

# Physics of Atoms and Molecules



October 26, 2020





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# Chapter 1

## Statistical Mechanics

### 1.1 Introduction

Differential expression of the first principle of thermodynamics:

$$dE = TdS - pdV$$

Boltzmann relation between entropy  $S$  and number of microstates at a given energy  $g(E)$  :

$$S = k \log(g(E))$$

The above defines an extensive property of the system, i.e. if we have two sub-systems at  $S_1, S_2$  then  $S = S_1 + S_2 = k \log(g_1 g_2) = k \log(g)$  .

### 1.2 Canonical ensemble

Let us assume that the reservoir temperature  $T$  does not change. The probability that the system has a given energy  $E$  is given by\* [1] :

$$P(E) = \frac{1}{Z} g(E) e^{-\frac{E}{kT}}$$

The above is called *Boltzmann distribution*. The quantity  $Z$  is called *partition function* and it's given by:

$$Z_{Can} = \sum_E g(E) e^{-\beta E}$$

Thus, the mean value of the energy in such an ensemble is given by:

$$\langle E \rangle = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial \log Z}{\partial \beta}$$

In such an ensemble the *Helmoltz free energy* takes the role of a thermodynamic potential:



$$F = E - TS = -kT \log Z_{Can}$$

We do present here some useful relations that involve  $F$  and its differential form:

- $dF = -pdV - SdT$
- $dF = \frac{\partial F}{\partial T}dT + \frac{\partial F}{\partial V}dV$
- $p = -\frac{\partial F}{\partial V}$
- $S = -\frac{\partial F}{\partial T}$

Using and  $p = -\frac{\partial F}{\partial V}$  it can be proved that

$$pV = kNT$$

That is the equation of state for ideal gases. The partition function of a single particle can be written as <sup>\*</sup>[2]:

$$Z_1 = \sum_{\epsilon_n} e^{-\beta\epsilon_n} = \frac{L^3}{2\pi^2} \left( \frac{2m}{\beta\hbar^2} \right)^2 \frac{\sqrt{\pi}}{4} = Vn_Q$$

The value  $n_Q$  is called *quantum density*, i.e. the total number of accessible states per unit of volume. We do define the *DeBroglie thermal wavelength* as the  $\lambda$  of a free particle with kinetic energy given by  $\pi k_B T$ :  $\lambda_{Th}: \pi k_B T = \frac{\hbar^2}{2m} \left( \frac{2\pi}{\lambda_{Th}} \right)^2$ . Hence we can rewrite  $Z_1$  as:  $Z_1 = \frac{V}{\lambda_{Th}^3}$ . Using we can find the expression of the *Sackur-Tetrode entropy*:

$$S = kN \log \left( \frac{n_Q}{n} \right) + \frac{5}{2}kN$$

All these considerations hold for non-degenerate system, that is for systems where  $\frac{n}{n_Q} \ll 1$ : meaning that we do assume that the number of particles is way smaller than the number of allowed energy states.

### 1.2.1 Gibbs free energy

This quantity is defined as the Legendre transformation of  $F$  within respect to  $V$ . Hence:

$$G = F - \frac{\partial F}{\partial V}V = F + pV = E - TS + pV$$

Some important relations involving  $G$  and its differential form:

- $dG = \frac{\partial G}{\partial T}dT + \frac{\partial G}{\partial p}dp$
- $dG = -SdT + Vdp$



- $S = -\frac{\partial G}{\partial T}$
- $V = \frac{\partial G}{\partial p}$

[1] Usually the term  $\frac{1}{kT}$  is called  $\beta$ , and so

$$P(E) = \frac{1}{Z} g(E) e^{-\beta E}$$

[2] In the derivation of this relation,  $L$  is the dimension of the discrete element of space where the w.f. is constrained.

### 1.3 Microcanonical ensemble

In such an ensemble the total energy  $E$ , instead of the temperature  $T$ , is fixed. If we do define\* [1] the *density operator*  $\hat{\rho} = \frac{e^{-\beta \hat{H}}}{Z}$ , in this ensemble it takes the form:  $\hat{\rho} = \sum_{i \in E} \frac{1}{g(E)} |i\rangle \langle i|$ . The mean value of any operator  $\hat{O}$  can be written as:  $\langle \hat{O} \rangle = Tr(\hat{O} \hat{\rho})$ . In this ensemble the entropy  $S$  takes the role of thermodynamic potential.

[1] This definition holds for any ensemble

### 1.4 Gran-canonical ensemble

In this type of ensemble the system can also exchange particles with the reservoir. The equilibrium within respect particles exchange is described by an intensive property of the system, called *chemical potential*  $\mu$ . Condition of equilibrium:  $\frac{dF_1}{dN_1} = \frac{dF_2}{dN_2}$ . More precisely:

$$-\frac{\partial S}{\partial N} T = \mu = \frac{\partial F}{\partial N}$$

The probability that the system has a given energy  $E$  and number of particles  $N$  is given by:

$$P(E, N) = \frac{1}{Z_{GC}} g(E, N) e^{-\beta(E - \mu N)}$$

Where  $Z_{GC}$  is the gran-canonical partition function:

$$Z_{GC} = \sum_{E, N} g(E, N) e^{-\beta(E - \mu N)}$$

In such an ensemble we also have:

$$dE = TdS - pdV + \mu dN$$

We can evaluate the mean value of energy and number of particles:



- $\langle N \rangle = \frac{1}{\beta} \frac{\partial \log Z_{GC}}{\partial \mu}$
- $\langle E - \mu N \rangle = \langle E \rangle - \mu \langle N \rangle = -\frac{\partial \log Z_{GC}}{\partial \beta}$

Since  $F = -kTN \log \left( \frac{V n_Q}{N!} \right)$  we can derive an expression for  $\mu$  :

$$\mu = \frac{\partial F}{\partial N} = kT \log \left( \frac{n}{n_Q} \right)$$

When we have to evaluate the partition function, we have to distinguish two cases: bosons and fermions.

- $Z_{GC}^{(f)} = 1 + e^{-\beta(\epsilon - \mu)}$
- $Z_{GC}^{(b)} = \frac{1}{1 - e^{-\beta(\epsilon - \mu)}}$

From where we can derive the mean number of particles per energy level in the two cases. More precisely what we do derive are two distributions: the *Fermi-Dirac* and the *Bose-Einstein* distributions.

- $f_{FD}(\epsilon) = \frac{1}{1 + e^{\beta(\epsilon - \mu)}}$
- $f_{BE}(\epsilon) = \frac{1}{e^{\beta(\epsilon - \mu)} - 1}$

## 1.5 Isobaric ensemble

In such an ensemble we have the reservoir with fixed temperature and pressure. Under these assumptions, the probability that the system has a certain value of energy  $E$  and volume  $V$  is:

$$P(E, V) = \frac{1}{Z_P} g(E, V) e^{-\beta(E + pV)}$$

Moreover, in such an ensemble we have:

$$G = -kT \log Z_P$$

## 1.6 Quantum gases

First of all we assume that we are dealing with a weakly quantum gas, i.e.  $\frac{n}{n_Q} < 1$ . The system is a grand-canonical ensemble. Hence the partition function is:

$$Z_{GC} = \sum_{N, E} e^{-\beta(E - N\mu)} g(E, N) = \sum_{n_1} \sum_{n_2} \dots \left( e^{-\beta \sum_{i=1}^N (n_i \epsilon_i - \mu n_i)} \right)$$

Which is equivalent to:





$$Z_{GC} = \prod_{i=1}^N \left( \sum_{n_i} e^{-\beta(\epsilon_i - \mu)n_i} \right) = \left\{ \prod_i (1 + e^{-\beta(\epsilon_i - \mu)}) \right. \\ \left. \prod_i \left( \frac{1}{1 - e^{-\beta(\epsilon_i - \mu)}} \right) \right\}$$

Where the first expression holds for fermions, while the second one for bosons. In a grand canonical ensemble, the thermodynamic potential is given by the *Landau thermodynamic potential*:

$$\Omega(V, T, \mu) = F - \frac{\partial F}{\partial N} N = F - \mu N = -kT \log Z_{GC}$$

Since it can be proved\* [1] that  $G = \mu N$ , we also have:  $\Omega = -pV$ . From where one can derive the equation of state for weakly quantum gases:

$$pV = kT \log Z_{GC} = nkT \left( 1 \pm \frac{n}{n_Q 2^{\frac{5}{2}}} \right)$$

Where the plus sign is for fermions, while the minus sign is for bosons.

### 1.6.1 Electrons in a metal

Electrons in a metal can be idealized as fermions (electrons) in a box. Electrons will occupy energy levels according to the Fermi-Dirac distribution. In particular we have to note that:

$$f(\epsilon) \xrightarrow{T \rightarrow 0} \theta(\epsilon - \mu) = \begin{cases} 0 & \epsilon > \mu \\ 1 & \epsilon < \mu \end{cases}$$

We do define *Fermi energy*, the maximum of the energy of the occupied level:  $\epsilon_F = \mu(T = 0)$ . If we define  $D(\epsilon)d\epsilon$  as the number of states, per unit volume, with energy in the interval  $(\epsilon; \epsilon + d\epsilon)$  we have\* [2]:

$$\int_0^{\epsilon_F} D(\epsilon) d\epsilon = n$$

The explicit expression of  $D(\epsilon)$  can be derived, obtaining:

$$D(\epsilon) = \frac{1}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \sqrt{\epsilon}$$

Meaning that the Fermi energy\* [3] equals to:

$$\epsilon_F = \frac{\hbar^2}{2m} k_F^2 = \frac{\hbar^2}{2m} (3\pi^2 n)^{\frac{2}{3}}$$

Hence we have that  $T_f = \frac{\epsilon_f}{k_B}$ . The chemical potential  $\mu$  depends on the temperature  $T$  with the relation:



$$\mu(T) = \epsilon_F \left( 1 - \frac{\pi^2}{12} \left( \frac{T}{T_F} \right)^2 \right)$$

The specific heat, at constant volume  $V$ , is defined as:

$$C_V = \frac{1}{V} \frac{\partial E}{\partial T} = \frac{\pi^2}{2} nk \frac{T}{T_F}$$

We now give three important relations that tell us what happens to the system when it happens a change in some quantity that describes it:

- $\Delta E^2 = kT^2 C_V$  in a canonical ensemble;
- $\Delta V^2 = -\frac{\partial V}{\partial p} kT$  in an isobaric ensemble;
- $\Delta N^2 = \frac{\partial N}{\partial \mu} kT$  in a gran-canonical ensemble.

## 1.6.2 Quantum superfluids

Quantum superfluids can be idealized as bosons in a box. Bosons in a box occupy energy levels according to the Bose-Einstein distribution. Moreover, if we do assume that all the particles occupy the level at  $\epsilon = 0$ , i.e. the lowest energy level, we have:

$$0 < f_{BE}(\epsilon = 0) = \frac{1}{e^{-\beta\mu} - 1}$$

Where we do expect that  $e^{-\beta\mu} > 1$ , that is  $\mu < 0$ . Here we are assuming that a *macroscopic number of particles* occupy a certain energy level, more precisely the lowest possible\* [4]! Actually, this is not a problem since bosons do not have to respect Pauli's exclusion principle. Meaning that the particles density is given by:

$$n = n_0 + \int_0^\infty \frac{D(\epsilon)}{e^{\beta(\epsilon-\mu)} - 1} d\epsilon$$

Where the contribute of  $n_0$  is fundamental for temperatures  $T < T_C$ , the Bose-Einstein condensation temperature. We also have that:

$$n_0(T) = n \left( 1 - \left( \frac{T}{T_C} \right)^{\frac{3}{2}} \right), T < T_C$$

The condensation temperature can be derived\* [5] and its value is:

$$kT_C = n^{\frac{2}{3}} \frac{\hbar^2}{2m} 4\pi \left( \frac{1}{2,612} \right)^{\frac{2}{3}}$$

And the condition  $T < T_C$  is equivalent to:



$$n > n_Q(2,612), \quad n_Q = \left( \frac{mkT}{2\pi\hbar^2} \right)^{\frac{3}{2}}$$

Bose-Einstein condensation is a necessary but not sufficient condition to the superfluidity. For such systems we can define the specific heat, at constant pressure  $P$  :  $C_P = T \frac{\partial S}{\partial T}$  . We have that:

$$C_P = -T \frac{\partial^2 G}{\partial T^2}$$

- [1] From  $G = G(P, T, N)$  and  $G = E - TS + pV$  , using  $dE = TdS - pdV + \mu dN$
- [2] For a gas, given its density  $\rho$  , its mass number  $A$  (expressed in u.a.m) and its atomic number  $Z$  we can write  $n = \frac{N}{V} = \frac{Z\rho}{Am_p}$  .
- [3] We can also note that:

$$\frac{E}{V} = \frac{N}{V} \langle \epsilon \rangle = \int_0^{\epsilon_F} D(\epsilon) \epsilon d\epsilon = \frac{3}{5} n \epsilon_F$$

Meaning that  $\langle \epsilon \rangle = \frac{3}{5} \epsilon_F$

- [4] This condition is called *Bose-Einstein condition*.
- [5] From

$$n = \int_0^{\infty} d\epsilon D(\epsilon) \frac{1}{e^{\frac{\epsilon}{T C^k}} - 1}$$



## Chapter 2

# Systems of identical particles

### 2.1 Many particles systems

For a single particle, we know the meaning of  $\psi(\vec{x})$  and  $|\psi(\vec{x})|^2$ . For many particles systems a natural extension of these concepts holds. We do distinguish two type of particles:

- Entire spin particles, are called *bosons*;
- Semi-entire spin particles, are called *fermions*.

The global w.f. of the system has to be:

- Completely symmetrical within respect the switch of coordinates for bosons;
- Completely anti-symmetrical within respect the switch of coordinates for fermions.

The global w.f. of the system can also be seen as the determinant of that matrix that has the energy levels  $u_i$  as rows and the particle states  $|j\rangle$  as columns. This determinant is called *Slater determinant* Since bosons have symmetrical w.f., all the negative signs have to be changed into positive signs when calculating this determinant in order to find a boson-system w.f.

#### Example

Let us assume that we are dealing with three fermions. Then we have:

$$M = \frac{1}{\sqrt{3!}} \begin{bmatrix} u_a(1) & u_a(2) & u_a(3) \\ u_b(1) & u_b(2) & u_b(3) \\ u_c(1) & u_c(2) & u_c(3) \end{bmatrix}$$

And the w.f. of the system is  $\psi = \det M$ .



## 2.2 Identical particles

Two particles are said to be identical if all their intrinsic properties, such as mass, spin, charge, are exactly the same. We can rephrase the definition saying that two particles are identical if no experiment can distinguish between them. An important consequence can be deduced from this definition: a system composed of identical particles must be invariant under the exchange of the particles roles.

Identical particles are of great importance in physics: all the electrons, protons, neutrons, etc in the universe are identical. Since we are dealing with the problem of an exhaustive quantum description of atoms and molecules, where lots of identical particles are concerned, we have to develop a proper quantum mechanical theory about identical particles.

In classical mechanics identical particles are treated just as they were different. In principle, indeed, it is always possible to distinguish between them following their orbits, and for this reason we can label the particles with (1), (2) . . . , labels which act as intrinsic properties that distinguish the particles and make them “no longer identical”. The problem of indistinguishability is purely quantum mechanical, since we have learned that particles no longer have definite trajectories. The labels (1), (2) . . . can’t be seen as intrinsic properties. Consider for example a system of two identical particles: when we detect one particle in a region of space in which both of them have a non-zero position probability, we have no way of knowing if the particle detected is the number (1) or the number (2) .

