

LS-coupling and *jj*-coupling

Spin-orbit interaction in multi-electron atoms

- We now have two effects to consider:
- 1: Interaction between \vec{s} and \vec{l} for every electron
 - $\vec{j} = \vec{l} + \vec{s}$
- 2: Angular part of the electrostatic interaction between the electrons
 - $$\begin{cases} \vec{l}_1 + \vec{l}_2 + \vec{l}_3 + \dots = \vec{L} \\ \vec{s}_1 + \vec{s}_2 + \vec{s}_3 + \dots = \vec{S} \end{cases}$$
- Both these effects have to be included in a total Hamiltonian

$$H = H_{\text{CF}} + H_{\text{res}} + H_{\text{SO}}$$

The parts of the Hamiltonian

- The central field Hamiltonian

$$H_{\text{CF}} = \sum_{i=1}^N H_i = \sum_{i=1}^N \left[-\frac{1}{2} \nabla_{r_i}^2 + V_{\text{CF}}(r_i) \right] = \sum_{i=1}^N \left[-\frac{1}{2} \nabla_{r_i}^2 - \frac{Z}{r_i} + S(r_i) \right]$$

- kinetic energy of all electrons
- Coulomb attraction to the nucleus for all electrons
- the central (radial) part of the Coulomb repulsion between all electrons

- The residual Coulomb Hamiltonian

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

- The angular (residual) part of the Coulomb interaction between electrons
 - coupling of the angular momenta of the individual electrons
- The spin-orbit Hamiltonian

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

- the sum of all spin-orbit interactions

Filled shells

- For a filled orbital :
 - half of the electrons spin-up, the other half spin-down
 - \Rightarrow contribution to S from filled shells : zero
 - all electrons with $+m_l$ are balanced by $-m_l$
 - \Rightarrow contribution to L from filled shells : zero
- For the sum in H_{SO} , we only need to include the electrons outside the last closed orbital

Total angular momentum

- The interactions between electrons (angular Coulomb + spin-orbit) will couple all electronic angular momenta together
- The only thing that will stay constant is the sum of all of them

$$\vec{J} = \vec{L} + \vec{S}$$

- where

$$\begin{cases} \vec{L} = \sum_i \vec{l}_i \\ \vec{S} = \sum_i \vec{s}_i \end{cases}$$

- A crucial point will be in which order all these momenta should be added
- That depends on in which order the perturbations are added

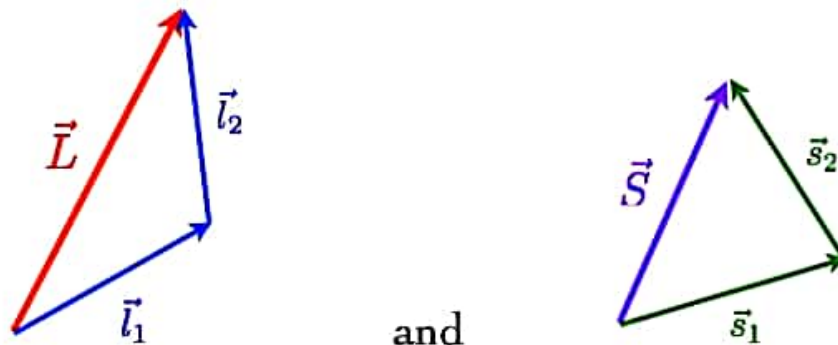
Ordering of the Hamiltonians

- We cannot solve the entire Hamiltonian analytically
 - perturbation theory is necessary
 - but, in which order should we take the Hamiltonians?
- Always true:

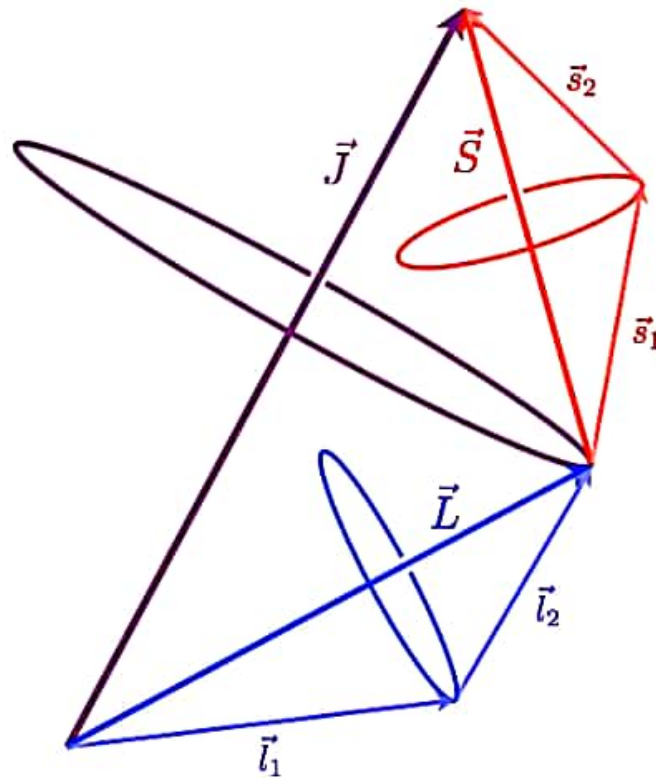
$$H_{CF} \gg H_{res} \quad \text{and} \quad H_{CF} \gg H_{SO}$$
- But then, there are two possibilities:
 - $H_{res} > H_{SO}$
 - $H_{SO} > H_{res}$

$$\underline{H_{res} > H_{SO}}$$

- In this case, the interaction between the electrons is stronger than the spin-orbit interaction in each of them
 - example with a 2-electron atom:



- Then, L and S couple to a total J

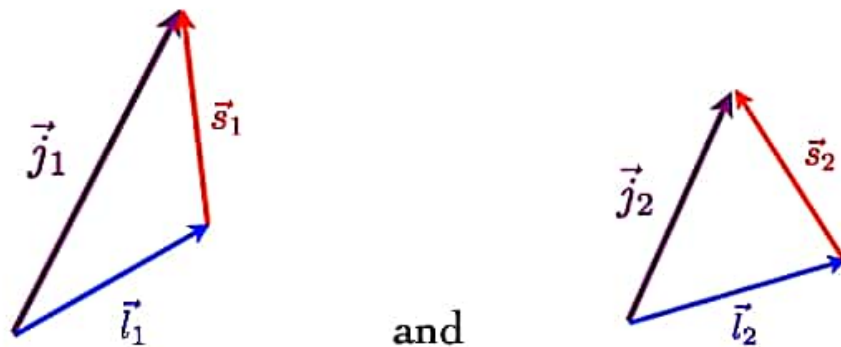


- This situation is called “ LS -coupling”
- This approximation is valid for most atoms
 - in particular for light atoms

