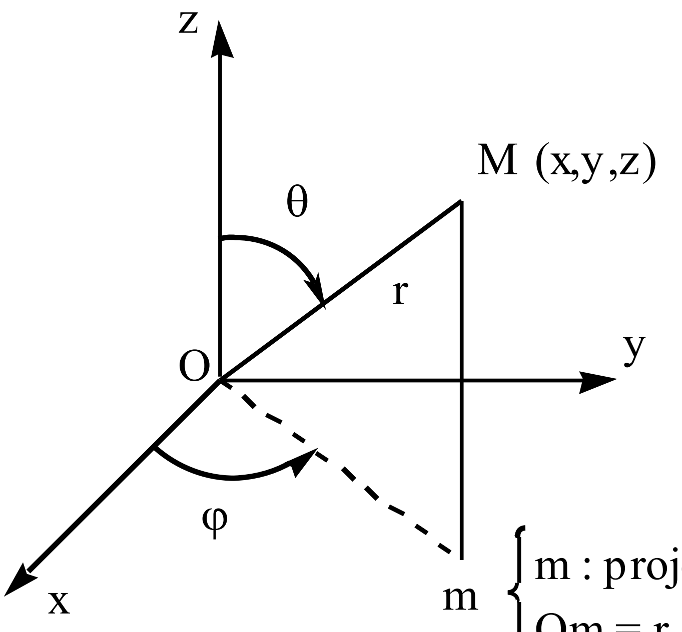
CHAPTER 01-
PERIODICITY AND IN-DEPTH STUDY OF THE PROPERTIES OF THE ELEMENTS _HALOGENS, CHALCOGENS, NITROGEN AND PHOSPHORUS, BORON.

