Chapter II: Energy quantification Part 2

I-3 Quantum model of the atom

Bohr's model, based on classical mechanics, does not allow us to correctly describe the behavior of atoms. Indeed, classical physics, which enables us to understand the evolution over time of a system on a macroscopic scale, is insufficient to account for phenomena on an atomic scale. At the beginning of the 20th century, a new mechanical theory was born, called wave mechanics or quantum mechanics, capable of studying microscopic systems.

I-3 -1 Heisenberg's uncertainty principle

The position x and momentum p (p=mv) of a particle cannot be determined simultaneously with more precision than that given by Heisenberg's relation:

$$\Delta \boldsymbol{x}.\Delta \boldsymbol{p} \geq \frac{\boldsymbol{h}}{\boldsymbol{2\pi}} = \hbar$$

This relationship admits an equivalent relationship:

$$\Delta \boldsymbol{E}.\Delta \boldsymbol{t} \geq \frac{\boldsymbol{h}}{\boldsymbol{2\pi}} = \hbar$$

where:

- **Δx (Δy,Δz)** position uncertainty ;
- **Δp** uncertainty in momentum**(Δp=mΔv)**;
- **ΔE** uncertainty in energy measurement ;
- **Δt** duration of energy measurement;
- **h** Planck's constant.

These uncertainty relations are applicable to any material system, but are only of practical importance in cases involving wave mechanics.

Example:

An e^- of mass $9.1.10^{-31}$Kg is part of a hydrogen atom with a diameter of 2.10^{-10}m. Its position is therefore known to within 10^{-10}m. What is the maximum accuracy I can obtain for the speed of this electron?

$$\Delta \boldsymbol{v} = \frac{\boldsymbol{h}}{\boldsymbol{m}\Delta \boldsymbol{x}} = \frac{\boldsymbol{6,62.10^{-34}}}{\boldsymbol{2.10^{-10}.3,14.9,1.10^{-31}}} = \boldsymbol{0,1158.10^{-7} = 1158Km/s}$$

Note

De Broglie's wave postulate (λ= h/p or λ= h/mv) and Heisenberg's uncertainty principle only have meaning in the microscopic world, i.e. on the scale of atoms and electrons.

I-3 -2 Atomic orbitals:

In this model, the stationary orbit becomes the atomic orbital: the region of space where the electron is most likely to be found.

An electronic layer corresponds to a set of atomic orbitals (A.O.) with the same value of the principal number n.

In wave theory, the electron's motion around the nucleus is associated with a standing wave. The amplitude of this wave is given by the Ψ wave function.Ψ.

Ψ is related to energy by solving a differential equation (Schrödinger). In fact, we consider Ψ^2, which has a meaning corresponding to the volume density of the electron's probability of presence P at a given point:

P = $|dP|$ = $\left|\Psi^2\right|$ dv = 1.

The electron's probability of presence is the same at every point of an A.O. Wave functions are characterized by the quantum numbers n, l and m.
Each Ψ orbital solution of the Schrödinger equation is represented by a quadruplet (n, l, m, m_s).

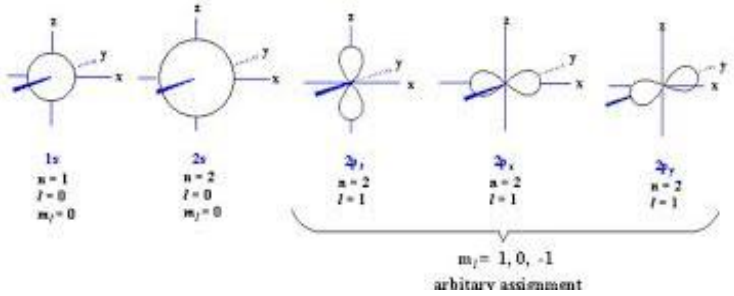
I-3 -3 Quantum numbers

I-3 -3- a The principal quantum number n, where n is an integer ≥1 It is the principal quantum number, denoted n, that determines the atom's principal energy level En and defines the energy layers.
An n-level can contain up to 2n2 electrons:
- For the n=1 level, the maximum number of electrons is 2 ;
- For the n=2 level, the maximum number of electrons is 8;
- For level n=3, the maximum number of electrons is 18;
- For the n=4 level, the maximum number of electrons is 32;

