

Energy levels of atoms and ions.

Single electron (Hydrogen-like) atoms or ions.

Positive nucleus of charge $+Ze$ and mass M , only one electron (mass m , charge $-e$). Since the Hamiltonian does not explicitly depend on the spin, the Schrödinger equation for Hydrogen-like atom is (in CGS units):

$$\mathbf{H} = -\frac{\hbar^2}{2M} \nabla_{\mathbf{r}_{nucleus}}^2 - \frac{\hbar^2}{2m} \nabla_{\mathbf{r}_e}^2 - \frac{Ze^2}{|\mathbf{r}_{nucleus} - \mathbf{r}_e|}$$

The three terms are the operators for kinetic energy of nucleus, of the electron, and the Coulombian potential energy.

In the center of mass reference system, the motion of the center of mass can be factored out. The Hamiltonian for the reduced mass is :

$$\mathbf{H} = -\frac{\hbar^2}{2\mu} \nabla_{\mathbf{r}}^2 - \frac{Ze^2}{r}$$

with $\mu = Mm/(M + m)$ is the reduced mass and r is the relative coordinate $r = |\mathbf{r}_{nucleus} - \mathbf{r}_e|$.

Electrons are spin $1/2$ particles; the spin projection onto the z axis, in units of \hbar , is the spin quantum number, m_s . It can take the values $\pm \frac{1}{2}$.

The Hamiltonian, however, does not depend on the spin. The wavefunction can be written as the product of the spatial component and of the Spin component:

$$\psi(\mathbf{q}) = \chi_{s,m_s} \psi(\mathbf{r})$$

Where χ_{s,m_s} are the eigenfunctions of the \mathbf{S} , \mathbf{S}^2 operators, with eigenvalues $1/2$, $\pm \frac{1}{2}$, and $\psi(\mathbf{r})$ is the solution of the Schrödinger equation:

$$\mathbf{H}\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

Introducing the angular momentum, we can group all the angular dependence on the angular momentum operator $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ and express the Schrödinger equation in polar coordinates:

$$\left[-\frac{\hbar^2}{2\mu} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{\mathbf{L}^2}{2\mu r^2} - \frac{Ze^2}{r} \right] \Psi(r, \vartheta, \varphi) = E \Psi(r, \vartheta, \varphi)$$

It can be shown that (both angular momentum and its projections are conserved); then the spatial eigenfunctions can be written as

$$\Psi(r, \vartheta, \varphi) = R(r) Y_{\ell, m_\ell}(\vartheta, \varphi),$$

where we introduced the spherical harmonics $Y_{\ell, m_\ell}(\vartheta, \varphi)$, which are defined as the simultaneous eigenfunctions of the operators \mathbf{L}^2 and \mathbf{L}_z .

They satisfy the eigenvalues equations:

$$\mathbf{L}^2 Y_{\ell, m_\ell}(\vartheta, \varphi) = \hbar^2 \ell(\ell + 1) Y_{\ell, m_\ell}(\vartheta, \varphi)$$

$$\mathbf{L}_z Y_{\ell, m_\ell}(\vartheta, \varphi) = \hbar m_\ell Y_{\ell, m_\ell}(\vartheta, \varphi)$$

The magnetic quantum number m_ℓ (also written as m) represents the projection of \mathbf{L} onto the z -axis, in units of \hbar . It can take on $2\ell + 1$ values: $m_\ell = -\ell, \dots, -1, 0, 1, \dots, \ell$. It characterizes the orientation of orbital. The eigenvalue of \mathbf{L} is $\hbar\sqrt{\ell(\ell + 1)}$.

The angular dependence of the wavefunctions, and of the angular distribution of electric charge in the orbitals, is enclosed in the spherical harmonics.

$$Y_{\ell, m_\ell}(\vartheta, \varphi) = \frac{1}{\sqrt{2\pi}} e^{im_\ell \varphi} P_{\ell, m_\ell}(\theta) \quad \text{normalized by}$$

$$\int |Y_{\ell, m_\ell}(\vartheta, \varphi)|^2 d\Omega = \int |Y_{\ell, m_\ell}(\vartheta, \varphi)|^2 \sin\theta d\theta d\varphi$$

The parity (behavior under $\mathbf{r} \rightarrow -\mathbf{r}$) of spherical harmonics is $(-1)^\ell$.

$P_{\ell, m_\ell}(\theta)$ are the associated Legendre polynomials.

Radial component of the wavefunction.

The radial component of the wavefunction and the energy eigenvalues can be found by solving the radial equation:

$$\left[-\frac{\hbar^2}{2\mu} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{\mathbf{L}^2}{2\mu r^2} - \frac{Ze^2}{r} \right] R(r) = ER(r)$$

Defining $R(r) = X(r)/r$ we obtain the radial equation:

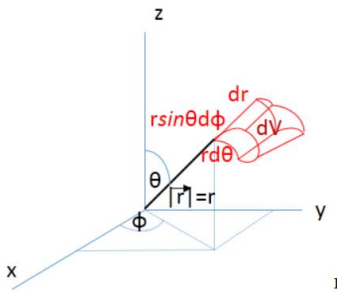
$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2} - \frac{Ze^2}{r} \right] X(r) = EX(r)$$

We notice that $V_{eff}(r) \equiv \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2} - \frac{Ze^2}{r}$ represents a Coulombian potential shielded by the centrifugal force of the electrons with $\ell \neq 0$.

The normalization is the following:

$$\int |\Psi(r, \vartheta, \varphi)|^2 r^2 dr d\Omega = 1 = \int |Y_{\ell,m}(\vartheta, \varphi)|^2 d\Omega$$

$$\begin{aligned} \int |Y_{\ell,m}(\vartheta, \varphi)|^2 d\Omega |R(r)|^2 r^2 dr &= \int |R(r)|^2 r^2 dr = 1 \\ \Rightarrow \int |X(r)|^2 dr &= 1 \end{aligned}$$



$$dV = r^2 \sin\theta dr d\theta d\varphi$$

The solutions of the radial equation are analytical and can be written with the associate Laguerre polynomials \mathcal{L} . They are labeled with the

values of the principal quantum number n and the orbital quantum number ℓ :

$$R_{n,\ell}(r) = N_{n,\ell} e^{-\frac{\rho}{2}} \mathcal{L}_{n+\ell}^{2\ell+1}(\rho)$$

With $\rho = 2 \frac{Z}{n} \frac{r}{a_0} \frac{\mu}{m}$ and

$$a_0 = \frac{\hbar}{mc\alpha} = \text{Bohr radius}$$

The Bohr radius is the radius of the innermost orbit of the electron, in the fundamental Hydrogen state.