Presented by Pr MOUSSACEB

THE HYDROGEN ATOM IN QUANTUM MECHANICS

Spherical symmetry

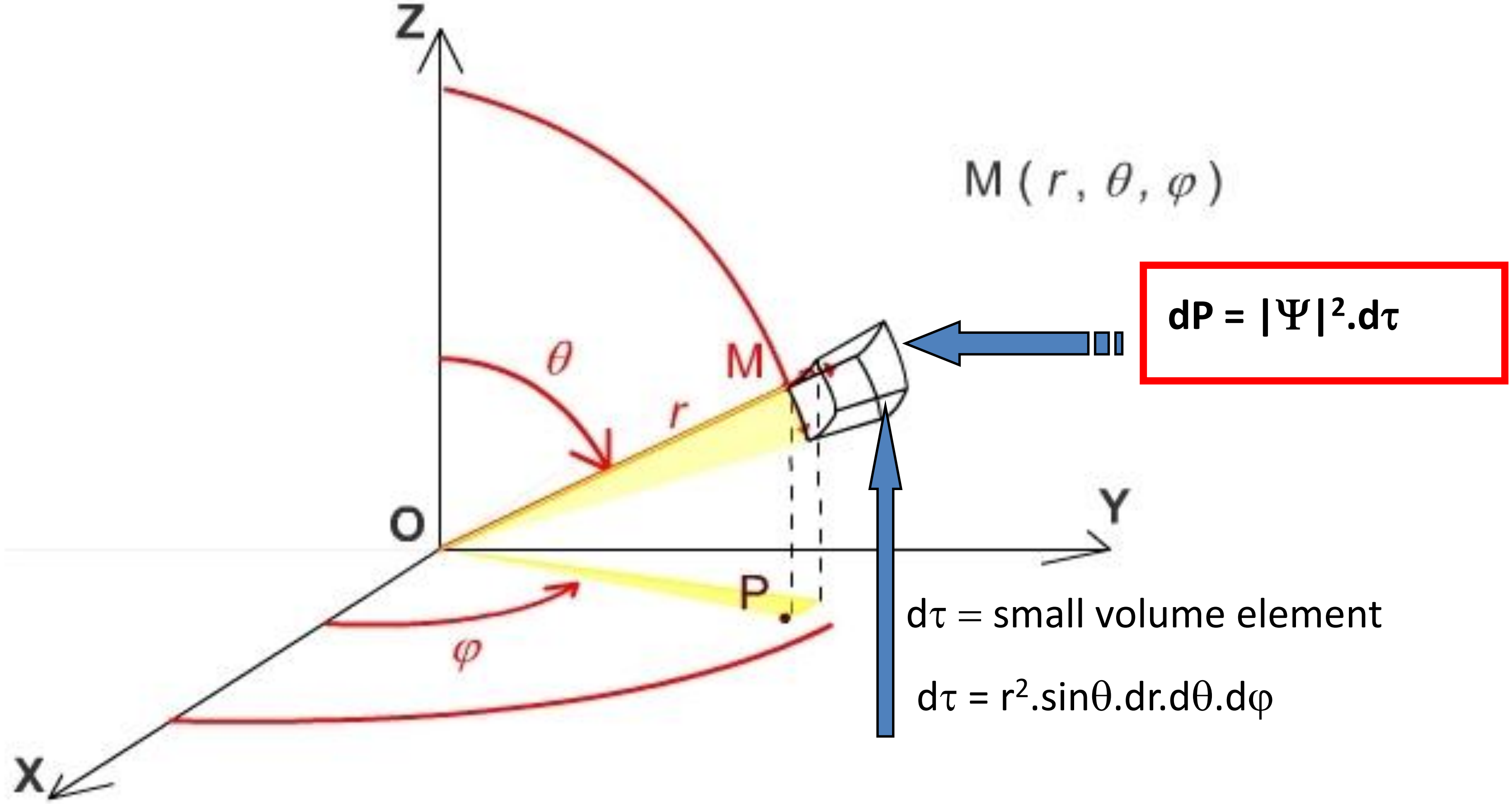


$$\begin{cases} x = r.\sin\theta.\cos\varphi \\ y = r.\sin\theta.\sin\varphi \\ z = r.\cos\theta \end{cases}$$

$$\begin{cases} r \in [0, \infty[\\ \theta \in [0, \Pi] \ \text{(co-latitude)} \\ \varphi \in [0, 2\Pi] \ \text{(longitude)} \end{cases}$$

$$\begin{cases} \text{m : projeté orthogonal de M dans le plan [xOy] (plan équatoria} \\ \text{Om} = r.\sin\theta \end{cases}$$

We write the wave function in the form $\boxed{\Psi(r,\theta,\varphi)}$



dP = $|\Psi|^2 . d\tau$

$d\tau$ = small volume element

$d\tau = r^2 . \sin\theta . dr . d\theta . d\varphi$

- $|\Psi|^2$ represents the probability density of the presence of the electron

- The probability dP of finding the electron in an infinitesimal volume **dτ** centered around a point M0 with coordinates (x0, y0, z0) is

$$\iiint_{\text{espace}} |\Psi|^2 . d\tau = 1$$

SCHRÖDINGER EQUATION

The motion of the electron is described by its wave function ψ

$$-\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right)+V\psi=E\psi$$

$\psi : wavefunction / eigenfunction$

$x, y, z : coordinates$

$m : mass$

$h : Planck's$

$E : totalenergy$

$V : potrntialenergy$

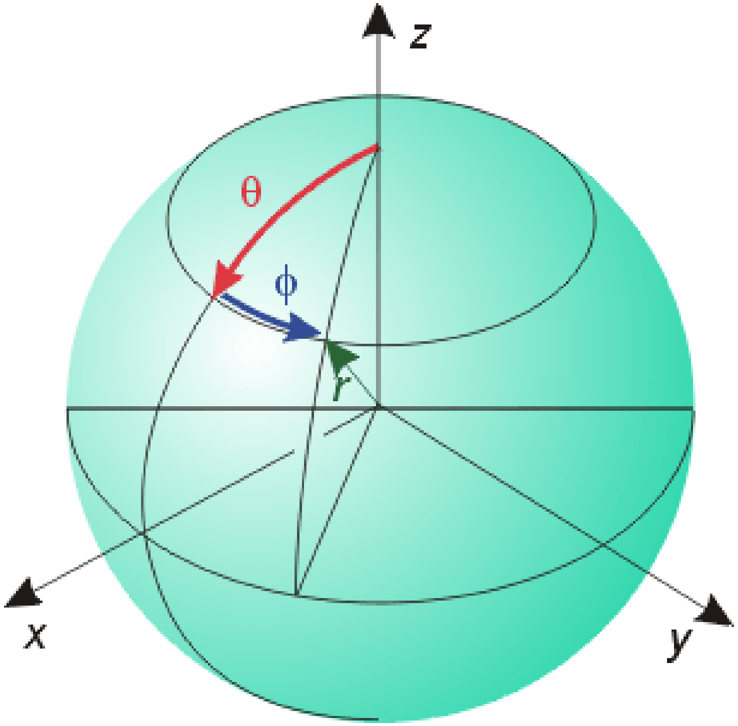
Solving the Schrödinger equation

Writing in polar coordinates and separation of variables:

