Atomes et molécules

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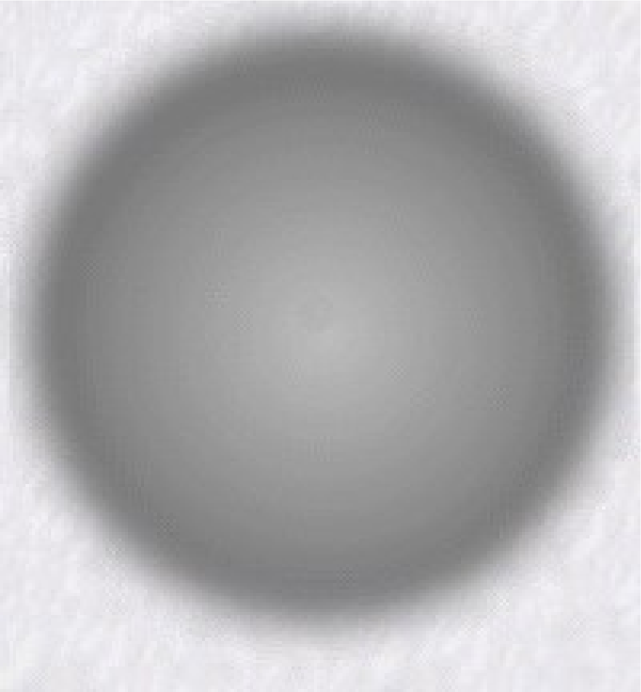
Chapter 10 : The atom in the wave model

I) The electron in wave mechanics

See Chapter 2 : Evolution of models of the atom



I-1) Introduction to wave mechanics

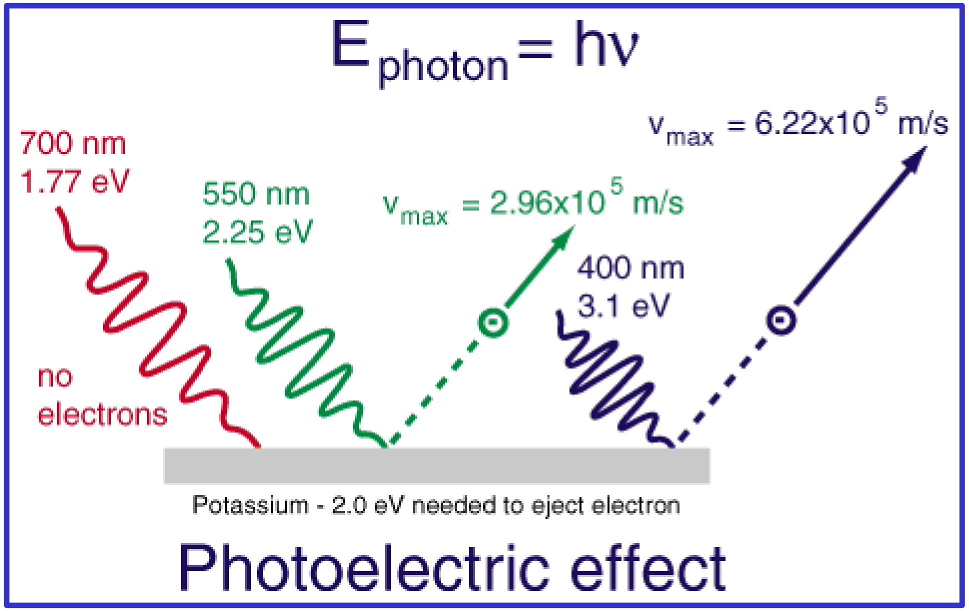
a/ Wave-particle duality

Light can be described as :

- a wave (characterized by its wavelength)
- a set of particles, photons with energy :

$$\boxed{E = h\nu = h\frac{c}{\lambda}}$$

ν is the frequency and λ is the wavelength



Photoelectric effect

Duality applies also to the electrons - And to all other particles with linear momentum p (p = Mass x Speed), a wavelength λ is associated (Louis de Broglie,1924)