α is the fine structure constant = (in CGS units) $\frac{e^2}{\hbar c} = \frac{1}{137}$

The probability *density* (probability in an infinitesimal volume element) of a configuration in space is given by

$$|\Psi(r, \theta, \varphi)|^2 = \Psi(r, \theta, \varphi) \cdot \Psi^*(r, \theta, \varphi).$$

The spatial wavefunctions are then defined by three quantum numbers, n, ℓ, m_ℓ :

$$\Psi(r, \vartheta, \varphi) = R_{n,\ell}(r) Y_{\ell,m_\ell}(\vartheta, \varphi),$$

And the corresponding energy eigenvalues are:

$$E_n = -\frac{1}{2} \mu c^2 \frac{(Z\alpha)^2}{n^2} = -R(\mu) \frac{Z^2}{n^2} = -\frac{\mu}{m} R_\infty \frac{Z^2}{n^2}$$

where $R_\infty = 12.6 \text{ eV} = 109737 \text{ cm}^{-1} = 2.17 \times 10^{-18} \text{ J}$ is the Rydberg constant. If there is no applied magnetic field, the energy of the orbital is independent of m_ℓ and of m_s .

We notice that:

- 1) There are infinite discrete levels, the Coulombian potential slowly tends to zero, so that the levels thicken at high n .
- 2) The energy eigenvalues depend on n only.

3) The states are degenerate in m_ℓ and ℓ (the degeneracy in ℓ is “accidental”, it depends on the $1/r$ dependence of the Coulombian potential).

4) The degeneracy of the energy levels is:

$d = 2 \sum_{\ell=0}^{n-1} (2\ell + 1) = 2n^2$, where we used the fact that $\ell = 0, \dots, n-1$, and that, for any value of ℓ , there are $(2\ell + 1)$ possible values of m_ℓ , and the spin degeneracy ($m_s = \pm 1/2$).

A given pair of quantum numbers n, ℓ (**subshell**) refers to $2(2\ell + 1)$ distinct electronic wave functions, which differs for the values of m_ℓ, m_s .

Finally, we have built the electron wavefunction as simultaneous eigenfunction of the operators H, L^2, L_z, S^2, S_z .

$$\psi(\mathbf{q}) = \chi_{s,m_s} \Psi_{n,\ell,m_\ell}(\mathbf{r}) = \chi_{s,m_s} R_{n,\ell}(r) Y_{\ell,m_\ell}(\theta, \varphi)$$

The quantum numbers are related by:

$$n = 1, 2, 3 \dots$$

$$\ell = 0, \dots, n-1$$

$$m_\ell = -\ell, -\ell + 1, \dots, \ell - 1, \ell$$

$$m_s = -\frac{1}{2}, \frac{1}{2}$$

A value of ℓ can be expressed as an “orbital”. Orbitals with $\ell = 0, 1, 2, 3$ are indicated with the letters s, p, f, d .

The “shell” n is sometimes indicated with letters: $n = 1, 2, 3, 4 \dots$ corresponding to shells K, L, M, N and so on. (I will not use this notation in the present notes, to avoid confusion with other literal symbols).

Configurations.

An atom or ion with a *single* electron can have its electron in any of the allowed orbitals or wave functions. The orbitals, in order of increasing energy, are $1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s$, and so on (Aufbau principle).

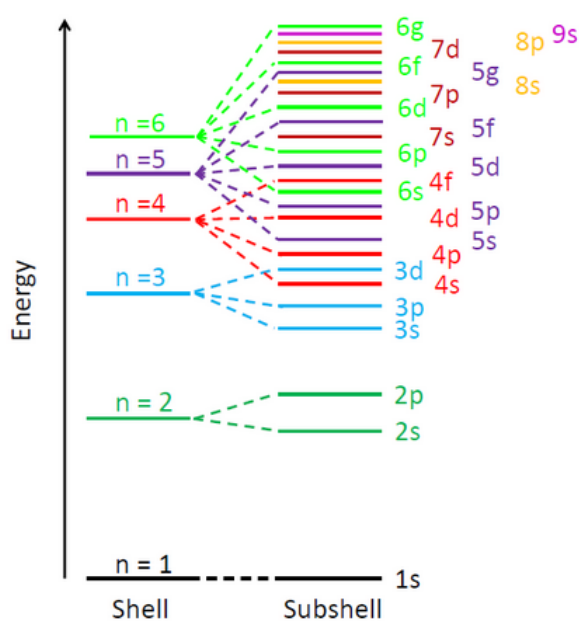
Note from the figure that 4s, 5s... are out of order: e.g., 4s subshell is closer to nucleus and effective potential gives it more binding energy than 3d.

According to the quantum mechanical theory of *multielectron* atoms, it is a good first *approximation* to think of the electrons as occupying “single-electron orbitals”, characterized by integer quantum numbers n and ℓ : $n=1,2,3,\dots$ and $0 \leq \ell < n$.

When the atom has more than one electron, the Pauli exclusion principle prevents two electrons to share the same wavefunction. In any subshell there can be at most $2(2\ell + 1)$ electrons.

The number of electrons occupying a subshell n, ℓ is designated by a superscript: for example, the neutral Sodium, with eleven electrons, has ground state configuration $1s^2 2s^2 2p^6 3s^1$. The value of m_s for the electron in the 3s subshell, however, is undetermined.

Another example: the ground state configuration of neutral Carbon is $1s^2 2s^2 2p^2$. The two electrons in the subshell 2p may be in any of the three 2p orbitals ($2p_x, 2p_y, 2p_z$) and with any of two the possible spin orientations allowed.



Aufbau principle: how electrons fill the orbitals in the atom ground state.

Multielectron atoms and spectroscopic terms.

For a given electronic configuration of a multielectron atom, its state depends on its total angular momentum, including spin and orbital components.

As seen above, the atomic electron configurations are ambiguous, as they do not specify in which orbital in the subshell the electrons are, in an uncomplete subshell. If a subshell has more than one electron and less than $4\ell + 1$ electrons, there is more than one way in which the electrons can arrange. Since, in principle, their energies may be different, it is important to remove any ambiguity.

In light atoms ($Z \leq 30$), electron spins \mathbf{s}_i interact *among themselves* (spin-spin interactions) so they combine to form a total spin angular momentum \mathbf{S} . The same happens with orbital angular momenta ℓ_i (orbit-orbit interactions) forming a total orbital angular momentum \mathbf{L} . The interaction between the quantum numbers \mathbf{L} and \mathbf{S} is called **Russell–Saunders coupling** or **L-S coupling**.¹ Coupling occurs between the resultant spin and orbital momenta of an electron which gives rise to \mathbf{J} the total angular momentum. The idea is to determine the total orbital angular momentum \mathbf{L} and the total spin \mathbf{S} , and then to

