Notes on atomic and molecular energy levels and fundaments of spectroscopy

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1   The hydrogenoid atoms spectrum

The hydrogen atom is a simple enough system to be fully studied analytically. In particular is possible to write down a Schrödinger equation for the electron, and find analytically the eigenfunctions:

$$\left[-\hbar^2 \frac{\nabla^2}{2m} + V(r)\right] \varphi(\vec{r}) = E\varphi(\vec{r}) \tag{1}$$

The solving technique is to write down the equation in spherical coordinates (since the potential has spherical symmetry) :

$$\left[\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]\psi(r,\theta,\varphi) + \tag{2}$$

$$+ \left[E - V(r)\right]\psi(r,\theta,\varphi) = 0 \tag{3}$$

and using the *separation of variables*

$$\psi(r,\theta,\varphi) = R(r)\,Y(\theta,\varphi)$$

we finally have:

$$\psi_{nlm}(r,\theta,\varphi) = R_{nl}(r)\,Y_{lm}(\theta,\varphi)$$

where

$$R_{nl}(r) = -\left\{\left(\frac{2Z}{na_\mu}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}\right\}^{1/2} e^{-\rho/2}\,\rho^l\,L_{n+l}^{2l+1}(\rho) \tag{4}$$

with

$$\rho = \frac{2Z}{na_\mu}r$$
$$a_\mu = \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2} = a_B\frac{m}{\mu}$$
$$a_B = \frac{4\pi\varepsilon_0\hbar^2}{me^2} \quad \text{(Bohr radius)}$$
$$\mu = \frac{mM}{m+M} \quad \text{(reduced electron mass)}$$

and where we used the *Laguerre polynomials* $L_{n+l}^{2l+1}(\rho)$:

$$L_{n+l}^{2l+1}(\rho) = \sum_{k=0}^{n_r} \frac{[(n+l]^2}{(n_r-k)!\,(2l+1+k)!} \frac{\rho^k}{k!}$$

with $n_r = n - l - 1$.

For the angular part, we have just the *spherical harmonics*:

$$Y_l^m(\theta, \varphi) = \sqrt{\frac{2\,l+1}{4\pi} \frac{(l-m)!}{(l+m)!}}\; P_l^m(\cos\theta)\, e^{i\,m\,\varphi} \tag{5}$$

in wich we find the Legendre functions $P_l^m(x)$:

$$P_l^m(x) = \frac{(-1)^m}{2^l\,l!}\,(1-x^2)^{m/2}\frac{d^{l+m}}{dx^{l+m}}\,(x^2-1)^l$$

For the eigenvalues we have:

$$E_n = -\frac{Z^2\,e^2}{2\,a_B\,n^2} \tag{6}$$

1.1   Ground state

Using the general formula, for n=1 we have the ground state:

$$\psi_{000}(r,\theta,\varphi) = \frac{1}{\sqrt{\pi}}\;\left(\frac{Z}{a_B}\right)^{3/2}\,e^{-\frac{Z}{a_B}\,r} \tag{7}$$

2   Angular momenta of hydrogenoid atoms

It is possible to show that (in general) the eigenvalues of the energy (Hemiltonian) have *degeneracy*: more than one of those eigenfunctions (eigenvectors) of the system, orthogonal to each other, have the same eigenvalue. In other words, the eigenspaces associated to each eigenvalue of the energy have (in general) a dimensionality bigger than one.

To completely resolve this degeneracy is sufficient to consider other three observables, that are "constants of motion" of the system, so that they have simultaneous eigenfunctions with energy. The three other observables are the magnitude of the (orbital) angular

momentum, it's projection on a direction (conventionally the z axis of a cartesian co-ordinate system), and the projection (usually on the same axis) of the spin angular momentum of the electron.

This means that the eigenfunctions of the Hamiltonian are also eigenfunctions of these other three operators.

Using these three operators the degeneracy is resolved: specifying three eigenvalues of these three observables, we univocally specify a single eigenfunction of the system (i.e. a monodimentional eigenspace).

Since the system is such that the spectra of those observables are discrete, we can specify the (discrete) eigenvalues using *quantum numbers*.

It is worth to point out that the angular momentum operators have a degeneracy on their own, and only considering all the operators the degeneracy is resolved.

2.1 Recalls about angular momenta

Let's introduce the operators that describe the orbital angular momentum, writing the squared modulus in terms of the cartesian components:

$$L^2 = L_x^2 + L_y^2 + L_z^2 \tag{8}$$

with the following commutation relations, typical of the angular momenta:

$$
\begin{aligned}
[L_x, L_y] &= i\hbar L_z & (9)\\
[L_y, L_z] &= i\hbar L_x & (10)\\
[L_z, L_x] &= i\hbar L_y. & (11)
\end{aligned}
$$

Using the Levi-Civita tensor $\epsilon_{i,j,k}$ defined as:

$$
\epsilon_{i,j,k} \equiv
\begin{cases}
+1 & \text{if } (i,j,k) = (x,y,z) \text{ or } (y,z,x) \text{ or } (z,x,y) & \text{(i.e. cyclic order)}\\
-1 & \text{if } (i,j,k) = (z,x,y) \text{ or } (x,z,y) \text{ or } (y,x,z) & \text{(i.e. inverted cyclic order)}\\
0 & \text{if } i = j \text{ or } j = k \text{ or } k = i & \text{(i.e. any other order)}
\end{cases}
\tag{12}
$$

we can summarize the commutation relations as

$$[L_i, L_j] = \epsilon_{i,j,k} i\hbar L_k. \tag{13}$$

It's easy to show that L^2 commutes with all the components:

$$\left[L^2, L_i\right] = 0 \quad \forall i = x, y, z \tag{14}$$

These two operators commute, so they have common eigenvectors that we denote with $|l, m\rangle$:

$$L^2|l, m\rangle = l(l+1)\hbar^2|l, m\rangle \tag{15}$$

$$L_z|l, m\rangle = m\hbar|l, m\rangle \tag{16}$$

Once we define the useful "step operators" as follow:

$$L_+ \equiv L_x + iL_y \tag{17}$$
$$L_- \equiv L_x - iL_y \tag{18}$$

with the properties:

$$L_+|l, m\rangle = \hbar\sqrt{(l-m)(l+m+1)}\,|l, m+1\rangle \tag{19}$$
$$L_-|l, m\rangle = \hbar\sqrt{(l+m)(l-m+1)}\,|l, m-1\rangle \tag{20}$$

it's possible to show the following properties:

- $l \in \{0, \frac{1}{2}, 1, \frac{3}{2}, 2, \cdots\}$

- $m \in \{-l, -l+1, \cdots l\}$

put it in words:

- l can take integer or "half-odd" numbers

- once l is fixed, m can take the $2l + 1$ values between $-l$ and l, starting with $-l$ and adding 1 up to l.