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

$$R_{n,l}(r)$$ Radial part

$$Y_{l,m_l}(\theta,\phi)$$ Angular part

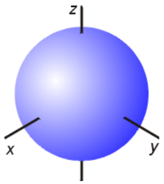


_n_ = 1, 2, 3, 4….= principal quantum number

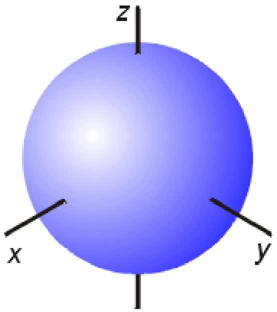
n determines the energy of the electron

n gives approximately the effective volume of the orbital

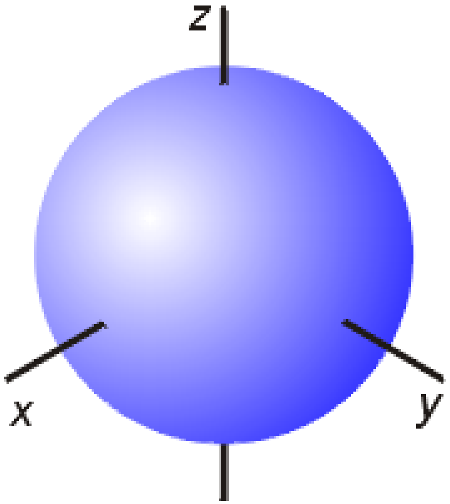
$$E_n = -\frac{\mu e^4}{8\varepsilon_0{}^2 h^2}\frac{1}{n^2} = -\frac{k}{n^2}$$



n = 1



n =2



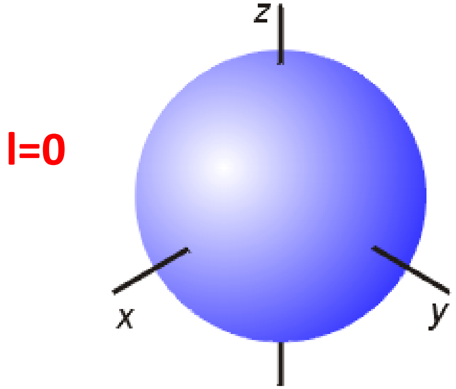
n = 3

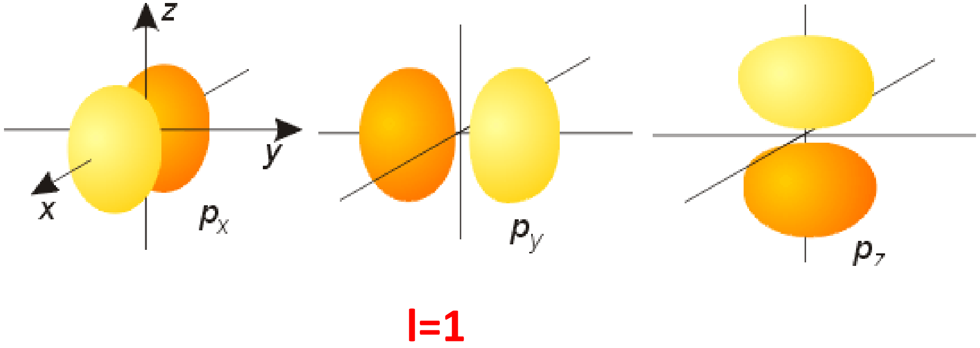
l is the secondary quantum number **$0<l<(n-1)$**

