

# Ay126: LS & JJ coupling, Spectroscopic Terms & Hund's rules

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## 1 General Framework

In the orbital approach, each electron is assigned an orbital and the primary Hamiltonian is the central-field approximation,  $H_{CF}$ , while the residual electrostatic repulsion is  $H_{res}$ . here

$$H_{CF} = \sum_{i=1}^N \left( -\frac{\hbar^2}{2m} \nabla_{r_i}^2 + V_{CF}(r_i) \right) \quad (1)$$

accounts for the kinetic energy of the electrons and Coulomb attraction between electrons and the nucleus and screening of the nucleus by the electrons and the residual Coulomb Hamiltonian accounts for the non-radial (angular) part of the Coulomb interaction which is sensitive to angular momentum  $l$ .

$$H_{res} = \sum_{j>i}^N \frac{1}{r_{ij}} - \sum_{i=1}^N S(r_i). \quad (2)$$

Each electron has the following quantum numbers:  $n, l, s$ . There is no interaction between the spin angular momenta and the spins. So,  $L = \sum l_i$  and  $S = \sum s_i$  are conserved quantities and are thus good quantum numbers. Furthermore, the sum of the angular and spin momenta of each shell is zero. So from the point of view of optical and UV emission lines (and also all of Chemistry!) it is only the valence electrons that matter.<sup>1</sup>

From hydrogen we know that spin-orbit interactions lead to lifting of degeneracy of levels.

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<sup>1</sup>We have seen that the UV/optical lines of Alkali elements has a striking resemblance to the Hydrogen spectrum. In a similar fashion, we can expect that the Alkaline elements (e.g.,  $1s^2 2s^2$  Beryllium or  $1s^2 2s^2 2p^6 3s^2$  Magnesium) should have spectrum resembling that of Helium. Here, we attack the model for more complex systems: Carbon ( $1s^2 2s^2 2p^2$ ), Nitrogen ( $1s^2 2s^2 2p^3$ ) and Oxygen ( $1s^2 2s^2 2p^4$ ), which also happen to be of great importance to astronomy.

So we now have an additional perturbing Hamiltonian,  $H_{SO}$ :

$$H_{SO} = \sum_{i=1}^N \xi(r_i) \vec{l}_i \cdot \vec{s}_i \quad (3)$$

**Keep in mind that  $H_{SO} \propto Z^4$  and  $H_{res} \propto Z$ .**

Let  $\vec{L} = \sum_i \vec{l}_i$  and  $\vec{S} = \sum_i \vec{s}_i$ . Let  $\vec{J} = \vec{L} + \vec{S}$  be the total angular momentum. All we can state is that  $\vec{J}$  is conserved. For now let us assume only two valence electrons. It is clear that the  $H_{SO}$  consists of terms of the following sort:

$$\begin{aligned} \Gamma_1 &= a_1 \mathbf{s}_1 \cdot \mathbf{s}_2 \\ \Gamma_2 &= a_2 \mathbf{l}_1 \cdot \mathbf{l}_2 \\ \Gamma_3 &= a_3 \mathbf{l}_1 \cdot \mathbf{s}_1 \\ \Gamma_4 &= a_4 \mathbf{l}_2 \cdot \mathbf{s}_2 \\ \Gamma_5 &= a_5 \mathbf{l}_1 \cdot \mathbf{s}_2 \\ \Gamma_6 &= a_6 \mathbf{l}_2 \cdot \mathbf{s}_1. \end{aligned} \quad (4)$$

The three terms correspond to spin correlation energy, electrostatic repulsion and spin-orbit interaction.

For light elements  $\Gamma_1$  and  $\Gamma_2$  dominate over  $\Gamma_3$  and  $\Gamma_4$  and the remaining two interactions are negligible. In this case,  $H_{res} > H_{SO}$ . A good approximation can be obtained treating  $L$  and  $S$  as “good quantum” numbers. This leads to the so-called “L-S” coupling approximation.

