# Atomes et molécules

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Chapter 3 : Electronic organization of atoms

## Introduction

## **1 – Organization of electrons in energy levels**

1.1 Concepts of shells, sub-shells and quantum boxes1.2 Organization of shells, sub- shells and quantum boxes1.3 Occupation of energy levels – Pauli exclusion principle

# 2 – Atom electronic configuration

- 2.1 Definition
- 2.2 Distribution of electrons in the fundamental state
- 2.3 Excited states of an atom
- 2.4 Concept of valence shells, LEWIS configuration of an atom

### Introduction

In all models of the atom the concepts of \_ quantified energy \_ 4 quantum numbers are valid.

On this basis we can build a scheme for the **atomic electrons organization** 

We can define the **electronic configuration** of an atom, based only on its atomic number Z (Z= number of protons = number of electrons in a neutral atom)

The task consists in arranging the electrons of an atom among a certain number of energy levels.

The hydrogen electron is in level n=1 with the energy  $E_1$ = -13.6 eV. What happens with a second and a third electron ? Experimentally, we obtain that the ionisation energy of Helium is 24.6 eV and for Lithium 5.39 eV. What is the interpretation?

## 1 - Organization of electrons...-1.1 shell, sub-shell, quantum boxes



Therefore the **shells**, sub-**shells** and quantum boxes are defined as sub-groups of electrons determined by their quantum numbers (n, l, m). These divisions correspond to the **possible** electron energy states, these states **being occupied or not**.

1 - Organization of electrons...- 1.2 shells organization

We know:

$$n: 1,2,3, ..., inf.$$
  

$$\ell = 0, 1, 2,..., n-2, n-1$$
  

$$m = -\ell, -\ell+1, ..., -1, 0, 1, ..., \ell-1, \ell$$

This dependency rule among quantum numbers has consequences:

\_ There are only a limited number of sub- shells in a shell

\_ There are only a limited number of quantum boxes in a sub- shell

1 - Organization of electrons...- 1.2 **shells** organization

| n<br>(shell) | 1<br>(sub-shell) | m<br>(quantum box) |
|--------------|------------------|--------------------|
| 1 (K)        | 0 (1s)           | 0                  |
|              | 0 (2s)           | 0                  |
| 2 (L)        |                  | -1                 |
|              | 1(2p)            | 0                  |
|              |                  | +1                 |
| 3 (M)        | 0 (3s)           | 0                  |
|              |                  | -1                 |
|              | 1 (3p)           | 0                  |
|              |                  | +1                 |
|              |                  | -2                 |
|              |                  | -1                 |
|              | 2 (3d)           | 0                  |
|              |                  | +1                 |
|              |                  | +2                 |

1 - Organization of electrons...- 1.2 shells organization

Quantum boxes representation



Represented independently of the presence of electrons

1 - Organization of electrons...-1.3 Occupation of energy levels- Pauli exclusion principle

1925: Pauli  $\rightarrow$  Exclusion principle: in an atom, two electrons cannot be described by the same combination of values for their quantum numbers.

I.e., they cannot occupy the same quantum state.

I.e., the electrons in an atom are in states which differ from each other at least in one of the 4 quantum numbers

In a quantum box (defined by **n**, *l*, **m**), the electrons state can only differ in **the value of s** 



There are at MOST 2 electrons per quantum box

1 - Organization of electrons...-1.3 Occupation of energy levels– Pauli exclusion principle

Definitions



A quantum box that has no electron is called **vacant** 



One electron in a box is called **odd** electron or **single** electron



If there are 2 electrons in the same box they are called **paired** electrons: they form a **doublet**.

## Pauli exclusion principle consequences

| n       | 1           | m              | S            | Number o    | of electrons |
|---------|-------------|----------------|--------------|-------------|--------------|
| (shell) | (sub-shell) | (quantum. box) |              | (sub-shell) | (shell)      |
| 1 (K)   | 0 (1s)      | 0 -1/2;+1/2 2  |              | 2           |              |
|         | 0 (2s)      | 0              | -1/2;+1/2    | 2           |              |
| 2 (L)   | 1(2p)       | -1             | -1/2;+1/2    |             |              |
|         |             | 0              | -1/2;+1/2    | 6           | 8            |
|         |             | +1             | -1/2;+1/2    |             |              |
| 3 (M)   | 0 (3s)      | 0              | -1/2;+1/2    | 2           |              |
|         | 1 (3p)      | -1             | -1/2;+1/2    |             |              |
|         |             | 0              | -1/2;+1/2    | 6           |              |
|         |             | +1             | -1/2;+1/2    | <u> </u>    |              |
|         | 2 (3d)      | -2             | -1/2;+1/2    |             |              |
|         |             | -1             | -1/2;+1/2    |             | 18           |
|         |             | 0              | -1/2;+1/2 10 |             | 10           |
|         |             | +1             | -1/2;+1/2    | Ĩ           |              |
|         |             | +2             | -1/2;+1/2    |             |              |

Ionisatio

Lithium:

The Z electrons of an atom are distributed among the layers, sub-layers and quantum boxes.