Wavelength

$$\lambda = \frac{\mathbf{h}}{\mathrm{p}} = \frac{\mathbf{h}}{\mathrm{mv}}$$

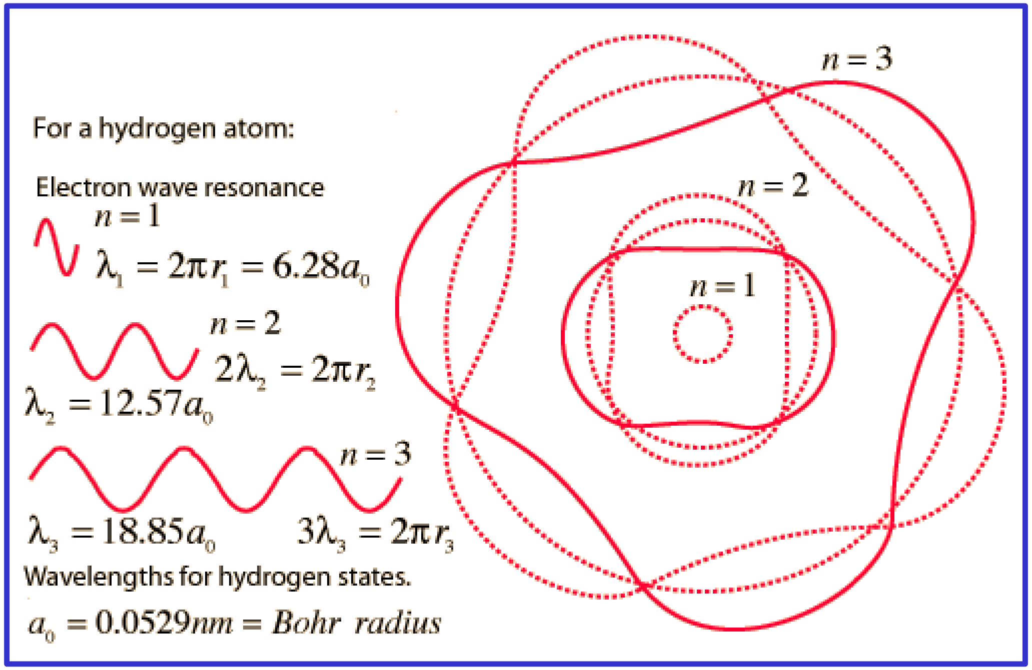
Linear momentum

Wave:

Quantum Wave Mechanic

Particle:

Classic mechanic description



The standing wave condition: circumference = whole number of wavelengths.

$$n\lambda = 2\pi r,\ \ n=1,\ 2,\ 3,\ldots$$

The angular momentum:

$$L = mvr = pr$$

$$= hr/\lambda = nh/2\pi = n\hbar$$

b) Heisenberg inequality (or uncertainty principle) :

1927: Werner Heisenberg → The momentum and position of a particle cannot be known simultaneously

For any particle :

$$\Delta x \, \Delta p > h / 2\pi$$

Δx : **uncertainty on the** position

Δp : **uncertainty on the momentum (speed):**

- The position and momentum of a particle cannot be simultaneously measured with arbitrarily high precision. There is a minimum for the product of the uncertainties of these two measurements. There is likewise a minimum for the product of the uncertainties of the energy and lifetime.

I-2) The wave function

a) Definition

- In wave mechanics, the electron is not described as a particle with a mass and a mechanical trajectory but as a **wave.**

- The electromagnetic wave associated to the electron is a stationary wave. Its amplitude at each point in space is time independent. This amplitude is given by a mathematical function:

the wave function written **Ψ (x,y,z)**,

- $\Psi(x,y,z)$ can be positive, negative, complex
- Ψ has no physical meaning but Ψ^2 has!
- Ψ must be finite, single-valued, continuous and vanish at infinity and Ψ^2 represents the probability density of finding the electron in a particular position in space.

- The probability dP of finding the electron in an infinitesimal volume dV centered at some point in space (x,y,z) is given by:

$$\mathbf{dP = |\,\Psi^2\,|\,dV}$$

- There is a normalization condition: the probability of finding the electron somewhere in space should be one:

$$\int_{\text{space}} \Psi^2 \, dV = 1$$

b) The Schrödinger equation

- Wave functions ψ are not determined experimentaly but can be calculated as solutions to a differential equation called :

The Schrödinger equation:

$$\frac{\delta^2\psi}{\delta x^2} + \frac{\delta^2\psi}{\delta y^2} + \frac{\delta^2\psi}{\delta z^2} + \frac{8\pi^2 m}{h^2}(E_t - E_p)\Psi = 0$$

E_t = total energy of the electron; E_p = potentiel energy applied to the electron
m = mass of the electron ; h = Planck constant

$$\frac{\delta^2}{\delta x^2} + \frac{\delta^2}{\delta y^2} + \frac{\delta^2}{\delta z^2} = \Delta$$

Δ : Laplace operator

$$\boxed{\Delta\Psi + \frac{8\pi^2 m}{h^2}(E_t - E_p)\Psi = 0}$$

II) Solutions to the Schrödinger equation

$$\boxed{\Delta\Psi + \frac{8\pi^2 m}{h^2}(E_t - E_p)\Psi = 0}$$

- **Solutions are functions ψ veryfying the equation in all points in space. The equation can be solved only for certain values of E_t : the quantum energy values that have been established experimentally (same values as the Bohr model).**

II-1) Case of hydrogen-like atoms

Only one é- : H (1 p, 1 é-);
He^+ (2 p, 1 é-);
Li^{++} (3 p, 1 é-);

- The only electron is in a central force field applied by the protons

- The Schrödinger equation can be solved analytically: solutions of ψ are possible for particular values of the energy E.