Indistinguishability creates fundamental difficulties, since it introduces an **exchange degeneracy**: when identical particles are concerned a complete measurement on each of the particle does not permit the determination of a unique ket of the state space of the system.

**Example** (Example 1)

Consider a system of two identical particles with spin degrees of freedom only. Each particle spin observable  $S_{i,z}$   $i = 1, 2$  constitutes a C.S.C.O in the state space of the single particle, and its eigenkets form a base of that space. We can construct an orthonormal base of the state space of the system taking the tensor product between the bases of the two state spaces.

$$\left\{ \begin{array}{l} \text{particle (1) state space spanned by } |+\rangle_1, |-\rangle_1 \\ \text{particle (2) state space spanned by } |+\rangle_2, |-\rangle_2 \\ \text{system state space spanned by } |+\rangle_1 |+\rangle_2, |+\rangle_1 |-\rangle_2, |-\rangle_1 |+\rangle_2, |-\rangle_1 |-\rangle_2 \end{array} \right.$$

Suppose we make a measurement of  $S_{1,z}$  and  $S_{2,z}$  and find  $\frac{+\hbar}{2}, \frac{-\hbar}{2}$  . Since the particles are identical we can’t know which particle has Oz spin component  $\frac{+\hbar}{2}$  and which has  $\frac{-\hbar}{2}$  . The state space of the system is then two dimensional, spanned by

$$|+\rangle_1 |-\rangle_2 = |+, -\rangle \quad , \quad |-\rangle_1 |+\rangle_2 = |-, +\rangle$$

Each ket of the form  $\alpha |+, -\rangle + \beta |-, +\rangle$ ,  $|\alpha|^2 + |\beta|^2 = 1$  represents the same physical state and in general physical predictions depends on the coefficients  $\alpha$



and  $\beta$ . This clearly shows the presence of exchange degeneracy (in this example in the initial state), which must be removed in order to make physical predictions.

**Example** (Example 2)

Consider a system of three identical particles (1), (2), (3) and an observable  $B(1)$  which form a C.S.C.O in the state space of particle (1). Since the particles are identical the observables  $B(2)$ ,  $B(3)$  exist and form a C.S.C.O in the state space of particle (2), (3). We can construct an orthonormal base of the state space of the system by taking the tensor product between each base of single-particle state spaces. Since the particles are identical we are not able to distinguish between  $B(1)$ ,  $B(2)$ ,  $B(3)$  and we can only measure the observable  $B$  for each of the particles. Suppose we find the values  $a, b, c$ . The final state of the system can be represented by any ket spanned by the six kets

$$\begin{array}{lll} |a(1), b(2), c(3)\rangle & |b(1), a(2), c(3)\rangle & |b(1), c(2), a(3)\rangle \\ |c(1), a(2), b(3)\rangle & |c(1), b(2), a(3)\rangle & |a(1), c(2), b(3)\rangle \end{array}$$

Examples clearly show the deep connection between exchange degeneracy and permutations. In the next chapter we're going to develop this connection by the introduction of **permutation operators**

## 2.3 Permutation operators

For a two-identical particles system we can define the permutation operator  $P_{21}$  as the linear operator whose action on the basis vector is given by:

$$\begin{aligned} P_{21} |u_i\rangle_1 |u_j\rangle_2 &= |u_i\rangle_2 |u_j\rangle_1 \\ P_{21} |u_i(1), u_j(2)\rangle &= |u_i(2), u_j(1)\rangle \end{aligned}$$

This operator satisfies the following properties:

- it is hermitian:  $P_{21} = P_{21}^\dagger$
- $P_{21}^2 = \mathbb{1}$
- from the previous properties it follows that  $P_{21}$  is *unitary*:  $P_{21}^\dagger P_{21} = P_{21} P_{21}^\dagger = \mathbb{1} \rightarrow P_{21}^\dagger = P_{21}^{-1}$

For a number  $N > 2$  of identical particles the situation is more complex. There are indeed  $N!$  permutation operators, which we'll call  $P_\alpha$ , with  $\alpha$  referring to an arbitrary permutation. It is simple to prove that the permutation operators do not commute with each other. Furthermore, the properties which we have seen to be valid for  $P_{21}$  are not necessarily respected by  $P_\alpha$ . However we can define transposition operators as linear operators which exchange the roles of two particles without changing the others. Of course the peculiarity of  $N = 2$  is that the only permutation operator is also a transposition operator. This is why it has the properties previously written. Since any permutation operators



can be broken down into the product of transposition operators, which are unitary,  $P_\alpha$  are also unitary. However they are not necessary hermitian and the decomposition is not unique, even if it can be shown that the parity of transposition operators that constitutes a permutation operator  $P_\alpha$  is always the same. This allows us to define a *parity* for permutation operators, according to the evenness or oddness of the number of transposition operators in their decomposition. Since permutation operators do not commute with each other it is not possible to form a basis of common eigenvectors. Nevertheless there exist special kets which are simultaneously eigenvectors of all permutation operators. These kets are the ones completely symmetric and completely antisymmetric with respect to all permutation operators:

$$\begin{aligned} \text{completely symmetric ket } P_\alpha |\phi_S\rangle &= |\phi_S\rangle \quad \forall \text{ permutation } \alpha \\ \text{completely antisymmetric ket } P_\alpha |\phi_A\rangle &= \epsilon_\alpha |\phi_A\rangle \quad \epsilon_\alpha = \begin{cases} +1 & \forall \text{ even permutation} \\ -1 & \forall \text{ odd permutation} \end{cases} \end{aligned}$$

### 2.3.1 The symmetrization postulate

The set of  $|\phi_S\rangle$  constitutes a vector subspace ( $\xi_S$ ) of the state space, as well as the set of  $|\phi_A\rangle$  ( $\xi_A$ ). However the state space  $\xi$  is not the direct sum of  $\xi_S$  and  $\xi_A$ . There exist indeed kets which aren't neither completely symmetric nor antisymmetric. However the **symmetrization postulate** saves us, since it states that in system composed of identical particles physical kets are, depending on the nature of the identical particles, either completely symmetric or completely antisymmetric with respect to permutation of these particles. Those particles whose physical kets are completely symmetric are called **bosons** and those for which physical kets are completely antisymmetric are called **fermions**. This postulate limits the state space: it is no longer the tensor product of the state spaces of each identical particle, but just a subspace, ( $\xi_S$ ) for bosons and ( $\xi_A$ ) for fermions. A never contradicted empirical rule enable us to identify **fermions** with particles of **half-integral spin** (electrons, positrons, neutrons, protons, muons, etc) and **bosons** with particles of **integral spin** (photons, mesons, etc). This is called **spin-statistics theorem** and it is proved in quantum field theory.

### 2.3.2 Permutation operators and exchange degeneracy

Let  $|u\rangle$  be a ket which can mathematically describe the state of a physical system of  $N$  identical particles. Then for all  $\alpha$   $P_\alpha |u\rangle$  is also a proper ket for the description of the system state, as well as any ket belonging to the subspace  $\xi_u$  spanned by  $|u\rangle$  and every  $P_\alpha |u\rangle$ . Depending on the ket  $|u\rangle$  the dimension of  $\xi_u$  can vary between 1 and  $N!$ . If this dimension is  $> 1$  there is an exchange degeneracy since several mathematical kets correspond to the same physical state. The new postulate restricts the class of mathematical kets which are proper description of a physical state: they have to belong to  $\xi_S$  or  $\xi_A$  according to the nature of identical particles. In order to prove the uniqueness of the mathematical ket able to describe a physical system (we can call it *physical ket*) we define the projectors  $[1]$  on  $\xi_S$  and  $\xi_A$  as:



$$S = \frac{1}{N!} \sum_{\alpha} P_{\alpha}$$

$$A = \frac{1}{N!} \sum_{\alpha} \epsilon_{\alpha} P_{\alpha}$$

\*[2]

They are also called *symmetrizer* and *antisymmetrizer* since they act on an arbitrary ket belonging to  $\xi$  and give respectively a completely symmetric and completely antisymmetric ket, belonging to  $\xi_S$  and  $\xi_A$ . These property can be written as:

$$P_{\alpha} S |\phi\rangle = S |\phi\rangle \quad S |\phi\rangle \text{ is completely symmetric}$$

$$P_{\alpha} A |\phi\rangle = \epsilon_{\alpha} A |\phi\rangle \quad A |\phi\rangle \text{ is completely antisymmetric}$$

They commute with each  $P_{\alpha}$  and the following properties hold:

$$P_{\alpha} S = S P_{\alpha} = S$$

$$P_{\alpha} A = A P_{\alpha} = \epsilon_{\alpha} A$$

Then

$$S |u\rangle = S P_{\alpha} |u\rangle$$

$$A |u\rangle = \epsilon_{\alpha} A P_{\alpha} |u\rangle$$

We have proved that the action of  $S$  and  $A$  on kets spanning  $\xi_u$  give collinear kets, which correspond to the same state. Finally we can state that there is a unique (within a constant factor) ket belonging to  $\xi_u$ , called physical ket, which is able to describe the physical state of the system:  $S |u\rangle$  for bosons and  $A |u\rangle$  for fermions.

- [1] the proof that they are projectors is left to the reader since it is irrelevant for the purpose of this discussion. Suggestion: in order to prove that  $S^2 = S$  and  $A^2 = A$  use the property:

$$P_{\alpha} S = S P_{\alpha} = S$$

$$P_{\alpha} A = A P_{\alpha} = \epsilon_{\alpha} A$$

- [2] with  $\epsilon_{\alpha}$  defined as previously done

## 2.4 Physical kets

So far we have seen that there exist a unique ket which properly describe the state of a system of identical particles. This ket is a completely symmetric ket for bosons and a completely antisymmetric ket for fermions. The problem is now to construct these kets. The procedure is theoretically simple:

- number the particles and construct the ket  $|u\rangle$  corresponding to the physical state and to the number given to the particles





- Apply  $S$  or  $A$  depending on the nature of the particles
- Normalize

This process allows us to construct easily the physical ket if the number of the particles is low. On the contrary for a system composed of a large number of particles we need a mechanical method in order to simplify calculations.

**Example** (Two identical particles)

Suppose we are dealing with a system with two identical particles, labeled with (1), (2). Assume that each particle can be in the orthogonal states  $|\varphi\rangle$  or  $|\chi\rangle$ . The state of the system can be:

$$\begin{aligned} |\varphi\rangle_1 |\chi\rangle_2 &= |\varphi(1), \chi(2)\rangle \\ |\varphi\rangle_2 |\chi\rangle_1 &= |\varphi(2), \chi(1)\rangle \end{aligned}$$

We chose  $|u\rangle = |\varphi(1), \chi(2)\rangle$ , then:

- if the particles are bosons we apply  $S$  on  $|u\rangle$  and normalize. We get the symmetric ket:

$$S|u\rangle = \frac{1}{\sqrt{2}} (|\varphi(1), \chi(2)\rangle + |\varphi(2), \chi(1)\rangle)$$

- if the particles are fermions we apply  $A$  on  $|u\rangle$  and normalize. We get the antisymmetric ket:

$$S|u\rangle = \frac{1}{\sqrt{2}} (|\varphi(1), \chi(2)\rangle - |\varphi(2), \chi(1)\rangle)$$

We can easily see that if  $|\chi\rangle = |\varphi\rangle$  there isn't any antisymmetric ket able to describe two fermions in the same state: this is a first insight in the **Pauli exclusion principle**, according to which two identical fermions cannot be in the same individual state.

### 2.4.1 Slater determinant

For a system of  $N$  identical particles there is a simple way to construct the symmetric and antisymmetric ket, based on the properties of a matrix determinant (remember that the definition of determinant is strictly linked to permutations). We summarize the procedure:

- number the particles  $1, 2, \dots, N$
- find the individual states accessible to the particles:  $|a\rangle, |b\rangle, |c\rangle, \dots, |z\rangle$ . There are  $N$  states, not necessary different.



- construct a squared matrix with dimension  $N \times N$  as follows:

$$\begin{bmatrix} |a(1)\rangle & \cdots & |z(1)\rangle \\ \vdots & \ddots & \vdots \\ |a(N)\rangle & \cdots & |z(N)\rangle \end{bmatrix}$$

- write down the expression for determinant. If you're dealing with bosons change each  $-$  with  $+$ , otherwise leave the determinant unchanged.
- normalize the expression found with the factor  $\frac{1}{\sqrt{N!}}$
- You have found the completely symmetric or completely antisymmetric ket describing the system!

### 2.4.2 When are antisymmetrization and symmetrization necessary?

If the application of the symmetrization postulate were always indispensable we should consider every electron in the universe even in the study of a single atom, since all electrons are identical. Clearly this is not the case. In fact under special conditions we can neglect the indistinguishability of the particles. Let us discuss when this approximation is appropriate.

Consider two identical particles (1), (2), one being in the individual state  $|\psi\rangle$  and the other in the individual state  $|\varphi\rangle$ . Assume that  $\langle x | \psi \rangle = \psi(x)$  vanishes outside a region  $\mathbb{D}$  and  $\langle x | \varphi \rangle = \varphi(x)$  vanishes outside a region  $\mathbb{B}$ , with  $\mathbb{D} \cap \mathbb{B} = \emptyset$ . The symmetric and antisymmetric waves function for the system are:

$$\begin{aligned} & \frac{1}{\sqrt{2}} (\psi(x_1)\varphi(x_2) + \psi(x_2)\varphi(x_1)) \\ & \frac{1}{\sqrt{2}} (\psi(x_1)\varphi(x_2) - \psi(x_2)\varphi(x_1)) \end{aligned}$$

Since the individual wave functions do not overlap, if  $x_1 \in \mathbb{D}$  and  $x_2 \in \mathbb{B}$  we have:

$$\begin{aligned} \psi(x_1) &\neq 0 && \text{since } x_1 \in \mathbb{D} \\ \varphi(x_2) &\neq 0 && \text{since } x_2 \in \mathbb{B} \\ \psi(x_2) &= 0 && \text{since } x_2 \notin \mathbb{D} \\ \varphi(x_1) &= 0 && \text{since } x_1 \notin \mathbb{B} \end{aligned}$$

The system wave functions then become:

$$\begin{aligned} & \frac{1}{\sqrt{2}} (\psi(x_1)\varphi(x_2) + 0) \\ & \frac{1}{\sqrt{2}} (\psi(x_1)\varphi(x_2) - 0) \end{aligned}$$

We can conclude that *if wave functions do not overlap symmetrization or antisymmetrization aren't necessary*



## 2.5 Pauli's exclusion principle

### 2.5.1 Pauli's exclusion principle

We've already mentioned the Pauli's exclusion principle: *each individual state can be occupied by a single fermion*. We have seen that it holds for two fermions. The introduction of Slater determinant allows us to see that this principle is valid for an arbitrary number of identical fermions: since the antisymmetric ket is a Slater determinant, if two states  $|a\rangle, |b\rangle$  are the same then the matrix has two identical columns and the determinant is 0. This is not true for bosons since every  $-$  has been changed into a  $+$ .

