



# Liaison Chimique '07

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## Chap. IV: Atome Multiélectronique



# Hamiltonien : système à n électrons

Unités : SI

$$\hat{H} = -\underbrace{\frac{\mathbf{h}^2}{2m_e} \sum_{i=1}^n \nabla_i^2}_{T_e \text{ énergie cinétique}} - \underbrace{\sum_{i=1}^n \frac{Ze^2}{4\pi\epsilon_0 r_i}}_{V_{eN} \text{ Attraction e-N}} + \underbrace{\sum_{i=1}^n \sum_{j>i}^n \frac{e^2}{4\pi\epsilon_0 r_{ij}}}_{V_{ee} \text{ Répulsion e-e}}$$

Problème : on ne peut pas séparer  $\hat{H}$  en termes indépendants à cause du terme biélectronique en  $1/r_{ij}$

Comment résoudre dans ce cas l'équation de Schrödinger ??



## Une approche possible (mais limitée)

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Première étape :

*A l'ordre 0, la fonction d'onde est égale, en première approximation, au produit de fonctions d'onde hydrogénoïdes (monoélectroniques)*

$$y^{(0)} = f_1(r_1, \mathbf{q}_1, \mathbf{f}_1) * f_2(r_2, \mathbf{q}_2, \mathbf{f}_2) * \dots * f_n(r_n, \mathbf{q}_n, \mathbf{f}_n)$$

avec :  $f = R_{n,l}(r) Y_l^m(\mathbf{q}, \mathbf{f})$

*Ceci revient à négliger le terme de répulsion biélectronique dans l'hamiltonien du système (approximation importante) !*



# Une approche possible (mais limitée)

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Seconde étape : méthode variationnelle (pour l'atome !)

- On considère des fonctions hydrogénoïdes avec une charge effective  $Z$  (paramètre variationnel) et on applique le principe variationnel

*Attention : erreur sur l'énergie de 1,9% pour l'hélium mais beaucoup plus élevée pour les atomes plus lourds !*

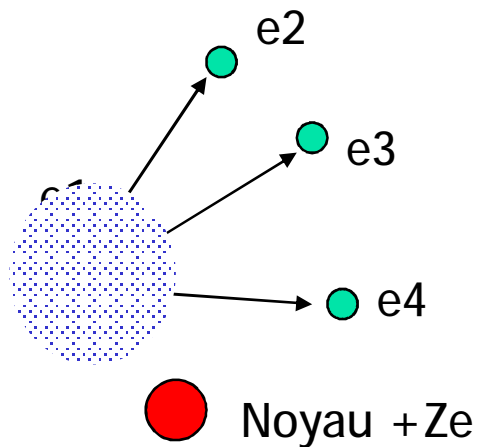
- **Amélioration :**

On minimise la fonction  $y = g_1(r_1, q_1, f_1) * g_2(r_2, q_2, f_2) \dots g_n(r_n, q_n, f_n)$  en appliquant le principe variationnel (le « paramètre » est ici **une fonction**) :

$$\frac{\partial W}{\partial g_i} = 0 \quad (W : \text{int. variationnelle}) \quad \text{avec : } g_i = h_i(\mathbf{r}_i) Y_{l_i}^{m_i}(q_i, f_i)$$

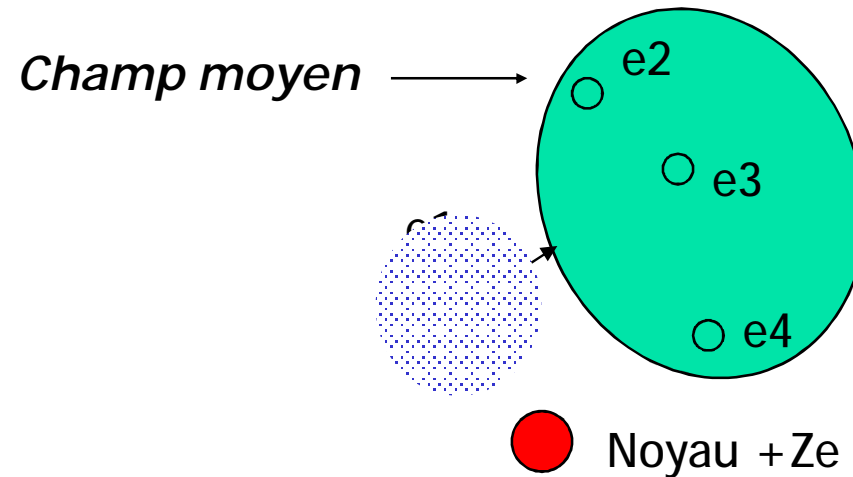
# Méthode de Hartree (1)

Méthode du champ auto-cohérent (SCF : self-consistent field)



Charges ponctuelles

$$\text{ex : } V_{12} = \frac{q_1 q_2}{4\pi \epsilon_0 r_{12}} = \frac{e^2}{4\pi \epsilon_0 r_{12}}$$



Distribution de charges

$$\text{ex : } V_{12} = \frac{q_1}{4\pi \epsilon_0} \int \frac{r_2}{r_{12}} du_2$$

avec:  $r_2 = -e |g_2|^2$

## Méthode de Hartree (2)

- En généralisant à l'ensemble des n-1 électrons :

$$V_{12} + V_{13} + \dots + V_{1N} = \sum_{j=2}^n \frac{e^2}{4\pi\epsilon_0} \int \frac{|g_j|^2}{r_{1j}} du_j$$

- **Potentiel effectif pour l'électron 1** (champ moyen électronique et noyau) :

$$V_1^{eff}(r_1, q_1, f_1) = \sum_{j=2}^n \frac{e^2}{4\pi\epsilon_0} \int \frac{|g_j|^2}{r_{1j}} du_j - \frac{Ze^2}{4\pi\epsilon_0 r_1}$$

$$V_1^{eff}(r_1) = \frac{\int_0^{2p} \int_0^p V_1^{eff}(r_1, q_1, f_1) \sin q_1 dq_1 df_1}{\int_0^{2p} \int_0^p \sin q_1 dq_1 df_1}$$

Approximation du champ  
Central (symétrie sphérique)



## Méthode de Hartree (3)

- On obtient alors une équation de Schrödinger monoélectronique :

$$\left[ \frac{-\hbar^2}{2m_e} \nabla_1^2 + V_1^{eff}(r_1) \right] t_1(1) = e_1 t_1(1)$$

→  $t_1(1)$  : orbitale améliorée pour électron 1 ( $\neq g_1(1)$ )

$$\text{avec } t_1(1) = R_{n,l}(r_1) Y_{l_1}^{m_1}(q_1, f_1)$$

→ Harmonique sphérique (car potentiel  $V_1^{eff}$  à symétrie sphérique)

→ Fonction radiale  $\neq$  fonction hydrogénoïde !!  
(car potentiel non coulombien)