In contrast, for heavier elements, the situation is the opposite:  $\Gamma_3$  and  $\Gamma_4$  dominate over  $\Gamma_1$  and  $\Gamma_2$  (whilst the remaining two terms continue to be negligible). This observation leads to “j-j” coupling. In this case, you sum  $j_i$  to yield  $J$ . In this case,  $H_{SO} > H_{res}$ . See Figure 1 for graphical summary.

## 2 L-S Coupling

In the L-S coupling approach, the primary Hamiltonian is  $H_{CF} + H_{SO}$ . These yield wave functions of the sort  $L, S, M_L, M_S$ . The interaction energy for light elements, ordered in decreasing energy, is as follows:

$$\Gamma_1 = \frac{1}{2} a_1 [S(S+1) - s_1(s_1+1) - s_2(s_2+1)] \quad (5)$$

$$\Gamma_2 = \frac{1}{2} a_2 [L(L+1) - l_1(l_1+1) - l_2(l_2+1)] \quad (6)$$

$$\Gamma_3 + \Gamma_4 = \frac{1}{2} A [J(J+1) - L(L+1) - S(S+1)]. \quad (7)$$

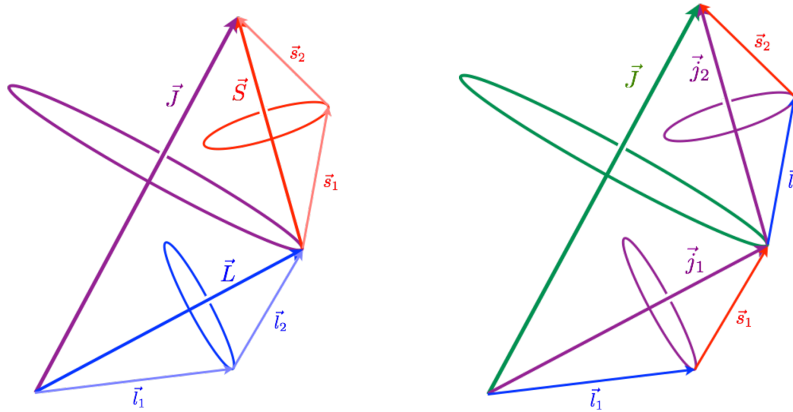


Figure 1: (Left) L-S coupling. (Right) j-j coupling.

Here,  $\mathbf{L} = \mathbf{l}_1 + \mathbf{l}_2$ ,  $\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2$  and  $\mathbf{J} = \mathbf{L} + \mathbf{S}$ .

A quick way to compute allowed values of L, S and J is the following: L ranges from  $|l_1 - l_2|$  to  $l_1 + l_2$ , S ranges from  $|s_1 - s_2|$  to  $s_1 + s_2$  and J varies from  $|L - S|$  to  $L + S$ . If either quantity (L or S) is zero then there is only one value for J (single term). For instance, if  $L = 0$ ,  $S = 1$  then  $J = 1$  as is also the case for  $L = 1$  and  $S = 0$ .

## 2.1 Spectroscopic Terms

Atomic spectroscopists developed “term” notation for each energy level. We will use the Helium atom to illustrate the term notation. The ground state of Helium atom is  $1s^2$ . The angular momenta of the two electrons are  $l_1 = 0$  and  $l_2 = 0$ . The spin of one electron is say  $+1/2$ . Then by Pauli’s principle the spin of the other must be  $-1/2$ . Thus the ground state has  $S = 0$  and  $L = 0$ . Since J ranges from  $L + S$  to  $|L - S|$  we have  $J = 0$ .