¹ Notice: This is true if the interactions $\ell_i \mathbf{s}_i$, the interactions between spin and orbital momentum of the single electron i , are smaller than the couplings with orbital momenta or spin of other electrons (coupling $\ell_i \ell_j$ or $\mathbf{s}_i \mathbf{s}_j$). For heavy atoms, the *individual* spin-orbit coupling of an electron may be as large as the spin-spin or orbit-orbit interactions with the other electrons; in that case, the *jj* coupling is used in place of the L-S coupling. Russell-Saunders is spin-orbit coupling, where spin-orbit coupling is small (light atoms where the electrons aren't particularly relativistic). In this case, the total orbital angular momentum and the total spin angular momentum are *both* good quantum numbers (meaning their operators commute with the Hamiltonian to a good approximation). So we obtain total angular momentum simply by adding total spin and total orbital angular momentum: $\mathbf{J} = \mathbf{L} + \mathbf{S}$. In heavier atoms, where the electrons are relativistic, the individual spin-orbit coupling is quite large, and total spin/orbital angular momentum are no longer good quantum numbers. In this case, we have to add the spin and orbital angular momenta for each electron separately (ℓ_i and \mathbf{s}_i , respectively) to get total angular momentum: $\mathbf{J} = \sum_i (\ell_i + \mathbf{s}_i)$. (*jj* coupling).

vectorially sum them to obtain the total angular momentum J .² In the all-electron system, the **total quantum numbers** for orbital L , spin S , and total J angular momenta are all **good quantum numbers**³, which are conserved. The result of the Russell-Saunders approach is presented as an *atomic term symbol*, or *spectroscopic term*, which has the form: $^{2S+1}L_J$.

A **term symbol** is an abbreviated description of the total spin and orbital angular momentum quantum numbers of the electrons: it specifies the total for *all* electrons in an atom (but may be also used to describe electrons in a given subshell).

Each allowed combination of L, S is a spectroscopic *term*. In an atomic term symbol, J is the total angular momentum quantum number, L is the total orbital angular momentum, and S is the total spin. The quantity $2S+1$ is called *spin multiplicity*.

As we assigned the letters s, p, d, f, ... to the values $\ell=0, 1, 2, 3, \dots$, we create the correspondence: $L=0, 1, 2, 3, \dots$ with the letter S, P, D, F, ...

For an atom with N electrons, the orbital angular momentum L is, in the L-S coupling approach, the vectorial sum of the electrons orbital angular momenta. Similarly, the individual electrons spins add (vectorially) to give a total spin angular momentum S .

$$\mathbf{L} = \sum_{i=1}^N \boldsymbol{\ell}_i ; \quad \mathbf{S} = \sum_{i=1}^N \mathbf{s}_i$$

For the module of \mathbf{L} it is still holding the relation $|\mathbf{L}| = \hbar \sqrt{L(L+1)}$ where L is the quantum number for total orbital angular momentum.

The z-components :

$$L_z \equiv M_L = \sum_{i=1}^N \ell_{z,i} = \sum_{i=1}^N m_{\ell,i} ; \quad S_z \equiv M_S = \sum_{i=1}^N s_{z,i} = \sum_{i=1}^N m_{s,i}$$

² This is an approximation holding if external magnetic fields are weak: otherwise, L and S decouple, producing a different splitting pattern in the energy levels : that is the Paschen-Back effect.

³ Given an operator O with eigenvalues and eigenvectors given by $O|q_i\rangle = q_i |q_i\rangle$, the q_i are said to be *good quantum numbers* if every eigenvector $|q_i\rangle$ remains an eigenvector of O with the same eigenvalues as time evolves, meaning that O is a constant of motion, and O commutes with the Hamiltonian, $[H, O] = 0$.

While the angular momentum sums up as a vector, the z-components sum up as scalars.

In analogy with the z-component of ℓ , which can take the $2\ell + 1$ values $m_\ell = -\ell, -\ell + 1, \dots, 0, \dots, \ell$, also the z-component of L can take $2L+1$ values $L_z = M_L = -L, -L + 1, \dots, 0, \dots, L$.

Similarly, M_S can have $2S+1$ values: $M_S = -S, -S + 1, \dots, 0, \dots, S$. The spin multiplicity is thus representing the number of projections that the total spin can have on the z-axis.

Now we want to learn how to relate microscopic configurations to spectroscopic terms.

- Consider the electronic configuration ns^2 (two electrons in an orbital ns , i. e. $\ell = 0$). There is only one set of values, $m_{\ell 1}, m_{s1}, m_{\ell 2}, m_{s2}$:

$m_{\ell 1}$	m_{s1}	$m_{\ell 2}$	m_{s2}	M_L	M_S
0	$\frac{1}{2}$	0	$-\frac{1}{2}$	0	0

The fact that there is only one value of $M_L = 0$ implies that $L=0$. In the same way, the fact that the only one value of $M_S = 0$ implies that $S=0$.

The total angular momentum is $J=L+S$. The z-component is $J_z \equiv M_J = L_z + S_z = M_L + M_S = 0$ which implies that $J = 0$.

It follows that an electronic configuration ns^2 , $L=S=J=0$. The corresponding spectroscopic term $^{2S+1}L_J$ is (indicating $L=0$ with the letter S) 1S_0 (*Singlet S zero*).

Also an electronic configuration like np^6 will have a term 1S_0 ; indeed, the six electrons in np^6 will have quantum numbers n, ℓ, m_ℓ, m_s given by: $(n, 1, 1, \pm \frac{1}{2})$; $(n, 1, 0, \pm \frac{1}{2})$; $(n, 1, -1, \pm \frac{1}{2})$. Summing up all the m_ℓ we obtain 0, as when we sum up all the m_s .

Then $M_L = 0$ and $M_S = 0$ and, as before, the term is 1S_0 .

Notice that M_L and M_S are necessarily $=0$ for totally filled subshells, because for any electron with negative m_ℓ there is a corresponding

electron with positive m_ℓ which cancels it out. Same for the m_s . We can thus ignore all the electrons which are in filled subshells, when discussing electronic configurations. For example, in the Carbon atom, we can neglect the $1s^2 2s^2$ electrons contribution in the configuration $1s^2 2s^2 2p^2$ of that atom .

- An electronic configuration which has a spectroscopic symbol different than 1S_0 is the *excited* electronic configuration of the *Helium atom* $1s^1 2s^1$. Since $\ell_1 = \ell_2 = 0$, the maximum value of $m_{\ell 1}$ and $m_{\ell 2}$ is zero. Then, the maximum value of $M_L = 0$, thus $L = 0$ is the only possible value of the total orbital angular momentum. Let us build a table with the possible M_S values in the columns, and fill it with the set of values of $m_{\ell 1}, m_{s1}, m_{\ell 2}, m_{s2}$:

		M_S (macrostate)		
		1	0 0	-1
M_L (macrostate)				
0	$0^+ 0^+$	$0^+ 0^-$	$0^- 0^+$	$0^- 0^-$ (microstates)

The notation 0^+ means that one electron has $m_\ell = 0$ and $m_s = +1/2$, while 0^- means that it has $m_\ell = 0$ and $m_s = -1/2$. The sets of possible values of $m_{\ell 1}, m_{s1}, m_{\ell 2}, m_{s2}$ corresponding to each pair (M_L, M_S) are called **microstates**. In the table above there are four microstates because there are two possible spins ($\pm 1/2$) for the electron in the orbital ns and two possible spins ($\pm 1/2$) for the electron in $n's$. Notice that we included both $0^+ 0^-$ and $0^- 0^+$ because the two electrons are in nonequivalent orbitals ($1s$ and $2s$). Since all the values of M_L are zero, they must correspond to $L=0$. In addition, the maximum value of M_S is 1. Therefore, $S = 1$ and $M_S = -1, 0, 1$. The corresponding term will be