### 2.5.2 Occupation numbers

If we have a system of identical particles, with each particle allowed to stay in one of the  $|u_i\rangle, |u_j\rangle, \dots, |u_p\rangle$  individual states, we can define the *occupation number*  $n_k$  as the number of particles being in the state  $|u_k\rangle$ . Occupation numbers are subjected to the restriction that  $\sum_k n_k = N$ . Clearly two mathematical state

$$\begin{aligned} &|u_1(1), u_1(2), \dots, u_1(n_1), u_2(n_1 + 1), \dots, u_2(n_1 + n_2) \dots \rangle \\ &|u_1(2), u_1(1), \dots, u_1(n_1), u_2(n_1 + 1), \dots, u_2(n_1 + n_2) \dots \rangle \end{aligned}$$

with the same occupation numbers are connected by the action of a permutation operator and represent the same physical state, that is under the action of  $S$  or  $A$  they give collinear kets. For this reason we can use occupation numbers to identify physical kets (and to span the physical state  $\xi_S$  or  $\xi_A$ ):

$$|n_1, n_2, \dots, n_k, \dots \rangle = cS |u_1(1), \dots, u_1(n_1), u_2(n_1 + 1), \dots, u_2(n_1 + n_2), \dots \rangle$$

This ket describes a state with  $n_1$  particles in the state  $u_1$ ,  $n_2$  particles in the state  $u_2$  and so on. From Pauli's exclusion principle it follows that:

- If the particle under study are bosons occupation numbers are arbitrary
- If the particle under study are fermions occupation numbers can only be 1 or 0, since a state can be empty or occupied by a single fermion

### 2.5.3 Statistical implications of Pauli's exclusion principle

Since statistical description of macroscopic properties is based on the number of microscopic states that corresponds to the same macroscopic state, the difference between bosons and fermions, the second being subjected to Pauli's exclusion principle, leads to different statistics:

- bosons are described by Bose-Einstein statistics, which takes into account the possibility of having an arbitrary number of particles in each individual state
- fermions are described by Fermi-Dirac statistics, which takes into account the restriction in the occupation numbers



## 2.6 Hamiltonian for identical particles

When identical particles are concerned it is intuitive that no physical property can be modified when the roles of the particles are permuted: any physical observable must be invariant under all permutations, that is: if  $G$  is a *physical* observable then  $[G, P_\alpha] = 0 \quad \forall \alpha$ . This also means that the spaces  $\xi_S$  and  $\xi_A$  are invariant under the action of a physical observable  $G$ : if  $|\psi\rangle \in \xi_S (\xi_A) \Rightarrow G|\psi\rangle \in \xi_S (\xi_A)$ . The hamiltonian of a system of identical particles is a physical observable (it corresponds to the energy) and must commute with all  $P_\alpha$ . This restricts the possible forms of the interacting potential.

Let us investigate deeply this fact. Consider a system of 2 non-interacting identical particles. The hamiltonian of this system is:

$$H = h(1) + h(2)$$

with  $h(1) = h(2)$  because of the indistinguishability of the particles. Now suppose that there is an interaction between the particles. In order to preserve the invariance of  $H$  under permutations of the particles ( $[H, P_{21}] = 0$ ), that is in order to keep the hamiltonian a physical observable, the interaction potential has to be of the form:

$$V(\mathbf{r}_1, \mathbf{r}_2) = V(|\mathbf{r}_1 - \mathbf{r}_2|)$$

### 2.6.1 Energy

For the sake of simplicity we are going to consider a system of  $N$  non-interacting identical particles. Then

$$H = h(1) + h(2) + \dots + h(N) \quad h(i) = h(j) \forall i, j = 1, \dots, N$$

$$h(1)|u_n\rangle = \epsilon_n |u_n\rangle \quad |u_n\rangle n^{th} \text{ individual state}$$

Suppose we are dealing with  $n_1$  particles in the state  $|u_1\rangle$ ,  $n_2$  particles in the state  $|u_2\rangle$  and so on. The total energy of each state is:

$$E_1 = n_1 \epsilon_1 \quad E_2 = n_2 \epsilon_2 \quad E_n = n_n \epsilon_n$$

and the total energy of the system is:

$$E = E_1 + E_2 + \dots + E_n$$

For bosons there are no restrictions on the numbers  $n_k$ . It follows that the ground state is the one with all the  $N$  bosons on the lowest energy level (we suppose it's  $\epsilon_1$ ), with energy

$$E_{\text{ground state}} = N\epsilon_1$$



The situation for fermions is different, since we have learned that  $n_k$  can only be 0 or 1. Thus if we have  $N$  fermions the ground state is the one with one fermion per quantum state.  $N$  quantum states will be “full” ( $n_k = 1$  for  $k \leq N$ ), the others will be empty ( $n_k = 0$  for  $k > N$ ). The situation is the following:

$$E_{\text{ground state}} = \epsilon_1 + \epsilon_2 + \cdots + \epsilon_N$$

The highest individual energy  $\epsilon_N$ , corresponding to the last full quantum state in the ground state is called **Fermi energy**

**Example** (Two identical non-interacting particles in an infinite potential well)

First consider the particles to be spinless. Since  $s = 0$  we’re dealing with bosons. It’s known from quantum mechanics that the wave function of a particle in such a system is given by

$$u_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

where  $L$  defines the width of the well.

Energy levels are given by

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2}$$

These expressions define the individual states and the individual energies. Suppose we have a particle on the state  $u_a$  and a particle on the state  $u_b$ . Taking into account the nature of the particles we can immediately write down the wave function of the system:

$$\psi_S(x_1, x_2) = \frac{1}{\sqrt{2}} (u_a(x_1)u_b(x_2) + u_a(x_2)u_b(x_1))$$

Now suppose that the particles have spin  $\frac{1}{2}$ .

- Individual states must take into account the spin degrees of freedom
- we’re now dealing with fermions

We know that a particle is on the level  $u_a$  with its spin up ( $m_s = \frac{\hbar}{2}$ ) and the other on the level  $u_b$  with its spin down ( $m_s = -\frac{\hbar}{2}$ ). Individual states are then given by:

$$u_a(i)\chi^+(i) \quad u_b(i)\chi^-(i) \quad i = 1, 2$$

Remembering that a permutation operator acts not only on the orbital variables but also on spin ones, antisymmetrization gives us the following wave function:

$$\psi_A(x_1, x_2) = \frac{1}{\sqrt{2}} (u_a(x_1)\chi^+(1)u_b(x_2)\chi^-(2) - u_a(x_2)\chi^+(2)u_b(x_1)\chi^-(1))$$



## 2.7 Physical predictions involving identical particles

We'll treat the problem only for a two-particle system. Consider two identical particles which can be in the individual states  $|u_a\rangle, |u_b\rangle$ , which include the spin-dependence and are orthogonal. The physical state of the system is:

$$\begin{aligned} |u_S\rangle &= \frac{1}{\sqrt{2}} (|u_a(1), u_b(2)\rangle + |u_a(2), u_b(1)\rangle) \quad \text{for bosons} \\ |u\rangle_A &= \frac{1}{\sqrt{2}} (|u_a(1), u_b(2)\rangle - |u_a(2), u_b(1)\rangle) \quad \text{for fermions} \end{aligned}$$

Suppose we want to measure on each particle the physical quantity  $G$

$$G |g_i\rangle = g_i |g_i\rangle \quad [G, P_{21}] = 0$$

What is the probability of finding  $g_n$  for one particle and  $g_{n'}$  for the other? The final state is:

$$\begin{aligned} |g_n, g_{n'}\rangle_S &= \frac{1}{\sqrt{2}} (|g_n(1), g_{n'}(2)\rangle + |g_n(2), g_{n'}(1)\rangle) \quad \text{for bosons} \\ |g_n, g_{n'}\rangle_A &= \frac{1}{\sqrt{2}} (|g_n(1), g_{n'}(2)\rangle - |g_n(2), g_{n'}(1)\rangle) \quad \text{for fermions} \end{aligned}$$

The desired probability is given by  ${}_S \langle g_n, g_{n'} | u \rangle_S$  for bosons and  ${}_A \langle g_n, g_{n'} | u \rangle_A$  for fermions, that is:

$$\begin{aligned} &\underbrace{\langle g_n | u_a \rangle \langle g_{n'} | u_b \rangle}_{\mathbf{J}} + \underbrace{\langle g_{n'} | u_a \rangle \langle g_n | u_b \rangle}_{\mathbf{K}} \quad \text{for bosons} \\ &\underbrace{\langle g_n | u_a \rangle \langle g_{n'} | u_b \rangle}_{\mathbf{J}} - \underbrace{\langle g_{n'} | u_a \rangle \langle g_n | u_b \rangle}_{\mathbf{K}} \quad \text{for fermions} \end{aligned}$$

The term **J** is called **direct term**, while the term **K** is called **exchange term**:

$$P = J \pm K$$

This shows the appearance of a sort of interference phenomenon when we're dealing with identical particles.



## Chapter 3

# Multi-electron atoms

### 3.1 Multi-electron atoms and term symbols

Multi-electron atoms are studied thanks to several approximations and assumptions. In particular, remember that:

- We assume to work in the particular reference frame of one electron;
- This electron feels the coulomb potential of the others, thus we introduce a charge distribution per unit volume:

$$\rho(\vec{x}) = \sum_i |\psi_i(\vec{x})|^2$$

- The potential introduced by the presence of this charge is called *Hartree potential*, and it's defined as:

$$V_H(\vec{x}) = \frac{e^2}{4\pi\epsilon_0} \int d^3x' \frac{\rho(\vec{x}')}{|\vec{x} - \vec{x}'|}$$

- A more precise result can be obtained taking into account another potential (actually it's an operator), called *Fock potential*:

$$\hat{V}_F \psi_i(\vec{x}) = \sum_j (-) \frac{e^2}{4\pi\epsilon_0} \int d^3x' \psi_j^*(\vec{x}') \frac{\psi_j(\vec{x}') \psi_i(\vec{x}')}{|\vec{x} - \vec{x}'|}$$

Light atoms ( $Z < 30/40$ ) are weakly affected from Spin-Orbit correction, so  $L_{tot}$  and  $S_{tot}$  are good quantum numbers that can be used to describe the state of these atoms. All these informations are given in the *term symbol*:

$$^{2S+1}L$$



Ltot	L
0	S
1	P
2	D
3	F

Where  $S$  stands for the total spin, while the letter  $L$  is fixed by the value of the total angular momentum according to these rules:

Where the values of total spin and angular momentum have to be chosen, starting from the electronic configuration, according to selection rules  $-L \leq M_L \leq L$  and  $M_S \leq S \leq M_S$ , Pauli's exclusion principle and *Hund's rules*:

1. Electrons take place in orbitals in such a way to minimize their total energy. Maximum multiplicity  $2S+1$  (i.e. maximum spin) corresponds to minimum energy.
1. Being the multiplicity maximum, the term with maximum angular momentum has the minimum energy.
1. For a given term, the level with lower energy corresponds to: the minimum value of  $J = L + S$  for atoms with outermost subshell half-filled or less, the maximum value of  $J$  for atoms with outermost shell more than half filled.

As a consequence of the third Hund's rule, the term symbol has to be written as:

$$^{2S+1}L_J$$

Note that term symbols have a particular recurrence: all the term symbols of the  $p^{n^{th}}$  level are the same of the symbols of the  $p^{(6-n)^{th}}$  level. When we construct the term symbol in this way we are working with the *LS coupling* (or scheme). In heavier atoms, the spin orbit correction has to be considered since it has an important effect on energy levels. Hence, each electron gives a contribute of  $j_i$  having its own angular momentum  $l_i$  and its own spin  $s_i$ . Now, all the  $j_i$  will couple up to give a generalized angular momentum  $J = \sum_i j_i$ . These informations are used to construct the term symbol indicating the split of the orbitals and the total value of  $J$ , as it follows:

$$\left( [ ] n_1 p_{j_i}^\alpha n_1 p_{j_k}^\beta \right)_J$$

Clearly this is just an example, since we can have more splitted levels. Anyway the total number of electrons  $\alpha + \beta$  has to sum up to the number of electrons in the starting orbital, and  $J$  has to be decided according to the third Hund's rule. The above scheme is called *jj coupling*.





## 3.2 Helium atom

### 3.2.1 Perturbative method

The hamiltonian describing the helium atom (  $Z = 2$  : two electrons and a nuclear charge of  $2e_0$  ) is :

$$\hat{H} = \underbrace{\frac{\hat{p}_1^2}{2m} - \frac{Ze_0^2}{4\pi\epsilon_0 r_1}}_{\hat{H}_1} + \underbrace{\frac{\hat{p}_2^2}{2m} - \frac{Ze_0^2}{4\pi\epsilon_0 r_2}}_{\hat{H}_2} + \underbrace{\frac{e_0^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|}}_{\hat{V}_{ee}}$$

Let us consider as *unperturbed hamiltonian*

$$\hat{H}^{(0)} = \hat{H}_1 + \hat{H}_2$$

The solutions of each  $H_i, i = 1, 2$  are

$$\langle r, \theta, \phi | n, l, m_l, m_s \rangle = R_{n,l}(r) Y_{l,m_l}(\theta, \phi) \chi_{m_s}$$

$$\epsilon_n = \frac{-Z^2 R_y}{n^2}$$

Since  $\hat{H}^{(0)}$  is the sum of  $\hat{H}_1$  and  $\hat{H}_2$  its solutions are tensor products of single-particle states, properly antisymmetrized according to [the symmetrization postulate](#). Let us discuss the ground state: two electrons on the 1s level, with opposite spins because of [Pauli's exclusion principle](#). We can obtain the appropriate anti-symmetric wavefunction using [Slater determinant](#)

$$\begin{aligned} \varphi(\vec{r}_1, \vec{r}_2) &= \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_{1s}(\vec{r}_1) \alpha(1) & \psi_{1s}(\vec{r}_1) \beta(1) \\ \psi_{1s}(\vec{r}_2) \alpha(2) & \psi_{1s}(\vec{r}_2) \beta(2) \end{vmatrix} \\ &= \frac{1}{\sqrt{2}} (\psi_{1s}(\vec{r}_1) \alpha(1) \cdot \psi_{1s}(\vec{r}_2) \beta(2) - \psi_{1s}(\vec{r}_1) \beta(1) \cdot \psi_{1s}(\vec{r}_2) \alpha(2)) \\ &= \frac{1}{\sqrt{2}} \psi_{1s}(\vec{r}_1) \psi_{1s}(\vec{r}_2) \underbrace{(\alpha(1) \beta(2) - \alpha(2) \beta(1))}_{\text{spin singlet } s=0} \end{aligned}$$

The  $0^{th}$  order energy value is

$$E^{(0)} = \epsilon_1 + \epsilon_2 \approx 108\text{eV}$$

Now we consider the electron-electron repulsion  $\hat{V}_{ee}$  as a perturbation and evaluate the first order correction to the ground-state energy:

$$\begin{aligned} E^{(1)} &= \langle G.S | \hat{V}_{ee} | G.S \rangle \\ &= \underbrace{\left( \frac{1}{2} \cdot \frac{e_0^2}{4\pi\epsilon_0} \cdot \int_0^{+\infty} d^3\vec{r}_1 d^3\vec{r}_2 |\psi_{1s}(\vec{r}_1)|^2 |\psi_{1s}(\vec{r}_2)|^2 \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right)}_{\text{direct integral}} \underbrace{\sum_{\text{spin part}}}_{=1} \end{aligned}$$



Before solving the direct integral it's important to give it a physical meaning:

- $-e_0 |\psi_{1s}(\vec{r}_1)|^2$  can be seen as a charge density associated with electron 1 since it's the product of a charge and a spatial probability distribution. Similarly  $-e_0 |\psi_{1s}(\vec{r}_2)|^2$  can be seen as the charge density associated with the other electron
- In this perspective it's easy to see that the direct integral represents the energy associated with coulomb interaction between electrons

The result of such an integral is  $\frac{5}{4}ZR_y$ , which is positive and thus increases the ground state energy. In the case of helium, with  $Z = 2$ , we obtain:

$$E^{(1)} = \frac{10}{4}R_y \approx 34eV$$

$$E_{G.S} = E^{(0)} + E^{(1)} \approx -74.8eV$$

This result has to be compared with the experimental value  $-79eV$ .