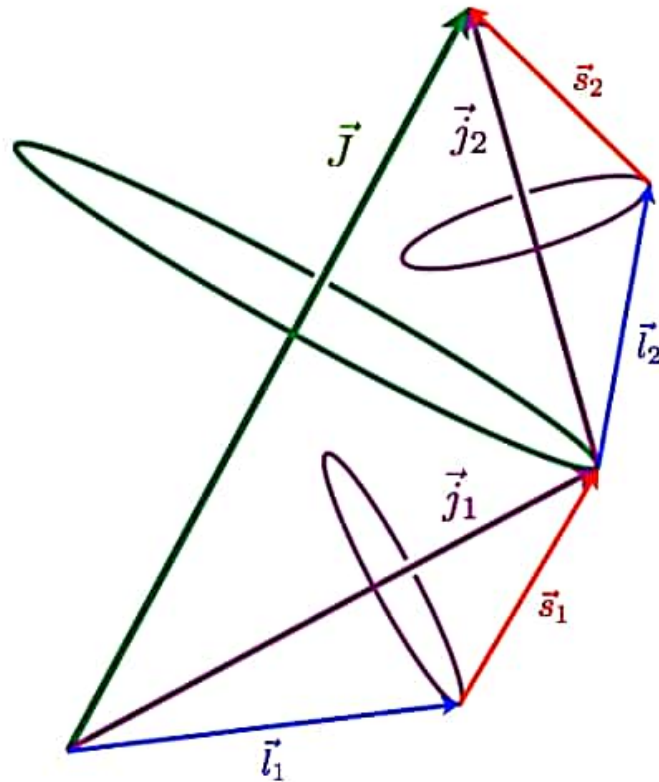
$$\underline{H_{SO} > H_{res}}$$

- In this case, the individual coupling between the electrons, via the spin-orbit interaction, is stronger than the electrostatic interaction between them

- example with a 2-electron atom:



- Then, j_1 and j_2 couple to a total J



- This situation is called “*jj*-coupling”
- This approximation has importance for heavy atoms
 - pure *jj*-coupling is rare
- There are often intermediate cases between *LS* and *jj*

LS-coupling

$$H = H_1 + H_{SO}$$

where

$$H_1 = H_{CF} + H_{res}$$

- Begin with :
 - $H_{CF} \psi_{CF} = E_{CF} \psi_{CF}$
 - $\Rightarrow |\psi_{CF}\rangle = |n_1 l_1, n_2 l_2, \dots, n_N l_N\rangle$
 - this gives the *electronic configuration*

- Then, calculate the first perturbation :
 - $\langle \psi_{CF} | H_{res} | \psi_{CF} \rangle$
 - (for the moment, we wait with the spin-orbit Hamiltonian)
 - $[H_{res}, L] = [H_{res}, S] = 0$
 - \Rightarrow this *atomic term* can be characterised by the quantum numbers L and S
 - $2S+1 L$
 - Eigenvector : $|\psi_{CF}\rangle = |\gamma L S M_L M_S\rangle$
 - (γ : the electronic configuration)
 - Degenerescence in M_L and M_S
 - $\Rightarrow (2L + 1)(2S + 1)$ degenerate states

How to find L and S

- Take into account :
 - Rules for addition of angular momenta
 - The Pauli principle

- For a filled shell :
 - $M_S = \sum_i m_{s_i}$ and $M_L = \sum_i m_{l_i}$
 - $\Rightarrow L = S = 0$
 - no contribution from the inner shells to the global L and S
 - It is enough to consider the valence electrons

Electrons in different orbitals (non-equivalent)

- The Pauli principle is already taken into account
- As an example, take a 2-electron atom :
 - $nl_1, n'l_2$ ($n \neq n'$)
 - $\begin{cases} L = |l_1 - l_2|, |l_1 - l_2| + 1, \dots, l_1 + l_2 \\ S = |s_1 - s_2|, |s_1 - s_2| + 1, \dots, s_1 + s_2 \end{cases}$
 - $(s_1 = s_2 = \frac{1}{2}) \Rightarrow S = 0$ or $S = 1$
 - (singlets and triplets)
- example 1 :
 - $l_1 = l_2 = 1 \Rightarrow$ configuration : $np, n'p$
 - $L = 0$ or $L = 1$ or $L = 2$
 - \Rightarrow possible terms are :
 - $^1S, ^1P, ^1D, ^3S, ^3P, ^3D$

- example 2 :
 - $l_1 = 1, l_2 = 2 \Rightarrow$ configuration : $np, n'd$
 - $L = 1$ or $L = 2$ or $L = 3$
 - \Rightarrow possible terms are :
 - $^1P, ^1D, ^1F, ^3P, ^3D, ^3F$
- More than 2 electrons
 - a bit more complicated

Electrons in the same orbital (equivalent electrons)