From this we can see that in general the eigenvalues of L have a degeneracy of $2l + 1$ with respect to L_z.

2.1.1   Multiplets

If we fix the quantum number j, i.e. the eigenvalue of J^2, we have an eigenspace of eigenvectors of J^2 that have all the $2j+1$ possible eigenvalues of J_z with $-j \le m \le +j$. The dimention of this eigenspace, let's call it V_j, is $2j + 1$, and its eigenbase, i.e. the set of the $2j + 1$ orthogonal eigenvectors $|j, m\rangle$ with $-j \le m \le +j$ will be called a *multiplet*. If $j = 0 \Leftrightarrow 2j + 1 = 1$ we have a *singlet*, if $j = 1/2 \Leftrightarrow 2j + 1 = 2$ we have a *doublet*, if $j = 1 \Leftrightarrow 2j + 1 = 3$ we have a *triplet*, and so forth. In the following we will deal with angular momenta that are the sum of several angular momenta (we well use the term "total angular momentum"). For example we will deal with the total angular momentum of a system made up of several particles, each of them with it's angular momentum. The definition of multiplet will hold for the total angular momentum as well.

2.2   Spin

2.2.1   Orbital and spin angular momentum

The Stern-Gerlak experiment lead the physicists to conclude that electrons possess an "intrinsic" angular momentum, called *spin*. Intuitively the spin can be thought as the angular momentum associated to the rotation of the particle around it's center. But this is not correct, for various reasons. First, in the quantum mechanics picture, particles as electrons have no extension, i.e. they are represented as mathematical points, so they cannot rotate around themselves. Another difference between the spin and an "ordinary"

angular momentum is that the component of the spin shows, in Stern-Gerlak and similar experiments, to be able to take only two different values. This means that the modulus of the spin has only one possible eigenvalue, the one with quantum number $s = \frac{1}{2}$. The $s = \frac{1}{2}$ value is peculiar of electrons, but for all the particles we have that the modulus of the spin has only one fixed value. Another contradiction (that led Pauli to initially dislike the idea of electron's spin) is that if we consider the intensity of the spin the hypothetic surface of the electron should move with a faster-than-light velocity. So the spin has to be seen as a peculiar angular momentum *associated* to the point-like particle.

2.2.2 General notation

Let's introduce the notation related with the spin. Here we have to remember that the spin is not a proper angular momentum, and is not related to a "rotation" of the electron. So we cannot represent it with operators on the $L^2(\mathbb{R}^3)$ Hilbert space that we use for the wave functions. We need to introduce a separate vector space, and the spin will be represented by an operator S on the vectors χ of this space. The state of a system "with spin" will be the tensor product of a vector of the "usual" Hilbert space $L^2(\mathbb{R}^3)$, and of a vector of this other vector space. This gives us the idea of the spin as an additional, intrinsic property of the particles. On the other hand the spin is an angular momentum: for example it's operators have the same commutation rules (13) and (14) we have seen in general for the angular momenta, and they have a similar spectrum degeneracy.

We will represent the squared modulus of the spin and it's components as:

$$S^2 = S_x^2 + S_y^2 + S_z^2 \tag{21}$$

with the usual commutation relations typical of the angular momenta:

$$[S_i, S_j] = \epsilon_{i,j,k} i\hbar S_k. \tag{22}$$

and

$$[S^2, S_i] = 0 \quad \forall i = x, y, z \tag{23}$$

In general the eigenvectors equations are:

$$S^2 \chi_{s,m_s} = s(s+1)\hbar^2 \chi_{s,m_s} \tag{24}$$

$$S_z \chi_{s,m_s} = m_s \hbar \chi_{s,m_s} \tag{25}$$

and the "step operators" are defined as:

$$S_+ \chi_{s,m_s} \equiv S_x + iS_y \tag{26}$$

$$S_- \chi_{s,m_s} \equiv S_x - iS_y \tag{27}$$

$$S_+ \chi_{s,m_s} = \hbar\sqrt{(s-m_s)(s+m_s+1)}\,\chi_{s,m_s+1} \tag{28}$$

$$S_- \chi_{s,m_s} = \hbar\sqrt{(s+m_s)(s-m_s+1)}\,\chi_{s,m_s-1} \tag{29}$$

Since each single particle has only a possible fixed value for the spin's modulus, the separate spin's vector space is the *multiplet* subspace we have discussed in general for angular momenta, relative to the same quantum number s of S^2 and all the possible $2s+1$ values of S_z's quantum number m_s.

2.2.3   Spin 1/2 particles

What we have seen since now is about a generic particle with spin. Let's now consider the specific case of electrons, that have $s = \frac{1}{2}$. In this case the spin's vector space (i.e the only *multiplet*) will have dimension $2s+1 = 2$, and the possible value for m_s will be $+\frac{1}{2}$ and $-\frac{1}{2}$. Let's denote the elements of the spin's vector space as two-elements columns, and it's orthonormal base as:

$$\begin{aligned} \chi_+ &\equiv \begin{pmatrix} 1 \\ 0 \end{pmatrix} \\ \chi_- &\equiv \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \end{aligned} \tag{30}$$

where:

$$S_z \chi_+ = +\frac{1}{2}\hbar \chi_+ \tag{31}$$

$$S_z \chi_- = -\frac{1}{2}\hbar \chi_- \tag{32}$$

(remember that this vector space is the *multiplet* of the spin angular momentum).
The *step operators* in this space will act as follow:

$$\begin{aligned} S_+ \chi_+ = 0 \quad &; \quad S_+ \chi_- = \hbar \chi_+ \\ S_- \chi_+ = \hbar \chi_- \quad &; \quad S_- \chi_- = 0 \end{aligned} \tag{33}$$