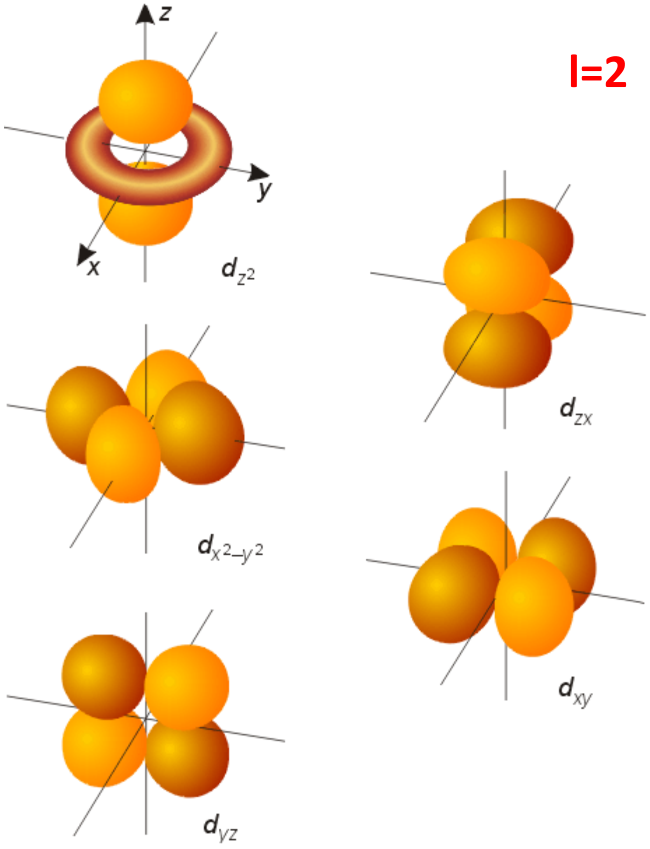
0, 1, 2, 3, 4 …

s, p, d, f …

l determines the general shape of the orbit



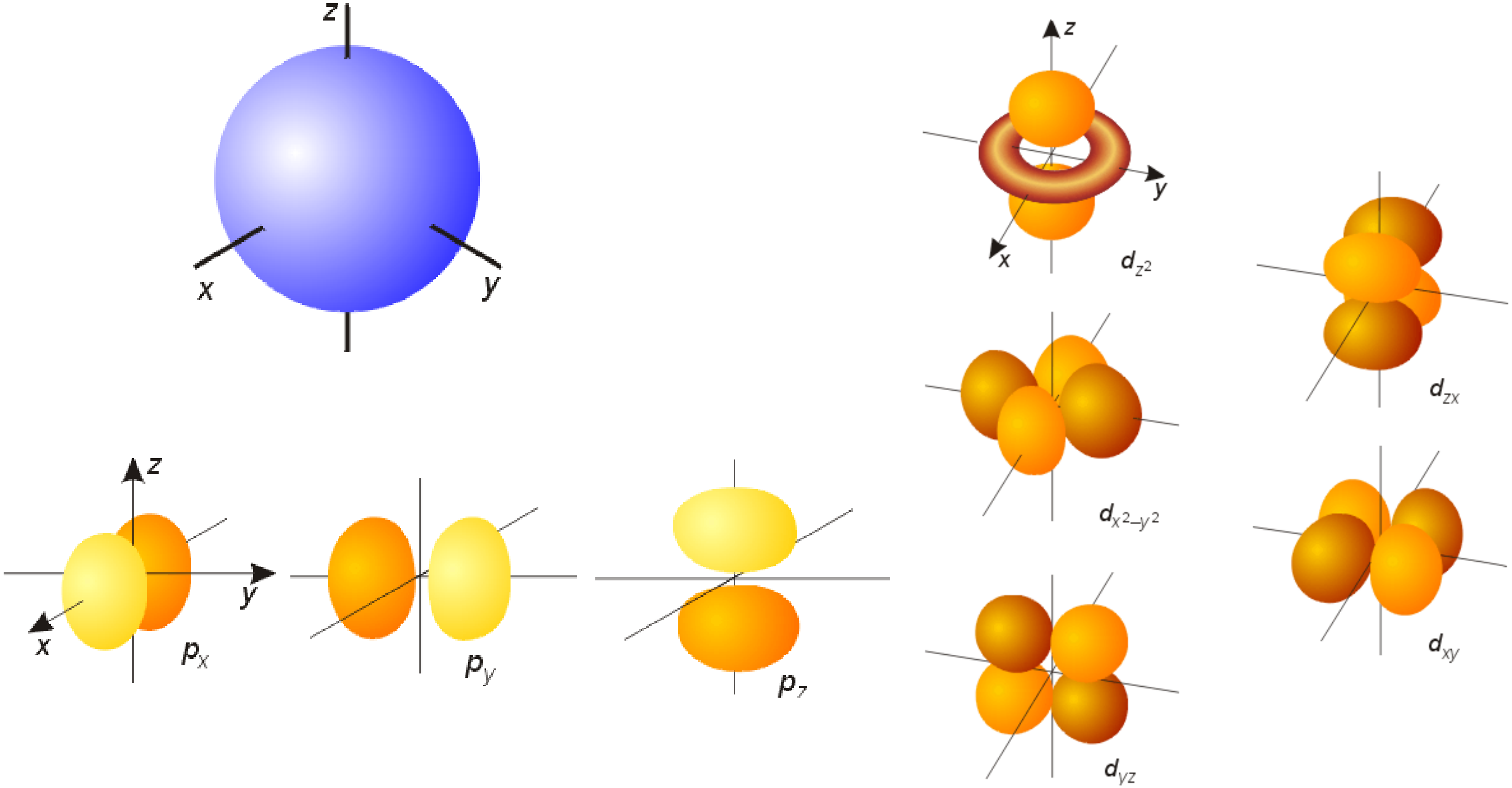