- This will normally be the case for ground state configurations
- More complicated, due to the Pauli principle
- Many states become forbidden
 - we will not cover this in detail
- Example 1 :
 - $n_1 = n_2, l_1 = l_2 = 1 \Rightarrow$ configuration : np^2
 - (the case for, for example : C, Si, Ge)
 - \Rightarrow possible terms : $^1S, ^1D, ^3P$
 - (other terms possible for $npnp'$ are forbidden due to the Pauli principle)
- Example 2 :
 - $n_1 = n_2 = n_3, l_1 = l_2 = l_3 = 1$
 - \Rightarrow configuration : np^3
 - (the case for, for example : N, P, As)
 - \Rightarrow possible terms : $^2P, ^2D, ^4S$

Electron configuration	Terms
ns	2S
ns^2	1S
np, np^5	2P
np^2, np^4	$^1S, ^1D$ 3P
np^3	$^2P, ^2D$
np^6	1S
nd, nd^9	2D
nd^2, nd^8	$^1S, ^1D, ^1G$ $^3P, ^3F$
nd^3, nd^7	$^2P, ^2D, ^2F, ^2G, ^2H$ (2) $^4P, ^4F$
nd^4, nd^6	$^1S, ^1D, ^1F, ^1G, ^1I$ (2) (2) (2) $^3P, ^3D, ^3F, ^3G, ^3H$ (4) (2) 5D
nd^5	$^2S, ^2P, ^2D, ^2F, ^2G, ^2H, ^2I$ (3) (2) (2) $^4P, ^4D, ^4F, ^4G$ 6S
nd^{10}	1S

More complicated cases

- More than two electrons
- Some equivalent and some non-equivalent electrons
- Configuration mixing

Fine structure in LS -coupling

- Now, we add the spin-orbit term of the Hamiltonian :
 - $H = H_1 + H_{SO}$
- The atomic terms have been found :
 - ^{2S+1}L , corresponding to the ket :
 - $|\gamma L S M_L M_S\rangle$
- We now have to find the corrections given by:
 - $\langle \gamma L S M_L M_S | H_{SO} | \gamma L S M_L M_S \rangle$
- Problem :
 - H_{SO} is not diagonal in this representation
 - ($[H_{SO}, L_z] \neq 0$ and $[H_{SO}, S_z] \neq 0$)

Change of basis

- We have to change to the diagonal basis :
 - $|\gamma L S J M_J\rangle$
 - (diagonalisation of H_{SO})

$$|L S J M_J\rangle = \sum_{M_L, M_S} C(L S J M_J; M_L M_S) |\gamma L S M_L M_S\rangle$$