### 3.2.2 Variational method

#### Theorem

We can improve the previous result by using a different approach, based on the following theorem:

$$\forall \varphi \langle \varphi | \hat{H} | \varphi \rangle \geq E_{\text{ground state}}$$

*Proof*

Let  $|u_n\rangle$  be the set of eigenstates of  $\hat{H}$ . Since they constitute a complete orthonormal system we can expand each  $\varphi$  on this set:

$$\hat{H} |u_n\rangle = \epsilon_n |u_n\rangle$$

$$|\varphi\rangle = \sum_n c_n |u_n\rangle$$

Computing  $\langle \varphi | \hat{H} | \varphi \rangle$  we have:

$$\begin{aligned} \langle \varphi | \hat{H} | \varphi \rangle &= \sum_{n,n'} c_n^* c_n \underbrace{\langle u_n' | \hat{H} | u_n \rangle}_{\delta_{n',n} \epsilon_n} \\ &= \sum_n \epsilon_n |c_n|^2 \geq \sum_n E_{\text{ground state}} |c_n|^2 = E_{\text{ground state}} \\ &\Rightarrow \langle \varphi | \hat{H} | \varphi \rangle \geq E_{\text{ground state}} \end{aligned}$$

We can take advantage of this fact choosing a ground-state single particle wave-function depending on a variational parameter:



$$\psi_{1s} \propto e^{-\frac{Z_{\text{eff}} r}{a_0}}$$

The wavefunction of helium ground state is thus:

$$\varphi(Z_{\text{eff}}, \vec{r}_1, \vec{r}_2) \propto e^{-\frac{Z_{\text{eff}} r_1 + r_2}{a_0}}$$

We have neglected both the spin part and the angular part of the wave function since they will not contribute to the following calculation. Now we apply the previous theorem:

$$\begin{aligned} \langle \varphi(Z_{\text{eff}}) | \hat{H} | \varphi(Z_{\text{eff}}) \rangle &= E(Z_{\text{eff}}) \\ E(Z_{\text{eff}}) &\geq E_{\text{ground state}}, \\ \hat{H} &= \hat{H}_1 + \hat{H}_2 + \frac{e_0^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}_1 - \vec{r}_2|} \end{aligned}$$

That means we have to find the minimum of  $E(Z_{\text{eff}})$  in order to get the best approximation, that is computing  $\frac{\partial E(Z_{\text{eff}})}{\partial Z_{\text{eff}}}$

$$\begin{aligned} \langle \varphi(Z_{\text{eff}}) | \hat{H}_{\text{tot}} | \varphi(Z_{\text{eff}}) \rangle &= \langle \varphi(Z_{\text{eff}}) | \hat{H}_1 + \hat{H}_2 + \frac{e_0^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}_1 - \vec{r}_2|} | \varphi(Z_{\text{eff}}) \rangle \\ &= \frac{5Z_{\text{eff}} R_y}{4} + 2 \langle \psi_{1s}(Z_{\text{eff}}) | \hat{H}_1 | \psi_{1s}(Z_{\text{eff}}) \rangle \end{aligned}$$

Now

$$2 \langle \psi_{1s}(Z_{\text{eff}}) | \hat{H}_1 | \psi_{1s}(Z_{\text{eff}}) \rangle = 2 \left\langle \psi_{1s}(Z_{\text{eff}}) \left| \frac{\hat{p}_1^2}{2m} - \frac{Ze_0^2}{4\pi\epsilon_0 r_1} \right| \psi_{1s}(Z_{\text{eff}}) \right\rangle$$

We need to evaluate two terms:

$$\begin{aligned} \left\langle \psi_{1s}(Z_{\text{eff}}) \left| \frac{\hat{p}_1^2}{2m} \right| \psi_{1s}(Z_{\text{eff}}) \right\rangle \\ \left\langle \psi_{1s}(Z_{\text{eff}}) \left| -\frac{Ze_0^2}{4\pi\epsilon_0 r_1} \right| \psi_{1s}(Z_{\text{eff}}) \right\rangle \end{aligned}$$

The latter is simple to evaluate since

$$\left\langle \psi_{1s}(Z_{\text{eff}}) \left| -\frac{1}{r_1} \right| \psi_{1s}(Z_{\text{eff}}) \right\rangle = \frac{Z_{\text{eff}}}{a_0}$$

so that this term gives



$$\begin{aligned} \left\langle \psi_{1s}(Z_{\text{eff}}) \left| -\frac{Ze_0^2}{4\pi\epsilon_0 r_1} \right| \psi_{1s}(Z_{\text{eff}}) \right\rangle &= -\underbrace{\frac{e_0^2}{4\pi\epsilon_0 a_0}}_{=\frac{R_y}{2}} Z Z_{\text{eff}} \\ &= -2R_y Z Z_{\text{eff}} \end{aligned}$$

The former can be easily computed writing

$$\frac{\hat{p}_1^2}{2m} = \hat{H}_1(Z_{\text{eff}}) + \frac{Z_{\text{eff}}e_0^2}{4\pi\epsilon_0 r_1}$$

so that

$$\begin{aligned} \left\langle \psi_{1s}(Z_{\text{eff}}) \left| \frac{\hat{p}_1^2}{2m} \right| \psi_{1s}(Z_{\text{eff}}) \right\rangle &= \left\langle \psi_{1s}(Z_{\text{eff}}) \left| \hat{H}_1 + \frac{Z_{\text{eff}}e_0^2}{4\pi\epsilon_0 r_1} \right| \psi_{1s}(Z_{\text{eff}}) \right\rangle \\ &= -Z_{\text{eff}}^2 R_y + \underbrace{\frac{e_0^2}{4\pi\epsilon_0 a_0}}_{=\frac{R_y}{2}} Z_{\text{eff}}^2 \\ &= -Z_{\text{eff}}^2 R_y + 2Z_{\text{eff}}^2 R_y \\ &= Z_{\text{eff}}^2 R_y \end{aligned}$$

With these result we can compute

$$\begin{aligned} E(Z_{\text{eff}}) &= \left\langle \varphi(Z_{\text{eff}}) \left| \hat{H}_{\text{tot}} \right| \varphi(Z_{\text{eff}}) \right\rangle \\ &= \frac{5Z_{\text{eff}}R_y}{4} + 2Z_{\text{eff}}^2 R_y - 4ZZ_{\text{eff}}R_y \end{aligned}$$

Differentiation with respect to  $Z_{\text{eff}}$  gives

$$\frac{\partial E(Z_{\text{eff}})}{\partial Z_{\text{eff}}} = \frac{5}{4} + 4Z_{\text{eff}} - 4Z$$

this result must equal 0 if we are looking for the minimum:

$$\begin{aligned} \frac{5}{4} + 4Z_{\text{eff}} - 4Z &= 0 \\ \Rightarrow Z_{\text{eff}} &= Z - \frac{5}{16} \end{aligned}$$

In case of helium we find  $Z_{\text{eff}} = \frac{27}{16}$ , which is greater than  $Z = 2$ : with this method electron screening has been taken into account. If we put this value of  $Z_{\text{eff}}$  in the function  $\varphi(Z_{\text{eff}}, \vec{r}_1, \vec{r}_2) \propto e^{-\frac{Z_{\text{eff}}r_1+r_2}{a_0}}$  we get the wavefunction of the ground state, and if we compute the energy we get

$$\begin{aligned} E_{\text{ground state}} \left( Z_{\text{eff}} = \frac{27}{16} \right) &= \frac{5Z_{\text{eff}}R_y}{4} + 2Z_{\text{eff}}^2 R_y - 4ZZ_{\text{eff}}R_y \\ &\approx -77.5eV \end{aligned}$$



Comparison with experimental value and the one obtained with perturbation theory lead us to conclude that this is a better approximation

SUMMARY:

The hamiltonian of this system can be written as:

$$\hat{H} = \frac{\vec{p}_1^2}{2m} + \frac{\vec{p}_2^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{Ze^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|}$$

Where the last term can be seen as a perturbation of a two electrons-system hamiltonian:

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \frac{e^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|} = \hat{H}_0 + \hat{H}_{pert}$$

Using the perturbation theory we find:

$$E_0^{(1)} = \langle \psi_0 | \hat{H}_{int} | \psi_0 \rangle = e^2 \int d^3\vec{r}_1 d^3\vec{r}_2 \frac{|\psi_{1s}(\vec{r}_1)|^2 |\psi_{1s}(\vec{r}_2)|^2}{4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|}$$

Solving the integral we get:

$$E_0^{(1)} = \frac{5}{4} Z R_y$$

While the unperturbed energy is:

$$E_0 = \epsilon_1^{(1s)} + \epsilon_2^{(1s)} = -2Z^2 R_y = -108eV$$

Let us state one important principle, called *variational principle*:

$$\langle \psi | \hat{H} | \psi \rangle \geq E_{GS}$$

Where  $E_{GS}$  stands for the ground state energy of the system. A more precise result for the energy  $E_0$  can be found looking for an “effective” charge  $Z_{eff}$  and by evaluating  $\langle \hat{H} \rangle$  at this  $Z_{eff}$ . We get\* [1]:

$$\langle \hat{H} \rangle = \frac{5}{4} Z_{eff} R_y + 2Z_{eff}^2 R_y - 4ZZ_{eff} R_y$$

And the value  $Z_{eff}$  can be derived looking for a minimum in the energy. Hence:

$$Z_{eff} = Z - \frac{5}{16}$$

For this particular hamiltonian we have that  $\langle \frac{\vec{p}^2}{2m} \rangle = -\frac{1}{2} \langle \mathcal{U} \rangle$ , which is just a consequence of the *virial theorem*:



$$\left\langle n \left| \frac{\hat{p}^2}{2m} \right| n \right\rangle = - \langle \vec{x} \nabla \mathcal{U} \rangle$$

Where  $|n\rangle$  is any eigenstate of the hamiltonian. Remember that the ground state wf of the He atom is given by the product of two hydrogen-like, ground state, wave functions. That is:

$$\psi_{100} = \psi_{1s}(\vec{r}_1)\psi_{1s}(\vec{r}_2)$$

Hence,  $\psi_{100}$  is an hydrogen-like wf and its expression is:

$$\psi_{100} = \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \frac{1}{\sqrt{\pi}} e^{-\frac{Zr}{a_0}}$$

Actually, this is just the radial part of the wf but for most exercises and applications this is what we need.

[1] This expression holds for any He-like hamiltonian.

### 3.3 Helium atom: excited states

We do consider the first excited state, that is  $1s2s$ . Since we have to dispoone two electrons on two different orbital levels we can get four global wf:

- $\psi = \frac{1}{\sqrt{2}} (\psi_{1s}(1)\psi_{2s}(2) - \psi_{1s}(2)\psi_{2s}(1)) \alpha(1)\alpha(2)$
- $\psi = \frac{1}{\sqrt{2}} (\psi_{1s}(1)\psi_{2s}(2) - \psi_{1s}(2)\psi_{2s}(1)) \beta(1)\beta(2)$
- $\psi_- = \frac{1}{\sqrt{2}} (\psi_{1s}(1)\psi_{2s}(2) - \psi_{1s}(2)\psi_{2s}(1)) \underbrace{\left[ \frac{\alpha(1)\beta(2) + \alpha(2)\beta(1)}{\sqrt{2}} \right]}_{\text{triplet state}}$
- $\psi_+ = \frac{1}{\sqrt{2}} (\psi_{1s}(1)\psi_{2s}(2) + \psi_{1s}(2)\psi_{2s}(1)) \underbrace{\left[ \frac{\alpha(1)\beta(2) - \alpha(2)\beta(1)}{\sqrt{2}} \right]}_{\text{singlet state}}$

For the mean value of the energy we have:

$$\langle \hat{H}_{tot} \rangle = \left\langle \psi_{\pm} \left| \frac{e^2}{4\pi\epsilon_0 |\vec{x}_1 - \vec{x}_2|} \right| \psi_{\pm} \right\rangle = J \pm K$$

Where  $J$  and  $K$  are called *direct* and *switch* integrals, and take on the values:

$$J = \frac{e^2}{4\pi\epsilon_0} \int d^3\vec{x}_1 d^3\vec{x}_2 \frac{\psi_{1s}^*(\vec{x}_2)\psi_{1s}(\vec{x}_2)\psi_{2s}^*(\vec{x}_1)\psi_{2s}(\vec{x}_1)}{|\vec{x}_1 - \vec{x}_2|} > 0$$



$$K = J(\vec{x}_i \mapsto \vec{x}_j) > 0, \quad i, j = 1, 2, i \neq j$$

Excited states allow us to introduce new energy levels, called *orbitals*. For the first excited state we have the configuration  $1s2p$ ;  $2p$  means that  $L = 1$ , and so  $M_L = \pm 1, 0$ . We thus have three possible wf for this state:  $\psi_{1,1}, \psi_{1,0}, \psi_{1,-1}$ . Actually only  $\psi_{1,0}$  is a real wf. Since we want to have real functions in order to describe orbitals\* [1], we take linear combinations of them:

$$\begin{cases} p_z \mapsto \psi_{1,0} \\ p_x \mapsto \frac{1}{\sqrt{2}} (\psi_{1,1} - \psi_{1,-1}) \\ p_y \mapsto \frac{1}{\sqrt{2}} (\psi_{1,1} + \psi_{1,-1}) \end{cases}$$

- [1] To be precise, here we should have taken only the radial part of the w.f. Since orbitals do describe the probability of occupation of a particular angular space region. Anyway, if you're given a state  $\psi$  in terms of orbitals  $p_i$  you can rewrite your state in terms of a w.f. using the combinations given below.

### 3.4 Hartree-Fock method

The Hartree-Fock method is an independent particle model which uses variational methods to find the best individual electron spin-orbitals.

Let us consider a many-electron atom with atomic number  $Z$ . The task is to find an equation describing the effective potential felt by a single electron.

Several effects have to be taken into account:

- the nucleus attraction:  $\hat{V}_{ne} = -\frac{Ze^2}{4\pi\epsilon_0 r}$
- the interaction with the other electrons
- the necessity for the system wavefunction to be a Slater determinant (antisymmetric)

Given the set of the electrons' wavefunctions  $\psi_i(\vec{r})$   $i = 1, \dots, Z$ , which constitute a starting ground state  $|\psi_1, \dots, \psi_Z\rangle_A$  (a Slater determinant), we can define a charge distribution

$$\rho(\vec{r}) = -e_0 \sum_i |\psi_i(\vec{r})|^2$$

We can now introduce the **Hartree potential**  $\hat{V}_H(\vec{r})$  as

$$\hat{V}_H(\vec{r}) = \int_0^{+\infty} d^3\vec{r}' \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|}$$

This potential represents the coulomb electron-electron repulsion. However it does not take into account spin effects and consider also the interaction of the electron with itself. These effects are taken into account by **Fock-potential**, which hasn't a classical interpretation



$$\hat{V}_F = \frac{e_0^2}{4\pi\epsilon_0} \sum_j - \int_0^{+\infty} d^3\vec{r}' \frac{\psi_j^*(\vec{r}') \psi_j(\vec{r}') \psi_i(\vec{r}')}{|\vec{r} - \vec{r}'|}$$

The sum  $\hat{V}_{H.F} = \hat{V}_H + \hat{V}_F$  is the *Hartree-Fock potential*

The **Hartree-Fock hamiltonian** for a single electron is then: \* [1]

$$\hat{H}_{H.F} = \frac{-\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} + \hat{V}_H(\vec{r}) + \hat{V}_F(\vec{r})$$

The equation we'd like to solve is then

$$\hat{H}_{H.F} \psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r})$$

It's important to note that both  $\rho(\vec{r})$  and  $\psi_j$ , which enter in the definition of  $\hat{V}_H$  and  $\hat{V}_F$  depend on the solutions of the hamiltonian equation and are not given "a priori". This is the reason why Hartree Fock equation is not, in fact, a Schrödinger equation for  $\psi_i$  until we fix in some way  $\rho(\vec{r})$  and  $\psi_j$

Hartree-Fock method consist in a **self-consistent** procedure:

- Chose an initial charge density, which means a starting ground state  $|\psi_1, \dots, \psi_Z\rangle_A$  and compute the corresponding  $\rho(\vec{r})$
- solve the hartree equation with that  $\rho$  and  $\psi_j$ , find the energy corresponding to it  $E_\rho$  and find the new wavefunctions  $\psi'_j$
- compute  $\rho'(\vec{r}) = -e_0 \sum_i \psi'_j(\vec{r})$
- put  $\rho'$  and  $\psi'_j$  in the hartree-fock potential and solve again the equation. If  $E_{\rho'} < E_\rho$   $\rho'$  and  $\psi'_j$  are better approximations for the ground state according to the variational principle.
- repeat the procedure until you reach a satisfactory agreement between the previous solutions and the latest.