ml (or simply m) is the magnetic quantum number

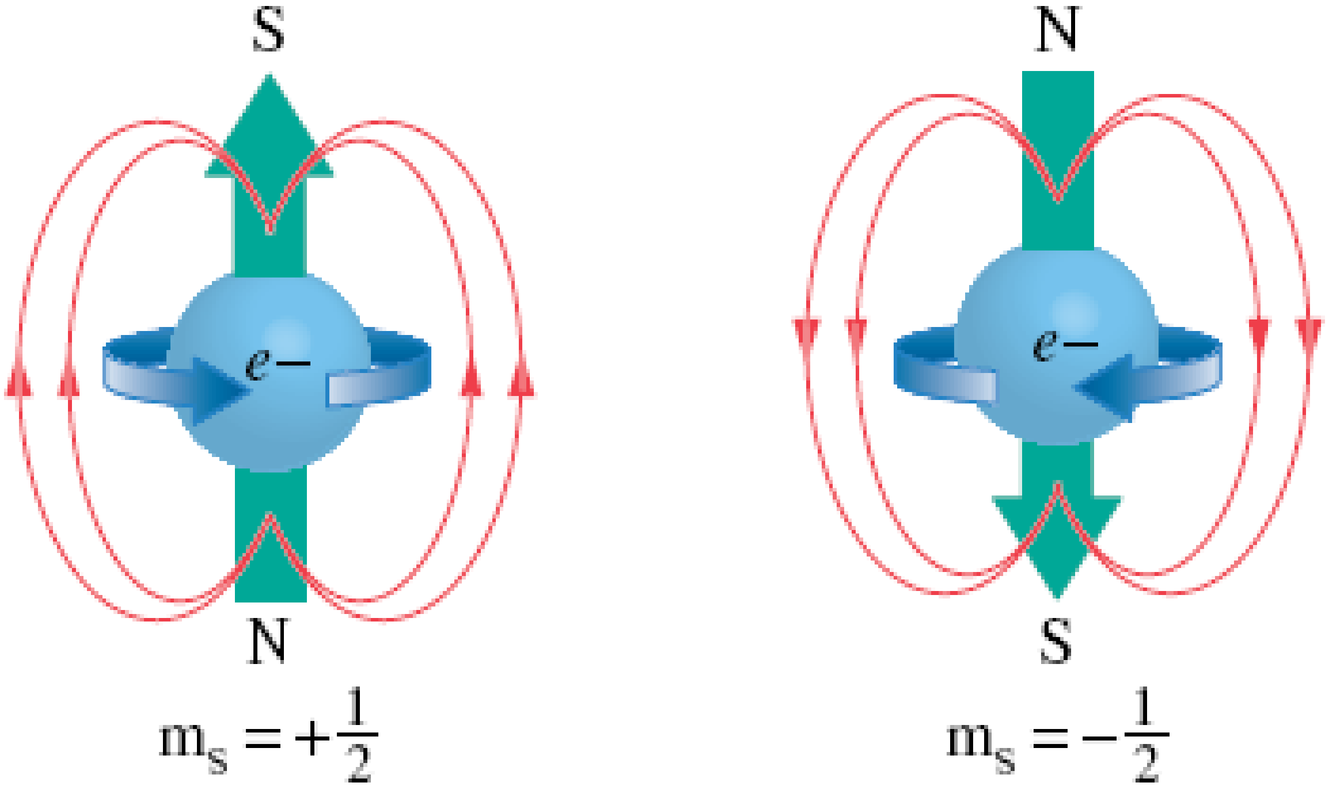
(+l)<=m<=(-l) $0, \pm 1, \pm 2, \pm 3 \ldots$