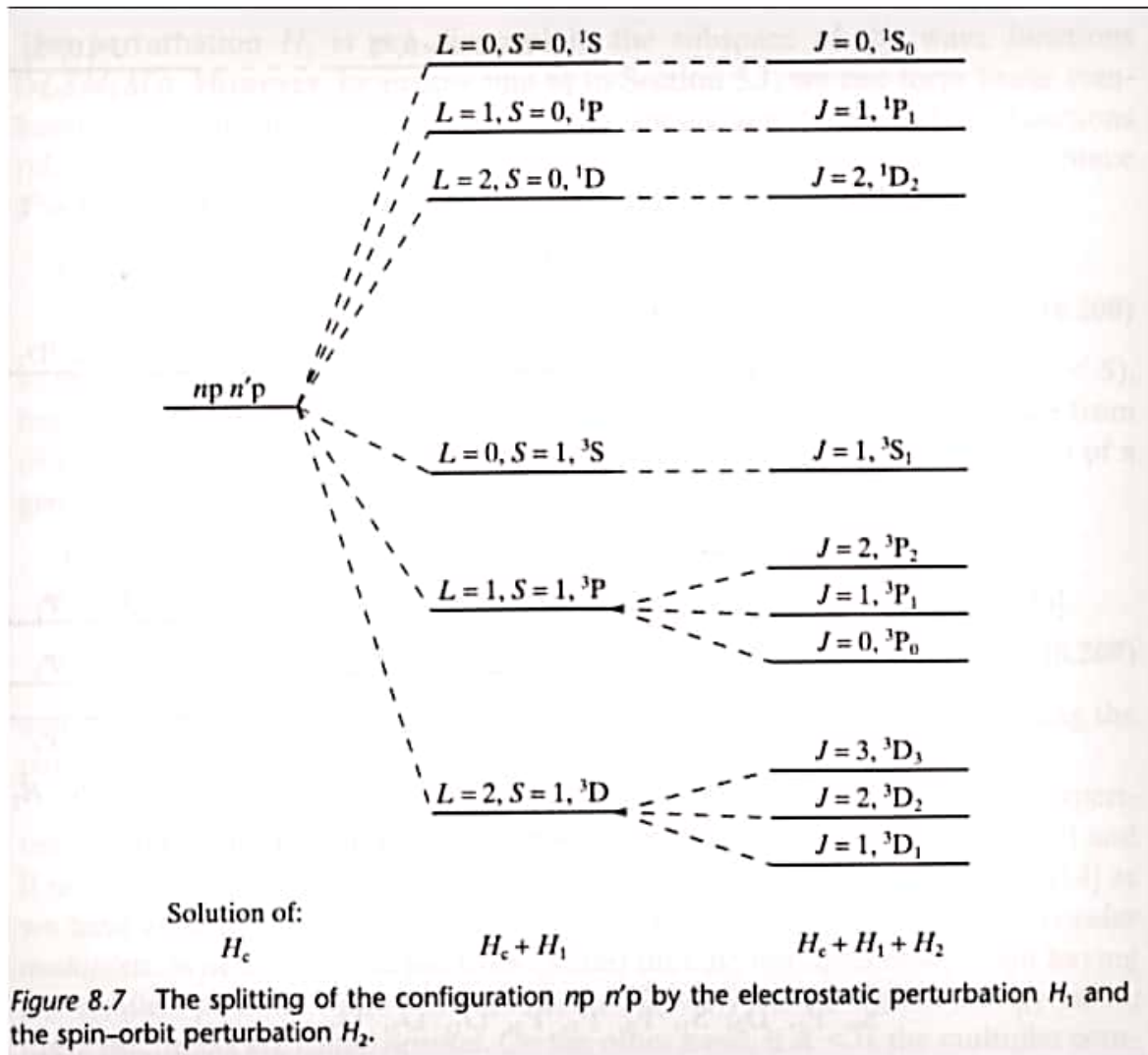
- The coefficients $C(L S J M_J; M_L M_S)$ are the "Clebsch-Gordan coefficients"