- The wave functions ψ, solutions to the Schrödinger equation, must satisfy a number of conditions (continuous, finite in space and normalised)

Solutions to the Schrödinger equation are quantified, three numbers need to be introduced :

the quantum numbers n, ℓ et m.

One set of n, ℓ and m defines the total energy and the wavefunction of the electron.

{ n, ℓ, m} defines

E_t

≡ energy of the electron

≡ **Quantum box**

□

ψ

≡Wave function of the electron

≡ψ^2 : probability to find the electron, information on the **spatial** distribution of the é:

The **orbital is the representation of this spatial distribution**

Atomic orbitals

The ORBITAL associated to $\{n,\ell,m\}$ defines the probability to find the electron and is described by the wave function $\psi_{n\ell m}$.

ORBITALS are equivalent to the quantum boxes.

They have the same name:

*Orbitals 1s, 2s $\{1,0,0\}$, $\{2,0,0\}$

*Orbitals 2p,3p $\{2,1,0\}$ $\{2,1,-1\}$ $\{2,1,+1\}$

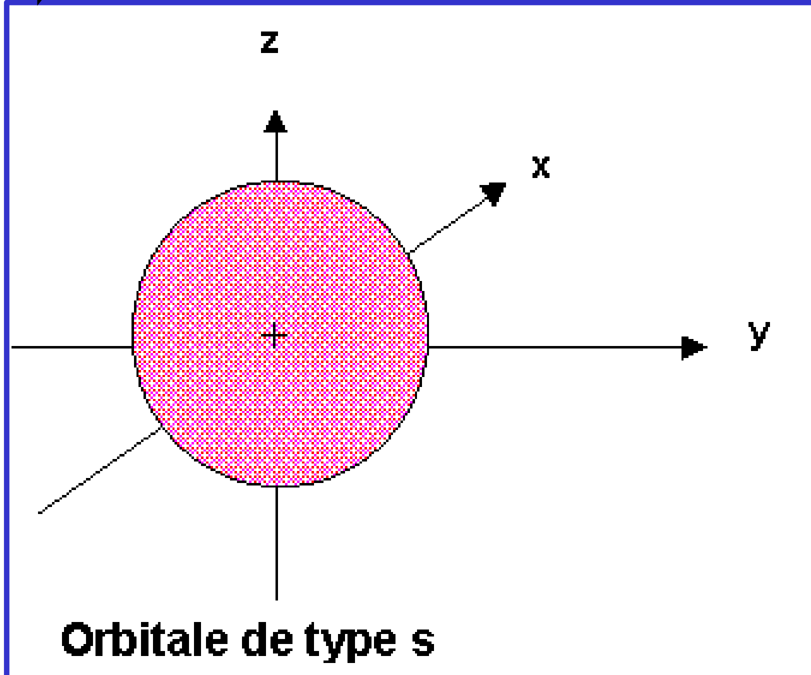
$\{3,1,0\}$,……..

Shape of the orbitals

- ℓ characterizes the shape and the symmetry of the orbitals.
- m characterizes the orientation of the orbitals in the reference system (x, y, z) of the nuclei.