m_l determines the spatial orientation of the orbit



For each l, there are 2l+1 possible value of ml

The spin quantum number



Enumeration

At a given level n are associated n^2 system states and $2\ n^2$ electrons

$0 \le l \le n-1$; $-l \le m \le +l$; $m_s = \pm ½$

$n = 1 \Rightarrow$ 1 state; $n = 2 \Rightarrow$ 4 states

$n = 3 \Rightarrow$ 9 states; $n = 4 \Rightarrow$ 16 states

$n = 1 \Rightarrow$ 2 e- ; $n = 2 \Rightarrow$ 8 e-

$n = 3 \Rightarrow$ 18 e- ; $n = 4 \Rightarrow$ 32 e-

Layers and under layers

	$l = 0$	$l = 1$	$l = 2$	$l = 3$	$l = 4$	$l = 5$	States	N^{bre} e^-
n = 1	1s						1	(2)
2	2s	2p					4	(8)
3	3s	3p	3d				9	(18)
4	4s	4p	4d	4f			16	(32)
5	5s	5p	5d	5f	5g		25	(50)
6	6s	6p	6d	6f	6g	6h	36	(72)

ELECTRONIC CONFIGURATION OF CHEMICAL ELEMENTS

The electronic configuration of an element (also called electronic structure) is the specification of the occupation of atomic orbitals by electrons.

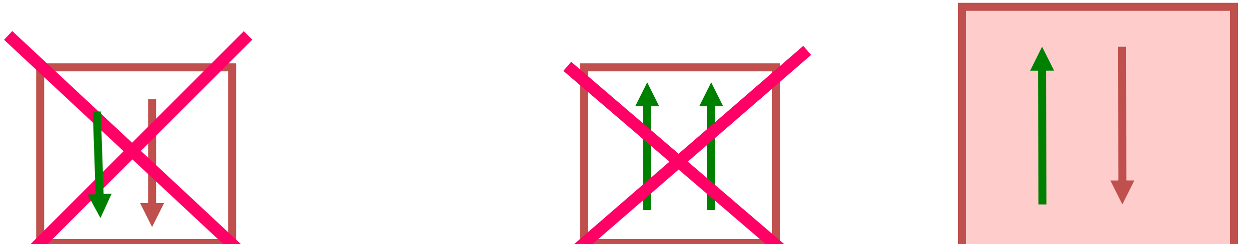
The electrons will successively fill the various orbitals while respecting certain rules.

RULES FOR FILLING OA

The Pauli Exclusion Principle:

1st statement: Two electrons of the same atom cannot have their four quantum numbers identical.

2nd statement: An atomic orbital can only contain a maximum of two electrons.



The Pauli Exclusion Principle

- a consequence of the Pauli principle is that an atomic orbital can only contain two electrons and one electron is necessarily of spin +1/2 and the other is necessarily of spin -1/2

because an atomic orbital can only have two electrons, and the two electrons are of opposite spins, the electron configurations of the first five elements are

H ($1s^1$) 1s ↑
He ($1s^2$) 1s ↑↓
Li ($1s^2 2s^1$) 1s ↑↓ 2s ↑
Be ($1s^2 2s^2$) 1s ↑↓ 2s ↑↓
B ($1s^2 2s^2 2p^1$) 1s ↑↓ 2s ↑↓ $2p_x$ ↑