$^{2S+1}L_J = ^3S_J$. This 3S_J term accounts for one microstate in each of the columns of the previous table. The central column contains two microstates, and it makes no difference which one we choose: after eliminating one microstate from each column (0^+0^+ ; 0^-0^- ; and 0^+0^- or 0^-0^+), we are just left with the element having $M_L=0$, $M_S=0$ (either 0^+0^- or 0^-0^+): this implies $L=0$ and $S=0$, corresponding to a term $^{2S+1}L_J = ^1S_J$. These two couples of macrostates, $(M_L=0, M_S=0)$ and $(M_L=0, M_S=1)$ can be resumed in this way:

$$L=0, S=1$$

$$M_L=0, M_S = -1, 0, 1$$

$$M_J = M_L + M_S = -1, 0, 1$$

which requires $J=1$

Spectroscopic term: 3S_1

("Triplet S one")

$$L=0, S=0$$

$$M_L=0, M_S = 0$$

$$M_J = M_L + M_S = 0$$

which requires $J=0$

Spectroscopic term: 1S_0

("Singlet S zero")

These two spectroscopic terms correspond to two electronic states having different energies: the triplet state 3S_1 having lower energy than the singlet one.

- As a final example on the deduction of the atomic term symbols, let us consider the *Carbon atom* in its *fundamental state*, $1s^2 2s^2 2p^2$

We have shown that we don't need to consider the completely filled subshells, since they necessarily have null values of M_L and M_S . We can focus on the configuration np^2 . We will build a table as we did before, with the possible values of $m_{\ell 1}, m_{s1}, m_{\ell 2}, m_{s2}$. We have to assign two electrons to two of six possible spin-orbitals:

$$n = 2, \ell = 1, m_{\ell} = 1, m_s = \frac{1}{2}$$

$$n = 2, \ell = 1, m_{\ell} = 1, m_s = -\frac{1}{2}$$

$$n = 2, \ell = 1, m_\ell = 0, m_s = \frac{1}{2}$$

$$n = 2, \ell = 1, m_\ell = 0, m_s = -\frac{1}{2}$$

$$n = 2, \ell = 1, m_\ell = -1, m_s = \frac{1}{2}$$

$$n = 2, \ell = 1, m_\ell = -1, m_s = -\frac{1}{2}$$

We have, for the first electron, six possible choices. For the second electron, just five. In total, we have $6 \times 5 = 30$ choices. Since electrons are indistinguishable, the order of the two spin-orbitals is irrelevant. Then, we have to divide by 2 the 30 possible choices, and we are left with 15 possible choices, i.e. 15 distinguishable ways to assign the two electrons to the six spin-orbitals above. In general, the number of distinguishable modes to assign N electrons to G spin-orbitals belonging to the same electronic shell (equivalent orbitals, e.g. all 2p) is given by

$$\frac{G!}{N!(G-N)!} = \binom{G}{N} \quad . \text{ For } G=6 \text{ and } N=2, \text{ this expression gives the value 15.}$$

To find the 15 possible sets of $m_{\ell 1}, m_{s1}, m_{\ell 2}, m_{s2}$ in the case of an electronic configuration np^2 , let's first determine the possible values of M_L and M_S . Since $m_{\ell 1}, m_{\ell 2}$ can both reach 1 as maximum value, M_L will be, at most, $M_L = 2$, so its possible values will be -2, -1, 0, 1, 2. Analogously, since m_{s1} and m_{s2} can both have $\frac{1}{2}$ as maximum value, M_S will be, at most, 1: then, the possible values of M_S are $M_S = -1, 0, 1$.

Using these informations, let's build a table with columns headed with the possible values of M_S and the lines headed with the possible values of M_L , where, for example, the notation $1^+ - 1^-$ stays for

$$m_{\ell 1} = 1, m_{s1} = +\frac{1}{2}, m_{\ell 2} = -1, m_{s2} = -\frac{1}{2}$$

Differently from the previous example, in which we treated non-equivalent orbitals, we now do not include both $1^+ 0^-$ and $0^- 1^+$ in the

cell $M_S = 0$, $M_L = 1$, because in this case the orbitals are equivalent (two orbitals $2p$): the two microstates 1^+0^- and 0^-1^+ are indistinguishable.

		M_S (macrostate)		
		1	0	-1
M_L (macrostate)				
2		1^+1^+	1^+1^-	1^-1^-
1		1^+0^+	0^+1^- ; 0^-1^+	1^-0^-
0		0^+0^+ ; 1^+-1^+	0^-0^+ ; -1^+1^- ; -1^-1^+	-1^-1^- ; 0^-0^-
-1		-1^+0^+	-1^+0^- ; -1^-0^+	-1^-0^-
-2		-1^+-1^+	-1^+-1^-	-1^--1^-

(microstates $m_{\ell 1}, m_{s1}, m_{\ell 2}, m_{s2}$ for a np^2 shell)

Now we have to deduce the values of L and S from the tabulated values of M_S and M_L . The six microstates circled in grey are excluded from the Pauli's principle: indeed, if the two electrons in the shell np have the same value of m_ℓ , they must have opposite spins. We cancel those states from our table.

The largest value of M_L is 2, (both electrons have $m_\ell = 1$), which appears *only* when $M_S = 0$. Then, there must exist a state with $L=2$ and $S=0$, i.e. 1D . Since $L=2$, $M_L = -2, -1, 0, 1, 2$, and 1D will contain a microstate for each line in the table. For those lines which contain more than one microstate (the second, the third and the fourth), it is not important which microstate one chooses. We can choose arbitrarily one of the microstates 0^+1^- , -1^+1^- , -1^+0^- . We choose -1^+1^- and we circle in red the microstates associated to 1D . Since its multiplicity is $(2S+1)(2L+1) = 1 \times 5$, it will account for 5 of the 15 possible quantum

states. As for the value of J , remember that $M_J = M_L + M_S$. For the five elements corresponding to 1D , $M_J = -2, -1, 0, 1, 2$, which implies $J=2$. The complete term symbol is then 1D_2 . Notice that the *degeneracy* of this state is $(2J+1)=5$.

The largest remaining value of M_L is 1, implying $L=1$. There are microstates with $M_L=-1, 0, 1$ associated to $M_S=-1, 0, 1$, circled in cyan. These nine microstates correspond to $L=1, S=1$, i.e. 3P (P triplet). For the nine microstates of 3P , $M_J = M_L + M_S = 2, 1, 0, 1, 0, -1, 0, -1, -2$.