- Orbitals characterized by ℓ=0 ⇔ s orbitals

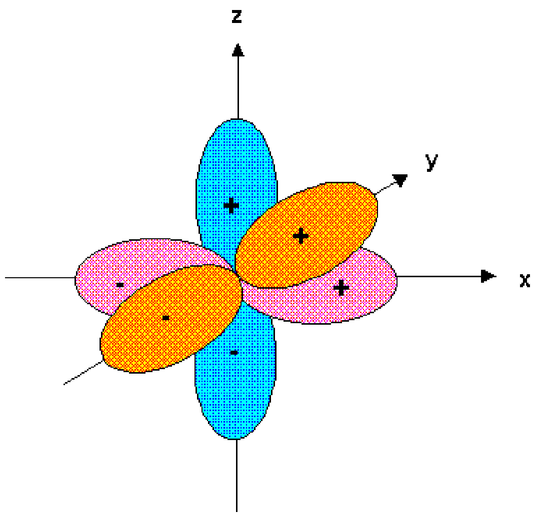
Spherical symmetry



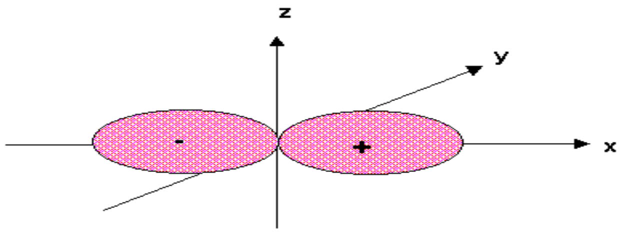
Orbitale de type s

- **Orbitals characterized by $\ell=1$ ↔ p orbitals**

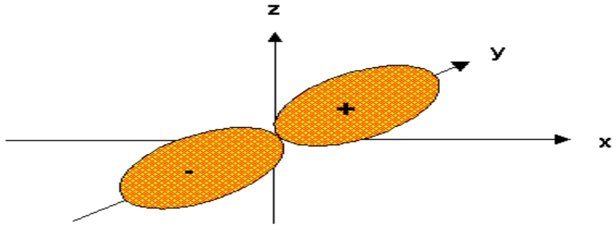
They are two-lobed shaped and oriented along coordinate x,y or z depending on the value of m.



