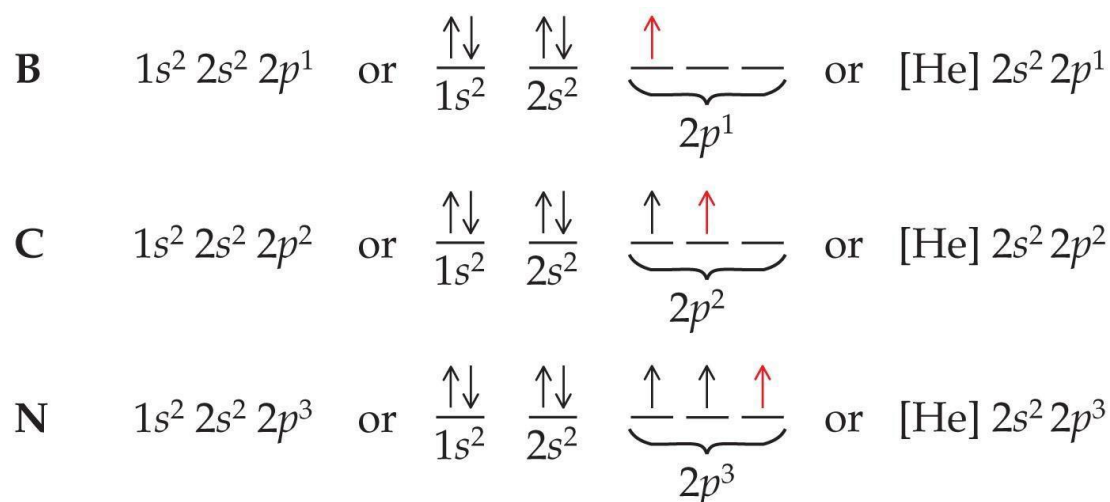


Example :

	Element	Atomic Number	Electron Configuration
H	Hydrogen	1	$1s^1$
He	Helium	2	$1s^2$
Li	Lithium	3	$1s^2 2s^1$
Be	Beryllium	4	$1s^2 2s^2$
B	Boron	5	$1s^2 2s^2 2p^1$
C	Carbon	6	$1s^2 2s^2 2p^2$
N	Nitrogen	7	$1s^2 2s^2 2p^3$
O	Oxygen	8	$1s^2 2s^2 2p^4$
F	Fluorine	9	$1s^2 2s^2 2p^5$
Ne	Neon	10	$1s^2 2s^2 2p^6$
Na	Sodium	11	$1s^2 2s^2 2p^6 3s^1$
Mg	Magnesium	12	$1s^2 2s^2 2p^6 3s^2$
Al	Aluminum	13	$1s^2 2s^2 2p^6 3s^2 3p^1$
Si	Silicon	14	$1s^2 2s^2 2p^6 3s^2 3p^2$
P	Phosphorus	15	$1s^2 2s^2 2p^6 3s^2 3p^3$
S	Sulfur	16	$1s^2 2s^2 2p^6 3s^2 3p^4$
Cl	Chlorine	17	$1s^2 2s^2 2p^6 3s^2 3p^5$
Ar	Argon	18	$1s^2 2s^2 2p^6 3s^2 3p^6$
K	Potassium	19	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
Ca	Calcium	20	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$

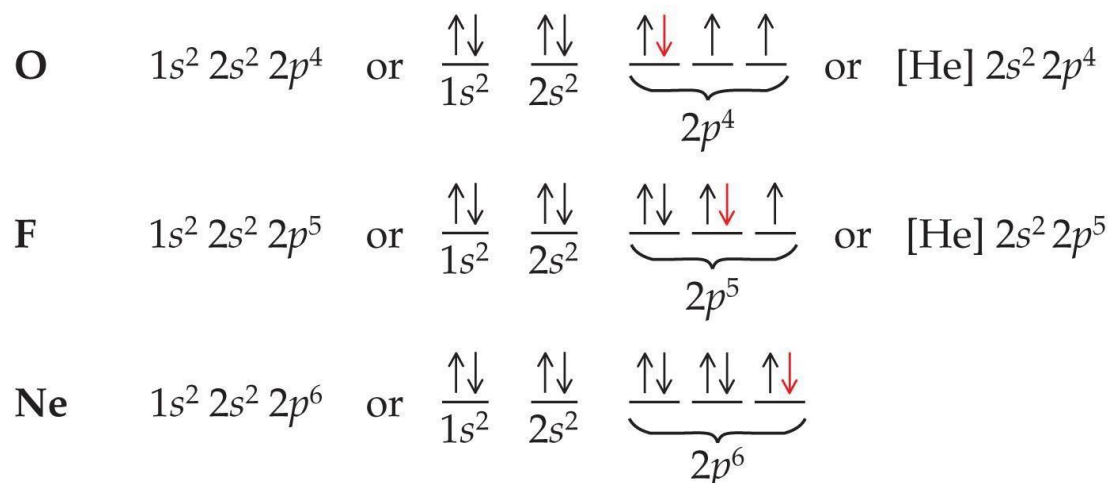
© 2013 Pearson Education, Inc.