### 3.4.1 Central field approximation

We can introduce further simplifications if we build  $\hat{V}_{H.F}$  as a central potential, since we are thus allowed to separate variables in the Hartree-Fock equation. Solutions are then of the form

$$\begin{aligned} \psi_i(\vec{r}) &= R_{n,l}(r) Y_{l,m_l}(\theta, \phi) \chi_{m_s} \\ \hat{H} |n, l, m_l, m_s\rangle &= \epsilon_{n,l} |n, l, m_l, m_s\rangle \end{aligned}$$

This decomposition is a feature shared by central potentials. However  $R_{n,l}$  is different from the radial function of hydrogenlike solutions. Furthermore, since the  $\frac{1}{r}$  dependence of Coulomb potential has been broken, energy eigenvalues depend not only on  $n$  but also on  $l$ : Hartree-Fock model thus provides an explanation for the *l-ordering* observed in atomic spectra. Indeed, because of the centrifugal





term  $\frac{\hbar^2 l(l+1)}{2mr^2}$  which grows with  $l$ , lower  $l$  implies lower energy (other things being equal). Electronic configuration of atoms is expressed specifying the number of electrons in each eigenstate: for example the expression  $1s^2 2s^2 2p^4$  means that 2 electrons are in the state  $n = 1, l = 0$ , 2 electrons in the state  $n = 2, l = 0$  and 4 electrons in  $n = 2, l = 1$ . In Hartree-Fock approximation there is no need for specifying  $m_l$  and  $m_s$  values since the energy does not depend on them.

1. same hamiltonian without  $\hat{V}_F$  is the **Hartree hamiltonian**, less correct but much easier to solve

### 3.5 Non-spherical corrections and LS scheme

The real Coulomb interaction between electrons is given by

$$\hat{V}_{ee} = \frac{1}{2} \frac{e_0^2}{4\pi\epsilon_0} \sum_{i \neq j} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

and the full hamiltonian is

$$\hat{H} = \sum_i \frac{-\hbar^2}{2m} \nabla_i^2 - \frac{Ze_0^2}{4\pi\epsilon_0} \sum_i \frac{1}{r_i} + V_{ee}$$

Instead, Hartree hamiltonian is

$$\hat{H}_H = \sum_i \frac{-\hbar^2}{2m} \nabla_i^2 - \frac{Ze_0^2}{4\pi\epsilon_0} \sum_i \frac{1}{r_i} + \sum_i V_H(\vec{r}_i)$$

Taking the difference between  $\hat{H}$  and  $\hat{H}_H$  we get

$$\hat{H}_1 = \hat{V}_{ee} - \sum_i \hat{V}_H(\vec{r}_i)$$

We can consider  $\hat{H}_1$  as a perturbation with respect to  $\hat{H}_H$ , representing the difference between the actual coulomb interaction between electrons and the average electron repulsion. The eigenstates of  $\hat{H}_H$  are labeled with the *good quantum numbers*  $|n_i, l_i, m_{l_i}, m_{s_i}\rangle$  and are degenerate in  $m_l$  and  $m_s$  since energies depend only on  $n$  and  $l$ . In order to deal with simpler calculations we'd like to find a basis that makes the perturbation  $\hat{H}_1$  diagonal together with  $\hat{H}_{H.F.}$ .

If  $\hat{H}_1$  is the most relevant perturbation \* [1] and thus we do not have to deal with other terms in the hamiltonian, we can proceed as follows.

Since  $\hat{H}_1$  does not contain spin-orbit energy terms it commutes not only with  $\hat{J} = \sum_i \hat{L}_i + \hat{S}_i$  but also with  $\hat{L} = \sum_i \hat{L}_i$  and  $\hat{S} = \sum_i \hat{S}_i$ . Furthermore,  $[\hat{H}_1, \hat{L}_i^2] = 0$  so that  $l_i$  is still a good quantum number together with  $n_i$ .

The right way of labeling states is thus:  $|\{n_i, l_i\}L, S, M_L, M_S\rangle$

Using Clebsch-Gordan coefficients we can easily change basis:



$$|\{n_i, l_i\}L, S, M_L, M_S\rangle = \sum_{m_{l_i}, m_{s_i}} \underbrace{(\dots)}_{\text{Clebsch-Gordan}} |n_i, l_i, m_{l_i}, m_{s_i}\rangle$$

The degeneracy of energy levels is partially removed by  $\hat{H}_1$  :

$$\langle \hat{H}_1 \rangle = E^{(1)}(\{n_i, l_i\}, L, S)$$

States with different  $L, S$  are no longer degenerate. This is the reason why when we take into account non-spherical corrections we label energy levels no longer with  $[n]s, [n]p, \dots$  but rather with **atomic terms in LS scheme**:

$$^{2S+1}L_J$$

where the capital letter  $L$  has to be replaced with  $S, P, D, F, \dots$  for  $L = 0, 1, 2, 3, \dots$ . A state  $1s^2 2s^2 2p^2$ , which represents 15 degenerate states, is now split in

$$^1D_2 (5 \text{ states}) \quad ^3P_0 \ ^3P_1 \ ^3P_2 (9 \text{ states}) \quad ^1S_{\frac{1}{2}} (1 \text{ state})$$

and each of these terms with a different capital letter  $L$  has different energy.\* [2]

After having taken into account non-spherical corrections, we can consider other less relevant perturbations such as spin-orbit coupling: as we'll see in the next chapter the effect of this perturbation is to split the terms according to their  $J$ , since

$$\langle \{n_i, l_i\}L, S, J, M_J | \hat{H}_{SO} | \{n_i, l_i\}L, S, J, M_J \rangle = A(\{n_i, l_i\}) \frac{\hbar^2}{2} (J(J+1) - L(L+1) - S(S+1))$$

This leads to a further removal of degeneracy, since states such as  $^3P_0 \ ^3P_1 \ ^3P_2$  no longer have the same energy.

The physical fact partially hidden by all the maths is that spins interact giving a total spin  $\hat{S}$  and so do the orbital angular momenta  $\hat{L}_i$ , which give rise to a total angular momentum  $\hat{L}$ . Then  $\hat{L}$  and  $\hat{S}$  couple into a  $\hat{J}$  (*LS coupling*).

### 3.5.1 Hund's rules

In order to find the term with the lowest energy the following empirical rules hold:

1. The term with the maximum spin has the lowest energy
2. If there still are more terms, choose the one with the highest angular momentum
3. if the shell is less than half-full the lowest energy term is the one with the lowest value of  $J$ , otherwise the one with the highest value of  $J$



1. in particular, if **spin-orbit** effects are small
2. For a detailed discussion about how to find atomic terms read **LS scheme**

### 3.6 Spin-orbit coupling and jj scheme

The hamiltonian representing spin-orbit interaction is

$$\hat{H}_{SO} = \frac{1}{2mc^2} \sum_i \hat{S}_i \hat{L}_i \frac{1}{r_i} \frac{\partial \hat{V}(r_i)}{\partial r_i}$$

$$\hat{V}(r) = \frac{-Ze^2}{4\pi\epsilon_0 r} + \hat{V}_H(r)$$

We can treat  $\hat{H}_{SO}$  as a perturbation to  $\hat{H}_{H.F.}$ . If we're not dealing with other perturbation of the same order ( which means spin-orbit corrections are the leading ones), we simply have to find a basis which is able to diagonalize  $\hat{H}_{SO}$  and  $\hat{H}_{H.F.}$  simultaneously. That basis is  $|n_i, l_i, j_i, m_{j_i}\rangle$ , where  $\hat{J}_i = \hat{L}_i + \hat{S}_i$  represent the total angular momentum of each electron. We can pass from the previous basis to the new one through Clebsch-Gordan coefficients:

$$|n_i, l_i, j_i, m_{j_i}\rangle = \sum_{m_{l_i}, m_{s_i}} \underbrace{(\dots)}_{\text{Clebsch-Gordan}} |n_i, l_i, m_{l_i}, m_{s_i}\rangle$$

The mathematical need for this basis represents the physical fact that when spin-orbit interaction becomes strong (in heavy atoms,  $Z \geq 40$ ), each orbital angular momentum tends to couple with its own spin:  $\hat{J}_i = \hat{L}_i + \hat{S}_i$ . The  $\hat{J}_i$  then combines to give the total  $\hat{J} = \sum_i \hat{J}_i$  (*jj coupling*)

Individual spin orbitals are now labeled with the new good quantum numbers:

$$[n][l][j]$$

The effect of spin-orbit coupling consists in a partial removal of degeneracy according to  $j$ - value:

$$\langle \hat{H}_{SO} \rangle = E^{(1)}(\{n_i, l_i\}, j_i)$$

For example  $2p$  level, characterized by  $l = 1, s = \frac{1}{2}$ , is split in  $2p_{\frac{1}{2}} 2p_{\frac{3}{2}}$ .

If we want to fill  $2p$  level with electrons we simply have to add an apix  $\alpha$  representing the occupation number. After placing all the electrons in the  $jj$  levels compute the possible values of the total  $J$ :  $(n l_j^\alpha n' l_{j'}^{\alpha'} \dots)_{J_1, J_2, \dots}$

When we take into account non-spherical corrections on these states  $m_{j_i}$  is no longer a good quantum number and we need to label states with  $\{|n_i, l_i, j_i\}, J, M_J$ . Degeneracy of configurations with same  $J$  is removed:

$$\langle \{n_i, l_i, j_i\}, J, M_J | \hat{H}_1 | \{n_i, l_i, j_i\}, J, M_J \rangle = E(\{n_i, l_i, j_i\}, J)$$



Each configuration with different value of  $J$  has now different energy. The lowest energy configuration is given by [Hund's third rule](#) <sup>[1]</sup>

**Remark**

- $[n][l]_{[j]}$  can have a maximum of  $2j + 1$  electrons
- If a level  $[n][l]$ , which can contain  $2(2l + 1)$  electrons is split in  $[n][l]_{[j_1]}, [n][l]_{[j_2]}$  the equality  $2(2l + 1) = (2j_1 + 1) + (2j_2 + 1)$  must hold. For example  $2p$  level is split in  $2p_{\frac{1}{2}} 2p_{\frac{3}{2}}$  and we have  $2(2 \cdot 1 + 1) = 6 = \underbrace{\left(2 \cdot \frac{1}{2} + 1\right)}_{=2} + \underbrace{\left(2 \cdot \frac{3}{2} + 1\right)}_{=4}$

1. For a detailed discussion about how to find atomic terms read [JJ scheme](#)



# Chapter 4

## Molecules

### 4.1 Born-Oppenheimer approximation

The aim of this section is to study the quantum description of the molecular bond. We are going to limit the analysis to diatomic molecules. First of all we consider a molecule composed by two atomic nuclei A and B, whose positions are defined by vectors  $\vec{R}_A$  and  $\vec{R}_B$ . The electrons positions are instead identified by  $\vec{x}_i$ . Both nuclei and electrons positions are referred to the center of mass of the two nuclei. The Hamiltonian we can write for a system like this is:

$$\hat{H} = \hat{T}_N + \hat{T}_e + U_{eN} + U_{ee} + U_{NN}$$

where  $\hat{T}_N$  and  $\hat{T}_e$  are the kinetic energies associated respectively to the nuclei and the electrons and  $U_{eN}$ ,  $U_{ee}$  and  $U_{NN}$  represent the Coulomb interactions. Now it's possible to isolate from this Hamiltonian an electron Hamiltonian:

$$\hat{H}_e = \hat{T}_e + U_{eN} + U_{ee}$$

This  $\hat{H}_e$  is a function of the nuclei positions and we can obtain an eigenvalues equation for the electrons:

$$\hat{H}_e \left( \left\{ \vec{R}_i \right\} \right) \psi_n^{el} \left( \left\{ \vec{R}_i \right\}; \left\{ \vec{x}_i \right\} \right) = E_n^{el} \psi_n^{el} \left( \left\{ \vec{R}_i \right\}; \left\{ \vec{x}_i \right\} \right)$$

It's possible to demonstrate that solving this equation for the electrons Hamiltonian leads to a solution  $\psi$  for the original complete eigenvalue equation which has the form:

$$\psi = \sum_n \chi_n \left( \left\{ \vec{R}_i \right\} \right) \psi_n \left( \left\{ \vec{R}_i \right\}; \left\{ \vec{x}_i \right\} \right)$$

where  $\chi_n$  is a wave function depending only on the nuclei positions. Such an equation is difficult to solve, but it can be simplified through the **Born-Oppenheimer adiabatic approximation**. This model is based on the fact that the mass of the nucleus is much greater than the electron one ( $m_p/m_e \approx 1800$ ). Being so, we can state that electrons move way faster than nuclei. Hence we



can assume that electrons follow the motion of the nuclei without changing the energy level they belong to. In other words, there is no energy exchange between nuclei and electrons. In this adiabatic approximation the solution  $\psi$  becomes:

$$\psi = \chi_n \left( \left\{ \vec{R}_i \right\} \right) \psi_n \left( \left\{ \vec{R}_i \right\}; \left\{ \vec{x}_i \right\} \right)$$

The sum over the quantum number  $n$  disappears, because of the impossibility for an electron to jump to an excited state. Now we can use these results to write an equation for the total Hamiltonian:

$$\left( \hat{T}_N + U_{NN} + \hat{H}_e \right) \chi_n \left( \left\{ \vec{R}_i \right\} \right) \psi_n^{el} \left( \left\{ \vec{R}_i \right\}; \left\{ \vec{x}_i \right\} \right) = E_{tot} \chi_n \left( \left\{ \vec{R}_i \right\} \right) \psi_n^{el} \left( \left\{ \vec{R}_i \right\}; \left\{ \vec{x}_i \right\} \right)$$

At this point we can observe that  $\hat{H}_e$  only acts on  $\psi^{el}$ , which is actually an eigenstate of  $\hat{H}_e$ , so we can substitute  $\hat{H}_e$  in the equation above with the corresponding eigenvalue  $E^{el} \left( \left\{ \vec{R}_i \right\} \right)$ . Moreover, again thanks to the greatness of nuclei masses in respect to electrons ones, we can assume that the application of the kinetic term  $\hat{T}_N$  to the  $\psi^{el}$  component of the total wave function gives a negligible contribution, then we can consider that  $\hat{T}_N$  acts only on  $\chi$ . Relying on this last approximation, it's possible to simplify the  $\psi^{el}$  term in order to obtain an eigenvalues equation for the sole  $\chi$  function:

$$\left[ \hat{T}_N + U_{NN} + E_n^{el} \left( \left\{ \vec{R}_i \right\} \right) \right] \chi \left( \left\{ \vec{R}_i \right\} \right) = E_{tot} \chi \left( \left\{ \vec{R}_i \right\} \right)$$