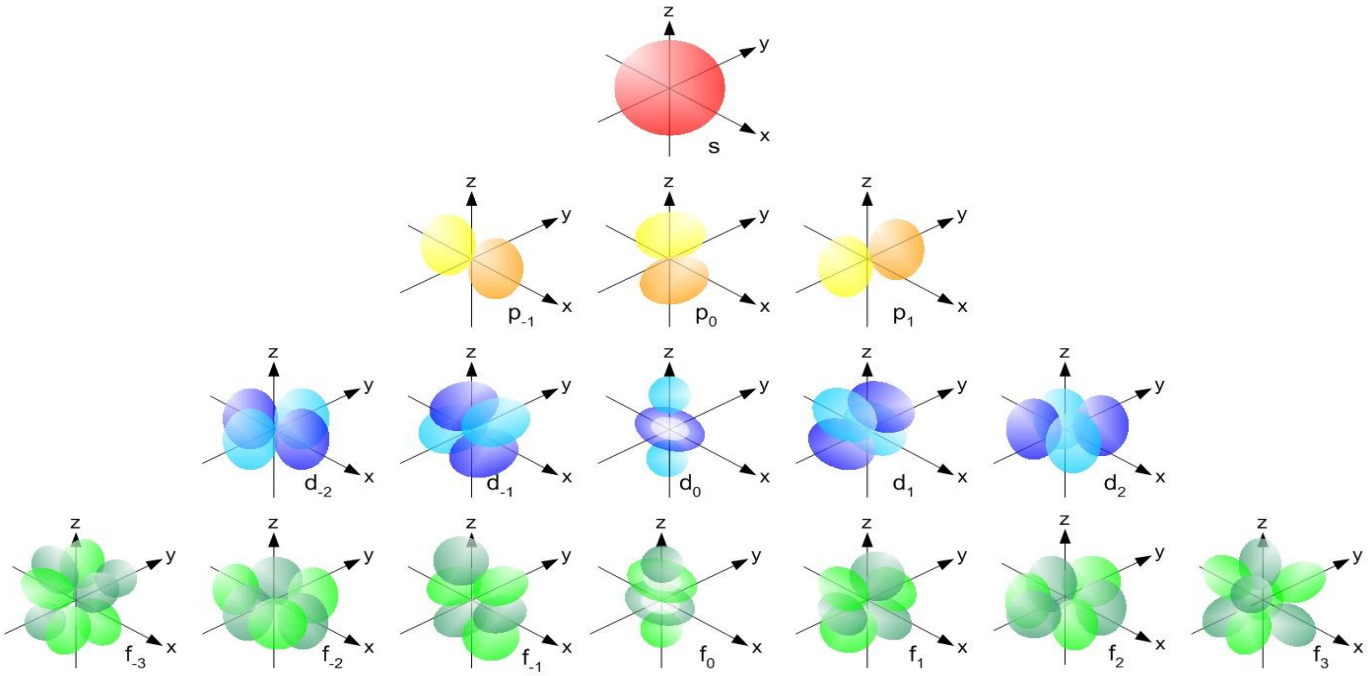
And so on, always following the same rule...

I-3 -3- b The secondary quantum number "l" or azimuthal, with "l" = 0, 1,..., n-1 The secondary quantum number, denoted ℓ (lower-case letter L (ℓ)), defines the notion of sublayers. It can take n values, from 0 to n - l, and determines the geometry of atomic orbitals so that the letter assigned to sublayer and orbital is the same. So we have :
- Orbital s for "l" = 0;
- Orbital p for "l" = 1;
- Orbital d for "l" = 2;
- Orbital f for "l" = 3.