These are the electron configurations for B to N in which the 2p shell begins to fill :



© 2013 Pearson Education, Inc.

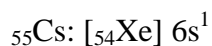
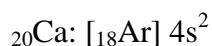
These are the electron configurations for O – Ne in which the 2p shell is completed :



© 2013 Pearson Education, Inc.

### III.1. Shorthand Electron Configurations

An electron configuration can also be written in an abbreviated (shorthand) configuration. In this method the electron configuration of the preceding noble gas is replaced by writing its symbol inside brackets.



### III.2. Orbital Diagrams

Another way to represent the order of fill for an atom is by using an orbital diagram often referred to as the littele boxes

➤ **Extra stability of half filled and completely filled orbitals : Exceptions to Klechkowski Filling Rules :**

The subshell d and f are more stable when it is full ( $d^{10}$ ) and ( $f^{14}$ ) or half full ( $d^5$ ) and ( $f^7$ ), a rule valid only for this subshell (case of the chromium and copper groups).

Example :

Elements with atomic number  ${}_{24}\text{Cr}$ ,  ${}_{42}\text{Mo}$  and  ${}_{74}\text{W}$  have configuration  $ns^1(n-1)d^5$  and not  $ns^2(n-1)d^4$  due to extra stability of these atoms.

Elements with atomic number  ${}_{29}\text{Cu}$ ,  ${}_{47}\text{Ag}$  and  ${}_{79}\text{Au}$  have configuration  $ns^1(n-1)d^{10}$  instead of  $ns^2(n-1)d^9$  due to extra stability of these atoms.

Case of chromium ( ${}_{24}\text{Cr}$ ):

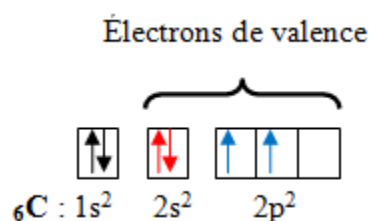
*Experimentally*  $\Rightarrow {}_{24}\text{Cr} : [{}_{18}\text{Ar}] 3d^5 4s^1$

Case of chromium ( ${}_{29}\text{Cu}$ ):

*Experimentally*  $\Rightarrow {}_{29}\text{Cu} : [{}_{18}\text{Ar}] 3d^{10} 4s^1$

### III. Core and valence electrons Lewis representation of an atom

Valence electrons are the electrons of the external shell (peripheral or valence).



**${}_{6}\text{C} : 1s^2 / 2s^2 2p^2$**

Valence number is: 4

Valence electrons are : 4 e<sup>-</sup>

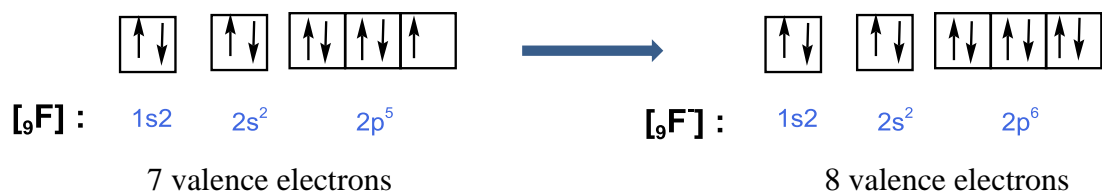
Core electrons: 2

### III.3. Electronic configuration of an ion

#### a. Case of anions

Addition of one or more electrons to the electronic configuration of the atom in its ground state while respecting the rules of Klechkowski, Pauli and Hund.

*Exemple* : Fluoride ion:  ${}_{9}\text{F}^-$



### b. Case of cations

Elimination of one or more electrons from the electronic configuration of the atom in its ground state while respecting the rules of Klechkowski, Pauli and Hund.

*Exemple* : Sodium ion:  $11\text{Na}^+$