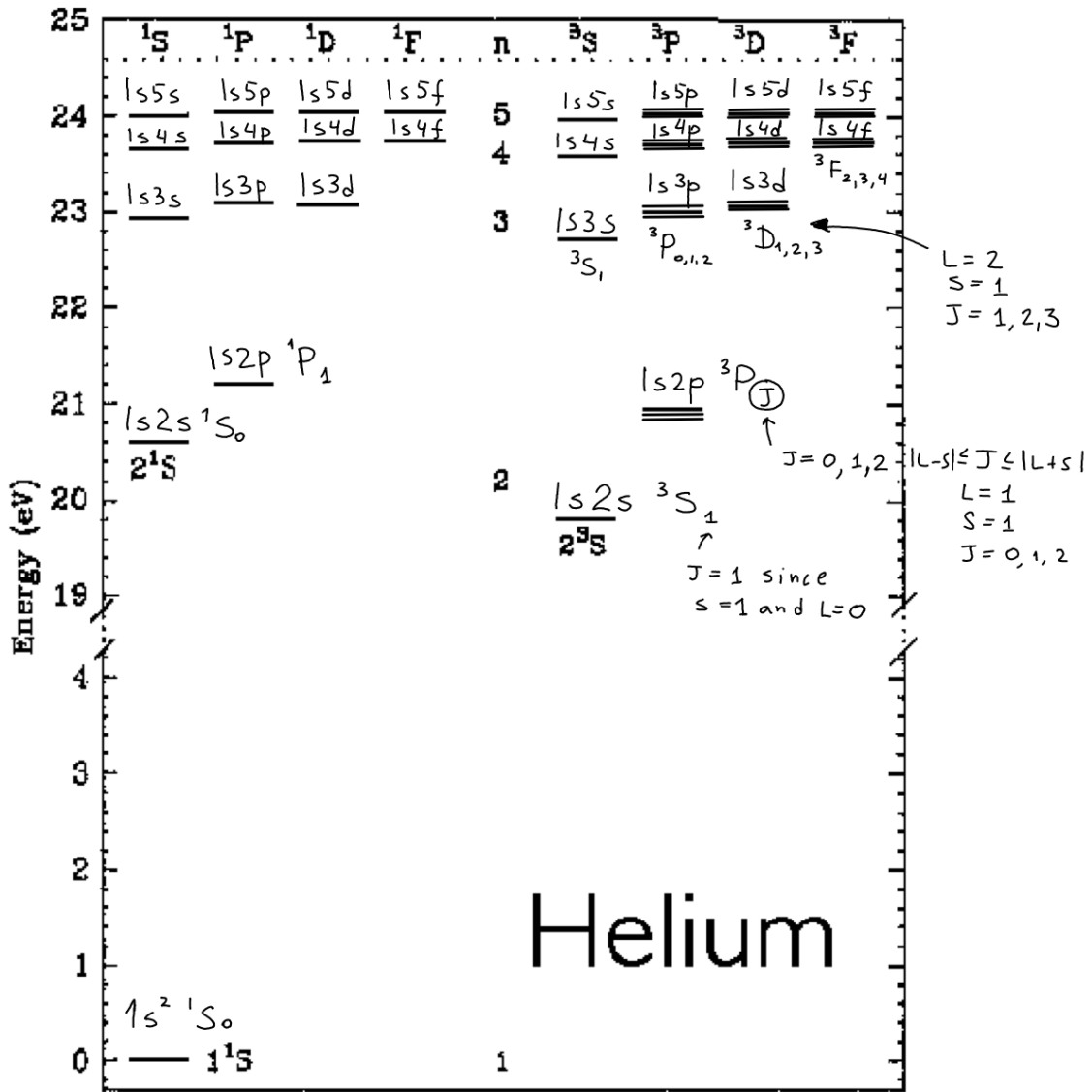
The spectroscopic symbol (as shown in Figure 2) is

$$\text{Spin-Multiplicity Angular_Orbital_Name}_{\text{J_values}}^{\text{Parity}} \quad (8)$$

Here Spin-multiplicity is  $2S + 1$  and Angular Orbital Name is S, P, D, F and so on.<sup>2</sup> Thus in our case the ground state is  $^1S_0$ .

<sup>2</sup>Do not confuse the Spin quantum number with the the S orbit!