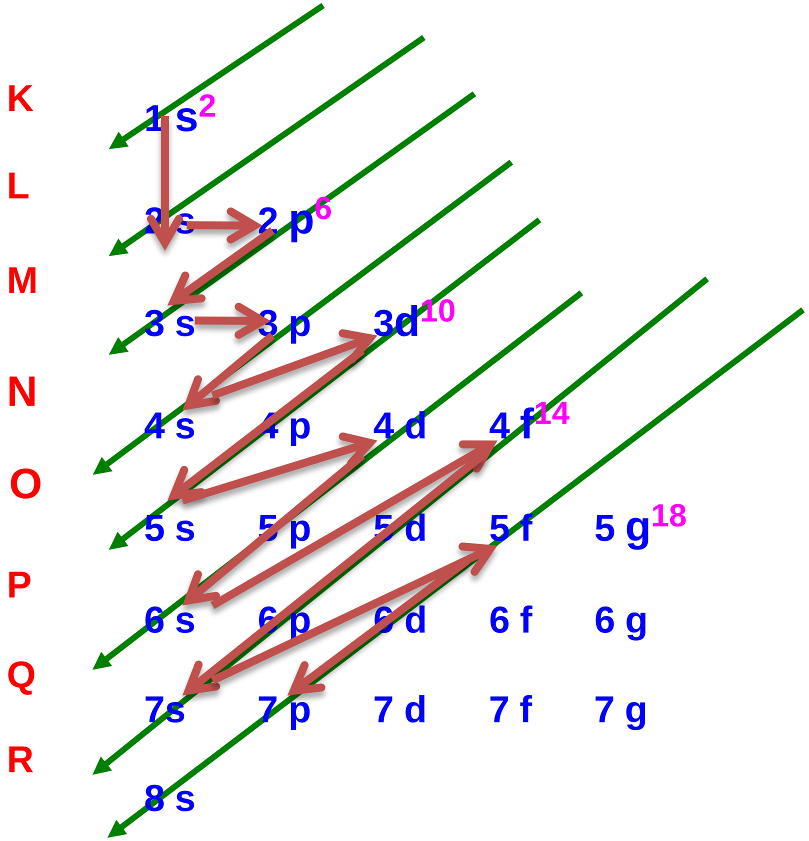
- KLECHKOWSKI FILLING RULE

Statement: The order of filling of the various layers and sub-layers is done by increasing values of the pair (n + l).

For the same value of (n + l), they will be classified in order of increasing n.

sous – couche	*n*	*ℓ*	*n + ℓ*	*ordre*
1 *s*	1	0	1	
2 *s*	2	0	2	
2 *p*	2	1	3	
3 *s*	3	0	3	
3 *p*	3	1	4	
4 *s*	4	0	4	
3 *d*	3	2	5	
4 *p*	4	1	5	
5 *s*	5	0	5	
4 *d*	4	2	6	
5 *p*	5	1	6	
6 *s*	6	0	6	
4 *f*	4	3	7	
5 *d*	5	2	7	
6 *p*	6	1	7	
7 *s*	7	0	7	
5f	5	3	8	
6d	6	2	8	

KLECHKOWSKI FILLING Principle



K	$1s^2$				
L	$2s$	$2p^6$			
M	$3s$	$3p$	$3d^{10}$		
N	$4s$	$4p$	$4d$	$4f^{14}$	
O	$5s$	$5p$	$5d$	$5f$	$5g^{18}$
P	$6s$	$6p$	$6d$	$6f$	$6g$
Q	$7s$	$7p$	$7d$	$7f$	$7g$
R	$8s$				

OA Filling Order

$1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^2$, $3d^{10}$, $4p^6$, $5s^2$, $4d^{10}$, 5p5 , $6s^2$, $4f^{14}$, $5d^{10}$, $6p^6$, $7s^2$, $5f^{14}$, $6d^{10}$, $7p^6$

Hund's Rule

It applies when using the formalism with quantum boxes. It is relative to the ground state, that of lowest energy.

Statement: Electrons having the values of n and l in common (called equivalent electrons) are distributed in such a way as to occupy the maximum number of atomic orbitals in such a way that the number of single electrons are at most in the same spin state.

- When we get to Carbon, we have three options

C ($1s^2 2s^2 2p^2$) 1s ↑↓ 2s ↑↓ $2p_x$ ↑↓

C ($1s^2 2s^2 2p^2$) 1s ↑↓ 2s ↑↓ $2p_x$ ↑ $2p_y$ ↓

C ($1s^2 2s^2 2p^2$) 1s ↑↓ 2s ↑↓ $2p_x$ ↑ $2p_y$ ↑

- Hund's rule states that the most stable electronic arrangement in a subshell is the one with the greatest number of parallel spins.
- The third option is the one that respects Hund's law

- The configurations of the other elements in the second row are

C ($1s^2 2s^2 2p^2$)	1s ↑↓	2s ↑↓	$2p_x$ ↑	$2p_y$ ↑	
N ($1s^2 2s^2 2p^3$)	1s ↑↓	2s ↑↓	$2p_x$ ↑	$2p_y$ ↑	$2p_z$ ↑
O ($1s^2 2s^2 2p^4$)	1s ↑↓	2s ↑↓	$2p_x$ ↑↓	$2p_y$ ↑	$2p_z$ ↑
F ($1s^2 2s^2 2p^5$)	1s ↑↓	2s ↑↓	$2p_x$ ↑↓	$2p_y$ ↑↓	$2p_z$ ↑
Ne ($1s^2 2s^2 2p^6$)	1s ↑↓	2s ↑↓	$2p_x$ ↑↓	$2p_y$ ↑↓	$2p_z$ ↑↓