We can then associate five microstates (with $M_J = 2, -1, 0, 1, 2$) to a value $J=2$, three microstates ($M_J = -1, 0, 1$) to $J=1$, and one microstate ($M_J=0$) to $J=0$. We see that the state 3P has three possible J values, corresponding to three atomic terms $^3P_0, ^3P_1, ^3P_2$.

The only microstate left has $M_L=0$ and $M_S=0$ at the table's center, which implies $L=0=S$ (S singlet 1S_0). A term with $L=0$ or $S=0$ can have only one value of J . The multiplicity of the term $2S+1$ can take values 1, 2, 3, 4 and leads to the designation of singlet, doublet, triplet, quartet, and so on.

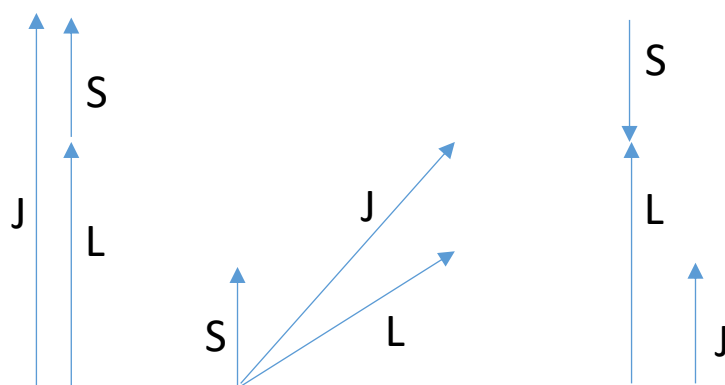
In summary, the electronic states associated to an np^2 configurations are two singlets $^1D_2, ^1S_0$ and three triplets, $^3P_0, ^3P_1, ^3P_2$:

$$^1D_2, ^3P_0, ^3P_1, ^3P_2, ^1S_0.$$

The values J of the atomic terms can be determined in relation to L and S , since $J=L+S$. The maximum value of J corresponds to L and S pointing to the same direction, $J=L+S$, while the minimum is when L and S point to opposite direction. i.e. $J=|L-S|$. The intermediate values are:

$$J = L+S, L+S-1, L+S-2, \dots, |L-S|. \quad (*)$$

This equation has a graphical representation: L and S are summed up in all the modes in which their sum is vector of length 0, 1, 2... if S is integer, or $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$ if $S=\frac{1}{2}, \frac{3}{2}, \frac{5}{2}$ and so on. For example, if $L=2$ and $S=1$, then L and S can be summed as vectors in this way:



Applying equation (*) to the previous 3P ($S=1, L=1$) term, we see that the values of J are given by $J=(1+1), (1+1)-1, 1-1$. Thus we have $J= 2, 1, 0$, as previously determined. Counting the possible M_J for each J , we see that 3P correspond to 9 macrostates.

Energy of the terms.

Different terms (e.g. for an np^2 configuration, the three possible terms $^3P, ^1D$ and 1S) will *differ in energy* by a significant fraction of the total binding energy of the electrons in the partially filled subshell. For atoms and low-ionization ions, the energy differences between different terms of the ground state configuration will be of order a few eV. Table 1 lists the terms for the ground state configurations of atoms and ions where the outermost subshell is ns or np . Higher energy states can be constructed by taking one of the electrons out of the ground state configuration and putting it into a higher orbital. For example, in the case of atomic carbon, this can be done by removing one of the $2s$ electrons and promoting it to a $2p$ orbital, giving $1s^2 2s^1 2p^3$ – the electrons in this configuration can also be organized into different terms. The energy levels are established by **Hund's rules**, which assume that the repulsion between the outer electrons is much greater than the spin-orbit interaction (L-S coupling regime):

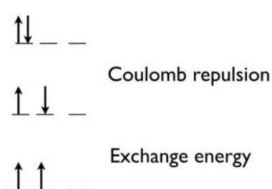
- 1) For a given electron configuration, the term with maximum multiplicity $2S+1$ has the lowest energy. ⁴
- 2) For a given multiplicity, the term with the largest value of the total orbital angular momentum J quantum number has the lowest energy.
- 3) For a given term (S and L fixed), in an atom with outermost subshell half-filled or less, the level with the lowest value of the total angular momentum quantum number J lies lowest in energy. If the outermost shell is more than half-filled, the level with the highest value of J is lowest in energy.

According to these rules, we can say, for example, that, in order of increasing energy, $^3P > ^1D > ^1S$, etc., as in Table 1:

Table 1 Terms for ns and np Subshells

Ground configuration	Terms (in order of increasing energy)	Examples
$\dots ns^1$	$^2S_{1/2}$	H I, He II, C IV, N V, O VI
$\dots ns^2$	1S_0	He I, C III, N IV, O V
$\dots np^1$	$^2P_{1/2,3/2}^o$	C II, N III, O IV
$\dots np^2$	$^3P_{0,1,2}, ^1D_2, ^1S_0$	C I, N II, O III, Ne V, S III
$\dots np^3$	$^4S_{3/2}^o, ^2D_{3/2,5/2}^o, ^2P_{1/2,3/2}^o$	N I, O II, Ne IV, S II, Ar IV
$\dots np^4$	$^3P_{2,1,0}, ^1D_2, ^1S_0$	O I, Ne III, Mg V, Ar III
$\dots np^5$	$^2P_{3/2,1/2}^o$	Ne II, Na III, Mg IV, Ar IV
$\dots np^6$	1S_0	Ne I, Na II, Mg III, Ar III

⁴ According to the first rule, electrons always enter an empty orbital before they pair up. Electrons are negatively charged and, as a result, they repel each other. Electrons tend to minimize repulsion by occupying their own orbitals, rather than sharing an orbital with another electron. Furthermore, the electrons in singly occupied orbitals are less effectively shielded from the nucleus. Besides the Coulomb repulsion, there's also a quantum mechanical effect. The *exchange energy* (which is favorable) increases with the number of possible exchanges between electrons with the same spin and energy. In transitioning from the top state to the middle state of figure below, we remove the Coulomb repulsion between electrons in the same orbital. Moreover, in transitioning from the middle state to the bottom state (most stable state predicted by Hund's first rule), we *gain* the *exchange energy*, because these two electrons are indistinguishable.



Fine-structure splitting due to spin-orbit interaction.

Remember that a term is defined as a couple (L,S). The multiplicity of a term with total spin S and orbital angular momentum L is $g = (2S + 1) \times (2L + 1)$. Thus, for example, the 3P term, with $S = 1$ and $L = 1$, has multiplicity $3 \times 3 = 9$.

When relativistic effects are small, a level (**term**) with a given $L \neq 0$ and a given $S \neq 0$ is split in a number of distinct levels **with different values of J**, because of the spin-orbit coupling. This coupling is a results of the interaction of the magnetic moment of the electron spin with the magnetic moment of the orbital motion. This fine-structure splitting is a small perturbation-of the order of $\alpha^2 Z^2$ with α the fine-structure constant, and Z the nuclear charge. Transitions among the fine-structure levels occur therefore at near to far-IR wavelength: the fractional energy shifts are of order $\sim 10^{-2}$ eV. This splitting of energy levels is the “fine structure”. In other words, as long as L and S are both non null, there are different ways in which L and S can combine to give total angular momentum J, corresponding to different energies: the spin-orbit interaction led to the “fine-structure” energy splitting of the terms, as in Figure 1.