### Helium energy level diagram



$$2s+1$$

$$L_J$$

**Helium ground state  $1s^2 \ ^1S_0$**

**Helium excited states  $1snl \ ^1L_J$  or  $^3L_J$**

Figure 2: Spectroscopic designations of excited states of Helium.

Now consider the first excited state of Helium,  $1s2s$ . For this state,  $S = 0$  or  $1$  (since the two electrons have different  $n$  quantum number Pauli principle does not place any restriction on spin). Clearly,  $L = 0$ . For  $S = 0$  and  $L = 0$  we get one term,  $^1S_0$  and for  $S = 1$  and  $L = 0$  we get another term,  $^3S_1$ .

## 2.2 The Ordering of Interaction Terms

From Figure 2 we see a big difference between  $1s2s$   $^1S_0$  and  $1s2s$   $^3S_1$ . This confirms the importance of the spin-spin interaction ( $\Gamma_1$  term in Equation 4). Now consider the relative placement of  $1s2s$  and  $1s2p$ . These configurations generate  $^1S_0$  and  $^1P_1$  in the singlet series and  $^3S_0$  and  $^3P_{0,1,2}$  in the triplet series. Notice the term value difference for the  $S$  and  $P$  states in each of the two series (Figure 3). The large difference justifies the dominant role of orbit-orbit interaction (cf.  $\Gamma_2$  in Equation 4). Finally, we can see that the spin-orbit interaction ( $\Gamma_3 + \Gamma_4$ ), so central in hydrogen, is a minor player for helium.

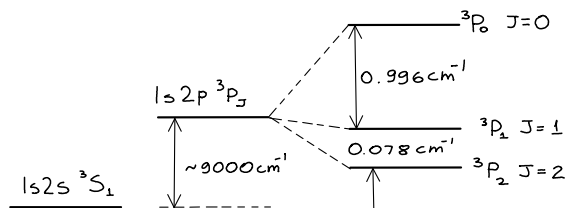


Figure 3: Fine structure of excited state of Helium.

As an aside. The discussion above shows that the spin multiplicity is indeed the multiplicity of the levels for a given spectroscopic term *provided*  $L \geq S$ . The spectroscopic term  $^1S_0$  has only one level whereas  $^3S_1$  also has one level, despite  $S = 1$ . It is best to call  $2S + 1$  as spin multiplicity and not loosely refer to it as multiplicity (and thus subtly change its meaning).

For atoms/electrons with multiple electrons there will be several spectroscopic terms even for the ground state. Hund's rule works to determine the ordering for the lowest energy state of an atom. For ions you are better off looking at Grotrian diagrams.

## 3 Parity

There is one other attribute that is needed to specify the spectroscopic term and that is parity (Draine, page 35). 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. The parity of a wave function of a single electron of orbital angular momentum  $l_i$  is  $(-1)^{l_i}$ . Thus  $s$  orbitals have even parity whereas  $p$  orbitals have odd parity. The parity of a spectroscopic term is given by the sum of the orbital momenta of the electronic system. If  $\sum_i l_i$  is even then the that term has even parity and otherwise. Odd parity is usually shown as “o” in the upper right corner. Absence of this symbol means that the parity is even.

## 4 Hund’s Rules

Hund from measurements of spectral lines formulated the following rules:

1. Rule I (also “The  $S$ -rule.”) For a given electron configuration, the term with maximum spin multiplicity  $(2S + 1)$  has the lowest energy.
2. Rule II (also “The  $L$  rule.”) For a given multiplicity, the term with the largest value of the total orbital angular momentum quantum number  $L$  has the lowest energy.
3. Rule III (also “The  $J$  rule.”) This rule is relevant to fine structure lines. For less than half-filled sub-shells, the lowest  $J$ -level lies lowest, but for more than half-filled sub-shells it is the reverse, that is, the highest  $J$ -level lies lowest in energy.