The last equation describes the nuclei dynamics and this means that the equations for  $\psi^{el}$  and  $\chi$  are now uncoupled.  $E_{tot}$  depends only on the distance between the nuclei:

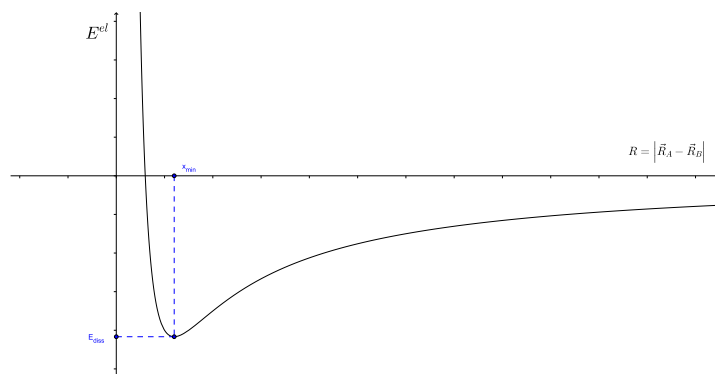
$$E_{tot} = E_{tot} \left( \left| \vec{R}_A - \vec{R}_B \right| \right)$$

Now we can redefine the quantity  $E^{el} \left( \left\{ \vec{R}_i \right\} \right)$  considering that  $U_{NN}$  is just a multiplicative operator:

$$E^{el} \left( \left\{ \vec{R}_i \right\} \right) = E_n^{el} \left( \left\{ \vec{R}_i \right\} \right) + U_{NN}$$

In other words,  $E^{el} \left( \left\{ \vec{R}_i \right\} \right)$  is the eigenvalue for the operator  $\hat{H}_e \left( \left\{ \vec{R}_i \right\} \right) + U_{NN}$  corresponding to the eigenfunction  $\psi^{el}$ . It's possible to plot  $E^{el} \left( \left\{ \vec{R}_i \right\} \right)$  in respect to the nuclear distance  $R = \left| \vec{R}_A - \vec{R}_B \right|$ :





In the graph, the value of the energy in correspondence of the  $x$  axis is  $E_A + E_B$ , where  $E_A$  and  $E_B$  are the energy associated to the hydrogenoid Hamiltonian for nucleus  $A$  and  $B$ . It can be seen that there is an  $R_{min}$  at which the energy is minimal. This is called **dissociation energy** and it's the energy that has to be given to the molecule in order to break the bond.

## 4.2 The Heitler-London model

There are two main models to approach the mathematical representation of the molecular bond:

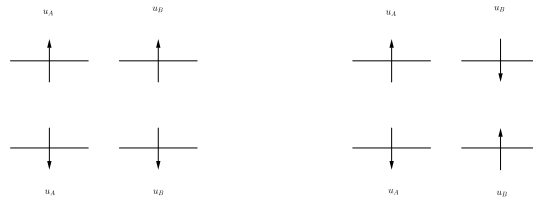
1. **Heitler-London**, or valence bond model;
2. **MO-LCAO**, that stands for Molecular Orbital from Linear Combination of Atomic Orbitals.

In this section we're going to illustrate the first of this two models. So, for simplicity, we consider the molecule  $H_2$  and we just try to find a way to describe the wave function which represents the two electrons orbiting around the bounded nuclei. Firstly we consider that both electrons, taken singularly, are described by the wave function corresponding to the ground state of Hydrogen (1s orbital). If the two nuclei were far enough, the superposition would be negligible and the two electrons could be described by a total wave function given by the multiplication of the two single wave functions for atom  $A$  and atom  $B$ :

$$\psi(\vec{x}_1; \vec{x}_2) = u_A(\vec{x}_1) u_B(\vec{x}_2)$$

where  $\vec{x}_1$  and  $\vec{x}_2$  represent the positions of the two electrons. In this case we can consider that the global Hamiltonian is separable, because the terms involving superposition between the effects of the two nuclei vanish when the distance between them is big. If the two nuclei are close to each other it is necessary to antisymmetrize the wave function (electrons are fermions). In order to do this we have to take in account all the possible electrons configuration:





It is fundamental to observe now that not all four states represented by the image above are eigenstates of the total spin operator  $S = S_1 + S_2$ . In particular, only the two states on the left ( $\alpha(1)\alpha(2)$  and  $\beta(1)\beta(2)$ ) are eigenstates of  $S$ . To obtain a complete system of eigenstates of  $S$  we have to consider, a part from the first two states, linear combinations between the two states on the right:

$$\chi_{\pm} = \frac{\alpha(1)\beta(2) \pm \beta(1)\alpha(2)}{\sqrt{2}}$$

$\chi_{-}$  is called a state of **singlet** ( $S = 0$ ), and from now we will denote it with  $\chi_{sing}$ , whereas the other three are states of **triplet** ( $S = 1$ ) and will be all denoted by  $\chi_{trip}$ . Of course we have to match the spin component of the wave function with the correct (symmetrical or antisymmetrical) spatial one, in order to obtain a totally antisymmetrical wave function. We denote:

$$\psi_{\pm} = (u_A(\vec{x}_1)u_B(\vec{x}_2) \pm u_A(\vec{x}_2)u_B(\vec{x}_1))$$

We get four antisymmetrical states:

- *Singlet* :  $\psi_{+}\chi_{sing}$
- *Triplet* :  $\psi_{-}\chi_{trip}$

It is possible to write the complete electrons Hamiltonian:

$$\hat{H}_e = \frac{\vec{p}_1^2}{2m_e} - \frac{e^2}{4\pi\epsilon_0|\vec{x}_1 - \vec{R}_A|} + \frac{\vec{p}_2^2}{2m_e} - \frac{e^2}{4\pi\epsilon_0|\vec{x}_2 - \vec{R}_B|} - \frac{e^2}{4\pi\epsilon_0|\vec{x}_1 - \vec{R}_B|} - \frac{e^2}{4\pi\epsilon_0|\vec{x}_2 - \vec{R}_A|} + \frac{e^2}{4\pi\epsilon_0|\vec{x}_1 - \vec{x}_2|}$$

The problem now is to normalize  $\psi_{sing}$  and  $\psi_{trip}$ . In fact, when superposition occurs, the quantity  $\langle u_a|u_b\rangle$  is not equal to 0, because the two states  $u_a$  and  $u_b$  are not orthogonal. We define the overlap  $S$  as:

$$S = \langle u_a|u_b\rangle$$

and the normalization coefficient that will appear in the correct expression of  $\psi_{sing}$  and  $\psi_{trip}$  will be  $\frac{1}{\sqrt{2(1\pm S^2)}}$ . It's easy to check that, if the overlap is null ( $S = 0$ ), the coefficient becomes  $\frac{1}{\sqrt{2}}$ .





$S = 0$  , distant atoms), the normalization coefficient is  $\frac{1}{\sqrt{2}}$  , which is consistent with the orthonormality of  $u_a$  and  $u_b$  . Taking in consideration the Hamiltonian we wrote above, we calculate:

$$\langle \psi_{\pm} | \hat{H} | \psi_{\pm} \rangle = 2E_{1s} + 2 \frac{J_{AB} \pm SK_{AB}}{1 \pm S^2} + \frac{e^2}{4\pi\epsilon_0 |\vec{R}_A - \vec{R}_B|} + \frac{J_{ee} \pm K_{ee}}{1 \pm S^2}$$

where  $E_{1s}$  represents the energy of the two atomic orbitals.  $J_{AB}$  and  $K_{AB}$  come from the interaction between electrons and nuclei.  $J_{AB}$  is called **direct integral** and represents the classical Coulomb potential energy:

$$J_{AB} = \frac{-e^2}{4\pi\epsilon_0} \int d^3\vec{x} \frac{|u_A(\vec{x})|^2}{|\vec{x} - \vec{R}_B|}$$

$K_{AB}$  is called **switch integral** and has no classical interpretation. It's defined as:

$$K_{AB} = \frac{-e^2}{4\pi\epsilon_0} \int d^3\vec{x} \frac{u_A^*(\vec{x}) u_B(\vec{x})}{|\vec{x} - \vec{R}_B|}$$

It can be demonstrated that  $J_{AB} < 0$  and  $K_{AB} < 0$  , moreover if we switch the labels  $A$  and  $B$  in the integrals, their values don't change. This is the reason of the factor 2 in the expression of the energy. The term  $\frac{e^2}{4\pi\epsilon_0 |\vec{R}_A - \vec{R}_B|}$  comes from the interaction between the two nuclei. Eventually the last term of the energy is due to the repulsive interaction between the two electrons.  $J_{ee}$  and  $K_{ee}$  are defined in analogy with  $J_{AB} < 0$  and  $K_{AB} < 0$  :

$$J_{ee} = \frac{e^2}{4\pi\epsilon_0} \int d^3\vec{x}_1 d^3\vec{x}_2 \frac{|u_A(\vec{x}_1)|^2 |u_B(\vec{x}_2)|^2}{|\vec{x}_1 - \vec{x}_2|}$$

$$K_{ee} = \frac{e^2}{4\pi\epsilon_0} \int d^3\vec{x}_1 d^3\vec{x}_2 \frac{u_A^*(\vec{x}_1) u_A(\vec{x}_2) u_B(\vec{x}_2) u_B^*(\vec{x}_1)}{|\vec{x}_1 - \vec{x}_2|}$$

with  $J_{ee} > 0$  and  $K_{ee} > 0$  . The minimum energy can be obtained taking the + between  $J_{AB}$  and  $K_{AB}$  . So the minimum energy state is the singlet state. We will denote  $E_+$  the energy of the singlet state and  $E_-$  the energy of the triplet state. It can be shown that it may happen, for certain values of interatomic distance that  $E_+ < 2E_{1s}$  , which means that the energy of the two atoms bounded in this state is lower than the energy they would have if they were completely separated. This is the reason why we call this state **bonding state**. On the other hand  $E_- > 2E_{1s}$  , so the triplet state is called **antibonding state**. This behaviour can be explained by talking about the charge density for the electrons. Considering the square module of the wave function as a probability density it's possible to write:

$$\frac{\rho(\vec{x})}{(-e)} = \int d^3\vec{x}_1 |\psi_{\pm}(\vec{x}_1; \vec{x})|^2 + \int d^3\vec{x}_2 |\psi_{\pm}(\vec{x}; \vec{x}_2)|^2$$



Because of the symmetry of  $\psi_{\pm}$  for the exchange between 1 and 2 indexes, the two integrals have the same value. This leads to:

$$\frac{\rho(\vec{x})}{(-e)} = 2 \int d^3\vec{x}_1 |\psi_{\pm}(\vec{x}_1; \vec{x})|^2 = \frac{|u_A(\vec{x})|^2 + |u_B(\vec{x})|^2 \pm 2u_A(\vec{x})u_B(\vec{x})}{1 \pm S^2}$$

where + sign is for the singlet state and – for the triplet. For the former state, in the middle of the molecule there is an increase of charge density, related to a higher probability to find the electrons between the two nuclei and to a stronger bond. The latter state, on the contrary, implicates a decrease of charge density and also of probability to find the electrons in the middle of the nuclei.

This model predicts a distance between bound nuclei of  $1 \text{ \AA}$  when the experimental value is  $0,74 \text{ \AA}$ . For the binding energy the theoretical values is  $3,14 \text{ eV}$  and the experimental one is  $4,75 \text{ eV}$ . These results are indicative that the Heitler-London model has some intrinsic limits. In order to overcome these problems it's useful to change point of view and consider the Molecular Orbital model.

### 4.3 The MO-LCAO model

In this section we are going to present the MO-LCAO model for the molecular bond. The acronym stands for Molecular Orbital obtained from Linear Combination of Atomic Orbitals.

### 4.4 Hückel method

The Hückel method is used to evaluate energy levels disposition in a molecule, following the linear combination of atomic orbitals theory (MO-LCAO). Let us assume a linear chain of identical atoms. We'd have to solve the stationary Schrödinger equation  $Hu = \epsilon u$ . We do recall  $\alpha \equiv \langle u_j^{pz} | H | u_j^{pz} \rangle$  the diagonal elements of the Hamilton operator  $H$ , representing the energy of the isolated atom, and  $\beta \equiv \langle u_j^{pz} | H | u_j^{pz} \rangle$  its off-diagonal elements, describing a first-neighbor coupling. Therefore, we can fill a matrix with the following elements:  $H_{ii} = \alpha$ ,  $H_{i,j+1} = H_{i+1,j} = \beta$ .

Assuming that an atom couples significantly only with its first neighbor, all the other matrix elements are equal to zero. The only exception is represented by the case of circular molecules, where also the matrix element that correspond to the first/last atom interaction must be taken equal to  $\beta$ . Hence:

$$H = \begin{bmatrix} \alpha & \beta & & \\ \beta & \alpha & \beta & \textcircled{0} \\ & \ddots & \ddots & \ddots \\ \textcircled{0} & \beta & \alpha & \end{bmatrix}$$

Energy levels now can be found solving  $H - \epsilon K = 0$ , that is:



$$\beta \begin{vmatrix} \frac{\alpha-\epsilon}{\beta} & 1 & & \\ 1 & \frac{\alpha-\epsilon}{\beta} & 1 & \textcircled{0} \\ & \ddots & \ddots & \ddots \\ & & \textcircled{0} & 1 & \frac{\alpha-\epsilon}{\beta} \end{vmatrix} = 0$$

Recall  $\frac{\alpha-\epsilon}{\beta} = x$  and solve in order to find energy levels. Remember that generally  $\beta < 0$ , and it is called *hopping parameter*.

## 4.5 Term symbol of homopolar molecules

Given the electronic configuration of a molecule, we can define its term symbol as follows:

$$^{2S+1}\Lambda_{u/g}^{\pm}$$

Where:

- $S$  indicates the value of the total spin;
- $\Lambda$  is the symbol that represents the eigenvalue of  $L_z$ , fixed by the value of  $M_L^{tot}$ ;
- $g/u$ , from the German *gerade* (even) or *ungerade* (odd), indicates whether the molecule has a defined parity with respect to its centre;
- $\pm$  indicates the rotational symmetry within respect to a molecular plane: we use  $+$  when the molecule is symmetrical,  $-$  when it's not.

Values of  $\Lambda$  has to be chosen according to these rules, in analogy with atomic orbitals:

$M_L^{* tot}$	$\Lambda$
0	$\Sigma$
1	$\Pi$
2	$\Delta$
3	$\Phi$

As for atomic orbitals, in a diatomic molecule we can have two electrons in the  $\Sigma$  orbital, in the  $\Pi$  orbital six due to the three-fold degeneracy and so on. In the molecular case however, the energy disposition of the molecular orbitals is non trivial, but it has to be derived from case to case.