2.2.4 Pauli martices

Let's work out the matricial representation of the spin operators S_x, S_y and S_z using as reference base $\{\chi_+, \chi_-\}$:

$$S_+ = \begin{pmatrix} \langle \chi_+|S_+|\chi_+\rangle & \langle \chi_+|S_+|\chi_-\rangle \\ \langle \chi_-|S_+|\chi_+\rangle & \langle \chi_-|S_+|\chi_-\rangle \end{pmatrix} = \begin{pmatrix} 0 & \hbar \\ 0 & 0 \end{pmatrix} = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \tag{34}$$

$$S_- = \begin{pmatrix} \langle \chi_+|S_-|\chi_+\rangle & \langle \chi_+|S_-|\chi_-\rangle \\ \langle \chi_-|S_-|\chi_+\rangle & \langle \chi_-|S_-|\chi_-\rangle \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ \hbar & 0 \end{pmatrix} = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}. \tag{35}$$

and since

$$\begin{cases} S_+ \equiv S_x + iS_y \\ S_- \equiv S_x - iS_y \end{cases} \Rightarrow \begin{cases} S_x = \frac{1}{2}\left(S_+ + S_-\right) \\ S_y = -\frac{i}{2}\left(S_+ - S_-\right) \end{cases} \tag{36}$$

we have

$$S_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \tag{37}$$

$$S_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}. \tag{38}$$

About S_z, we have chosen as base vector it's eigenvectors (cfr. (31) and (32)), so it's matricial representation will be a diagonal matrix with eigenvalues as diagonal elements:

$$S_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{39}$$

If we define the *pauli matrices* as:

$$\begin{cases} \sigma_x \equiv \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \\ \sigma_y \equiv \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \\ \sigma_z \equiv \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \end{cases} \tag{40}$$

we can write:

$$\begin{cases} S_x = \frac{\hbar}{2}\sigma_x \\ S_y = \frac{\hbar}{2}\sigma_y \\ S_z = \frac{\hbar}{2}\sigma_z \end{cases} \tag{41}$$

Pauli matrices diplay the following properties:

- $\forall i, \quad \sigma_i^2 = \mathbb{I}$

- $[\sigma_i, \sigma_j] = 2\, i\, \epsilon_{i,j,k}\, \sigma_k.$

The Pauli matrices are a basis for the space of *all the 2×2 matrices with trace equal zero*. If we add the identity 2×2 matrix, these four matices

$$\sigma_x \equiv \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad ; \quad \sigma_y \equiv \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad ; \quad \sigma_z \equiv \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad ; \quad \sigma_{\mathbb{I}} \equiv \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{42}$$

are a basis for the space of all the 2×2 matrices.

3   Addition of angular momenta

When we deal with atoms with more than one electron, we have to take into account the total orbital momentum and the total spin. Nevertheless, is useful to keep using the notation that comes from the hydrogen atom. So it is important to understand the relation between the "addenda" angular momenta and spins (i.e. the ang. mom. and spin of the single electrons) and the total ones.

We will start considering a generic angular momentum that is the sum of only two other ang. mom.:

$$\vec{J} = \vec{J_1} + \vec{J_2} \tag{43}$$

The total angular momentum is an angular momentum itself, so for J^2 and J_z we will have common eigenvectors:

$$J^2|j,m\rangle = j(j+1)\hbar^2|j,m\rangle \tag{44}$$

$$J_z|j,m\rangle = m\hbar|j,m\rangle \tag{45}$$

and will be valid the same rules that we have seen for a single angular momentum:

- $j \in \{0, \frac{1}{2}, 1, \frac{3}{2}, 2, \cdots\}$

- $m \in \{-j, -j+1, \cdots j\}$

3.0.5   Angular momentum coupling theorem

Let's go back to the case in which we sum just two ang. mom..

Let's write the common eigenstate of J^2 and J_z as a tensor product of two eigenstates of the addenda angular momenta:

$$|j,m\rangle = |j_1,m_1\rangle \otimes |j_2,m_2\rangle. \tag{46}$$

We have an intuitive justification for this if we think at the total angular momentum as obtained summing the angular momenta of two different parts of our system. For

example the total orbital angular momentum of an atom that has two electrons. It's possible to demonstrate that things are the same in much "odd" situations, as if we add the spin ang. mom. and the orbital ang. mom. of the same particle. Is worth to keep in mind that the two addenda ang. mom. have to commute, so that we can measure each of them without disturb the state of the other.

This said, the following theorem holds:

Theorem 3.1 (Angular momentum theorem)

$$|j_1 - j_2| \leq j \leq j_1 + j_2 \tag{47}$$

This theorem just express the triangular property. It says that the modulus of the sum of two vectors cannot be longer than the sum of the two moduli of the two addenda, and shorter than their difference (see fig 1).
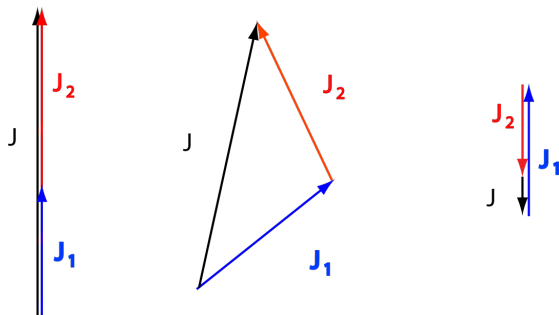
Figure 1: triuangular property

Is worth to say that j is not the modulus of the angular momenta, but is just the quantum number associated to the square modulus operator. So this is just an "intuitive" demonstration of the theorem. A more rigorous and complicated demonstration exist.

4   Identical particles - symmetrization

If we have a system made of several "parts", and two or more of these parts are identical, the state of the system has to be the same if we swap two of these identical particles.

We have such a situation wen we study atoms with more than one electron. For example we can write

$$\psi(\vec{r_1}, \vec{r_2}) = \phi_1(\vec{r_1}) \, \phi_2(\vec{r_2}) \qquad \underset{\text{exchange}}{\Rightarrow} \qquad \bar{\psi}(\vec{r_2}, \vec{r_1}) = \phi_1(\vec{r_2}) \, \phi_2(\vec{r_1}). \tag{48}$$

In general ψ and $\bar{\psi}$ are two different wave functions, and can be even orthogonal. So we have different states that have to describe the same physical state (by definition of identical particles). This situation is called *exhange degeneracy*.