## 5 Determining the Spectroscopic Terms for two electrons

Now let us consider an atom with two valence electrons which have different energy quantum numbers. We have already seen that  $1s2s$  electronic configuration yields  $^1S_0$  and  $^3S_1$ . Now consider  $1s2p$ . Here we have  $S = 0, 1$  and  $L$  goes from  $l_1 + l_2$  to  $|l_1 - l_2|$  or  $L = 1$ . Thus we obtain two terms:  $^1P_1$  and  $^3P_{0,1,2}$ . For  $pd$  we find  $S = 0, 1$  and  $L = 1, 2, 3$ . Thus the terms are singlets  $PDF$  and triplets  $PDF$ . The terms that result from other two valence electrons is given in the table below. Note that the  $\cdot$  means that the electrons have different values of  $n$ .

combo				
$s \cdot s$	$^1S_0$			
	$^3S_1$			
$s p$		$^1P_1$		
		$^3P_{0,1,2}$		
$s d$			$^1D_2$	
			$^3D_{1,2,3}$	
$p \cdot p$	$^1S_0$	$^1P_1$	$^1D_2$	
	$^3S_1$	$^3P_{0,1,2}$	$^3D_{1,2,3}$	
$p d$		$^1P_1$	$^1D_2$	$^1F_3$
		$^3P_{0,1,2}$	$^3D_{1,2,3}$	$^3F_{2,3,4}$

## 5.1 Pair of electrons in the same $n$ state

A state is characterized by  $(n, l, m_l, m_s)$ . If the two electrons are in the same energy state (same  $n$ ) and have the same angular momentum,  $l_1 = l_2$  then by Paul exclusion principle states which are identical are excluded. For this reason,  $1s^2$  of Helium has only a single state,  $^1S$  and the triplet  $^3S$  is excluded. The table below summarizes the spectroscopic terms of a pair of electrons with the same energy and angular momentum quantum numbers.

Table 1: Spectroscopic terms for a pair of valence electrons with same  $n$  quantum number.

$s^2$	$^1S$				
$p^2$	$^1S$	$^3P$	$^1D$		
$d^2$	$^1S$	$^3P$	$^1D$	$^3F$	$^1G$

We will work out the spectroscopic term for Carbon,  $1s^2 2s^2 2p^2$ . For each electron  $m_l = 1, 0, -1$  and  $m_s = 1/2, -1/2$  and this leads to six combinations per electron. Thus, the number of combinations for two electrons is 36. Of this, we eliminate identical quantum numbers. This leaves 30 combinations. However, the electrons are not distinguishable and so the number of unique combinations is 15. For each of these 15 “microstates”<sup>3</sup> we sum  $m_l$  and  $m_s$  to get  $M_L = m_{l,1} + m_{l,2}$  and  $M_S = m_{s,1} + m_{s,2}$ . Figure 4 summarizes the calculations.

### 5.1.1 The Simplest Approach

In the simplest approach, you compute the matrix elements (see Figure 4) and then write down the 15 elements. We search for the largest values of  $M_L$ . We find only one value

<sup>3</sup>A micro state is characterized by  $m_l, m_s$ .