I-3 -3- b The magnetic quantum number m, with m ∈ [-ℓ, + ℓ] The magnetic quantum number, denoted m, is a relative integer between - ℓ and +ℓ. This number describes the electron's orientation in the magnetic field of other charges. In other words, m determines the orientation of the orbital. Example 1: for ℓ =1, we can have m= -1, 0 or 1.
Example n°2: for ℓ =3, we can have m = -3, -2, -1,



Representation of the s and p atomic orbitals of an atom.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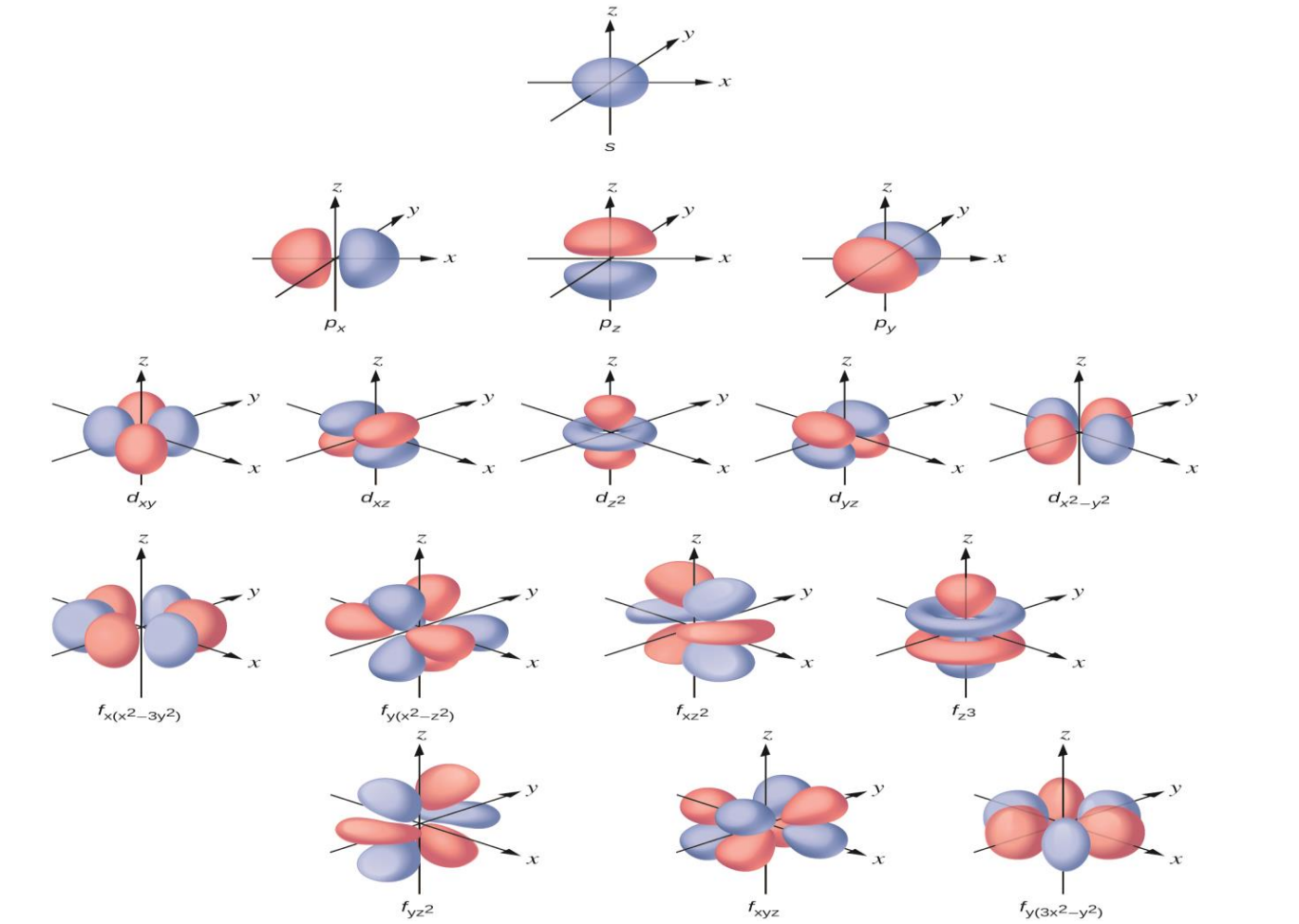
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fy(x2−z2)
fxz2
fz3
fyz2
fxyz
fy(3x2−y2)