4.1 States with defined symmetry

The *symmetric* and *antisimmetric* states are defined as:

$$\psi^S(\vec{r_1}, \vec{r_2}) = \frac{1}{\sqrt{2}} \left[\phi_1(\vec{r_1}) \, \phi_2(\vec{r_2}) \; + \; \phi_1(\vec{r_2}) \, \phi_2(\vec{r_1}) \right] \tag{49}$$

$$\psi^A(\vec{r_1}, \vec{r_2}) = \frac{1}{\sqrt{2}} \left[\phi_1(\vec{r_1}) \, \phi_2(\vec{r_2}) \; - \; \phi_1(\vec{r_2}) \, \phi_2(\vec{r_1}) \right]. \tag{50}$$

These special states stay the same or just change their sign after the exchange of particles.

In this notation we supposed that is possible to factorize the state of the total system as a product of functions of the "components" systems (non entangled particles). A more general notation is

$$\psi^S(\vec{r_1}, \vec{r_2}) = \frac{1}{\sqrt{2}} \left[\psi(\vec{r_1}, \vec{r_2}) \; + \; \bar{\psi}(\vec{r_2}, \vec{r_1}) \right] \tag{51}$$

$$\psi^A(\vec{r_1}, \vec{r_2}) = \frac{1}{\sqrt{2}} \left[\psi(\vec{r_1}, \vec{r_2}) \; - \; \bar{\psi}(\vec{r_2}, \vec{r_1}) \right]. \tag{52}$$

States like these are said to have *defined symmetry*.

Is possible to demonstrate the following:

Theorem 4.1 (about symmetry of eigenstates) *The eigenstates of the Hamiltonian have a defined symmetry.*

4.2 Symetrization postulate

States with no defined symmetry would introduce contradiction to theory. Such states would make possible to tell wether the identical particles have been exchanged, contradicting the definition itself on *identical particles*. To overcome this contradiction, a postulate is introduced:

Postulate 4.1 (Symetrization postulate) *the state of a system with two or more identical subparts can be only symmetrical or anti-symmetrical with respect to the subparts exchange.*

This postulate "resolves" the contraddiction.

4.3 Spin-statistic theorem

Is possible to demonstrate this theorem, that relates the symmetry of the wave functions of a system made of identical parts, with the spin of the single particles:

Theorem 4.2 (spin-statistic theorem) *The wave function of a system made out of identical particles with* semi-integer *spin quantum number is an* anti-symmetric *function with respect to the subparts exchange. The wave function of a system made out of identical particles with* integer *spin quantum number is an* symmetric *function with respect to the subparts exchange.*

Particles with *semi-integer* spin quantum number are called *fermions*, Particles with *integer* spin quantum number are called *bosons*.

4.3.1 Slater's determinant and Permanent

The wave function of a system made out of multiple identical fermions has to be anti-symmetric, i.e. it has to change sign for any exchange of two paticles. It can be built

as linear combination of wave functions of single parts (particles) in the following way:

$$\begin{vmatrix} \phi_1(\vec{r}_1) & \phi_2(\vec{r}_1) & \cdots & \phi_n(\vec{r}_1) \\ \phi_1(\vec{r}_2) & \phi_2(\vec{r}_2) & \cdots & \phi_n(\vec{r}_2) \\ \cdots & \cdots & \cdots & \cdots \\ \phi_1(\vec{r}_n) & \phi_2(\vec{r}_n) & \cdots & \phi_n(\vec{r}_n) \end{vmatrix} \tag{53}$$

This linear combination is known as the *Slater's determinant.*

The wave function of a system made out of multiple identical bosons has to be symmetric, i.e. it has to remain unchanged for any exchange of two paticles. It can be built as linear combination of wave functions of single parts (particles) in the following way:

$$\sum_{\sigma \in S_n} \prod_{i=1}^{n} \phi_i(\vec{r}_{\sigma(i)}) \tag{54}$$

Where S_n is the set of all possible permutations of vectors of length n, and $\sigma(i)$ with $\sigma \in S_n$ is the the $i-$th element of a permutation.

This linear combination is known as the *permanent.*

5 Multielectron atoms

The energy eigenvalue of the total system doesn't depend any more only on the energy of the single particles. Since more than one electron are in place, the "shielding" effect of other electrons affect the energy of each other. So, in the expression of the eigenvalue of the energy we will find also the quantum numbers related to the angular momenta.

5.1 Two electrons atoms

Let's give an example: let's consider an atom with two electrons. It can be the helium atom itself, or any atom that has been ionized up to live it with only two electrons left. Electrons are fermions, so the wave function has to be anti-symmetric, so we have to write it as a *Slater's determinant.* We have also to take into account the spin: the state

of a single electron is the product of a *spatial* wave function and of a vector of the spin vector space:

$$\begin{vmatrix} \psi_1(\vec{r_1})\chi_+(1) & \psi_2(\vec{r_1})\chi_-(1) \\ \psi_1(\vec{r_2})\chi_+(2) & \psi_2(\vec{r_2})\chi_-(2) \end{vmatrix} \tag{55}$$

where we have two different spatial wave functions, identified by the footer, and they can be associated to one or the other indistinguishable particles, identified by the spatial positions $\vec{r_i}$. About the spin vectors, as we have seen in paragraph 2.2.3, for electrons there are two orthogonal spin vectors χ_+ and χ_-, and in parenthesis we have indicated the particle to which they are referred to.

Now, this is a wavefunction of the total system, written in terms of the wave functions of the single electrons. Let's focus on the spin part. Since spins are angular momenta we have to use what we have learned from the *angular momenta coupling*: the total spin of the atom will be the sum of the spins of the two electrons. Since for a single electron $s_1 = s_2 = \frac{1}{2}$ we know that the quantum number associated to the squared modulus of the total spin will be $0 \leq s \leq 1$, and since it will take values spaced by one unity, the actual values will be actually 0 and 1.

So we will have two multiplets, i.e. two subspaces of orthogonal autovectors of S_z that are degenerate in respect to S^2. In particular we will have a singlet and a triplet.