→  $e_1$  : énergie de l'orbitale de l'électron 1

# Méthode de Hartree (4)

- On résoud le même type d'équation monoélectronique pour *tous les électrons* :

$$\left[ \frac{-\hbar^2}{2m_e} \nabla_i^2 + V_i^{eff}(r_i) \right] t_i(i) = e_i t_i(i)$$

Systeme de n équations couplées

$$\hat{h}_i(i)$$

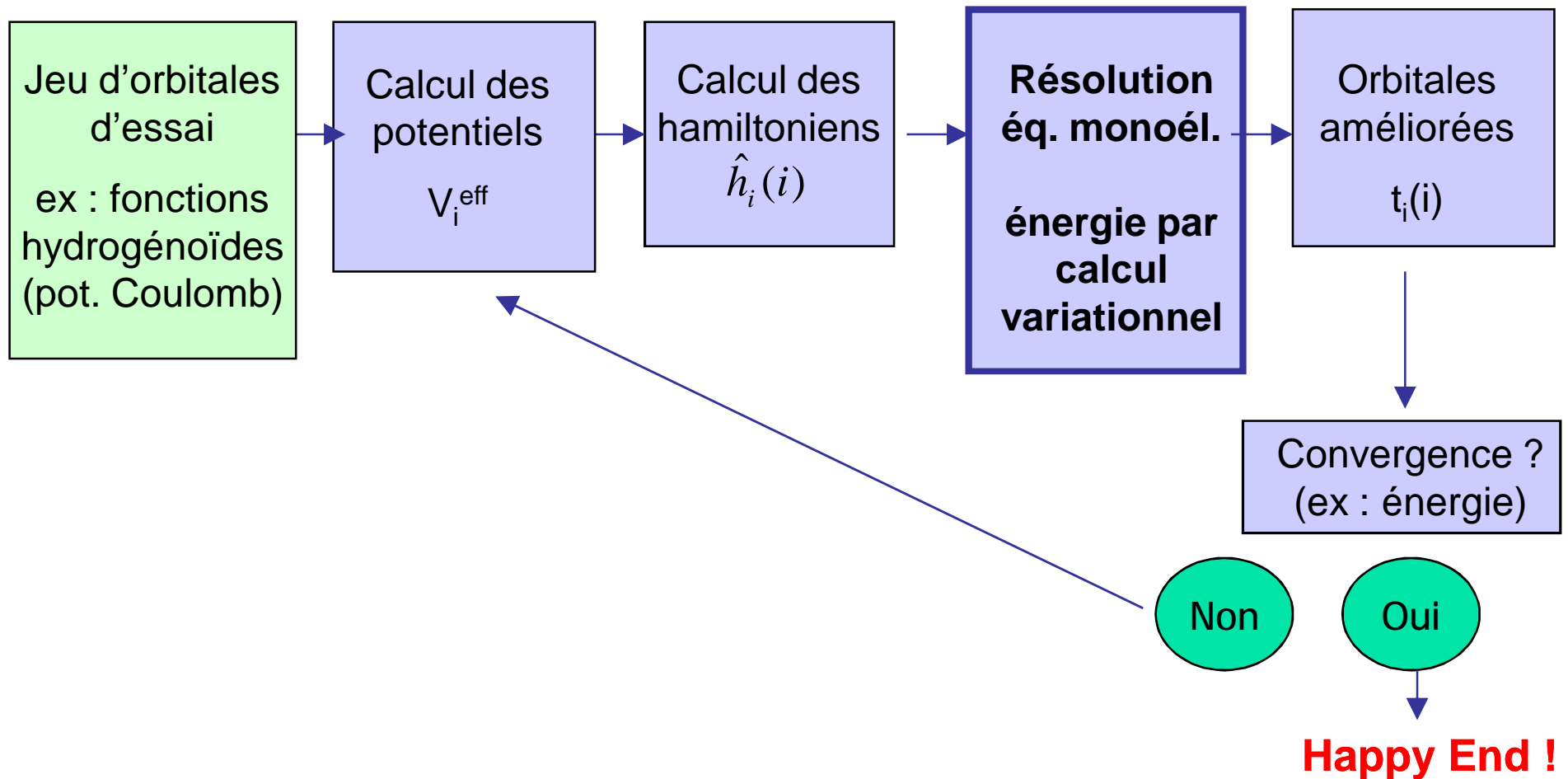
Procédure SCF  
jusqu'à convergence

On obtient alors une série d'orbitales améliorées :

$$t_1(1), t_2(2), t_3(3), t_4(4) \dots t_n(n)$$

Nouveaux potentiels  $V_i'^{eff}$  pour chaque électron

# Procédure SCF : récapitulatif





# Energie de Hartree

**Attention !** L'énergie électronique totale *n'est pas égale* à la somme des énergies orbitales !!

$$E = \sum_{i=1}^n e_i - \sum_{i=1}^{n-1} \sum_{j=i+1}^n \iint \frac{e^2 |t_i(i)|^2 |t_j(j)|^2}{4\pi\epsilon_0 r_{ij}} du_i du_j$$

$$E_{Hartree} = \sum_{i=1}^n e_i - \sum_{i=1}^{n-1} \sum_{j=i+1}^n J_{ij}$$



$J_{ij}$  : intégrales coulombiennes

$e_i$  : énergies des orbitales monoélectroniques



*Afin d'éviter de comptabiliser  
deux fois les  
répulsions interélectroniques*

# Méthode Hartree-Fock (1)

- Dans la méthode de Hartree, la fonction d'onde utilisée est une approximation à l'ordre 0 :

$$\Psi = g_1(r_1, \mathbf{q}_1, \mathbf{f}_1) * g_2(r_2, \mathbf{q}_2, \mathbf{f}_2) \dots g_n(r_n, \mathbf{q}_n, \mathbf{f}_n)$$

*Problème : cette fonction d'onde (produit de Hartree) n'est pas antisymétrique !!*

- On utilise alors (**méthode Hartree-Fock**) une combinaison linéaire antisymétrique de produits de spinorbitales = déterminant de Slater