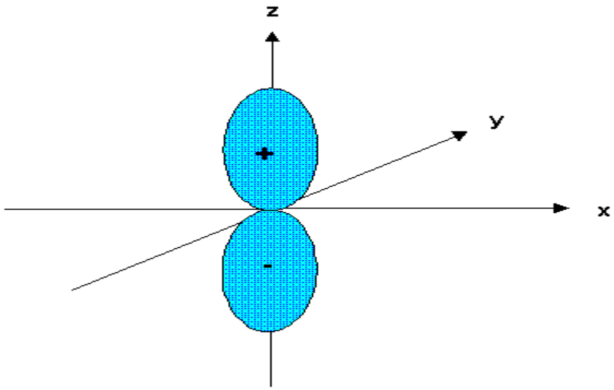
Les trois orbitales p



Orbitale p_x

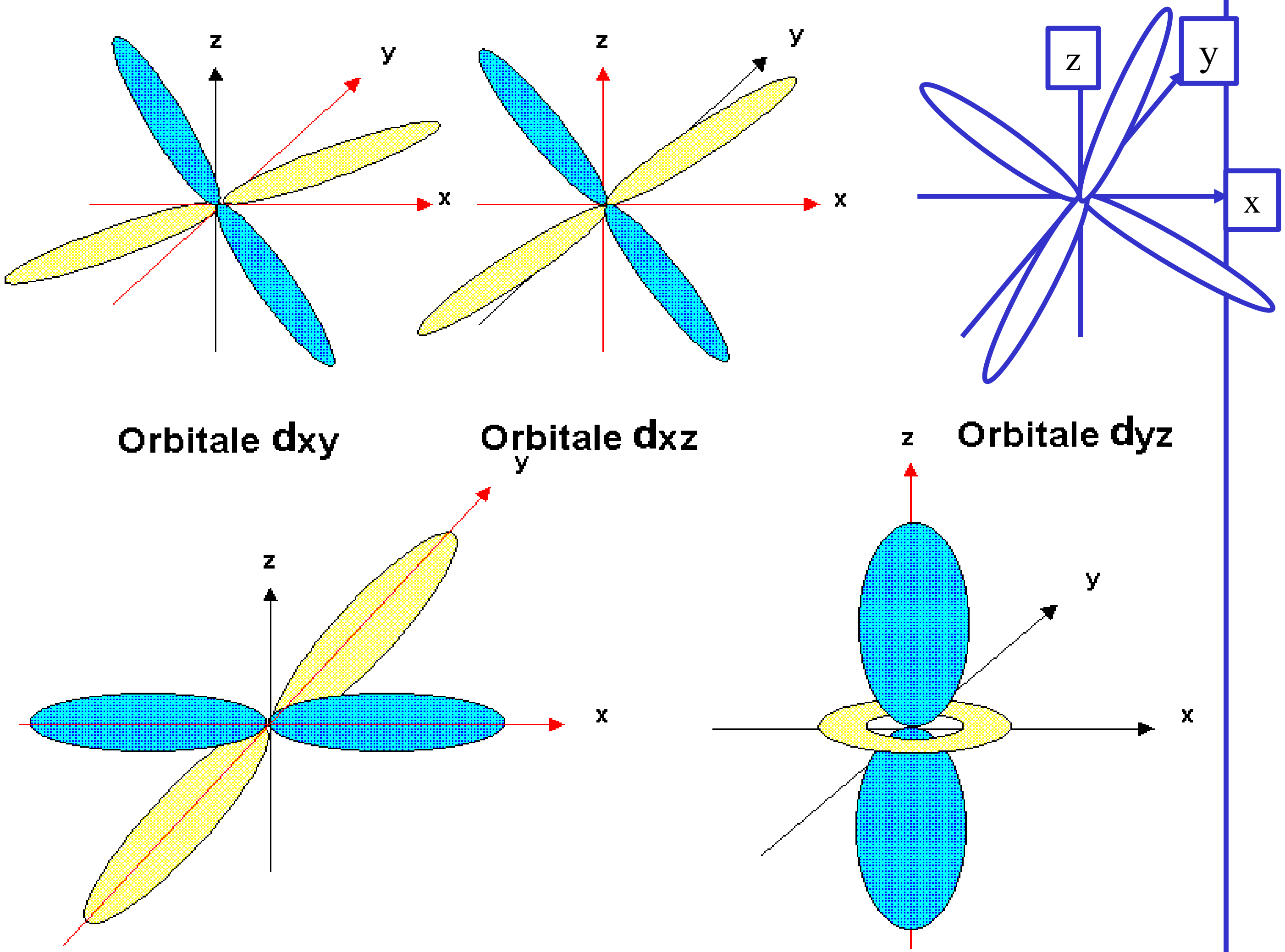


Orbitale p_y



Orbitale p_z

- **Orbitals characterized by ℓ=2 ⟺ d orbitals.**



Orbitale dxy

Orbitale dxz

Orbitale dyz

Orbitale dx^2- y^2

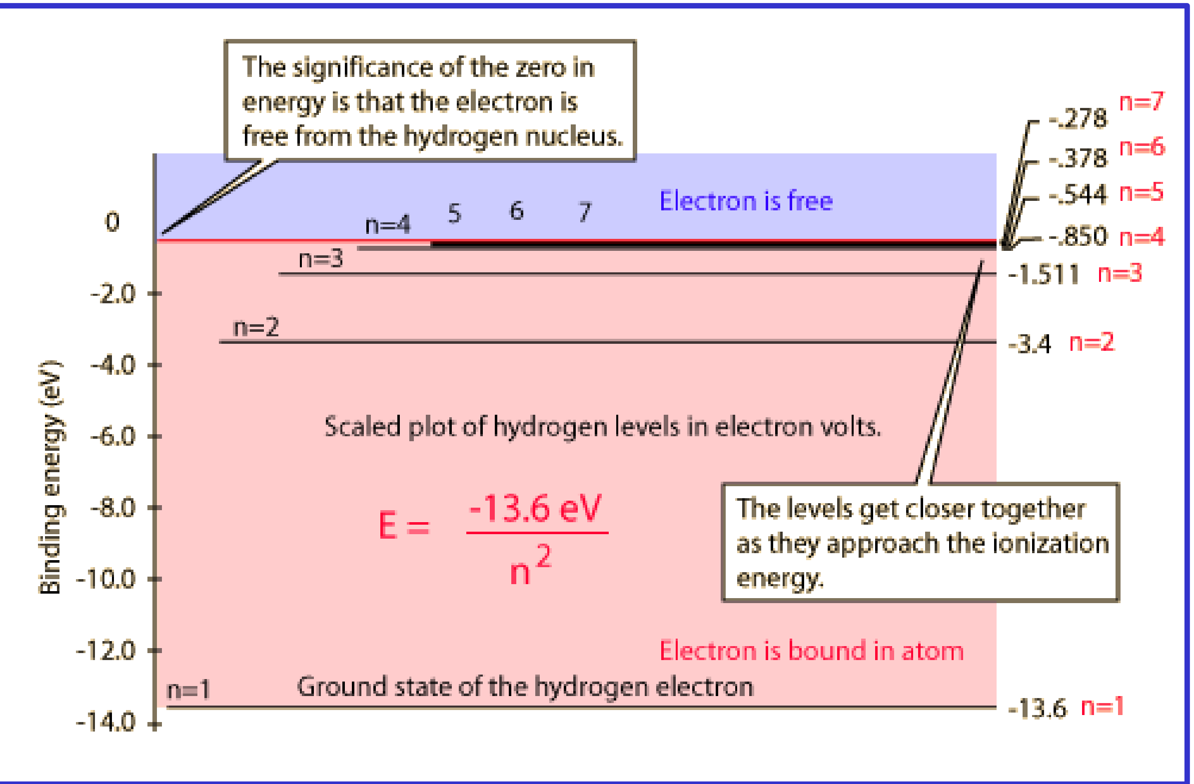
Orbitale dz^2

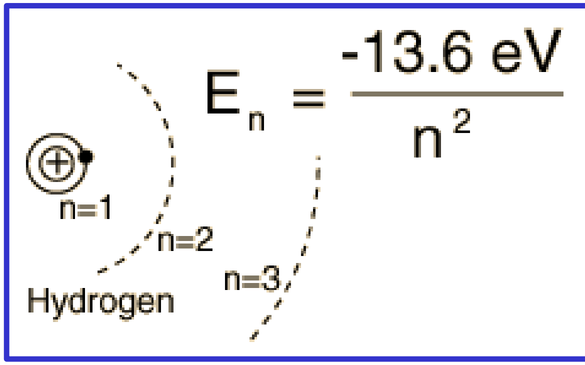
La fonction d'onde est positive pour les lobes bleus et négatives pour les lobes jaunes