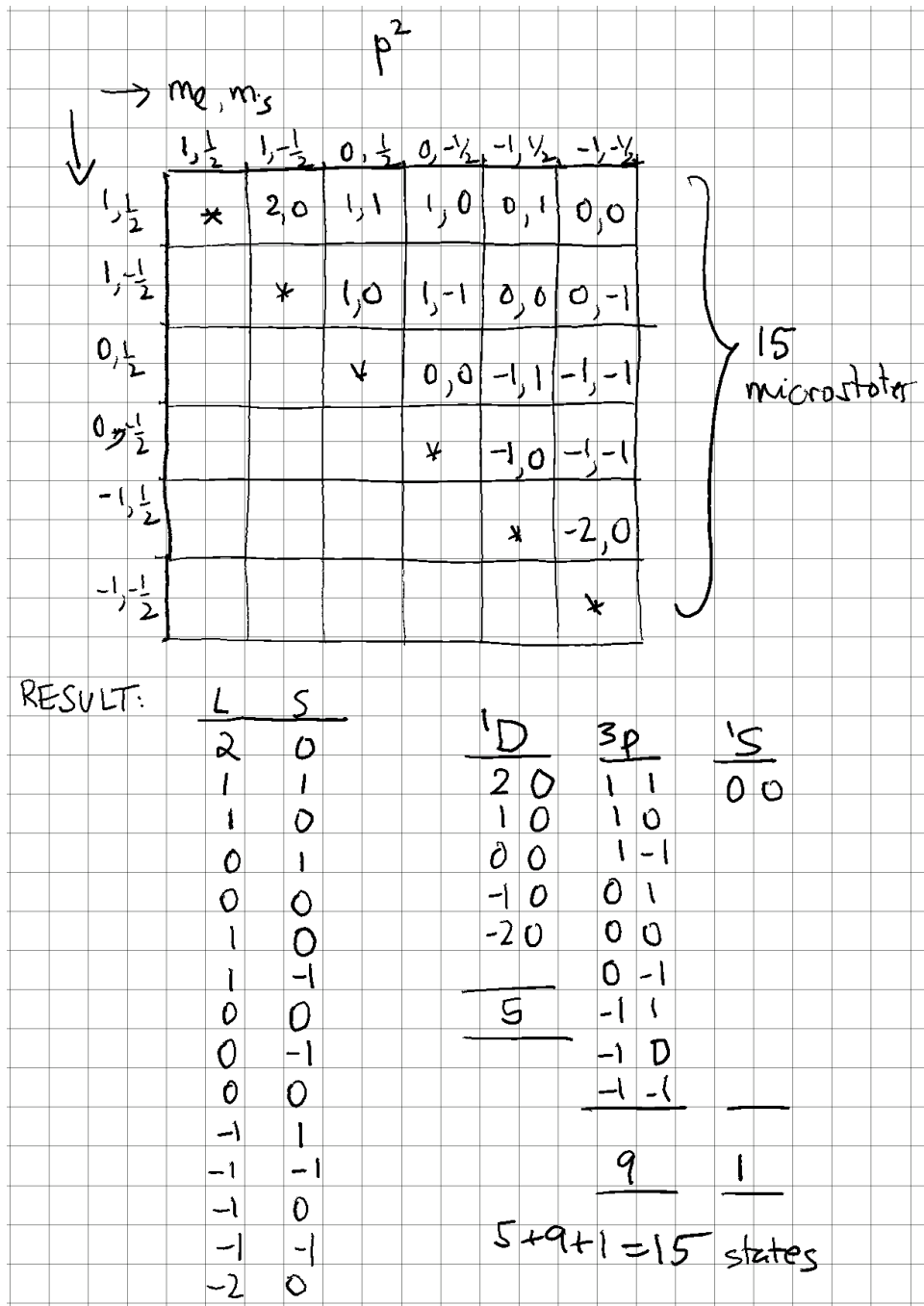


Figure 4:



and that is  $M_L = 2$  for which  $M_S = 0$ . This must be  ${}^1D_2$  term. The corresponding  $(M_L, M_S)$  are  $(2, 0), (1, 0), (0, 0), (-1, 0), (-2, 0)$ . We mark off the corresponding five entries in the above column. [The specific entry you pick is not important (a state with a given  $m_l$  and  $m_s$  is not distinguishable from another with same pair of quantum numbers)]. The next highest value is  $L = 1$ . There are three entries: for  $M_L$ :  $(1, 1), (1, 0), (1, -1)$ . Clearly, this is a triplet term,  ${}^3P$ . This term has  $(2L + 1)(2S + 1) = 9$  micro states. These are  $(1, 1), (1, 0), (1, -1), (0, 1), (0, 0), (0, -1), (-1, 1), (-1, 0), (-1, -1)$ . We mark off the corresponding nine entries as P. We are left with only entry  $(0, 0)$ . This is a  ${}^1S_0$  state. We conclude that the spectroscopic terms for the ground state of Carbon are  ${}^1D_2, {}^3P_{0,1,2}$  and  ${}^1S_0$ .