Finding the fine-structure levels

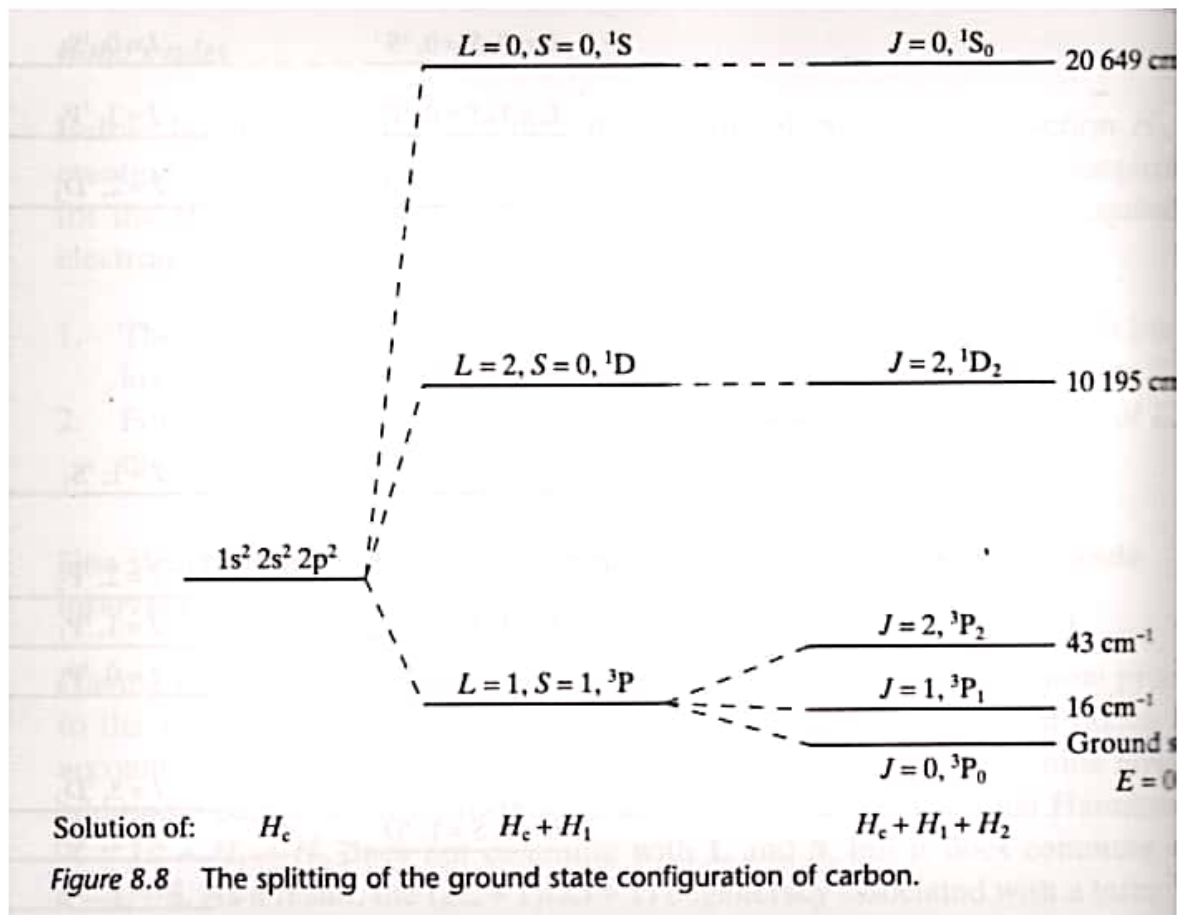
- $\vec{J} = \vec{L} + \vec{S}$
- addition of angular momenta

$$\begin{cases} J = |L - S|, |L - S| + 1, \dots, L + S \\ M_J = -J, J + 1, \dots, J \end{cases}$$
- For every atomic term, there are $(2S + 1)$ fine-structure levels
 - (or $(2L + 1)$ if $L < S$)
- example 1 :
 - configuration : $npnp'$

3D	\Rightarrow	$J = 3, 2, 1$	\Rightarrow	${}^3D_1, {}^3D_2, {}^3D_3$
1D	\Rightarrow	$J = 2$	\Rightarrow	1D_2
3P	\Rightarrow	$J = 2, 1, 0$	\Rightarrow	${}^3P_0, {}^3P_1, {}^3P_2$
1P	\Rightarrow	$J = 1$	\Rightarrow	1P_1
3S	\Rightarrow	$J = 1$	\Rightarrow	3S_1
1S	\Rightarrow	$J = 0$	\Rightarrow	1S_0



- example 2 :
 - configuration : np^2
 - 1D_2 , 3P_2 , 3P_1 , 3P_0 , 1S_0



Spin-orbit energies

- The energy corrections due to the spin-orbit interaction, the fine-structure splitting, can be found via the Hamiltonian