Ex : He

$$\Psi_0 = \frac{1}{\sqrt{n!}} \begin{vmatrix} u_1(1) & u_2(1) & u_3(1) & \mathbf{L} & u_n(1) \\ u_1(2) & u_1(2) & u_1(2) & \mathbf{L} & u_n(2) \\ \mathbf{L} & \mathbf{L} & \mathbf{L} & \mathbf{L} & \mathbf{L} \\ u_1(n) & u_2(n) & u_3(n) & \mathbf{L} & u_n(n) \end{vmatrix}$$

$$\Psi_0 = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1)a(1) & 1s(1)b(1) \\ 1s(2)a(2) & 1s(2)b(2) \end{vmatrix}$$

ou

$$\Psi_0 = \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1) & \overline{1s}(1) \\ 1s(2) & \overline{1s}(2) \end{vmatrix} = |1s\overline{1s}|$$

avec  $1s(1) = 1s(1)a(1)$  et  $\overline{1s}(1) = 1s(1)b(1)$



# Méthode Hartree-Fock (2)

## Equations Hartree-Fock

$$\hat{F}u_i(i) = e_i u_i(i)$$

## Système de n équations couplées

$\hat{F}$  = opérateur de Fock

$$u_i = t_i * S_i = i^{\text{ème}} \text{ spinorbitale}$$

= fonction d'espace  $f$  \* fonction de spin  $s$

$e_i$  = énergie de la  $i^{\text{ème}}$  spinorbitale

## Energie Hartree-Fock

$$E_{HF} = \sum_{i=1}^n e_i - \sum_{i=1}^{n-1} \sum_{j=i+1}^n (J_{ij} - K_{ij})$$

(ou énergie SCF)

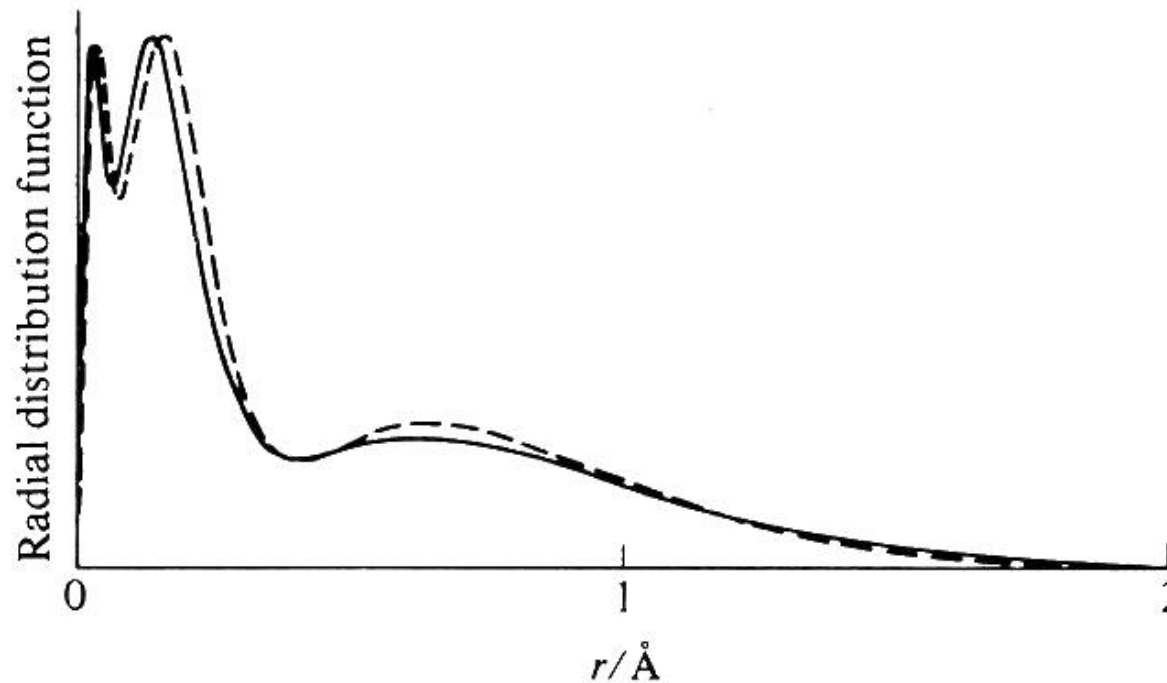
$J_{ij}$  = intégrales de Coulomb

$K_{ij}$  = intégrales d'échange

(effet purement quantique dû à

l'antisymétrisation de la fonction d'onde)

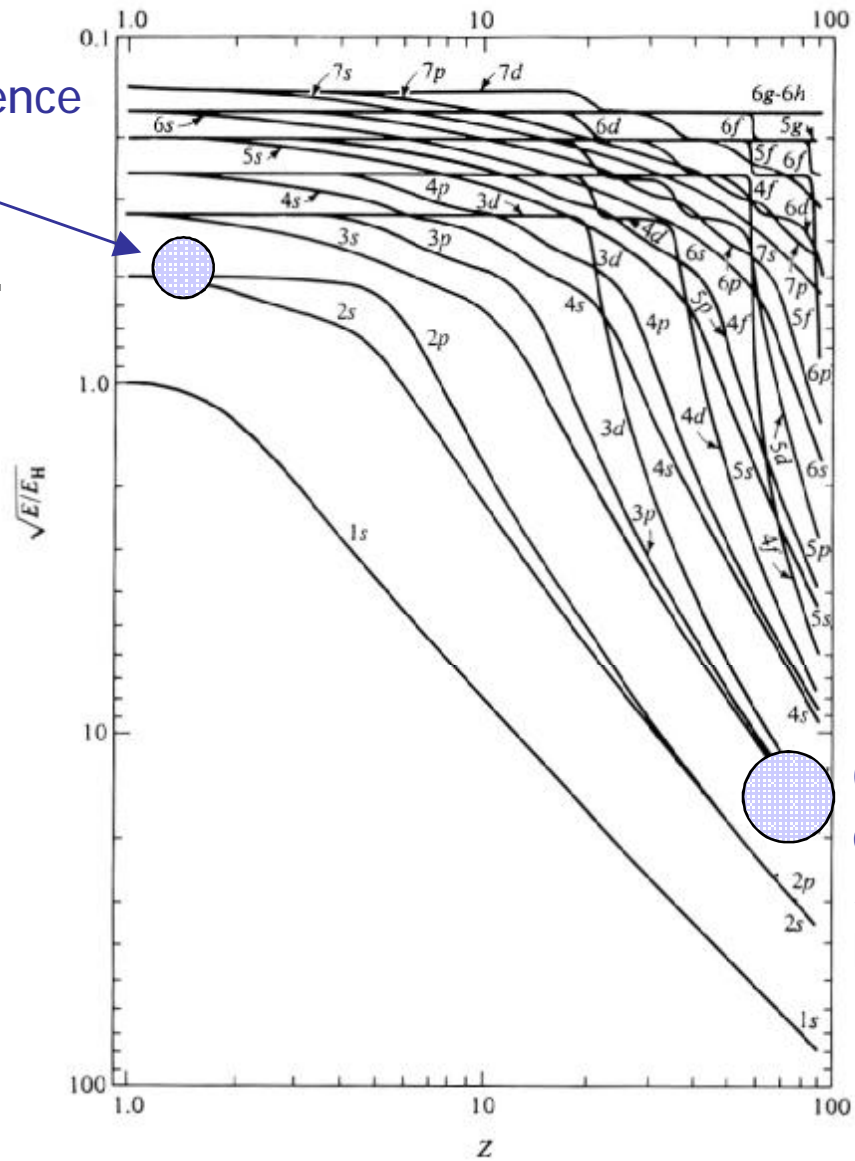
## Exemple de calcul : $D(r)$ pour Ar



**Figure 11.1** Radial distribution function in Ar as a function of  $r$ . The broken line is the result of a Hartree–Fock calculation. The solid line is the result of electron-diffraction data. [From L. S. Bartell and L. O. Brockway, *Phys. Rev.*, **90**, 833 (1953). Used by permission.]