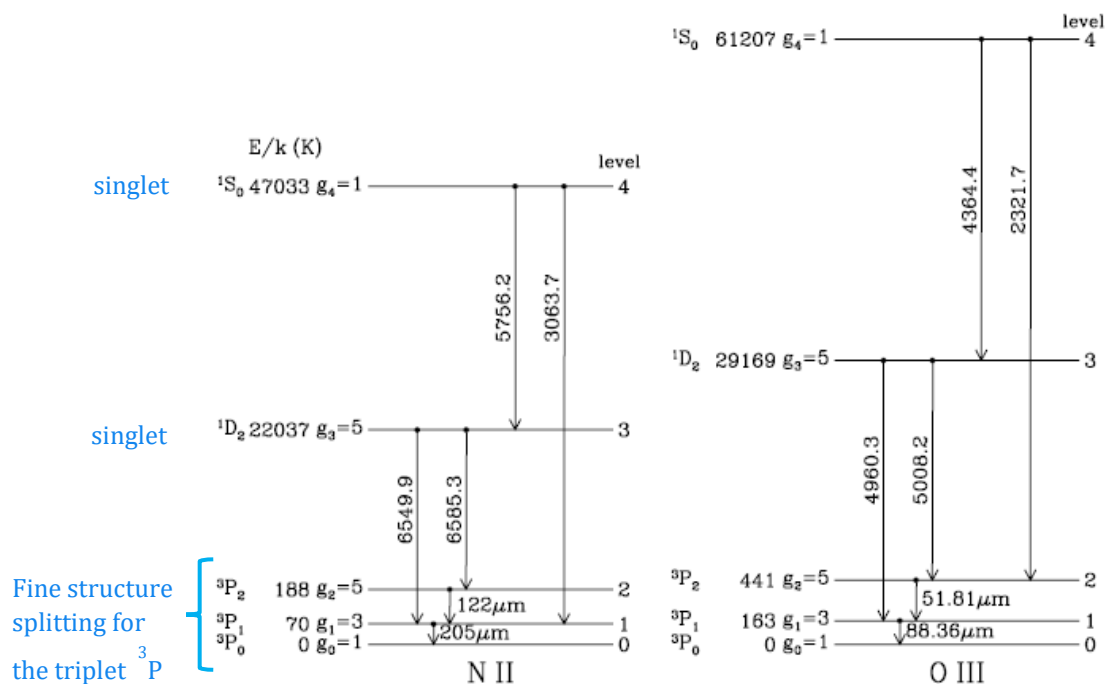


Figure 1

Energy-level diagram for the ground configuration of the $2p^2$ ions N II and O III. (Fine-structure splitting is exaggerated for clarity.) Forbidden transitions connecting these levels are shown, with wavelengths in vacuo.

Note that the adopted notation for designating energy levels overlooks possible hyperfine structure arising from interaction of the electrons with the magnetic moment of the nucleus.

● Exercise. Find the terms describing $ns np$ (e.g., C III with one electron in an excited state: instead of being $1s^2 2s^2$, one of the electrons jumped to the $1p$ orbitals.)

You should obtain $1P_1$, $3P_2$, $3P_1$, $3P_0$.

Parity of the state.

In the spectroscopic notation, it is customary to indicate in the spectroscopic term also the parity of the state, so the energy level in spectroscopic notation will be

$2S+1 \mathcal{L}_J^p$ where $L=0,1,2,3\dots$ ($\mathcal{L} = S,P,D,F$) and

$p = \text{blank for state of even parity; } o \text{ for state of odd parity.}$

The parity of an energy level is “even” or “odd” depending on whether the electronic wave function changes sign under reflection of **all** of the electron positions through the origin. If ℓ_i are the orbital angular momenta of the individual electron orbitals, then the parity is:

even if $\prod_i (-1)^{\ell_i} = 1$ ($\sum_i \ell_i = \text{even}$)
 odd if $\prod_i (-1)^{\ell_i} = -1$ ($\sum_i \ell_i = \text{odd}$)

Hyperfine splitting: interaction with nuclear spin.

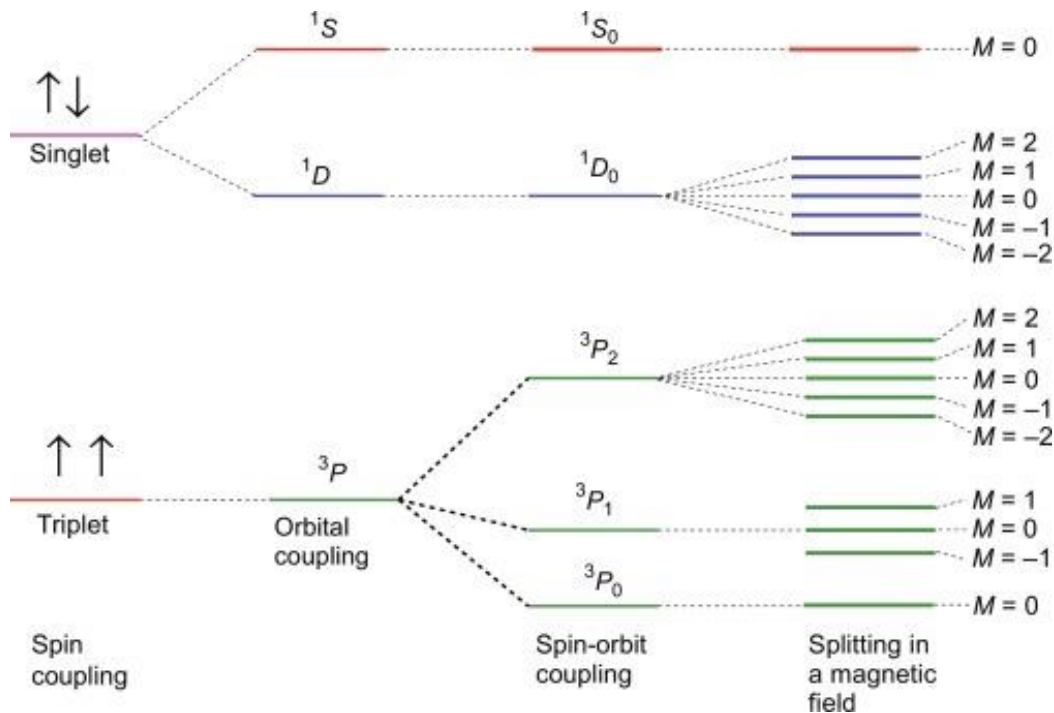
If the nucleus has nonzero spin, it will have a nonzero magnetic moment. If the nucleus has a magnetic moment, then fine-structure levels with nonzero electronic angular momentum J can themselves be split due to interaction of the electrons with the magnetic field produced by the nucleus. Each term with nonzero value of J is indeed still degenerate with respect to the orientation of J : J is space quantized in a magnetic field. Designating M_J as the component of J along the magnetic field, M_J can take the values $J, (J-1), (J-2), \dots, -J$ (i.e., $g_J = 2J + 1$). For example, the 3P term corresponds to nine macrostates, with $L=1$, $S=1$ and $J=0,1,2$, and M_J varying accordingly from $-J$ to J . Each of the J values corresponds to $2J+1$ values of M_J .