Using the Clebsch-Gordan coefficients we can express the total spin in terms of the single particle's spins:

$$\begin{aligned} \chi_{0,0}(1,2) &= \tfrac{1}{\sqrt{2}}\left[\chi_+(1)\,\chi_-(2) - \chi_-(1)\,\chi_+(2)\right] \\ \chi_{1,-1}(1,2) &= \chi_+(1)\,\chi_+(2) \\ \chi_{1,0}(1,2) &= \tfrac{1}{\sqrt{2}}\left[\chi_+(1)\,\chi_-(2) + \chi_-(1)\,\chi_+(2)\right] \\ \chi_{1,1}(1,2) &= \chi_-(1)\,\chi_-(2) \end{aligned} \tag{56}$$

About the symmetry of the functions with respect to the exchange of particles, for this case of two identical particles we can see that the spin vector on it's own has a definite symmetry, and since the total function has to be anti-symmetric, this means that the spatial wave function has to have a definite symmetry too. In particular we see that:

- for the *singlet* the spin vector is *anti-symmetric* so the wave function has to be *symmetric*

- for the *singlet* the spin vector is *symmetric* so the wave function has to be *anti-symmetric*.

The transition between a singlet and a triplet state is forbidden in the dipole approximation, in case the spin-orbit interaction can be neglected, as is the case in ions with $Z \leq 40$ (cfr [2] pag 255). So, historically helium in a singlet state or in one of the triplet states were seen as two different elements, and two names were used: orthohelium for the triplet state, and parahelium for the singlet state.

Is interesting to show how, using electrostatic ideas, we can tell that the orthohelium (singlet state) has a lower energy. Indeed, we know that the spatial wave function of a singlet state is anti-symmetric. For a two-particles anti-symmetric wave function, to be anti-symmetric means that the the more the particles are far apart, the higher is it's value (the extreme if to have $\vec{r}_1 = \vec{r}_2$, that gives $\psi(\vec{r}_1, \vec{r}_2) = 0$). So in general, the probability for small separations of the two electrons is smaller than for a symmetric space wavefunction. But if the average distance between electrons is higher for the singlet state, then there will be less shielding of the nucleus by the ground state electron, and the excited state electron will therefore be more exposed to the nucleus. This will make it more tightly bound to the nucleus, and so the energy of such a state will be lower.

6 Perturbative theory

To study systems more complex than the hydrogen atom, the analytical approach is no more suitable. So we have to use the perturbative theory.

6.1 Time independent perturbative theory

Let's consider a system that has an Hamiltonian of the form:

$$H_0 + \varepsilon H_I \tag{57}$$

where:

- H_0 is an hamiltonian operator of which is completely known the spectrum

- ε is an *adimensional* parameter

- H_I is an operator of wich are at least known the matrix element, in the rapresentation on the eighenbase of H_0

The paradigm of this approach is as follows:

we have a so called *unperturbated system*, wich is completely known, and is *simpler*, and then we have a more complex system, which is difficult or impossible to "diagonalize" (i.e. find the spectrum), but can be written in the form (57), so to separate the well-known, simpler "sub-system", and a *perturbation H_I*. The parameter ε has the meaning of a "tuning" parameter, that enables us to change the magnitude of the perturbation: for $\varepsilon \to 0$ the perturbated system "approaches" the umperturbated one.

Let's now introduce some notation. Let be

$$H_0|\varphi_n\rangle = E_n^{(0)}|\varphi_n\rangle \tag{58}$$

the eigenvalues equation for the unperturbated system (for the sake of simplicity we suppose that the spectrum is only discrete)

and let be

$$[H_0 + \varepsilon H_I]|\psi_l\rangle = E_l|\psi_l\rangle \tag{59}$$

the eigenvalues equation for the complete system's Hemiltonian H.

Let's now consider that since the umperturbated Hamiltonian is an Hermitian operator, the set of its eigenvectors is a base of the Hilbert space (eigenbase). so we can expand each eigenvector of H on the eigenbasis of H_0:

$$|\psi_l\rangle = \sum_n a_{nl}|\varphi_n\rangle. \tag{60}$$

Hypotheses   What we have seen since now is completely general. Let's now introduce some hypotheses, necessary for the further development of the perturbative theory.

- it is possbile to expand the eigenvalues of the complete systems in series of powers of ε:

$$E_l = E_l^{(0)} + \varepsilon E_l^{(1)} + \varepsilon^2 E_l^{(2)} + \cdots \tag{61}$$

- it is possible to expand the coefficients $a_{l\,n}$ of (60) in series of powers of ε

$$a_{l\,n} = \delta_{l\,n} + \varepsilon\, a_{l\,n}^{(1)} + \varepsilon^2\, a_{l\,n}^{(2)} + \cdots \tag{62}$$

- H and H_0 have the same domain (of essential eigenadjointness)

- H_0 has only discrete spectrum, and all the eigenvalues are non-degenerate

(note: the last two hypotheses can be released afterward)

Under these hypotheses, the terms of the expansion of the *eigenvalues* of the complete (perthurbated) system are as follows:

$$E_l^{(1)} = (H_I)_{ll} \equiv \langle \varphi_l | H_I | \varphi_l \rangle$$

$$E_l^{(1)} = \sum_{n \neq l} \frac{(H_I)_{l\,n}\,(H_I)_{n\,l}}{E_l^{(0)} - E_n^{(0)}} = \frac{|(H_I)_{l\,n}|^2}{E_l^{(0)} - E_n^{(0)}}$$

while the terms of the expansion of the coefficients of the (62) are:

$$a_{l\,n\,l \neq n}^{(1)} = \frac{(H_I)_{l\,n}}{E_l^{(0)} - E_n^{(0)}}$$

$$a_{l\,l}^{(1)} = 0$$

so that the (60) becomes

$$\psi_l \simeq \varphi_l + \varepsilon \sum_{n \neq l} \frac{(H_I)_{l\,n}}{E_l^{(0)} - E_n^{(0)}}\, \varphi_n \tag{63}$$

where we are taking the first order approximation

6.2 Time dependent perturbative theory - Harmonic perturbation

(cfr. [1] cap II, $XIII$ and A_{XIII})

Let's consider a physical system that is described by an hamiltonian of this form:

$$H(t) = H_0 + \varepsilon V(t) \tag{64}$$

where is possible to separate a so called "inperturbed hamiltonian" H_0, and a *time-dependent* perturbative term $V(t)$.