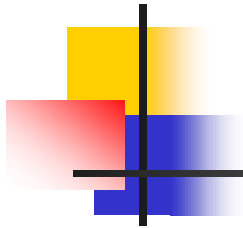
# Energies orbitales atomiques

Levée de dégénérescence pour  $Z > 1$  (2s,p)  
(effet :  $1/r_{ij}$ )



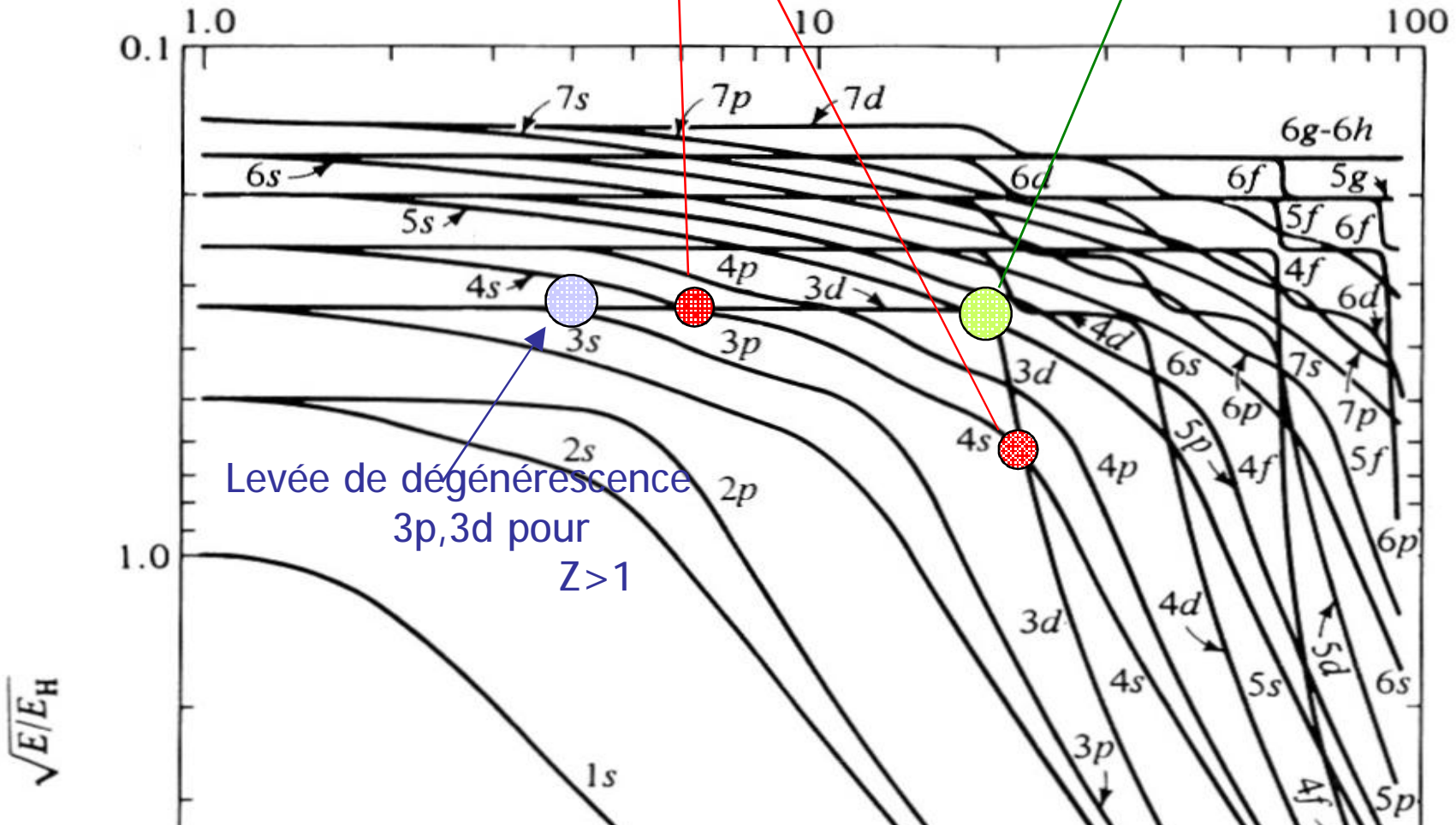
Quasi-dégénérescence 3s,p,d  
Pour Z élevé  
( $V_{ee} \ll V_{eN}$ )

**Figure 11.2** Atomic-orbital energies as a function of atomic number for neutral atoms, as calculated by Latter. [Figure redrawn by M. Kasha from R. Latter, *Phys. Rev.*, **99**, 510 (1955). Used by permission.] Note the logarithmic scales.  $E_{11}$  is the ground-state hydrogen-atom energy,  $-13.6$  eV.



Inversion  
orbitale 4s/3d  
4s < 3d pour  
7 ≤ Z ≤ 20

Chute soudaine en  
énergie (3d) pour Z=21  
(mauvais écranage)





## Small complement: atomic terms

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Remember.....

The total wave function,  $\psi(r, \theta, \phi)$  depends on  $n$ ,  $\ell$ , and  $m_\ell$ . The wave function becomes

$$\Psi_{nlm_\ell}(r, \theta, \phi) = R_{nl}(r)Y_{lm_\ell}(\theta, \phi)$$



## Orbital Angular Momentum Quantum Number $\ell$

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Energy levels are **degenerate** with respect to  $\ell$  (the energy is independent of  $\ell$ ).

Chemists use letter names for the various  $\ell$  values:

$\ell =$	0	1	2	3	4	5 . . .
Letter =	<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>	<i>g</i>	<i>h</i> . . .

Atomic states are usually referred to by their values of  $n$  and  $\ell$ .

A state with  $n = 2$  and  $\ell = 1$  is called a  $2p$  state.