Exceptions to Klechkowski's Rule:

Z	Name	Symbol	Configuration according to Klechkowski	Actual configuration
24	Chrome	Cr	(Ar) $3d^{4}\ 4s^{2}$	(Ar) $3d^{5}\ 4s^{1}$
29	Cuivre	Cu	(Ar) $3d^{9}\ 4s^{2}$	(Ar) $3d^{10}\ 4s^{1}$
41	Niobium	Nb	(Kr) $4d^{3}\ 5s^{2}$	(Kr) $4d^{4}\ 5s^{1}$
42	Molybdène	Mo	(Kr) $4d^{4}\ 5s^{2}$	(Kr) $4d^{5}\ 5s^{1}$
44	Ruthénium	Ru	(Kr) $4d^{6}\ 5s^{2}$	(Kr) $4d^{7}\ 5s^{1}$
45	Rhodium	Rh	(Kr) $4d^{7}\ 5s^{2}$	(Kr) $4d^{8}\ 5s^{1}$
46	Palladium	Pd	(Kr) $4d^{8}\ 5s^{2}$	(Kr) $4d^{10}$
47	Argent	Ag	(Kr) $4d^{9}\ 5s^{2}$	(Kr) $4d^{10}\ 5s^{1}$
57	Lanthane	La	(Xe) $4f^{1}\ 6s^{2}$	(Xe) $5d^{1}\ 6s^{2}$
58	Cérium	Ce	(Xe) $4f^{2}\ 6s^{2}$	(Xe) $4f^{1}\ 5d^{1}\ 6s^{2}$
64	Gadolinium	Gd	(Xe) $4f^{1}\ 6s^{2}$	(Xe) $4f^{7}\ 5d^{1}\ 6s^{2}$
78	Platine	Pt	(Xe) $4f^{14}\ 5d^{8}\ 6s^{2}$	(Xe) $4f^{14}\ 5d^{9}\ 6s^{1}$
79	Or	Au	(Xe) $4f^{14}\ 5d^{9}\ 6s^{2}$	(Xe) $4f^{14}\ 5d^{10}\ 6s^{1}$
89	Actinium	Ac	(Rn) $5f^{1}\ 6d^{0}\ 7s^{2}$	(Rn) $6d^{1}\ 7s^{2}$
90	Thorium	Th	(Rn) $5f^{2}\ 6d^{0}\ 7s^{2}$	(Rn) $6d^{2}\ 7s^{2}$
91	Protactinium	Pa	(Rn) $5f^{3}\ 6d^{0}\ 7s^{2}$	(Rn) $4f^{2}\ 6d^{1}\ 7s^{2}$
92	Uranium	U	(Rn) $5f^{4}\ 6d^{0}\ 7s^{2}$	(Rn) $4f^{3}\ 6d^{1}\ 7s^{2}$
93	Neptunium	Np	(Rn) $5f^{5}\ 6d^{0}\ 7s^{2}$	(Rn) $4f^{4}\ 6d^{1}\ 7s^{2}$
96	Curium	Cm	(Rn) $5f^{8}\ 6d^{0}\ 7s^{2}$	(Rn) $4f^{7}\ 6d^{1}\ 7s^{2}$

$4s^{2}\ 3d^{4}$ $4s^{1}\ 3d^{5}$

$4s^{2}\ 3d^{9}$ $4s^{1}\ 3d^{10}$

- All these exceptions concern elements having an incomplete d or f sublayer.

- This rule that we will admit is the following:

- **A fully filled or half-filled subshell provides greater stability to the atoms.**

- This rule applies particularly to configurations of the type (n-1)d^9 ns^2 (Cu, Ag and Au) and (n-1)d^4 ns^2 (Cr, Mo) which will transform respectively into d^{10} s^1 and d^5 s^1.

- We can consider that an electron from the s subshell "jumps" to the d subshell to complete it to 5 or 10 electrons.

- The configuration obtained is then more stable than the initial configuration.