What the theory delivers is a "probability of transition": given an initial state $|\varphi_i\rangle$ and a final state $|\varphi_f\rangle$, we can know the first order (second, third etc.) approximation of the probability that the transition between those states takes place. The general expression of the (first order approximation for the) transition probability is:

$$P_{i \to f}(t) = \frac{\varepsilon^2}{\hbar^2} \left| \int_0^t e^{i\,\omega_{fi}\,t'}\; V_{fi}(t')\; dt' \right|^2 \tag{65}$$

where

$$\omega_{fi} \equiv \frac{E_f - E_i}{\hbar} \tag{66}$$

is called *Bohr frequency*

and

$$V_{fi}(t) \equiv \langle \varphi_f | V(t) | \varphi_i \rangle \tag{67}$$

is the *matrix element* of the perturbation.

We will focus our discussion on the specific (nevertheless with some generality) case where the perturbative term in the (64) has an harmonic dependance on the time:

$$V(t) = V_0 \cos \omega t \tag{68}$$

and is referred to as the *harmonic perturbation.*

We have also to distinguish the easier case when the initial and final states are both part of the discrete spectrum, from the case when the final case is part of the continuous spectrum.

6.2.1   Discrete→discrete transition

If we substitute the (68) in the (65) and we use the Euler formulae and calculate the integrals, with some algebra we get:

$$P_{fi}(t) = \frac{|V_{0\,fi}|^2}{4\,\hbar^2} \left| \frac{e^{i(\omega_{fi}+\omega)t} - 1}{(\omega_{fi} + \omega)} + \frac{e^{i(\omega_{fi}-\omega)t} - 1}{(\omega_{fi} - \omega)} \right|^2 \tag{69}$$

where ω is the frequency (pulsation) of the harmonic perturbation and $V_{0\,fi}$ is the matrix element of its amplitude V_0:

$$V_{0\,fi} \equiv \langle \varphi_f | V_0 | \varphi_i \rangle \tag{70}$$

and is a constant quantity.

Up to this point there is no approximation.

The two terms that are summed in the square modulus in the (69) are called *resonant term* and *anti-resonant term* respectively.

It is possible to use an approximate expression for the probability of transition (69), where we use just one of the two terms. In what follows we will show this approximation and the conditions in which it is valid.

The resonant term   Before we study the hypotheses under which is possible to use the approximation with only the resonant term, let's study this term.

First, we can apply some algebra, and write the resonant term as:

$$F(t, \omega - \omega_{fi}) \equiv \left[\frac{\sin(\omega_{fi} - \omega)t/2}{(\omega_{fi} - \omega)/2} \right]^2 . \tag{71}$$

In fig. 2 we can see a plot, with the typical shape of the *diffraction pattern*.

The maximum probability is achieved when the frequency of the harmonic perturbation equals the Bohr frequency (66) of the two levels: $\omega = \omega_{fi}$. For this (resonant) frequency the probability is:

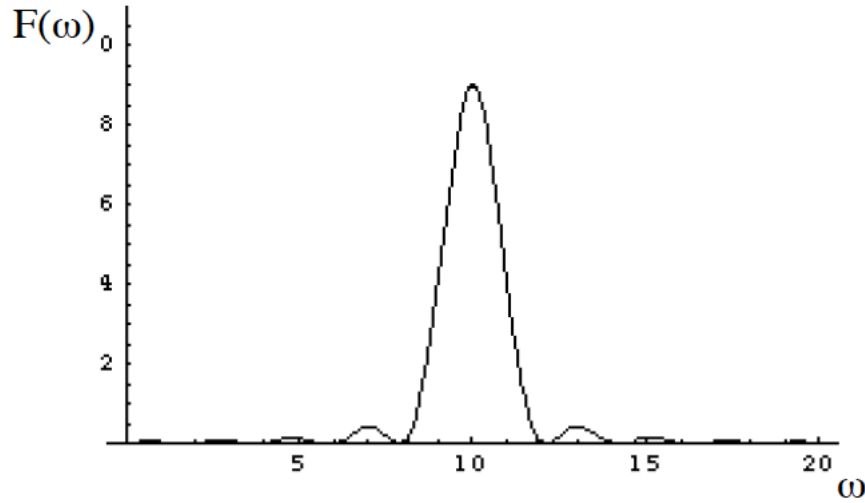$$P(\omega = \omega_{fi}) = \frac{|V_{0\,fi}|^2}{4\,\hbar^2} \tag{72}$$

$F(\omega)_0$

Figure 2: a plot of the resonant term

The width of the central maximum, i.e. the biggest difference between ω and ω_{fi} that is allowed to still have an appreciable probability of transition is:

$$\Delta\omega = \frac{4\pi}{t} \tag{73}$$

It's also worth to note that the probability on the secondary maxima is about the 5% of the probability at the resonance.

conditions to approximate only to the resonant term   Let's consider the (69). If we carry out the square, the complete form would have the resonant term, the anti-rensonant term, and the double product. About the transition, once we set the two energy levels, we know whether the Bohr frequency is positive or negative, i.e. whether the transition is an *emission* or an *absorption*. On the other hand, the frequency of the harmonic perturbation can be only positive. So, once is set whether we have an absorption or an emission, we can only have $\omega \simeq \omega_{fi}$ or $\omega \simeq -\omega_{fi}$ respectively.
When $\omega \simeq \omega_{fi}$ or $\omega \simeq -\omega_{fi}$ is possible to neglect the resonant or anti-resonant term, and the double product.
About the time, we have seen that either the maximum value and the width of the peak of probability (diffraction pattern) are functions of time. For this reason some

conditions about time have to be fulfilled in order for the approximation to be valid.

- We want that the two peaks of the resonant and the anti-resonant term are separated. Since the width of the peaks is $\Delta\omega \frac{4\pi}{t}$ the first condition is that the two width are less than the distance $2\omega_{fi}$ between the maxima:

$$t \gg \frac{2\pi}{\omega_{fi}} \tag{74}$$

- If the time grows indefinitely, the maximum probability (72) becomes greater than 1, loosing significance. This can happen because we are using formula (65) that comes from an approximated theory (time-dependent perturbation theory, approximated at the first order). So we have to impose for the maximum probability of transition to be less than the unity:

$$t \ll \frac{|V_{0\,fi}|}{2\,\hbar} \tag{75}$$

To summarize, provided that the harmonic perturbation lasts a time t such that

$$\frac{2\pi}{\omega_{fi}} \ll t \ll \frac{|V_{0\,fi}|}{2\,\hbar} \tag{76}$$

we can approximate the probability of a transition with an expression containing only the resonant (ant-resonant) term, depending whereas is an emission or an absorption:

$$P_{fi}(t,\omega) = \frac{|V_{0\,fi}|^2}{4\,\hbar^2} \left[\frac{\sin(\omega_{fi} \pm \omega)t/2}{(\omega_{fi} \pm \omega)/2} \right]^2 \tag{77}$$

6.2.2 Discrete→continuous transition

If the final state is part of the continuous spectrum, a different approach is needed.