I-3 -3- c Spin quantum number

- Permissible values of quantum numbers A 4th quantum number is introduced to take account of the fact that the electron behaves as a particle that can spin on itself in either direction, hence its name: spin quantum number s. This number can take only two values: +1⁄2 or -1⁄2. This number can take only two values: +1⁄2 or -1⁄2. It defines the electron's orientation in the magnetic field...

Applications 1. Give the electron sublayers included in the n = 4 layer.

2. How many orbitals does an electronic sublayer 2p contain?

Answers 1. For **n = 4**, the permitted values of ℓ are 0, 1, 2, 3. The electronic sublayers in the n = 4 layer are: 4s, 4p, 4d and 4f.

2. p corresponds to **ℓ = 1**. The permitted values of **m** are -1, 0 and 1, so there are three orbitals in the 2p electron sublayer. The same applies to the sublayer 3p, 4p,...

Table of possible values of quantum number:

Number	Symbol	Possible Values
Principal Quantum Number	n	$1, 2, 3, 4, \ldots$
Angular Momentum Quantum Number	ℓ	$0, 1, 2, 3, \ldots, (n-1)$
Magnetic Quantum Number	m_l	$-\ell, \ldots, -1, 0, 1, \ldots, \ell$
Spin Quantum Number	m_s	$+1/2, -1/2$

Summary table of the various states of an atom for the first five levels:

n	*l*	*ml*	m_s	Number of orbitals	Orbital Name	Number of electrons	Total Electrons
1 (K shell)	0	0	½ - ½	1	1*s*	2	2
2 (L Shell)	0	0	½ - ½	1	2*s*	2	8
	1	-1, 0, +1	½ - ½	3	2*p*	6	
3 (M-shell)	0	0	½ - ½	1	3*s*	2	18
	1	-1, 0, +1	½ - ½	3	3*p*	6	
	2	-2, -1, 0, +1, +2	½ - ½	5	3*d*	10	
4 (L-shell)	0	0	½ - ½	1	4*s*	2	32
	1	-1, 0, +1	½ - ½	3	4*p*	6	
	2	-2, -1, 0, +1, +2	½ - ½	5	4*d*	10	
	3	-3, -2, -1, 0, +1, +2, +3	½ - ½	7	4*f*	14	

I-3-4 Electronic structure of poly-electronic atoms (electronic configuration)

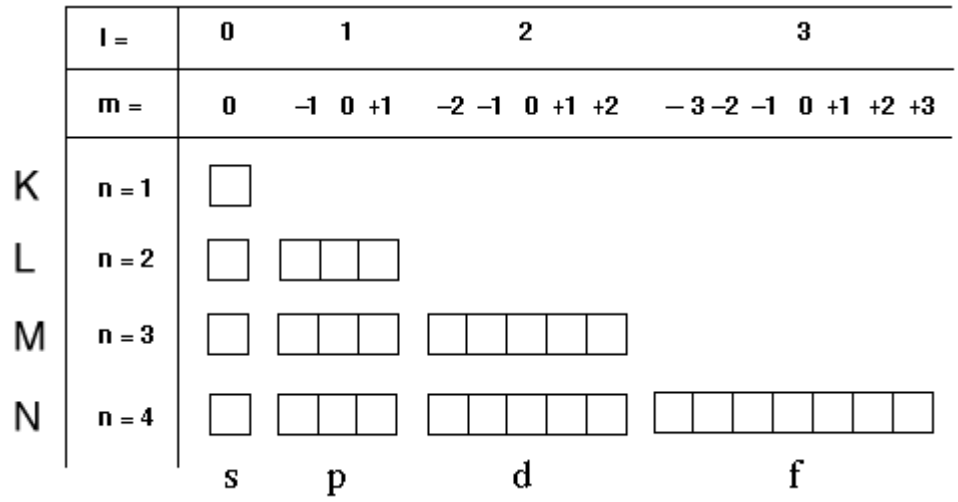
The electronic configuration of an atom is the distribution of Z electrons of the atom in a ground state over the atomic orbitals. Atomic orbitals are filled using the four general rules.