This distribution is called **electronic configuration**.

The electronic configuration is determined considering that the atom adopts naturally the state with minimum energy Fundamental state = Most stable state

| 3 electrons   | Lithium,<br>Beryllium,<br>Boron,<br>Carbon,<br>Nitrogen,<br>Oxygen,<br>Fluorine,<br>Neon, | Li<br>Be<br>C<br>N<br>G<br>F | 1s <sup>2</sup> 2s <sup>1</sup><br>1s <sup>2</sup> 2s <sup>2</sup><br>1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>1</sup><br>1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>2</sup><br>1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>3</sup><br>1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>4</sup><br>1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>5</sup><br>1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> |    | 1         1 | 2px 2py 2pz       1 | 11 electrons   |
|---------------|---|------------------------------|--|----|---|---|--|
|               |   |                              |  | 1s | 25  | 2p <sub>x</sub> 2p <sub>y</sub> 2p <sub>z</sub>   |  |
| 3 electrons   | Lithium,  | Li                           | 1s <sup>2</sup> 2s <sup>1</sup>  | ţ↑ | 1   |   | 11 electrons   |
|               | Beryllium,  | Be                           | 1s <sup>2</sup> 2s <sup>2</sup>  | ţţ | ţ↑  |   |  |
|               | Boron,  | в                            | 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>1</sup>  | ţţ | ţţ  | 1   |  |
|               | Carbon,   | с                            | 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>2</sup>  | ţţ | †↓  | <u>†</u> †  | $\left( \left( \begin{array}{c} \mathbf{Na} \end{array} \right) \right)$ |
|               | Nitrogen,   | N                            | 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>3</sup>  | ţţ | ţţ  | <u> </u>  |  |
|               | Oxygen,   | ο                            | 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>4</sup>  | ţţ | ţţ  | <u>↑↓</u> ↑ <u></u> ↑   |  |
|               | Fluorine,   | F                            | 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>5</sup>  | 1↓ | ţ↓  | ↑↓↑↓ ↑  | Invitation anarous of  |
| hium: 5.39 eV | Neon,   | Ne                           | 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup>  | 1↓ | 1↓  | Ţ↓Ţ↓Ţ↓  | Sodium: 5.14 eV  |

2 - Atom electronic conf. - 2.2 Distribution of electrons in the fundamental state

2.2.a Order of sub-layers energy levels

To determine the electronic configuration of an atom in the fundamental state we 'fill' progressively the sub-layers with electrons, in increasing energy order, up to the point where all Z electrons are placed.

There is an **inversion in the order of the sub-layer energies**.



2 - Atom electronic conf. - 2.2 Distribution of electrons in the fundamental state

- For Sodium, level 4s is shifted down below the n= 4 level of Hydrogen and finds itself below the 3d level which is not shifted compared to the n= 3 of Hydrogen.
- In general, for most atoms, s levels are lower in energy than p levels and d levels.



2 - Atom electronic conf. - 2.2 Distribution of electrons in the fundamental state

It can be shown that for any atom, the distribution of sub-shell energies defined by the pair  $\{n, l\}$  follows the diagram:



2 - Atom electronic conf. - 2.2 Distribution of electrons in the fundamental state

The order of quantum box energy levels is dictated by the Klechkovski rule (also known as Madelung rule):



2 - Atom electronic conf. - 2.2 Distribution of electrons in the fundamental state

Finally, we get the following order:

In the framework of quantum boxes



## 2.2.b – Hund's rule

In an isolated atom, the quantum boxes within the same sub-shell correspond to the same energy level. That is why we represent them by joint squares:





Sub-shell of type p

Sub-shell of type d



Sub-shell of type f

The electrons are placed 1 per box, and are **only paired in doublets if there are more electrons than boxes** 

The electrons are placed in as many quantum boxes as possible before completing one of them.

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"Equivalent to spin maximization: it's a question of energy minimization"

2 - Atom electronic conf. - 2.2 Distribution of electrons in the fundamental state



#### Example:

Iron (Fe) electronic structure in the fundamental state

Fe (Z=26), 26 electrons to be distributed in the sub-shells of increasing energy:

1s<sup>2</sup>, 2s<sup>2</sup>, 2p<sup>6</sup>, 3s<sup>2</sup>, 3p<sup>6</sup>, 4s<sup>2</sup>, 3d<sup>6</sup>



2 - Atom electronic conf. - 2.2 Distribution of electrons in the fundamental state

There are exceptions, in particular the electronic configurations with halffilled or full sub-shells are favored, as these configuration provide more stability.