- **Energy levels**

In the case of hydrogen-like atoms, it can be shown that each value of n (each value of E_n) corresponds to **n^2 orbitals with the same energy (because of ℓ and m)**

This is called the degeneracy of the energy level.





$$E_n = \frac{-13.6\ \text{eV}}{n^2}$$

- Consequence in the case of the H atom:

orbitals

⇕

possible energy (quantum cell)

⇕

$\{n\}$

The electron in the H atom can take different energies depending <u>only on the principal quantum number *n*</u>

$$E_t = - \frac{e^4 m}{8\varepsilon_0^2 h^2} \frac{1}{n^2} = - \frac{13.6 \text{ eV}}{n^2}$$

The sub shells (defined by ℓ) and the sub levels (defined by m) belonging to the same shell (defined by n) have the same energy:

they are degenerated.

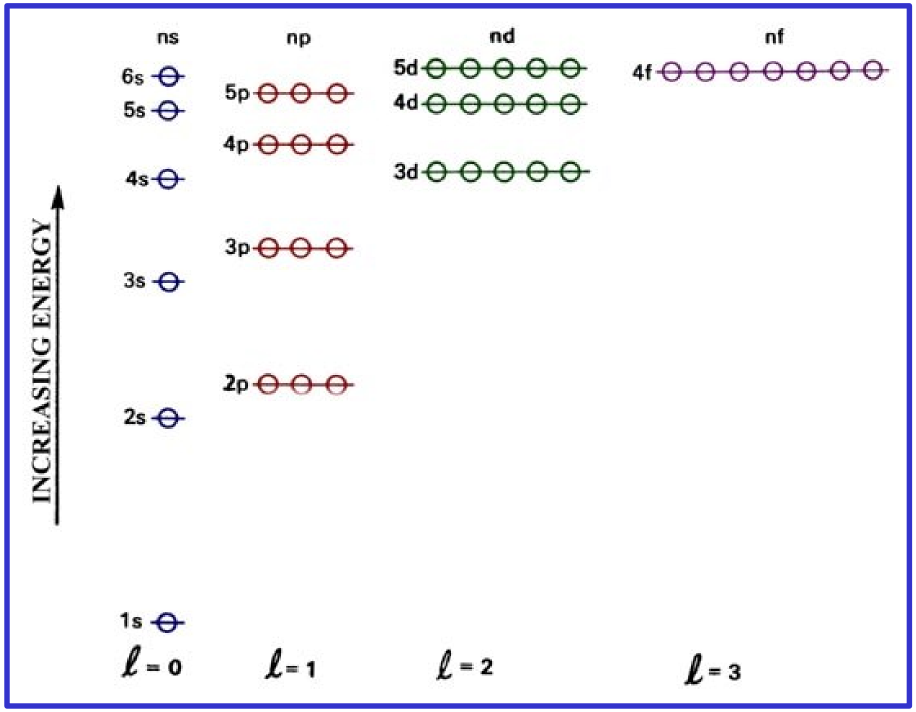
All orbitals with the same *n* have the same energy