Generally, the nuclear spin is of little concern: this “hyperfine” splitting is typically of order 10^{-6} eV. However, for HI, the hyperfine structure, resulting from the interaction of the magnetic moment of the electron and the nucleus, is of particular interest because it gives rise to the 21cm line ($h\nu = 5.9 \times 10^{-6}$ eV).

Zeeman effect

When a static magnetic field \mathbf{B}_0 is applied, each of the fine-structure levels splits into $2J+1$ energy levels, with energies depending on the value of $\mathbf{J} \cdot \mathbf{B}_0$. The energy splittings are small, $\mu_B B_0 \approx 5.78 \times 10^{-15} (B_0 / \mu G)$ eV, where $\mu_B \equiv e\hbar/2m_e c$ is the Bohr magneton.

Interstellar magnetic field strengths are of order $1\text{--}100 \mu G$ and therefore the Zeeman shifts are too small to be measured for transitions in the sub-mm or shortward ($h\nu \geq 10^{-4}$ eV)



Radiative transitions

Selection rules.

Selection rules for electronic transitions merely reflect conservation principles. Angular momentum has to be conserved under vector addition and, since the photon has one unit of angular momentum, this leads to the

Strong transitions are driven by electric dipoles. **Electric dipole** selection rules are two types: rigorous rules - must always be obeyed; propensity rules - lead to weaker transitions.

Rigorous rules:

(1) $\Delta J = 0, \pm 1$ with $J = 0 \rightarrow 0$ forbidden

(2) $\Delta M_J = 0, \pm 1$

(3) parity must change (Laporte rule): the dipole operator in the transition moment integral (proportional to the transition probability) has odd parity and hence couples states with opposing parity .

Additional set of rules which is not rigorously satisfied by complex atoms (propensity rules):

(4) $\Delta S=0$ The spin multiplicity is unchanged. The electron spin can only be changed by a magnetic field.

(5) Δn arbitrary, $\Delta l = \pm 1$ Only one electron jumps: the configuration of the two states must differ by only the movement of a single electron.

(6) $\Delta L=0, \pm 1$, with $L=0 \rightarrow 0$ forbidden

Configuration interaction weakens this rule: e.g. ground state of Be $1s^2 2s^2$ is in fact mixed with 5% contribution from $1s^2 2p^2$..

In many-electrons systems, there can be **transitions that violate rule 4** and change the total spin (**semi-forbidden** transitions): they are called **intercombination lines** (e.g. CIII]). Semi-forbidden transitions, resulting in intercombination lines, are electric dipole transitions for which the selection rule of spin conservation is violated as a result of the failure of LS coupling .

Transitions which violate the propensity rule 5 and/or 6 are strictly **forbidden**, and are labelled by *two* square brackets (e.g. [CIII]).

Table 2 gives examples of the 3 types of transitions.

Table 2

Species	f	\leftarrow	i	$\lambda(\text{\AA})$	$A_{ul}(s^{-1})$	ΔJ	Parity [†]	ΔS	Δl
NII	$2p^2 \ ^3P_0^e$	\leftarrow	$2p3s \ ^3D_1^o$	1084.0	2.18×10^8	-1	$o \rightarrow e$	0	+1
CIII]	$2s^2 \ ^1S_0^e$	\leftarrow	$2s2p \ ^3P_1^o$	1908.7	114	+ 1	$o \rightarrow e$	-1	-1
[CIII]	$2s^2 \ ^1S_0^e$	\leftarrow	$2s2p \ ^3P_2^o$	1906.7	0.0052	+ 2	$o \rightarrow e$	-1	-1

How do I calculate the parity of a term?

You don't know it just by the term. Only electrons in odd orbitals (with ℓ odd) contribute to the total parity. An odd number of electrons in odd orbitals (those with an odd ℓ such as in p, f,...) correspond to an odd term symbol, while an even number of electrons in odd orbitals correspond to an even term symbol. For any closed subshell, the summation is always an even number, because there is an even number of electrons. We have to sum only the ℓ of electrons in open subshells of odd orbitals. For example, $2p3s$ is odd. $2p^2$ is even. $2s2p$ is odd. $2p^3s$ is odd.

Photons do not change spin usual, thus the rule $\Delta S=0$. However, relativistic effects mix spin states, especially for high Z ions.

Example: [Weak spin changing transitions](#) → [intercombination lines](#). Doubly ionized Carbon, CIII or C^{2+} , is observed to have the semi forbidden transition: CIII] $2s^2\ ^1S_0^e - 2s2p\ ^3P_1^o$ at $\lambda = 1908.7\ \text{\AA}$ (in the UV band).

$2s2p\ ^3P_1^o$ state is metastable - no allowed radiative decay.

The abundant nebular emission features in the far-UV, including CIII] $\lambda\lambda 1907, 1909$, C IV $\lambda\lambda 1548, 1550$, HeII $\lambda 1640$, O III] $\lambda\lambda 1661, 1666$ and Si III] $\lambda\lambda 1882, 1892$, are especially important in probing the ionized gas in HII regions. These lines can be combined to infer various physical parameters, such as metallicity, abundance pattern, and ionization parameter, and provide valuable constraints on the ionizing stellar populations. (see, e.g. CIII] Emission in Star-forming Galaxies at $z \sim 1$ Du et al., 2017)

Doublet : C III] $\lambda\lambda 1907, 1909$. The C III] doublet is a collisionally excited forbidden/semi-forbidden transition, which is typically observed in HII regions in star-forming galaxies. The doublet ratio is determined by the electron density.

Other examples: transitions between singlet and triplet levels of Helium.