This is the case of the transition elements (incomplete filling of sub-shells (n-1)d)

Examples :

**Chromium (Cr : Z=24)**  $1s^2$ ,  $2s^2$ ,  $2p^6$ ,  $3s^2$ ,  $3p^6$ ,  $4s^1$ ,  $3d^5$ 



**Copper (Cu : Z=29)**  $1s^2$ ,  $2s^2$ ,  $2p^6$ ,  $3s^2$ ,  $3p^6$ ,  $4s^1$ ,  $3d^{10}$ 



#### Atoms are not always in their fundamental state:

One atom receiving some energy (heat, radiation, etc.) can "jump" in a quantum state not corresponding to the minimal energy state. The electronic configuration changes: **one electron** is found in a different quantum box than in the fundamental state.

This state is called an excited state. It is unstable and short-lived.

The excess of energy is rapidly returned in the form of light by the emission of a photon and the atom is back to its fundamental state.



2 - Atom electronic configuration

Magnesium (Mg : Z=12)



**Fundamental state** 

Example of 3 excited states (others are also possible):



2 - Atom electronic conf. - 2.4 Concept of valence layer, LEWIS configuration of an atom

The electrons in the shell of highest principal quantum number (n) in the fundamental state play a main role in chemical reactions.

These are the electrons that participate to the **formations of bonds**.

Shell of highest n = external shell = peripheric shell = valence shell

Chemical properties are determined by the presence in the shell of doublets of electrons, single electrons or the absence of electrons.

We will provide a description of the valence layer based on the Lewis representation.

The element symbol represents the nucleus and the NON external electrons.

We represent only the external electrons, i.e., those in the valence shell.

2 - Atom electronic conf. - 2.4 Concept of valence shell, LEWIS configuration of an atom

Symbolism and conventions:

- \_ an isolated point: : an isolated electron in a quantum box
- \_ by a dash: : 2 paired electrons, in the same quantum box
- \_ by a square: **[**] : empty quantum box or hole

Examples :



"The Lewis configuration is mostly used for atoms belonging to the first three lines in the periodic table of elements"

#### **QCM 2**

On considère les atomes de phosphore  ${}^{31}_{15}P$  et de soufre  ${}^{32}_{16}S$ . Parmi les propositions suivantes, préciser celle(s) qui est(sont) exacte(s) :

- A. L'atome de soufre, S, comporte 32 neutrons.
- **B.** Le numéro atomique de l'atome de soufre, S, est 16.
- C. Les atomes de P et de S appartiennent à une même famille d'éléments chimiques et se trouvent donc dans une même période du tableau de la classification périodique.
- **D.** L'atome de P a une couche de valence du type  $\rm ns^2np^4.$
- E. Aucune des propositions précédentes (A à D) n'est exacte.

#### QCM 3

On donne O (Z=8) et S (Z = 16), parmi les propositions suivantes, préciser celle(s) qui est(sont) exacte(s) :

- A. L'atome de soufre, S, et l'atome d'oxygène, O, ont une couche de valence de même configuration.
- **B.** L'atome de soufre, S, et l'atome d'oxygène, O, se situent dans une même période du tableau de la classification périodique.
- C. L'atome d'oxygène est un halogène.
- **D.** L'atome de S comporte 5 électrons sur sa couche externe.
- **E.** L'atome de soufre est un alcalino-terreux.

#### QCM 5

Quel(s) atome(s) contien(nen)t, à l'état fondamental, trois électrons non-appariés sur leur couche de valence?

**A.** Li (Z = 3) **B.** N (Z = 7) **C.** Ne (Z = 10) **D.** Be (Z = 4) **E.** P (Z = 15)

#### QCM 6

Quelle couche électronique peut contenir un maximum de 18 électrons? Celle caractérisée par :

**A.** n = 1 **B.** n = 2 **C.** n = 3 **D.** n = 4 **E.** n = 5

#### QCM 7

Parmi les configurations électroniques suivantes, quelle(s) est (sont) celle(s) qui ne respecte(nt) pas le principe d'exclusion de Pauli?

- **A.**  $1s^3 2s^2 2p^6$ .
- **B.**  $1s^22s^22p^5$ .
- C.  $1s^22s^22p^43s^13p^1$ .
- **D.**  $1s^22s^22p^63s^23p^63d^{14}4s^2$ .
- E.  $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}4s^1$