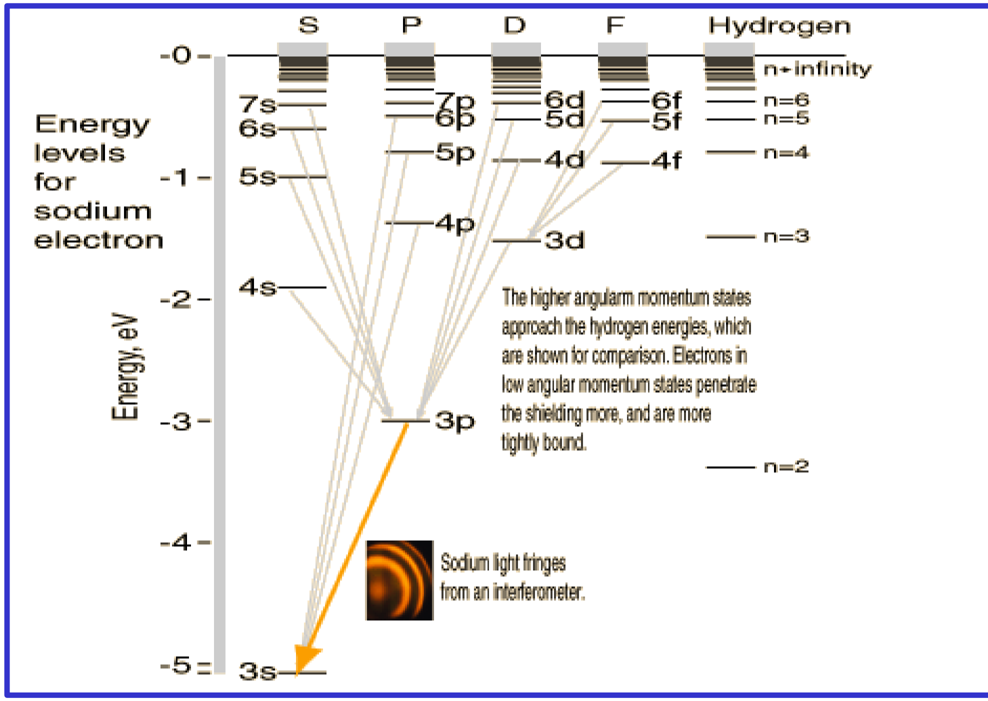
II-2) Case of many-electron atoms

- The atom is not a central force field system anymore. In addition to the nuclei/e- attraction, repulsion between electrons appear.

- The full resolution of the Schrödinger equation is no longer possible. Approximations need to be done.

- It can be shown that the **energy of a given electron of the atom now depends on both quantum numbers : n and ℓ (but not m)**





The higher angularm momentum states approach the hydrogen energies, which are shown for comparison. Electrons in low angular momentum states penetrate the shielding more, and are more tightly bound.

Sodium light fringes from an interferometer.

orbitals

↕

Possible energy (quantum cell)

↕

{n, ℓ}

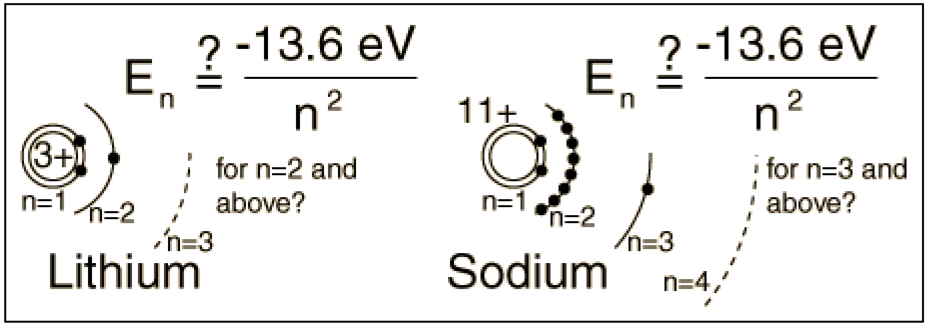
The orbitals belonging to the same shell (same n) no longer have the same energy. It **depends on ℓ**:

$$E_{3s} < E_{3p} < E_{3d}$$

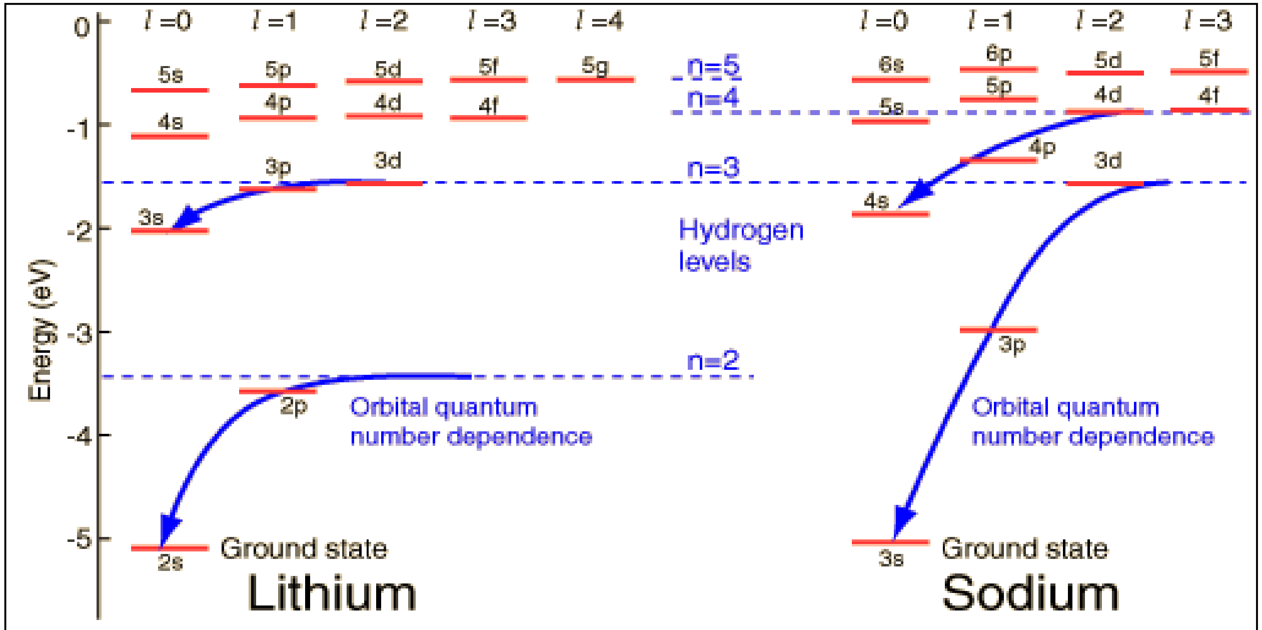
When belonging to the same subshell (same ℓ) sublevels with **different m** still have the same energy (they are degenerated)