## Magnetic Quantum Number $m_\ell$

Classically, the orbital angular momentum

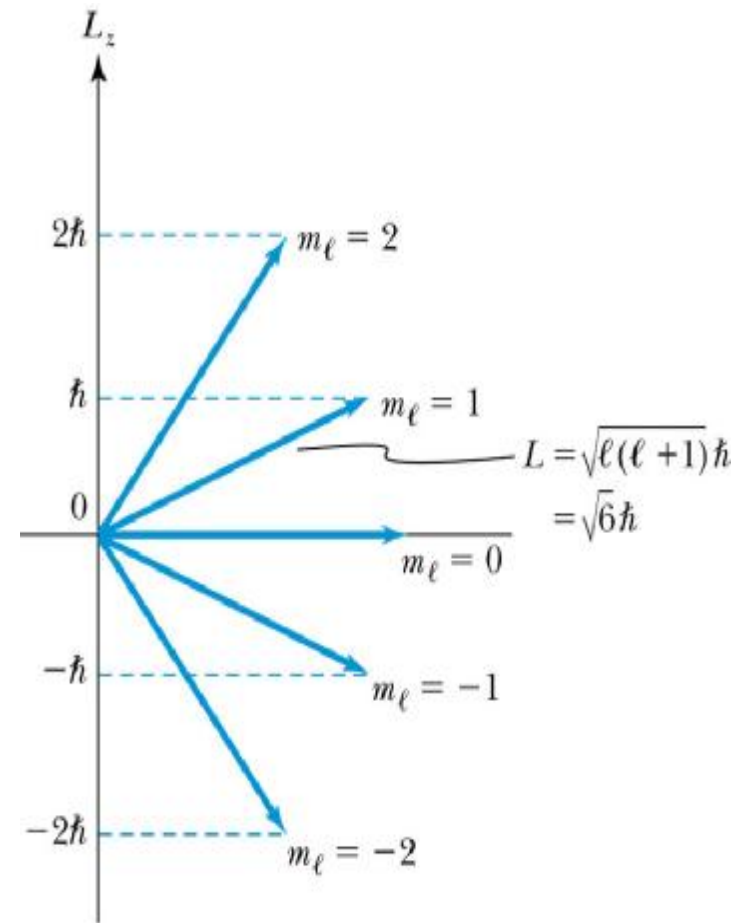
$$\vec{L} = \vec{r} \times \vec{p} \quad \text{with } L = mv_{\text{orbital}}r.$$

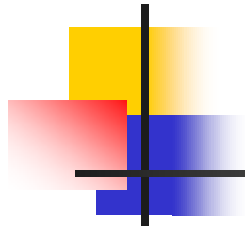
$L$  is related to  $\ell$  by

$$L = \sqrt{\ell(\ell + 1)}\hbar$$

The solution for  $g(f)$  specifies that  $m_\ell$  is an integer and is related to the  $z$  component of  $L$ :

$$L_z = m_\ell \hbar$$

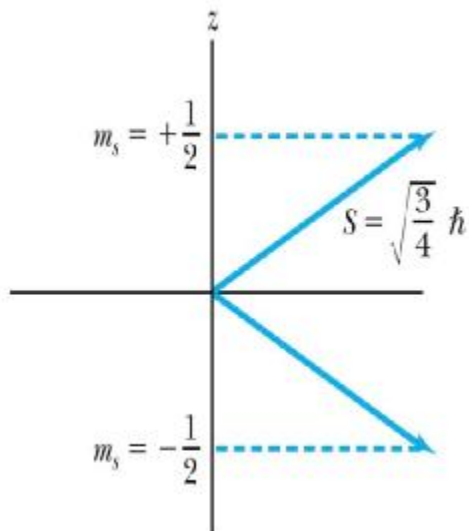
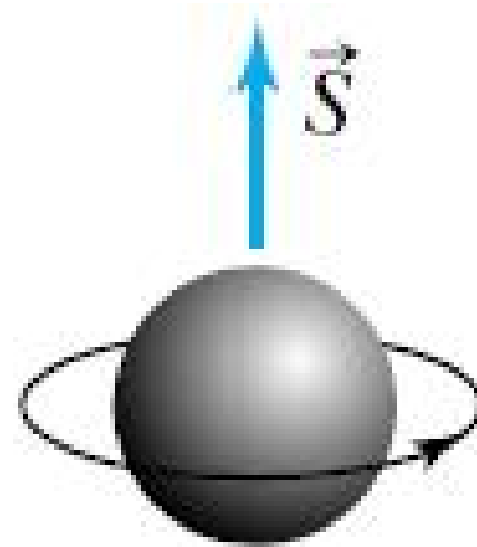




# Spin

The spinning electron reacts similarly to the orbiting electron in a magnetic field.

The **magnetic spin quantum number**  $m_s$  has only two values,  $m_s = \pm 1/2$ .



The electron's spin will be either “up” or “down” and can never be spinning with its magnetic moment  $\mu_s$  exactly along the  $z$  axis.

$$|\vec{S}| = \sqrt{s(s+1)}\hbar = \sqrt{3/4}\hbar$$



# Atomic States and Atomic Terms

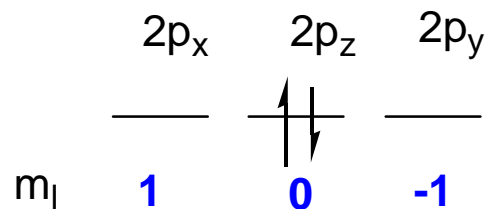
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An atom can exist in several electronic states of different **energy** (*atomic states*). *The atomic states* differ one from another by the way available  $\alpha$ - and/or  $\beta$ -electrons are distributed among atomic orbitals.

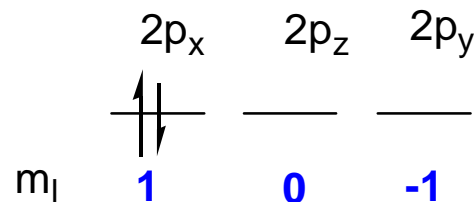
Examples of atomic states:

- a) H atom in  $1s^1$ ,  $2p^1$  or  $3s^1$  configuration
- b) C atom in the  $[\text{He}]2s^2 2p^2$  configuration:

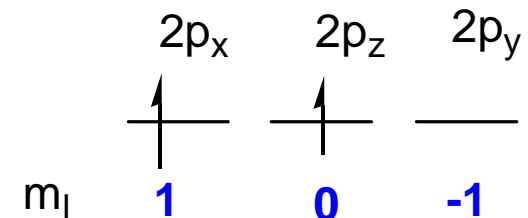
state at  $21648 \text{ cm}^{-1}$



state at  $10194 \text{ cm}^{-1}$



state at  $4460 \text{ cm}^{-1}$





# How to identify an Atomic State

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Each atomic state is characterized by:

- (a) the electronic configuration,
- (b) by spin **S**,
- (c) the **orbital angular momentum L**
- (d) the **total electron angular momentum J**.

The state of the lowest energy is called the ground state



## Russell-Saunders coupling

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The **total spin  $\mathbf{S}$**  and the **total orbital angular momentum  $\mathbf{L}$**  for light elements can be obtained as a vector sum:

$$\mathbf{S} = \sum \mathbf{s}_i \text{ and } \mathbf{L} = \sum \mathbf{l}_i$$

(LS- or Russell-Saunders coupling).