## Chapter 5

# Exercises

### 5.1 Notation

#### 5.1.1 Notation

- $\mathbf{L}$  denotes the *total* orbital angular momentum  $\mathbf{L} = \sum_i \mathbf{l}_i$ , with  $\mathbf{l}_i$  single-particle angular momentum. The eigenvalues of  $L^2$  are such that  $L^2|\varphi\rangle = \hbar^2 L(L+1)|\varphi\rangle$  and are simply denoted by the letter  $L$ . The eigenvalues of  $\mathbf{L}_z$  are such that  $\mathbf{L}_z|\varphi\rangle = \hbar m_L|\varphi\rangle$  and are simply denoted by the letter  $m_L$ .
- $\mathbf{S}$  denotes the *total* spin  $\mathbf{S} = \sum_i \mathbf{s}_i$ , with  $\mathbf{s}_i$  single-particle spin. The eigenvalues of  $S^2$  are such that  $S^2|\varphi\rangle = \hbar^2 S(S+1)|\varphi\rangle$  and are simply denoted by the letter  $S$ . The eigenvalues of  $\mathbf{S}_z$  are such that  $\mathbf{S}_z|\varphi\rangle = \hbar m_S|\varphi\rangle$  and are simply denoted by the letter  $m_S$ .
- $\mathbf{J}$  denotes the *total* angular momentum  $\mathbf{j}_i = \mathbf{l}_i + \mathbf{s}_i$ ,  $\mathbf{J} = \sum_i \mathbf{j}_i$ . The eigenvalues of  $J^2$  are such that  $J^2|\varphi\rangle = \hbar^2 J(J+1)|\varphi\rangle$  and are simply denoted by the letter  $J$ . The eigenvalues of  $\mathbf{J}_z$  are such that  $\mathbf{J}_z|\varphi\rangle = \hbar m_J|\varphi\rangle$  and are simply denoted by the letter  $m_J$ .
- Keep in mind the **addition rules for angular momenta**: let us call  $\mathbf{J}_1, \mathbf{J}_2$  two arbitrary angular momenta.

$$\mathbf{J}_{\text{tot}} = \mathbf{J}_1 + \mathbf{J}_2$$

$$m_{J_{\text{tot}}} = m_{J_1} + m_{J_2}$$

$$|J_1 - J_2| \leq J_{\text{tot}} \leq J_1 + J_2$$

$$-J_{\text{tot}} \leq m_{J_{\text{tot}}} \leq +J_{\text{tot}}$$

### 5.2 Atomic terms

#### LS scheme

The LS scheme is appropriate for light atoms ( $Z < 40$ ), when spin-orbit hamiltonian can be treated as a perturbation to the hartree hamiltonian with non spherical corrections. The good quantum number are fixed by the necessity of



diagonalizing non-spherical corrections hamiltonian and are  $n_i, l_i, L, S, m_L, m_S$ . Spin orbit effects will split these states according to their  $J$  value.

The problem of finding the atomic terms of a particular electronic configuration simply reduces to the determination of the total angular momentum  $\mathbf{L}$  eigenvalue and the total spin  $\mathbf{S}$ . The term is then of the form:

$$\begin{aligned} {}^{2S+1}L \quad L = S \quad \text{if } L = 0 \\ = P \quad \text{if } L = 1 \\ = D \quad \text{if } L = 2 \\ = F \quad \text{if } L = 3 \\ = \dots \end{aligned}$$

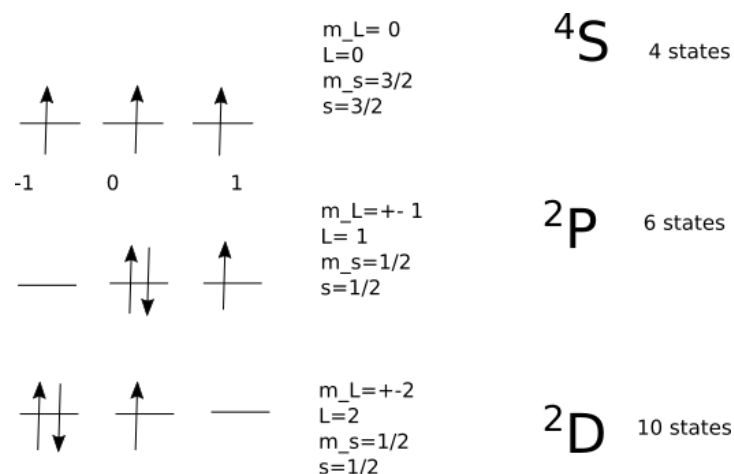
Let us discuss a concrete example in order to point out the general procedure to follow. Consider the atom  ${}^7N$ . An electronic configuration is an expression of the form  $1s^2 2s^2 2p^3$ , which specifies the number of electrons in each atomic orbital. The previous expression is the electronic configuration of nitrogen ground state. Another possible configuration for our atom is the excited one  $1s^2 2s^1 2p^3 3d^1$ . Now, how can we find the terms corresponding to these configurations?

- First of all remove the closed shells: they do not participate in the determination of the atomic terms
- Find the number of possible states for each atomic orbital. The reason for doing this will be clear in the following discussion. The number is easy to find with the little help of combinatorial analysis. Let us call  $g = 2 \cdot (2L + 1)$  and  $n$  the number of electrons in the  $L$ -orbital. Then

$$\text{number of states} = \binom{g}{n} = \frac{g!}{n!(g-n)!}$$

For the ground-state configuration  $1s^2 2s^2 2p^3$  the number of states for the  $2p$  orbital with 3 electrons in it is  $\frac{6!}{3!3!} = 20$

- Put the electrons in the orbitals and find the possible values of  $m_S, m_L$ . According to the values found you can deduce that of  $L$  and  $S$ , since  $-L \leq m_L \leq L$  and  $-S \leq m_S \leq S$ . In our example we find for the nitrogen ground state:



- Check that the number of states given by the terms is the same you previously calculated.
- The exercise may ask you to find the term which correspond to the lowest energy. According to **Hund's rules** :
  - The term with the maximum spin has the lowest energy
  - If there still are more terms, choose the one with the highest angular momentum
- For the ground-state terms the lowest energy term is thus  $^4S$
- In doing exercises remember that terms are symmetric with respect to the half-full level:  $p^4$  terms are the same of  $p^2$  and so on.
- Let us consider the excited configuration of nitrogen  $1s^2 2s^1 2p^3 3d^1$  . We now have three not completely full orbitals. If you are asked for this configuration's terms we can proceed as follows:
  - Find the terms for each orbital as previously done for the ground state configuration. We get:

Orbital	Terms	Number of states
$2s^1$	$^2S$	2
$2p^3$	$^4S \quad ^2P \quad ^2D$	$4 + 6 + 10 = 20$
$3d^1$	$^2D$	10

- • Sum the terms according to angular momenta addition rules:

Configuration	First terms	Second terms	Resulting terms
$2s^1 2p^3$	$^2S$	$^4S, ^2P, ^2D$	$^2S + ^4S \rightarrow ^3S, ^5S$ $^2S + ^2P \rightarrow ^3P, ^1P$ $^2S + ^2D \rightarrow ^3D, ^1D$
$2s^1 2p^3 3d^1$	$^2D$	$^3S, ^5S, ^3P, ^1P, ^3D, ^1D$	$^2D + ^3S \rightarrow ^2D, ^3S$ $^2D + ^5S \rightarrow ^3D, ^5S$ $^2D + ^3P \rightarrow ^4P, ^2P, ^4D, ^2D$ $^2D + ^1P \rightarrow ^2P, ^2D$ $^2D + ^3D \rightarrow ^2S, ^4S, ^2P, ^4P, ^2D, ^4D, ^2F, ^4F$ $^2D + ^1D \rightarrow ^2S, ^2P, ^2D$

- If you are asked for the term with lowest energy use Hund's rules to select the term. In this example it's  $^6D$  . However if the exercise do not ask to find every term you can simplify the problem selecting in each orbital the lowest energy term and then adding just these terms



- If we consider spin-orbit effects as a perturbation to the hamiltonian we have to introduce an additional index representing the total angular momentum eigenvalue,  $J$ . For the ground state term  ${}^4S_{\frac{3}{2}}$   $-\frac{3}{2} \leq J \leq \frac{3}{2} + 0 = \frac{3}{2}$  and we can write the term as:

$${}^4S_{\frac{3}{2}}$$

For the excited term  ${}^6D$   $L = 2, S = \frac{5}{2}$  so that  $\frac{1}{2} \leq J \leq \frac{9}{2}$  and the possible terms are:

$${}^6D_{\frac{1}{2}} \quad {}^6D_{\frac{3}{2}} \quad {}^6D_{\frac{5}{2}} \quad {}^6D_{\frac{7}{2}} \quad {}^6D_{\frac{9}{2}}$$

Which of these terms has the lowest energy? The **third Hund's rule** saves us from complex calculations: if the shell is less than half-full the lowest energy term is the one with the lowest value of  $J$ , otherwise the one with the highest value of  $J$ . In our example the shell less than half-full so the lowest energy term is  ${}^6D_{\frac{1}{2}}$ .

### JJ scheme

For heavy atoms ( $Z > 40$ ) the spin-orbit effects can be stronger than non-spherical corrections, so we must include  $H_{SO}$  in the hartree hamiltonian and then treat non-spherical corrections as a perturbation. The good quantum numbers describing the single-particle unperturbed states are  $n, l, j, m_j$ . In order to take into account non-spherical corrections we then have to find  $J, M_J$ . Let us discuss the general procedure through a concrete example. Consider the lead atom  ${}^{82}Pb$  in the ground state  $[Xe]4f^{14}5d^{10}6s^26p^2$ . In the following discussion we'll not take into account 4f orbital.

- Find the  $j$ 's for each orbital corresponding to a single electron placed in it:

Hartree orbital	l	s	j	jj orbital	max number of electrons
5d	2	$\frac{1}{2}$	$\frac{3}{2}, \frac{5}{2}$	$d_{\frac{3}{2}} \quad d_{\frac{5}{2}}$	4 6
6s	0	$\frac{1}{2}$	$\frac{1}{2}$	$s_{\frac{1}{2}}$	2
6p	1	$\frac{1}{2}$	$\frac{1}{2}, \frac{3}{2}$	$p_{\frac{1}{2}} \quad p_{\frac{3}{2}}$	2 4

- Place the electrons in the jj-orbitals so found: 10 electrons in 5d, 2 in 6s, 2 in 6p

$$[5d_{\frac{3}{2}}^4 5d_{\frac{5}{2}}^6 6s_{\frac{1}{2}}^2 6p_{\frac{1}{2}}^2 6p_{\frac{3}{2}}^0]$$

- Find  $J$ -values for the shell which is not completely full. The others would give  $J=0$  and do not contribute. In this case we have to find  $J$  for the shell  $6p^2 \rightarrow 6p_{\frac{1}{2}}^2, 6p_{\frac{3}{2}}$ . We can have just  $m_J = 0$  so that  $J = 0$
- If you're asked for the lowest energy configuration choose the  $J$ -value according to Hund's third rule. Here we have just one possible value of  $J$  so there is no need for doing this. However we write the lowest energy state for lead in the jj-scheme in order to highlight the notation:

$$\left( [5d_{\frac{3}{2}}^4 5d_{\frac{5}{2}}^6 6s_{\frac{1}{2}}^2 6p_{\frac{1}{2}}^2 6p_{\frac{3}{2}}^0] \right)_0$$



Let us discuss a more complex situation with 3 electrons in the  $d_{\frac{5}{2}}$  jj-orbital:  $d_{\frac{3}{2}}^4 d_{\frac{5}{2}}^3$ . There are  $\binom{6}{3} = 20$  states corresponding to this configuration. Keeping in mind that for Pauli's exclusion principle we can have just one electron with fixed  $l, j, m_j$  we have these possibilities:

$m_j$	-5/2	-3/2	-1/2	1/2	3/2	5/2	$m_J$
	◻●	◻●	◻●	◻	◻	◻	9/2
	10 states						
	◻●	◻	◻●	◻●	◻	◻	5/2
	6 states						
	◻	◻●	◻●	◻●	◻	◻	3/2
	4 states						

We have selected time by time the configurations with the highest  $m_J$ . Indeed, rigorously speaking if we find  $m_J = \frac{5}{2}$  we can just say that  $J \geq m_J$ . However since we have already counted the states with  $J = \frac{9}{2}$  and no other value of  $J$  between  $\frac{9}{2}$  and  $\frac{5}{2}$  is allowed because of Pauli's exclusion principle we can say that  $m_J = \frac{5}{2} \Rightarrow J = \frac{5}{2}$ . Counting the states allows us to verify that these configurations exhaust the multiplicity of  $d_{\frac{5}{2}}^3$

We then have these possible terms:

$$\left( d_{\frac{5}{2}}^3 \right)_{\frac{9}{2}, \frac{5}{2}, \frac{3}{2}}$$

If we are now looking for the lowest energy term we take into account that a  $d$  orbital can have a maximum of 10 electrons so that with 7 electrons we are in a more than half-full shell and we have to pick the highest value of  $J$ . The lowest energy term is thus

$$\left( d_{\frac{5}{2}}^3 \right)_{\frac{9}{2}}$$

### 5.3 Molecular terms

Molecular terms refer to MO-LCAO theory of molecular orbitals.

#### Homonuclear molecules

A molecule is said to be homonuclear if it's made of two identical atoms. For this kind of molecules there are special symmetries in the hamiltonian:





- symmetry with respect to the center :  $[H, P] = 0$
- symmetry with respect to the bound axis, which we choose to be the z axis:  
 $[H, L_z] = 0$
- symmetry with respect to every plane orthogonal to the bound axis :  $[H, P_\pi] = [H, P_{xy}] = 0$  . However  $[L_z, P_\pi] \neq 0$  and we can't construct a C.S.C.O of eigenstates common to  $H, L_z, P, P_\pi$  . We have to choose  $H, L_z, P$  or  $H, L_z, P_\pi$  , but since  $L_z, P_\pi = L_z P_\pi + P_\pi L_z = 0$  ( $L_z$  anticommutes with  $P_\pi$ ) the eigenstates of  $L_z$  with  $m = 0$  are also eigenstates of  $P_\pi$  and we can classify these states with an additional index

A molecular orbital is a linear combination of atomic orbitals of atom (1) with that of atom (2) and is described by a greek small letter identifying m-value plus a subscript for the parity,  $g$  for even orbitals or  $u$  for odd orbitals.

$$\begin{aligned}
 m = 0 &\rightarrow \sigma \\
 m = \pm 1 &\rightarrow \pi \\
 m = \pm 2 &\rightarrow \delta \\
 &\dots \\
 \text{even orbitals} & \quad [\sigma, \pi, \dots]_g \\
 \text{odd orbitals} & \quad [\sigma, \pi, \dots]_u
 \end{aligned}$$

Furthermore we have to keep in mind that every pair of atomic orbitals gives rise, when combined, to a bonding orbital and an antibonding orbital (denoted with a superscript  $*$  ). Once we have found molecular orbitals we fill them with the electrons. The **molecular terms** are then given by the assignment of the total angular momentum projection  $M_z$  ,a superscript on the left for spin multiplicity and the subscript for the overall parity, plus the  $\pm$  superscript for  $\Sigma$  terms.

$$^{2s+1} [\Sigma, \Pi, \Delta, \Phi, \dots]_{g/u}$$

Let us discuss an example, the  $C_2$  molecule.

- Write the expression for each atom electronic configuration:  $C_{\text{ground state}} = [He]2s^2 2p^2$
- Since  $[H, P] = 0$  and parity is governed by  $l$  -values we can combine atomic orbitals with  $\mathbf{l} = \mathbf{l}'$  . Furthermore since  $[H, L_z] = 0$  we must have  $\mathbf{m} = \mathbf{m}'$  . Thus we are allowed to combine  $2s_{C_1}$  with  $2s_{C_2}$  and  $2p_{C_1}$  with  $2p_{C_2}$  .