All orbitals with same {*n*, ℓ} have the same energy

Hydrogen-like atoms such as lithium and sodium might be expected to exhibit similar energy levels. They consist of closed shells with a single electron outside. Envisioning a Bohr-type shell structure with just a single electron in the outer shell, the net charge inside that shell is just one net positive charge. This leads to the following expectation:

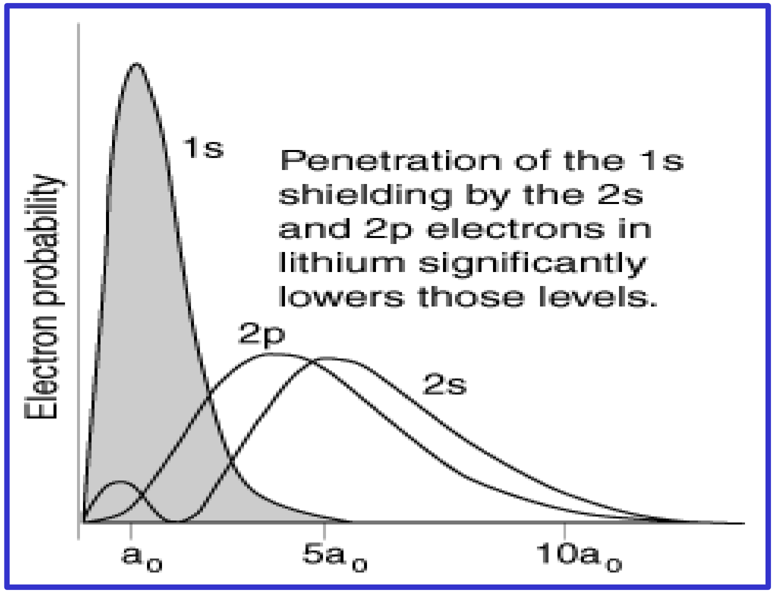


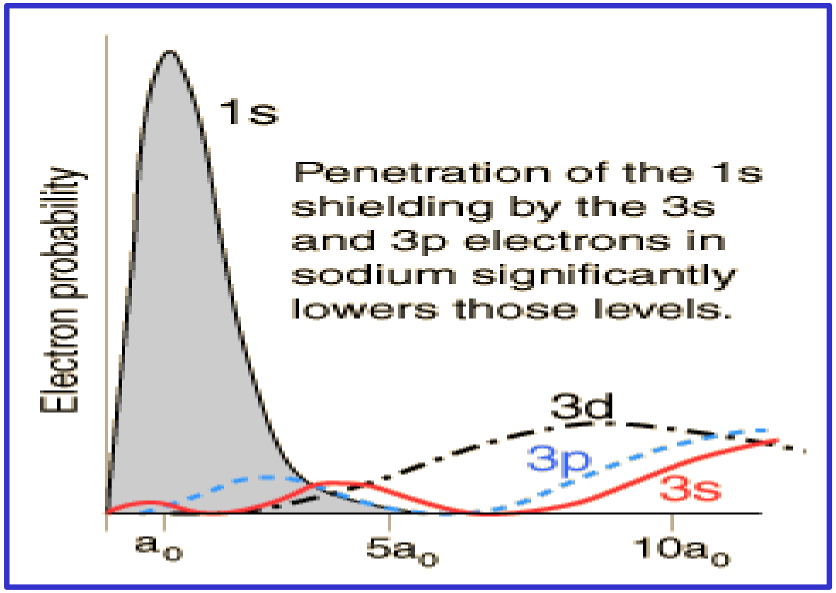
However, when data from spectra are used to build energy level diagrams for these atoms, a strong orbital dependence of the energy is found for the electrons of low angular momentum as shown below.



- **Origin of Orbital Quantum Number Dependence of Electron Energies**

When the wavefunctions for electrons with different orbital quantum numbers are examined, it is found that there is a different amount of penetration into the region occupied by the **1s electrons**. This penetration of the shielding 1s electrons exposes them to more of the influence of the nucleus and causes them to be more tightly bound, lowering their associated energy states.





In the case of lithium, the 2s electron shows more penetration inside the first Bohr radius and is therefore lower than the 2p. In the case of sodium with two filled shells, the 3s electron penetrates the inner shielding shells more than the 3p and is significantly lower in energy.