$$H_{\text{SO}} = \beta_{LS} \vec{L} \cdot \vec{S}$$

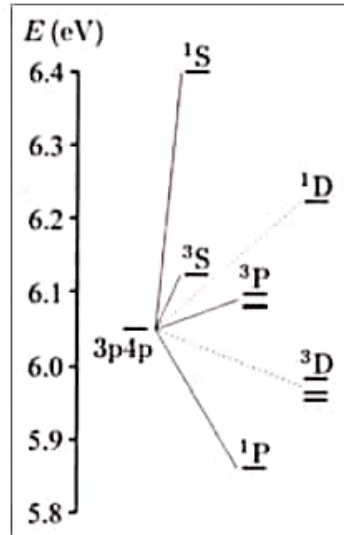
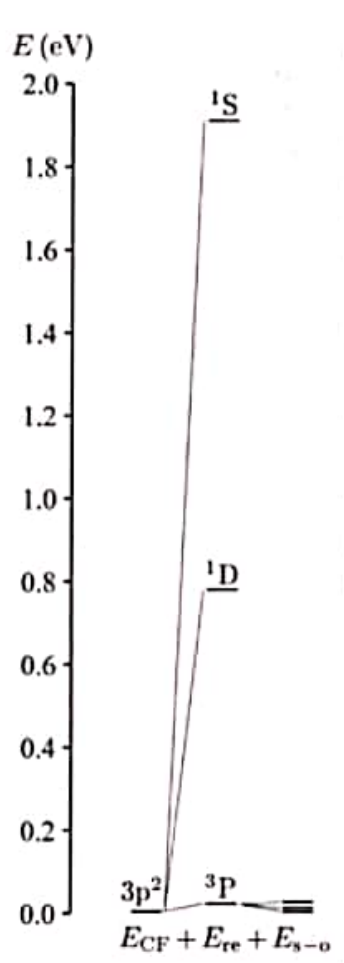
- here, β_{LS} is a constant typical for the term $|\gamma L S\rangle$

$$\begin{aligned} E_{\text{SO}} &= \langle \gamma L S J M_J | H_{\text{SO}} | \gamma L S J M_J \rangle \\ &= \beta_{LS} \langle L S J M_J | \vec{L} \cdot \vec{S} | L S J M_J \rangle \\ &= \frac{\beta_{LS}}{2} \langle L S J M_J | J^2 - L^2 - S^2 | L S J M_J \rangle \\ &= \frac{\beta_{LS}}{2} [J(J+1) - L(L+1) - S(S+1)] \end{aligned}$$

- Separation between two fine-structure levels

$$\begin{aligned} E(J) - E(J-1) &= \\ &= \frac{\beta_{LS}}{2} \{ [J(J+1) - L(L+1) - S(S+1)] \\ &\quad - [(J-1)J - L(L+1) - S(S+1)] \} \\ &= \frac{\beta_{LS}}{2} [J^2 + J - J^2 + J] \\ &= \frac{\beta_{LS}}{2} J \end{aligned}$$

- “Landé’s interval rule”
 - This rule can be used as a test of how well system can be described by LS-coupling



jj -coupling

- This applies when $H_{SO} > H_{res}$
 - The Hamiltonians have to be applied in a different order

$$H = H_2 + H_{res}$$

where

$$H_2 = H_{CF} + H_{SO}$$

- Remember that :
 - $H_{SO} \propto Z^4$
 - $H_{res} \propto Z$
 - $\Rightarrow jj$ -coupling will be relevant for heavy atoms

$$H_2 = \sum_{i=1}^N \left(-\frac{1}{2} \nabla_{r_i}^2 - \frac{Z}{r_i} + S(r_i) \right) + \sum_{i=1}^N \xi(r_i) \vec{L} \cdot \vec{S}$$

- In this case, we have to begin with the SO-coupling for the individual electrons :
 - we form :
 - $\vec{j}_1 = \vec{l}_1 + \vec{s}_1, \vec{j}_2 = \vec{l}_2 + \vec{s}_2 \dots, \vec{j}_N = \vec{l}_N + \vec{s}_N$
- The jj -coupling terms, we write as a parentheses with all the j -values
- As an example, take a 2-electron atom :
 - $l_1 = 0, l_2 = 1 \Rightarrow$ configuration : $ns, n'p$
 - $\begin{cases} l_1 = 0 \\ l_2 = 1 \end{cases}$ and $\begin{cases} s_1 = 1/2 \\ s_2 = 1/2 \end{cases}$

- $(j_i = |l_i - s_i|, |l_i - s_i| - 1, \dots, l_i + s_i)$
- $\Rightarrow j_1 = 1/2$ and $j_2 = 3/2, 1/2$
- \Rightarrow Two possibilities :
- $\left(\frac{1}{2}, \frac{1}{2}\right)$ and $\left(\frac{1}{2}, \frac{3}{2}\right)$

Fine-structure in jj -coupling.