Let's newly consider our physical system, made of an unperturbed part and a time dependent perturbation (cfr. (64)). Let's consider an initial state $|\varphi_i\rangle$ and a final state $|\varphi_f\rangle$. Be $|\psi(t)\rangle$ the state at generic time t given that at $t = 0$ the system was in the initial state $|\varphi_i\rangle$, as we can obtain solving the schrödinger evolution equation for the system.

Following the postulates of quantum mechanics, the probability that at time t the system is in the final state is

$$P(t)_{fi} = |\langle \varphi_f | \psi(t) \rangle|^2. \tag{78}$$

What we have written is true if the initial and final state are part of the discrete spectrum of the hamiltonian of the unperturbed system H_0. If the final state is part of the continuous spectrum, the (78) is just a a probability density, and to have a finite probability we have to integrate over some interval.

Let's suppose that the elements of the continuous spectrum of H_0, of wich $|\varphi_f\rangle$ is part, are individuated by a set of continuous indices (among which there is the energy), that we will synthetically denote with α. So we can also write $|\varphi_f\rangle = |\alpha\rangle$.

This said, in the case that the final state is part of the discrete spectrum, we can re-write the (78). The probability that at time t the system is in a state belonging to the interval $\Delta\alpha$, given the initial state $|\varphi_i\rangle$, is obtained integrating over the interval $\Delta\alpha$:

$$P_{\Delta\alpha i}(t) = \int_{\Delta\alpha} |\langle \alpha | \psi(t) \rangle|^2 d\alpha. \tag{79}$$

In the following is useful a change of variables in the integration: we "extract" the energy out of the synthetic notation: $|\alpha\rangle = |\beta, E\rangle$. To complete the change of variables in the integration, we have to take into account the Jacobian of the transformation $\rho(\beta, E)$, so that the differential is:

$$d\alpha = \rho(\beta, E) d\beta dE. \tag{80}$$

The jacobian $\rho(\beta, E)$ here can e seen as a *density on final states* as function of β and E.

Using this, the (79) becomes

$$P_{\Delta\beta\Delta E i}(t) = \int_{\Delta\beta\Delta E} \rho(\beta, E) |\langle \beta E | \psi(t) \rangle|^2 d\beta dE. \tag{81}$$

Now, if we use the time-dependent perturbation theory, we can substitute the (78):

$$|\langle \beta E | \psi(t) \rangle|^2 \simeq \frac{1}{\hbar^2} |\langle \beta E | V_0 | \varphi_i \rangle|^2 \left[\frac{\sin(\omega_{fi} - \omega)t/2}{(\omega_{fi} - \omega)/2} \right]^2$$

where now in the Bohr frequency $\omega_{fi} = \frac{E-E_i}{\hbar}$ there is the continuous parameter E.

In the limit of $t \to \infty$ we can use $\lim_{t\to\infty} \left[\frac{\sin(\omega_{fi}-\omega)t/2}{(\omega_{fi}-\omega)/2} \right]^2 = 2\hbar\pi t\delta(E - E_i)$, so, if we substitute this expression in the (81), and consider the action of the delta-function in the integral, we obtain the so called *Fermi's golden rule*:

$$P_{fi} = \frac{2\pi}{\hbar}\rho(\beta_f\, E_i)|\langle\beta_f\, E_i|V_0|\varphi_i\rangle|^2 \tag{82}$$

6.3   Atom-radiation interaction

We want to apply the results of the time-dependent perturbation theory to the interaction between the electromagnetic radiation and an atom. Of course the atom will lay the role of the unperturbated system, and the electromagnetic radiation will play the role of the time-dependent harmonic perturbation.

The unperturbated hamiltonian, i.e. the energy of an electron in an atom, will have the form:

$$H_0 = \frac{P^2}{2m} + V(r) \tag{83}$$

where $V(r)$ is the *average central potential* that describes the total interaction with the other electrons and with the nucleus (cfr. e.g. Thomas-Fermi model).

When we take into account the electromagnetic radiation, and we assume some simplifying hypotheses (e.g. planar monochromatic wave, linearly polarized along the z axis and propagating along the y axis) the complete hemiltonian becomes:

$$
\begin{aligned}
H &= \frac{\left[\vec{P} - \frac{q}{c}\vec{A}(\vec{r},t)\right]^2}{2\,m} + V(r) - \frac{q}{m\,c}\,\vec{S}\cdot\vec{B} \\
H &= \frac{P^2}{2\,m} - \frac{q}{c\,m}\vec{P}\cdot\vec{A} + \frac{q^2}{2\,c^2m}A^2 + V(r) - \frac{q}{m\,c}\,\vec{S}\cdot\vec{B}
\end{aligned}
$$

and finally, reordering (the unperturbated hamiltonian is represented by the first two terms, in square brackets):

$$H = [\frac{P^2}{2\,m} + V(r)] - \frac{q}{c\,m}\vec{P}\cdot\vec{A} + \frac{q^2}{2\,c^2m}A^2 - \frac{q}{m\,c}\,\vec{S}\cdot\vec{B} \tag{84}$$

Here:

- $\vec{A}(\vec{r}, t)$ is the *magnetic vector potential* operator

- $\vec{B}$ is the magnetic field operator

- $\vec{S}$ is the spin operator

- P is the *momentum* operator

- m is the electron mass

- q is the electron charge

- c is the light's velocity.