The **total electron angular momentum  $\mathbf{J}$**  is also defined as a vector sum  $\mathbf{J} = \mathbf{L} + \mathbf{S}$ , which holds true in the absence of significant spin-orbit coupling (LS-coupling). Possible values of  $\mathbf{J}$  are  $\mathbf{L} + \mathbf{S}$ ,  $\mathbf{L} + \mathbf{S} - 1$ , ...  $|\mathbf{L} - \mathbf{S}|$ .

# Atomic Terms

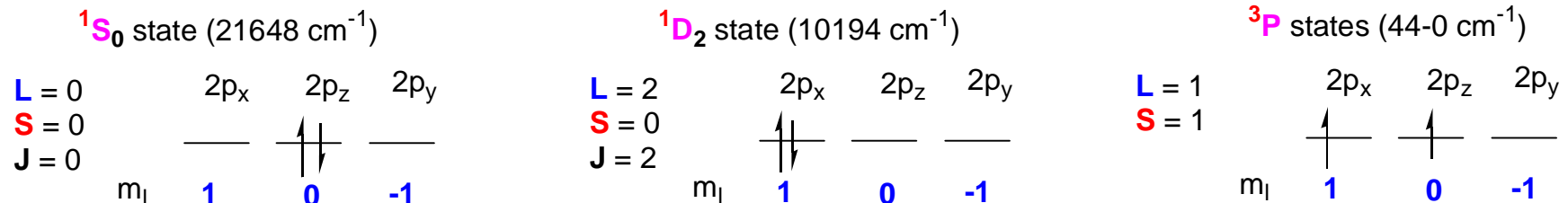
To distinguish between atomic states, besides electronic configuration, each of them is assigned an *atomic term* symbol

$$2S+1L_J$$

Where **2S+1** is the **spin multiplicity** and **J** **total angular momentum**

As for the orbitals, the symbols **S, P, D, F, G, H** etc. are used for the **total orbital angular momentum L = 0, 1, 2, 3, 4, 5**

C atom in the [He]2s2p2 configuration





## Assigning atomic term symbols

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Any atom with *completely-filled shells or subshells* has the total spin  $S=0$ , multiplicity  $2S+1=1$ ,  $L=0$ ,  $J=0$  and can exist in the  $^1S_0$  atomic state only (He  $1s^2$ , Be  $[\text{He}]2s^2$  etc.).

Atoms with not completely filled subshells can exist in several *atomic states*. Hund's rules define the *lowest energy atomic state* for each given *electronic configuration*.



## Assigning atomic term symbols

**H 1s<sup>1</sup> or Li [He]2s<sup>1</sup> or H 3s<sup>1</sup> (excited state)**

total spin **S** (vector) = 1/2;  $M_S$  (allowed projections of **S**) = 1/2, -1/2 ( $2S+1=2$  values);

**spin multiplicity**  $2S+1=2$ ;

**orbital angular momentum L** (vector) = 0;  $M_L$  (allowed projection of **L**) = 0, ( $2L+1=1$  value);

**total electron angular momentum J** = 1/2 (single value)

The state is  $^2S_{1/2}$

**B [He]2s<sup>2</sup>2p<sup>1</sup> or H 2p<sup>1</sup> (excited state)**

total spin **S** = 1/2,  $M_S$  = 1/2, -1/2 (2 values);

**spin multiplicity**  $2S+1=2$ ;

**orbital angular momentum L** = 1;  $M_L$  = 1, 0, -1 (three possible values);

**total electron angular momentum J** = 3/2, 1/2 (two possible values)

The possible states are  $^2P_{3/2}$  and  $^2P_{1/2}$

# Experimental evidence for electron spin

Consider two excited states of the hydrogen atom:

**H 3s<sup>1</sup>** (excited state); **S** = 1/2; **L** = 0; **J** = 1/2;

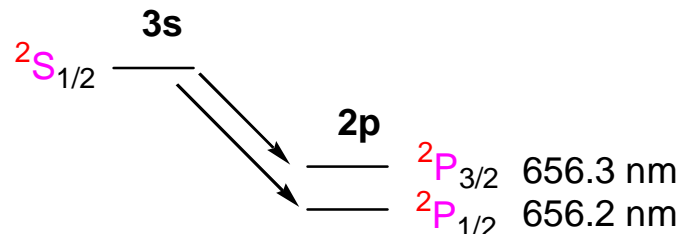
The term is **<sup>2</sup>S<sub>1/2</sub>**

**H 2p<sup>1</sup>** (excited state); **S** = 1/2; **L** = 1; **J** = 3/2, 1/2;

There are two possible states, **<sup>2</sup>P<sub>3/2</sub>** and **<sup>2</sup>P<sub>1/2</sub>**

These two terms arise from the fact that **L** ≠ 0 interacts with **S** ≠ 0. In turn, the latter is due to electron spin. If electron spin did not exist, a single term would correspond the **2p<sup>1</sup>** configuration only.

As an evidence for electron spin, in the atomic hydrogen emission spectrum **two** lines are observed, which both correspond to **H 3s<sup>1</sup> → 2p<sup>1</sup>** electron transition, at 656.3 and 656.2 nm:





## Two electrons in a not completely filled subshell

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Every possible distribution of  $X$  electrons among  $(2l+1)$  subshell orbitals is called a microstate.

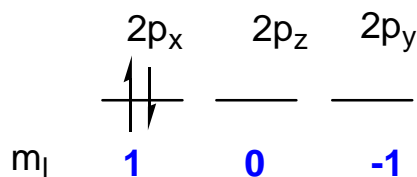
Total number of different microstates is  $N!/(X!(N-X)!)$ , where  $N = 2(2l+1)$  is the maximum occupancy of a subshell. Each term  $2S+1L$  corresponds to  $(2S+1)(2L+1)$  microstates.

## Two electrons in a not completely filled subshell

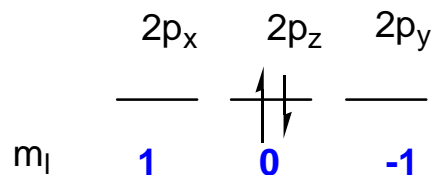
Consider an atom with two electrons in a not completely filled p-subshell, **C** [He]2s<sup>2</sup>2p<sup>2</sup>. s-Subshell contributes nothing to either **S** or **L**. We need to consider p-subshell only.

The number of microstates for doubly occupied 2p-subshell is 15. ( $N = 2(2 \cdot 1 + 1) = 6$ ;  $X = 2$ ;  $N! / (X!(N-X)!) = 6! / (2!4!) = 15$ ). They form 5 terms, <sup>1</sup>D<sub>2</sub>, <sup>1</sup>S<sub>0</sub>, <sup>3</sup>P<sub>2</sub>, <sup>3</sup>P<sub>1</sub> and <sup>3</sup>P<sub>0</sub>. The lowest energy state is <sup>3</sup>P<sub>0</sub>.