I-3-4-a Pauli Exclusion Principle

In an atom, two electrons cannot have their four quantum numbers identical: If two electrons of an atom occupy the same orbital (same values of n, ℓ,m), they necessarily differ in spin quantum number (one spin +1/2 and the other spin -1/2).

Note

- An orbital is defined by the three numbers n, ℓ and m. It's convenient to represent orbitals using quantum boxes:



- A quantum bin can only contain a maximum of 2 electrons of opposite spins.

- For a layer n, the number of squares is n2 and the number of electrons is 2n2.

I-3-4-b Stability principle

Electrons occupy the lowest energy levels within the limit of available space.

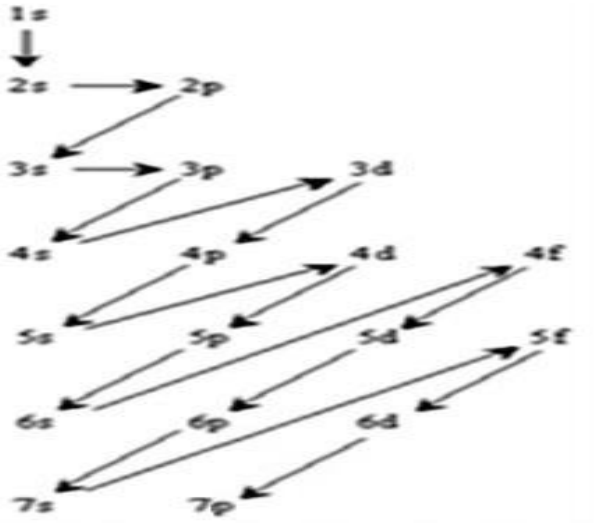
I-3-4-c HUND's rule

In the ground state, when electrons are placed in a multiple sublayer (p, d, f), they occupy the maximum number of orbitals of the same energy with single electrons having parallel spins (same value of s).

I-3-4-d KLECHKOWSKI rule

Sublayers are filled in ascending order of n+l values. For two equal values, the sublayer with the smallest n is filled first. For example, for 2p and 3s, n+l = 2+1 and n+l = 3+0 respectively, so 2p is filled first (smaller n), and only then 3s.

The order in which the sublayers are filled can be represented as follows:



- 1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s 4f 5d 6p 7s 5f 6d... If we fill in according to Klechkowski's rule, we usually note the configuration in ascending n order.
- The electronic configuration of an element's ground state is the signature of its internal structure and governs its chemical properties. When writing down electronic configurations, we make this distinction by defining two categories of electrons:

I-3-4-d-1 Core electrons

- Core electrons are those that populate the inner orbitals. For a given element, they correspond to the configuration of the rare gas that precedes this element in the classification. The configuration of core electrons is symbolized by the rare gas symbol in brackets.

I-3-4-d-2 Valence electrons

- Valence electrons populate the orbitals of occupied peripheral layers. The valence configuration is classically noted by aligning the symbols of the sublayers and superscripting the number of electrons in the sublayer. The valence layer represents the layer with the largest n.

Note: for transition elements whose electronic configuration ends in $(n-1)d^x\ ns^y$, their valence layer is not strictly limited to the largest n. In this case, consider that the valence electrons of the (n-1)d sublayer are part of the valence layer. So we don't have ns in the valence layer, but (n-1)d ns. Logically, the electrons d.

As we've seen, an atom's valence shell is its last electronic shell, i.e. the one furthest from the nucleus. It is characterized by the highest principal quantum number n. An atom can ionize by losing one or more electrons, or it can ionize by gaining electrons to complete its last layer.