We can neglect the last term $-\frac{q}{cm}\vec{S}\cdot\vec{B}$ if the wavelenght of the electromagnetic radiation is of the order of magnitude of the visible light. We can neglect the one-before-the-last term $\frac{q^2}{2c^2m}A^2$ if the intensity of the radiation is low (linear perturbation regime). Finally, we can expand power series the first term of the harmonic perturbation:

$$V(t) = -\frac{q}{cm}P_z A_0 \left[e^{i(ky-\omega t)} - e^{-i(ky-\omega t)} \right] \tag{85}$$

$$e^{\pm iky} = 1 \pm iky - \frac{1}{2}k^2y^2 \pm \ldots$$

This power series expansion is called *multipoles expansion*. The first order approximation of this electromagnetic harmonic perturbation is called *electric dipole approximation*:

$$V_{ED}(t) = -\frac{q A_0}{cm}P_z \left[e^{-i\omega t} - e^{i\omega t} \right]$$

$$V_{ED}(t) = \frac{q E_0}{\omega m}P_z \sin\omega t \tag{86}$$

where E_0 is the amplitude of the oscillating electric field.

Finally, we write the matrix element of this electric dipole approximation of the electro-magnetic harmonic perturbation, between two states. Using some commutation properties of the momentum operator P_z we have:

$$\langle \varphi_f | V_{ED}(t) | \varphi_i \rangle = iqE_0 \frac{\omega_{fi}}{\omega} \langle \varphi_f | Z | \varphi_i \rangle \sin \omega t \qquad (87)$$

where ω_{fi} is the Bohr frequency and Z is the position operator along the z axis (direction of the polarization of the electromagnetic wave).

7 Selection rules

We have seen that the time-dependent perturbation theory can describe the interaction of the electromagnetic radiation with an atom.

In particular set the initial and the final states, we can calculate a probability of transition.

We have seen that this probability of transition depends on the matrix element of the perturbation "between" the initial and final states. We have also seen that we can expand the perturbation operator (multipoles expansion), so that we have several orders of approximation, the first and most important being the *electric dipole term.*

On the other hand we know that the initial and final states are eigenstates of the unperturbated hamiltonian, i.e. eigenstates of hydrogenoid atom. These eigenfunctions are made of a *radial* part and a *spherical harmonic.*

So, without carry out the calculations for the transition probabilities, but just using the orthonormality properties of the spherical harmonics, we can predict that the transitions between many hydrogenoid eigenstates will be zero.

We can build a set of *transition rules.* We will have transition rules that take into account only the electric dipole approximation, then other rules that take into account transitions that would have been forbidden (i.e. zero probability) using the electric dipole approximation, but become possible (non-zero probability) although with a smaller probability, taking into account higher terms of the multipoles expansion.

Let's list the rules.

Electric Dipole - linear polarization
$$\begin{cases} l_f - l_i \equiv \Delta l = \pm 1 \\ m_f - m_i \equiv \Delta m = 0 \end{cases}$$

Electric Dipole - circular polarization
$$\begin{cases} l_f - l_i \equiv \Delta l = \pm 1 \\ m_f - m_i \equiv \Delta m = \pm 1 \end{cases}$$

Electric Dipole - taking into account the spin
$$\begin{cases} j_f - j_i \equiv \Delta j = 0, \pm 1 \\ \Delta m_j = 0, \pm 1 \\ \Delta l = \pm 1 \end{cases}$$

Magnetic Dipole
$$\begin{cases} \Delta l = 0 \\ \Delta m_l = \pm 1 \\ \Delta m_s = \pm 1 \end{cases}$$

Electric Quadrupole
$$\begin{cases} \Delta l = 0, \pm 2 \\ \Delta m_l = 0, \pm 1, \pm 2 \end{cases}$$

8 Molecules

[...]

8.1 Linear Combination of Atomic Orbitals

[...]

8.2 Molecular Orbital

[...]

9 The spectroscopic notation

9.1 Notation for the hydrogen atom

To specify the eigenstate of the electron in an hydrogen atom a notation is used, with the following conventions:

- the energy level of the electron is in relation with the *energy quantum number* $n \in \{1, 2, 3, \ldots\}$, and is specified by the quantum number itself.

- the eigenvalue of the modulus of the (orbital) angular momentum is in relation with the *orbital quantum number* $l \in \{0, 1, 2, \ldots\}$, and is specified by a subscript letter at the right of the energy quantum number, with the following convention: $s \Leftrightarrow l = 0$; $p \Leftrightarrow l = 1$; $d \Leftrightarrow l = 2$; $f \Leftrightarrow l = 3$. The meaning of the letter is related to the early observations of the spectroscopists, and is as follow: "sharp", "principal", "diffuse", and "fine". Higher values are named with the letters following in alphabetical order, with no particular meaning.

- the eigenvalue of the projection of the (orbital) angular momentum is in relation with the *magnetic quantum number* $m_l \in \{-l, -l+1, \ldots, 0, \ldots +l\}$, for a total of $2l + 1$ possible vaues, and is in general not specified.

- sometimes a footer is added, to specify the spin projection quantum number $\pm 1/2$.

An example of the notation is:

$$2s_{1/2}$$

that denotes an electron state with $n = 2$ (energy), $l = 0$ (orbital angular momentum modulus) and $s = \frac{1}{2}$ (spin angular momentum modulus).

9.2 Notation for multielectrons atoms

To build the label for a multielectron atom state, tree things are taken into account:

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- the total *spin* angular momentum S

- the total *orbital* angular momentum L

- the total angular momentum J.

The symbol is built with L at the center, with $2S + 1$ as apex on the left, and J as footer on the right:

$$^{2S+1}L_J \tag{93}$$

The angular momentum symbol follows the spectroscopic notation scheme: $s \Leftrightarrow l = 0$; $p \Leftrightarrow l = 1$; $d \Leftrightarrow l = 2$; $f \Leftrightarrow l = 3$ etc..

9.3 Hund's rules

1. The term with maximum spin multiplicity (i.e. the highest S value) lies lowest in energy

2. For a given multiplicity, the term with the largest value of L lies lowest in in energy

3. For atoms with less than half-filled shells, the level with the lowest value of J lies lowest in energy.
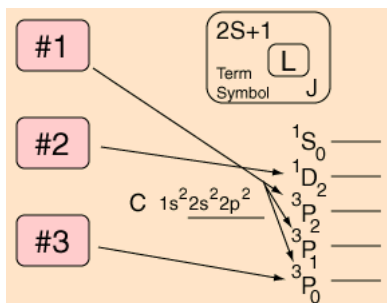

Figure 3: Illustration of the Hund's rules

9.4 Notation for molecules

9.4.1 symmetry groups

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