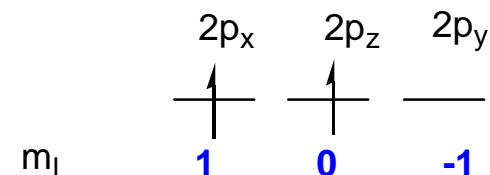
Why <sup>3</sup>P<sub>0</sub>?



**L** = 2  
**S** = 0    <sup>1</sup>D<sub>2</sub>, 5 microstates  
**J** = 2    (M<sub>L</sub>=2, 1, 0, -1, -2)  
           (M<sub>S</sub>= 0)



**L** = 0  
**S** = 0    <sup>1</sup>S<sub>0</sub>, 1 microstate  
**J** = 0    (M<sub>L</sub>=0, M<sub>S</sub>=0)



**L** = 1  
**S** = 1    <sup>3</sup>P<sub>2</sub>, <sup>3</sup>P<sub>1</sub>, <sup>3</sup>P<sub>0</sub>  
**J** = 2, 1, 0    3 states,  
                   9 microstates  
                   (M<sub>L</sub>=1, 0, -1)  
                   (M<sub>S</sub>=1, 0, -1)



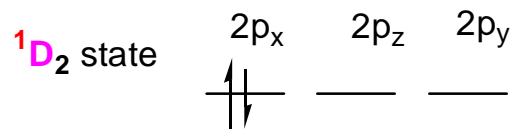
# Hund's Rules

Hund's rules allow to establish which of the several atomic states is the lowest in energy.

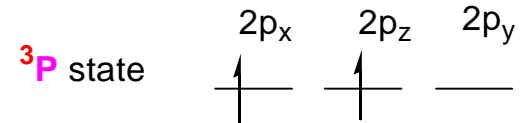
Consider C [He]2s<sup>2</sup>2p<sup>2</sup> as an example

Following states are possible: <sup>1</sup>D<sub>2</sub>, <sup>1</sup>S<sub>0</sub>, <sup>3</sup>P<sub>2</sub>, <sup>3</sup>P<sub>1</sub> and <sup>3</sup>P<sub>0</sub>

**1<sup>st</sup> Hund's rule.** The ground state term is that of the highest multiplicity: <sup>3</sup>P



Two electrons repel each other stronger  
Exchange energy is zero



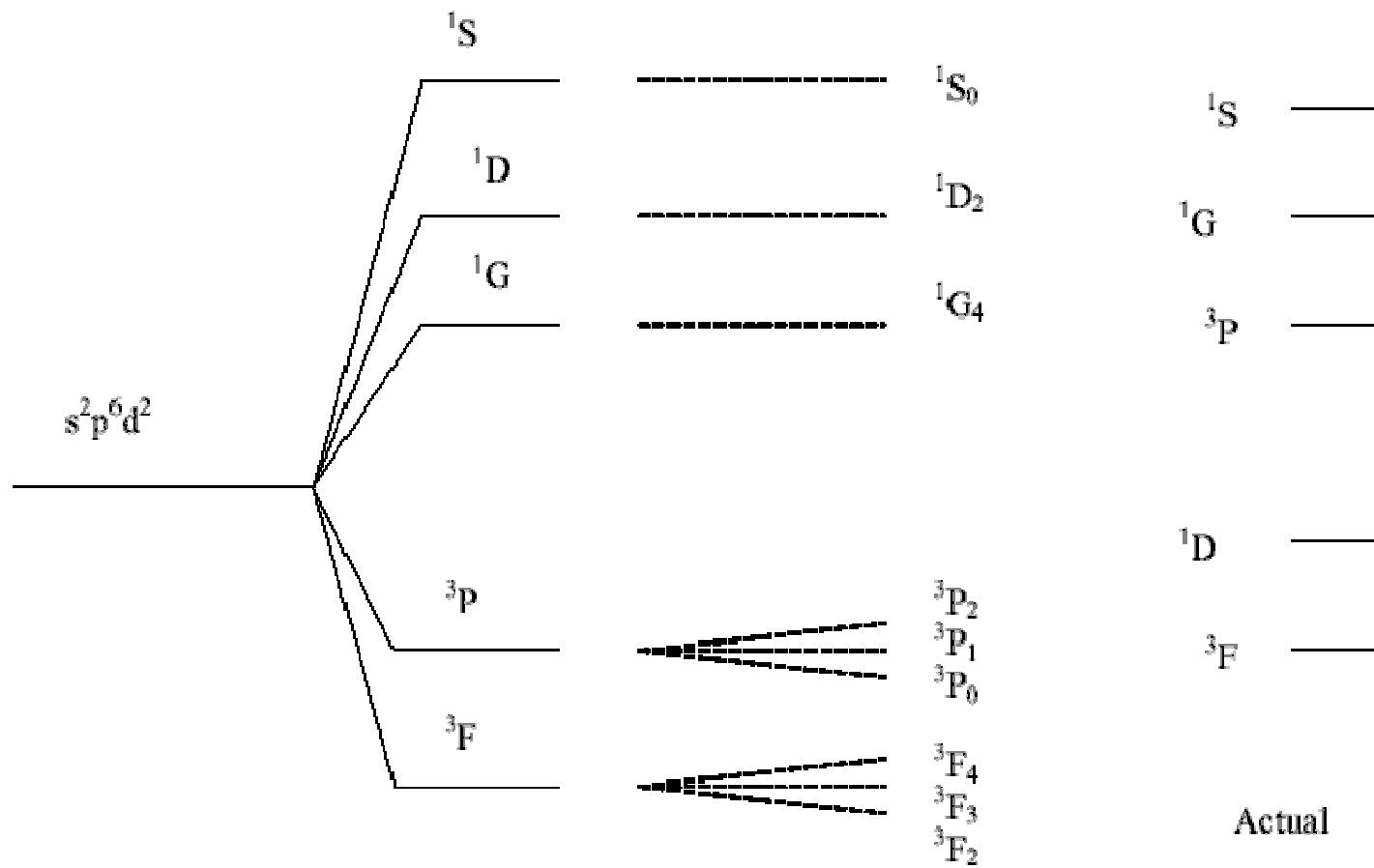
Two electrons repel each other weaker  
Exchange energy stabilizes the system

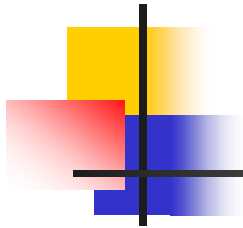
**2<sup>nd</sup> Hund's rule.** Among terms of the same multiplicity the term with the highest **L** value corresponds to the most stable atomic state.

**3<sup>rd</sup> Hund's rule.** The lowest energy state is that of lowest **J** value if the subshell is less than half-filled and of highest **J** value in the opposite case.