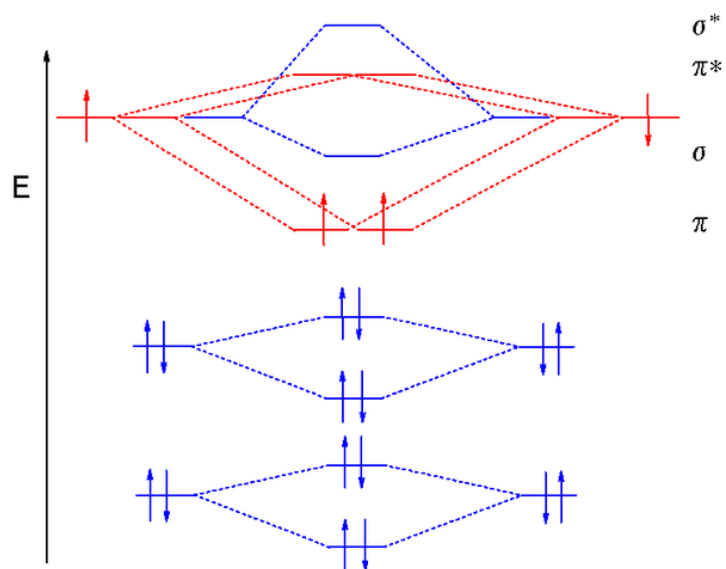
$$\begin{aligned}
 2s_1 + 2s_2 &\rightarrow 1\sigma_g \quad 1\sigma_u^* \\
 2p_{z1} + 2p_{z2} &\rightarrow 2\sigma_g \quad 2\sigma_u^*
 \end{aligned}$$

(linear combination of  $p_{x1}$  and  $p_{y1}$ ) + (linear combination of  $p_{x2}$  and  $p_{y2}$ )  $\rightarrow 1\pi_u \quad 1\pi_g^*$

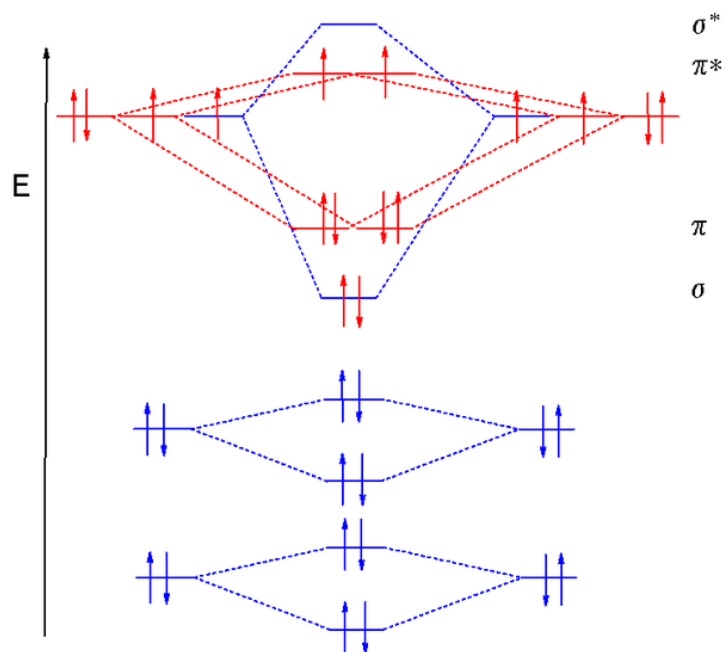
$$\pi_u \quad \underbrace{\quad \rightarrow \quad}_{\text{composed of}} \quad \pi_u^+ \quad m = 1 \quad + \quad \pi_u^- \quad m = -1$$



- Put the electrons in the so-found molecular orbitals starting from the lowest energy orbital. There isn't a general rule which regulates the energy scale of molecular orbitals. However for homonuclear molecules experiments show that:



- energy diagram of  $B_2$ . The order of filling is the same for  $C_2$ ,  $N_2$



- energy diagram of  $O_2$ . The order of filling is the same for  $F_2$

In our example the electronic configuration of  $C_2$  is then



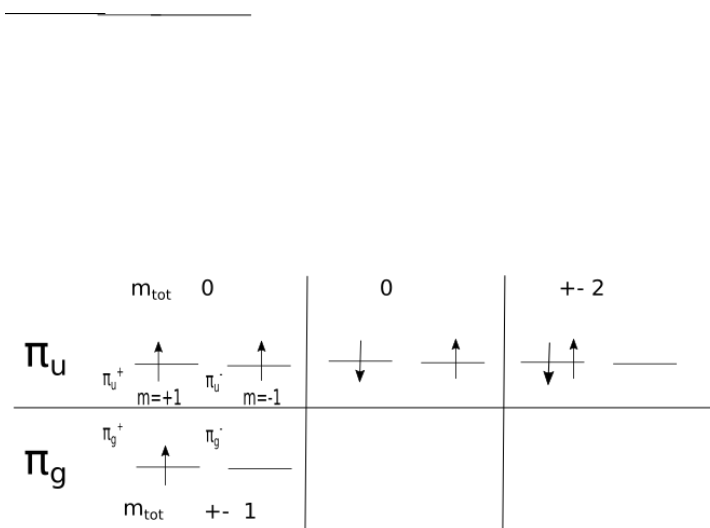
$$[He]1\sigma_g^2 1\sigma_u^2 1\pi_u^4$$

- Closed shells do not contribute to the molecular terms, so consider just not completely full shells. Find the possible values of  $M = \sum m_i$  and  $s$  looking at the allowed configurations. For each configuration find the corresponding  $g/u$  and, eventually,  $\pm$  indexes with the help of the following rules:

$$\begin{aligned}
 g \cdot u &= u \cdot g = u \\
 g \cdot g &= u \cdot u = g \\
 + \cdot - &= - \cdot + = - \\
 + \cdot + &= - \cdot - = +
 \end{aligned}$$

. The molecular term for  $C_2$  ground state is then  $^1\Sigma_g^+$ .

Let us discuss the problem of finding molecular terms for the excited configuration of  $C_2^+$ :  $1\sigma_g^2 1\sigma_u^2 1\pi_u^2 1\pi_g^1$ . We neglect the  $\sigma$ 's orbitals since they're full. Possible configurations are:



So that we have for  $\pi_u$  the terms (following the order of the image):  $^3\Sigma_g^+$   $^1\Sigma_g^+$   $^1\Delta_g$ . For  $\pi_g^*$  there is just one term that is  $^2\Pi_g$ . Now we add each term corresponding to  $\pi_u$  possible configurations to the term related to  $\pi_g^*$ , and we obtain:

$$\begin{aligned}
 ^2\Pi_g + ^3\Sigma_g^+ &\rightarrow \underbrace{^4\Pi_g}_{8\text{states}} \quad \underbrace{^2\Pi_g}_{4\text{states}} \\
 ^2\Pi_g + ^1\Sigma_g^+ &\rightarrow \underbrace{^2\Pi_g}_{4\text{states}} \\
 ^2\Pi_g + ^1\Delta_g &\rightarrow \underbrace{^2\Phi_g}_{4\text{states}}, \quad \underbrace{^2\Pi_g}_{4\text{states}}
 \end{aligned}$$



The number of states is easily found considering that each term (except  $\Sigma$ 's) represents 2 possible values of  $M$  so that the total states are  $2 \cdot (2s + 1)$  for each non- $\Sigma$  term and  $2s + 1$  for  $\Sigma$ 's terms. Let us verify our result. The configuration  $1\pi_u^2 1\pi_g^1$  corresponds to  $\binom{4}{2} \cdot \binom{4}{1} = 6 \cdot 4 = 24$  states, which is just the number found.

### Non-homonuclear molecules

A molecule is said to be non-homonuclear if it's made of two atoms of different species. For this kind of molecules there are less symmetries than in homonuclear molecules:

- There isn't symmetry with respect to the center :  $[H, P] \neq 0$
- The symmetry with respect to the bound axis, which we choose to be the z axis, is still present:  $[H, L_z] = 0$
- The symmetry with respect to every plane orthogonal to the bound axis is still present and the same considerations hold.

The procedure for finding molecular orbitals and molecular terms is almost the same sketched for homonuclear molecules. The main difference is:

- Since symmetry with respect to the center has been broken there is no superscript  $g/u$  neither in molecular orbitals nor in molecular terms. Furthermore we can combine **also** atomic orbitals with  $l \neq l'$  if they have  $\mathbf{m} = \mathbf{m}'$ . For example  $2s$  and  $2p_z$  can mix together. Because of the energy difference between different  $n$  shells and in order to simplify calculations we will not assume  $2s - 2p$  (and other analogue pairs) mixing to be possible if one of these orbitals is completely full.



## Chapter 6

# Appendix

### 6.1 Some useful constants

- Bohr radius  $a_0 = 5.29 \times 10^{-11} m = 0.525 \text{ \AA}$
- Rydberg's constant  $R_y = 13.6 eV$
- Plank's constant  $h = 6,62 \times 10^{-34} Js$
- Electronvolt  $1eV = 1,602 \times 10^{-19} J$
- Mass of the proton  $m_p = 1,7 \times 10^{-27} Kg$
- Mass of the electron  $m_e = 9,1 \times 10^{-31} Kg \simeq m_p/1800$
- Boltzmann's constant  $k_B = 1,38 \times 10^{-23} JK^{-1}$
- Fine-structure constant  $\alpha = \frac{1}{4\pi\epsilon_0} \frac{e^2}{\hbar c} \simeq \frac{1}{137}$

### 6.2 Fermi energies, temperatures and velocities

### 6.3 Magnetic susceptibility and Curie's law

If an atom is exposed to an external magnetic field, its energy levels will be splitted due to (at least) the Zeeman effect. Thus the hamiltonian of the system is\* [1]:

$$\hat{H} = \frac{e}{m} B \hat{S}_z$$

We want to evaluate  $C_v = \frac{d\langle E \rangle}{dT}$  and  $\langle \mu_z \rangle$ . Being  $\Delta$  the energy levels split, we have:

$$Z = e^{\beta\Delta} + e^{-\beta\Delta}$$



Element	Fermi Energy [eV]	Fermi Temperature [ $\times 10^4$ K]	Fermi Velocity [ $\times 10^6$ m/s]
Li	4.74	5.51	1.29
Na	3.24	3.77	1.07
K	2.12	2.46	0.86
Rb	1.85	2.15	0.81
Cs	1.59	1.84	0.75
Cu	7.00	8.16	1.57
Ag	5.49	6.38	1.39
Au	5.53	6.42	1.40
Be	14.3	16.6	2.25
Mg	7.08	8.23	1.58
Ca	4.69	5.44	1.28
Sr	3.93	4.57	1.18
Ba	3.64	4.23	1.13
Nb	5.32	6.18	1.37
Fe	11.1	13.0	1.98
Mn	10.9	12.7	1.96
Zn	9.47	11.0	1.83
Cd	7.47	8.68	1.62
Hg	7.13	8.29	1.58
Al	11.7	13.6	2.03
Ga	10.4	12.1	1.92
In	8.63	10.0	1.74
Tl	8.15	9.46	1.69
Sn	10.2	11.8	1.90
Pb	9.47	11.0	1.83
Bi	9.90	11.5	1.87
Sb	10.9	12.7	1.96

Using (Canonical ensemble) we get:

$$\langle E \rangle = -\Delta \tanh(\beta\Delta)$$

Hence:

$$C_v = -\frac{1}{kT^2} \frac{\partial \langle E \rangle}{\partial \beta}$$

Being  $\vec{\mu} = -\frac{e}{2m}g\vec{S}$ , where  $g$  is called *Lande factor* and it takes on the value  $g \simeq 2$  for the spin operator, we get:

$$\begin{aligned} \langle \mu_z \rangle &= \mu_B \frac{e^{-\beta\Delta}}{Z} - \mu_B \frac{e^{\beta\Delta}}{Z} = -\mu_B \tanh(\beta\Delta) \simeq -\mu_B \beta\Delta \\ \Rightarrow \langle \mu_z \rangle &= \frac{\mu_B^2 B}{ZkT} \end{aligned}$$

In a more general case, that is if we do consider both the spin and the angular momentum, we have:



$$\hat{H} = g_{LSJ} \frac{e}{2m} \underline{B} \underline{J}$$

Since this new hamiltonian is of the form  $\hat{H} = -\underline{\mu}_{eff} \underline{B}$ , we have that  $\underline{\mu}_{eff} = -g_{LSJ} \frac{e}{2m} \underline{J}$ . Hence  $\mu_{eff}^2 = g_{LSJ}^2 \mu_B^2 j(j+1)$  and thus  $\mu = \frac{\mu_{eff}^2 B}{3kT}$ . In conclusion we get the *Curie's law*:

$$\chi = \frac{\mu_{eff}^2}{3kT} = \frac{C}{T}$$

Where the quantity  $\chi$  is called *magnetic susceptibility*, while  $C = \frac{\mu_{eff}^2}{3k}$  is the Curie constant. Actually all these quantities have to be defined per number of particles per unit of volume, that is:

$$\chi = \frac{N \mu_{eff}^2}{V 3kT} = \frac{C}{T}$$

This is a quantum result, but it can be derived classically. In this case we'd have:

$$\langle \mu_z \rangle = \mu \left( \coth(\gamma) - \frac{1}{\gamma} \right)$$

Being  $\gamma = \beta \mu B$ , this function is called *Langevin function*.

[1] We do have:  $\hat{H} = -\vec{\mu} \vec{B}$ . Being  $\vec{\mu} = -\frac{e}{2m} g \vec{S} \vec{S}$  (if we do consider only spin), and  $g$  is the Lande (or gyromagnetic) factor which takes on the value  $g = 2$  for  $\vec{S}$ . Concluding that:  $\hat{H} = \frac{eB}{m} \hat{S}_z$ .

## 6.4 Magnetism and Lande factor

When an atom is placed in a magnetic field region, we can have two possibilities:  $B_{ext} \gg B_{int}$ , when the external field is way greater than the internal field produced by the motion of electrons, and viceversa  $B_{int} \gg B_{ext}$ . These two cases give two different hamiltonians of perturbation. Hence we do distinguish the normal and anomalous Zeeman effects:

- Normal Zeeman effect\* [1]:

$$\hat{H} = \frac{eB_{ext}}{2m} (L_z + 2S_z) \Rightarrow E_{M_L, M_S} = \frac{eB_{ext} \hbar}{2m} (M_L + 2M_S)$$

- Anomalous Zeeman effect\* [2]:

$$\langle \hat{H} \rangle = \frac{eB}{2m} \langle J_z \rangle \underbrace{\left[ 1 + \frac{\langle \hat{S} \hat{J} \rangle}{\langle \hat{J}^2 \rangle} \right]}_{\text{Lande factor}}$$



$$\Rightarrow E_{J^2, L^2, S^2} = \frac{eB\hbar^2}{2m} M_J \left[ 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} \right]$$

In exercises, unless it is specified, you can not determine whether a given  $B_{ext}$  is greater than  $B_{int}$  or not and so you have to evaluate both energy split terms and . In conclusion we want to remember the hamiltonian of the spin-orbit coupling:

$$\hat{H}_{SO} = \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{m_e^2 c^2} \frac{\mathbf{S}\mathbf{L}}{r^3}$$

And its energy spectrum, in the  $n, l, m$  basis, is:

$$E_{n,l} = -\frac{1}{2} m_e c^2 (Z\alpha)^2 \left[ \frac{2(Z\alpha)^2}{n^2(2l+1)} - \frac{3(Z\alpha)^2}{4n^4} \right]$$

- [1] Spin-orbit effect can be neglected. Hence  $H_B$  is a perturbation for a normal hydrogen-like hamiltonian. Hence here we work in the  $|L^2, M_L\rangle |S^2, M_S\rangle$  basis.
- [2] Spin-orbit can not be neglected, hence it has to be considered as part of the global hamiltonian to which  $H_B$  is a perturbation. Hence here we work in the  $|J^2, M_J, L^2, S^2\rangle$  basis.





## Chapter 7

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