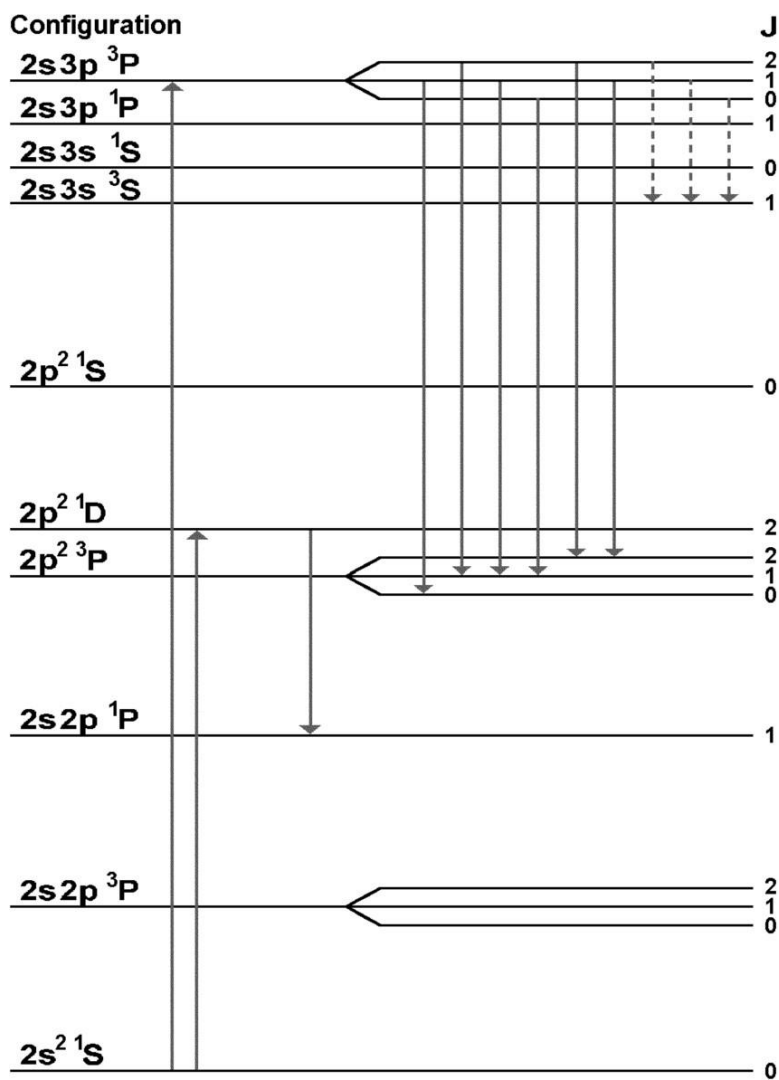
Or N II] $2143.4\ \text{\AA}\ ^3P_2 - ^5S_2^o$. The A-coefficients are a million times weaker

- Exercise. Is $2s^2 - 2s2p$ allowed? Is $2s^2 - 2s3d$ allowed? Is $2s^2 - 3p^2$ allowed?

Is $^1S - ^1P^o$ allowed? And is $^3D - 3P^o$ allowed? Is $^1S - ^1S^o$ allowed? And $^3S - ^3D^o$?

Table 5.1 Selection rules for atomic spectra. Rules 1, 2 and 3 must always be obeyed. For electric dipole transitions, intercombination lines violate rule 4 and forbidden lines violate rule 5 and/or 6. Electric quadrupole and magnetic dipole transitions are also described as forbidden.

	Electric dipole	Electric quadrupole	Magnetic dipole
1.	$\Delta J = 0, \pm 1$ Not $J = 0 - 0$	$\Delta J = 0, \pm 1, \pm 2$ Not $J = 0 - 0, \frac{1}{2} - \frac{1}{2}, 0 - 1$	$\Delta J = 0, \pm 1$ Not $J = 0 - 0$
2.	$\Delta M_J = 0, \pm 1$	$\Delta M_J = 0, \pm 1, \pm 2$	$\Delta M_J = 0, \pm 1$
3.	Parity changes	Parity unchanged	Parity unchanged
4.	$\Delta S = 0$	$\Delta S = 0$	$\Delta S = 0$
5.	One electron jumps Δn any $\Delta l = \pm 1$	One or no electron jumps Δn any $\Delta l = 0, \pm 2$	No electron jumps $\Delta n = 0$ $\Delta l = 0$
6.	$\Delta L = 0, \pm 1$ Not $L = 0 - 0$	$\Delta L = 0, \pm 1, \pm 2$ Not $L = 0 - 0, 0 - 1$	$\Delta L = 0$



Allowed transitions for the $2s3p$ P and $2p$ D levels of the CIII ion. Upward lines indicate the excitation from the ground level and the downward lines the radiative transitions. Dotted lines represent emissions in the visible

$$\begin{array}{ll}
P_0(x) = 1 & P_3(x) = \frac{1}{2}(5x^3 - 3x) \\
P_1(x) = x & P_4(x) = \frac{1}{8}(35x^4 - 30x^2 + 3) \\
P_2(x) = \frac{1}{2}(3x^2 - 1) & P_5(x) = \frac{1}{8}(63x^5 - 70x^3 + 15x)
\end{array}$$

Table 10 – 1. The First Six Legendre Polynomials.

$$\begin{array}{ll}
P_{0,0}(x) = 1 & P_{2,0}(x) = \frac{1}{2}(3x^2 - 1) \\
P_{1,1}(x) = -\sqrt{1-x^2} & P_{3,3}(x) = -15(\sqrt{1-x^2})^3 \\
P_{1,0}(x) = x & P_{3,2}(x) = 15x(1-x^2) \\
P_{2,2}(x) = 3(1-x^2) & P_{3,1}(x) = -\frac{3}{2}(5x^2 - 1)\sqrt{1-x^2} \\
P_{2,1}(x) = -3x\sqrt{1-x^2} & P_{3,0}(x) = \frac{1}{2}(5x^3 - 3x)
\end{array}$$

Table 10 – 2. The First Few Associated Legendre Polynomials.

$$\begin{array}{l}
L_0(x) = 1 \\
L_1(x) = -x + 1 \\
L_2(x) = x^2 - 4x + 2 \\
L_3(x) = -x^3 + 9x^2 - 18x + 6 \\
L_4(x) = x^4 - 16x^3 + 72x^2 - 96x + 24 \\
L_5(x) = -x^5 + 25x^4 - 200x^3 + 600x^2 - 600x + 120 \\
L_6(x) = x^6 - 36x^5 + 450x^4 - 2400x^3 + 5400x^2 - 4320x + 720
\end{array}$$

Table 10 – 3. The First Seven Laguerre Polynomials.

$$\begin{array}{ll}
L_0^0(x) = L_0(x) & L_0^2(x) = 2 \\
L_1^0(x) = L_1(x) & L_3^0(x) = L_3(x) \\
L_1^1(x) = -2x + 4 & L_3^1(x) = -4x^3 + 48x^2 - 144x + 96 \\
L_0^1(x) = 1 & L_2^3(x) = 60x^2 - 600x + 1200 \\
L_2^0(x) = L_2(x) & L_3^3(x) = -120x^3 + 2160x^2 - 10800x + 14400 \\
L_2^1(x) = 3x^2 - 18x + 18 & L_3^2(x) = -20x^3 + 300x^2 - 1200x + 1200 \\
L_2^2(x) = 12x^2 - 96x + 144 & L_1^3(x) = -24x + 96 \\
L_1^2(x) = -6x + 18 & L_0^3(x) = 6
\end{array}$$

Table 10 – 4. Some Associated Laguerre Polynomials.

Further reading

Bransden B.H, Joachain (2003), *Physics of Atoms and Molecules*, John Wiley & Sons: provides a comprehensive discussion of the spectroscopy of atoms and ions.