<sup>3</sup>P<sub>0</sub> is the most stable atomic state

A More complex example  $\text{Ti}(1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2)$

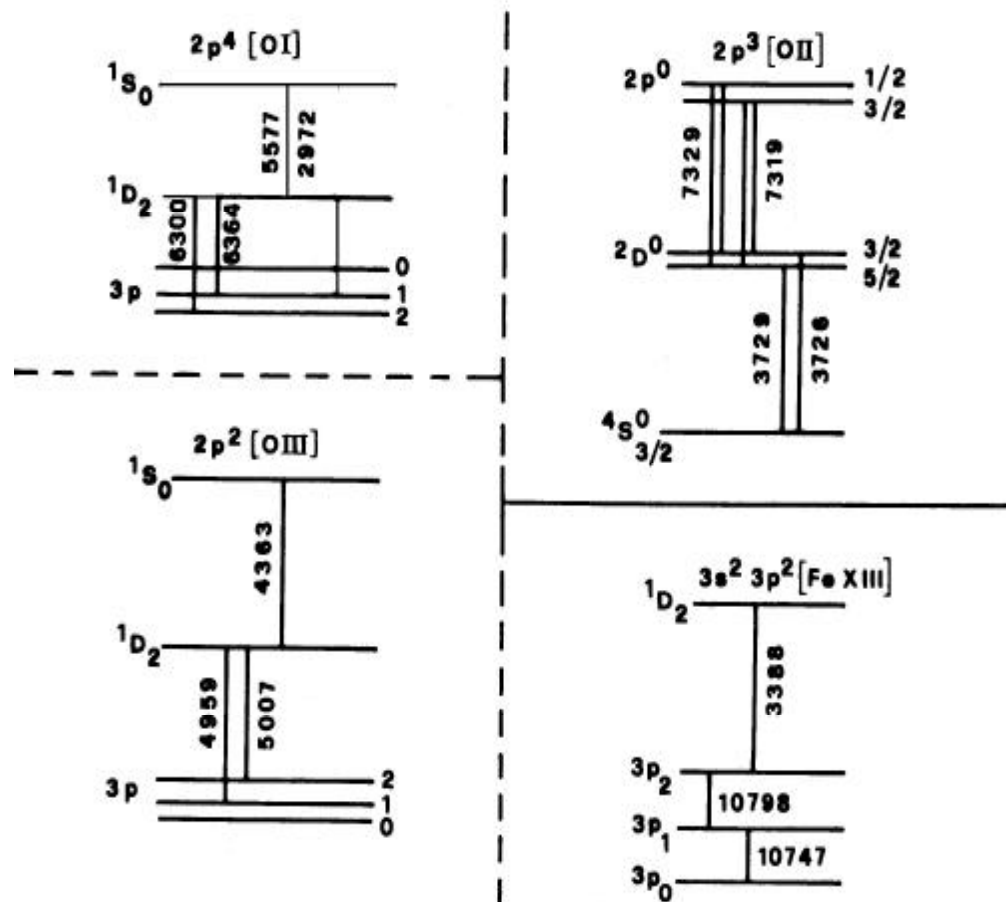




Some results of this procedure for your amusement:

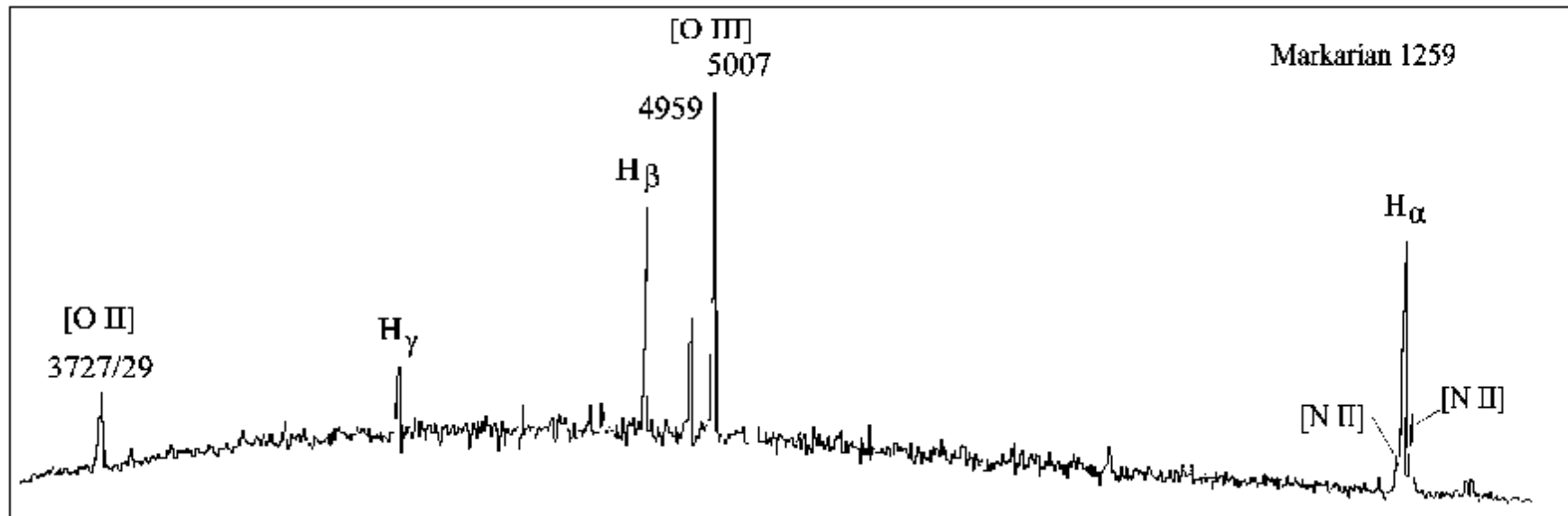
Configuration	Terms
$p^1, p^5$	$^2P$
$p^2, p^4$	$^3P, ^1D, ^1S$
$p^3$	$^4S, ^2P, ^2D$
$d^1, d^9$	$^2D$
$d^2, d^8$	$^3P, ^3F, ^1S, ^1D, ^1G$
$d^3, d^7$	$^2P, ^2D, ^2D, ^2F, ^2G, ^2H, ^4P, ^4F$
$d^4, d^6$	$^1S, ^1S, ^1D, ^1D, ^1F, ^1G, ^1G, ^1I, ^3P, ^3P, ^3D, ^3F, ^3F, ^3G, ^3H, ^5D$
$d^5$	$^2S, ^2P, ^2D, ^2D, ^2D, ^2F, ^2F, ^2G, ^2G, ^2H, ^2I, ^4P, ^4D, ^4F, ^4G, ^6S$

# Oxygen and Nitrogen atomic spectra





# A galaxy spectrum



# Spectra of Halley's Comet