## 6 Two Tricks

**Trick 1:** For identical electrons it can be shown that only terms that obey Pauli's exclusion principle is those even  $L + S$ . Thus an easy to figure out the allowed spectroscopic combinations is to compute all possible spectroscopic terms assuming non identical electrons and then apply this trick to only accept those which are allowed by the exclusion principle. Thus in Table 1 we inspect the six terms that result from  $p \cdot p$ . Applying this trick we see that only the following three terms are allowed:  ${}^1S, {}^3P$  and  ${}^1D$ .

**Trick 2:** The terms for complementary electronic configuration is the same. The electronic configuration for Oxygen is  $1s^2 2s^2 2p^4$  whereas that for Carbon is  $1s^2 2s^2 2p^2$ . The  $p$  shell has a maximum of 6 electrons. These two configurations are complementary to each other. The spectroscopic terms for Oxygen and Carbon are the same (except Hund's J-rule is reversed; see §4).

I have written a Unix/bash program which can compute allowed spectroscopic terms for any number of identical electrons. See the next lecture for this program. Running this program and reviewing the intermediate output files will improve your understanding of spectroscopic terms.

## 7 $jj$ coupling

Recall that spin-orbit Hamiltonian as  $Z^4$  whereas the residual electrostatic Hamiltonian as  $Z$ . So for high- $Z$  elements spin-orbit Hamiltonian dominates. As a result, the principal Hamiltonian is  $H_2 = H_{CF} + H_{SO}$  and the perturbing Hamiltonian is  $H_{res}$ .

$$H_2 = \sum_{i=1}^N -\frac{1}{2} \nabla_{r_i}^2 - \frac{Z}{r_i} + S(r_i) + \xi(r_i) l_i \cdot s_i$$

In this scheme, each  $j_i$  is a good quantum number. It is computed as  $|(l_i - s_i)|, \dots, l_i + s_i$ . Consider a two-electron system with electronic configuration of  $ns, n'p$ . We have  $j_1 = 1/2$  and  $j_2 = 1/2, 3/2$ . The resulting two states are These are written as

$$(1/2, 1/2) \quad \text{and} \quad (1/2, 3/2).$$

Application of  $H_{\text{res}}$  leads to  $J = |j_1 - j_2|, \dots, j_1 + j_2$ . Thus, we get the following levels

$$(1/2, 1/2) \Rightarrow J = 1, 0 \Rightarrow \begin{cases} (1/2, 1/2)_0 \\ (1/2, 1/2)_1 \end{cases}$$

$$(1/2, 3/2) \Rightarrow J = 2, 1 \Rightarrow \begin{cases} (1/2, 3/2)_1 \\ (1/2, 3/2)_2 \end{cases}$$

See Figure 5 to see the evolution of the energy levels as  $Z$  increases.

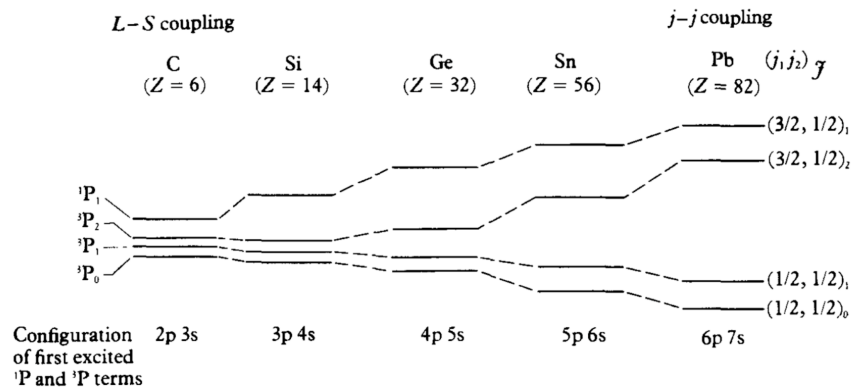


Figure 5: Evolution of the energy levels as  $Z$  increases.