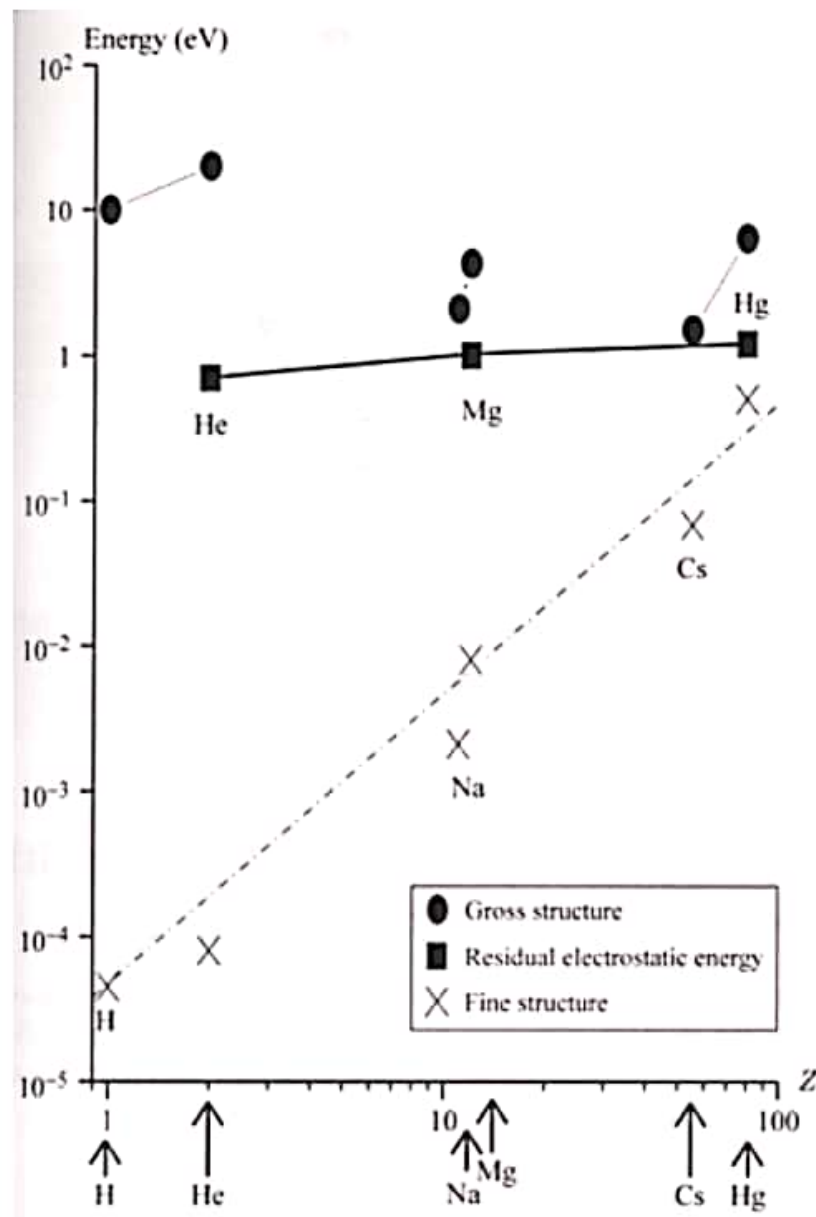
- When the terms are determined, H_{res} is added as a perturbation
 - this leads to fine-structure levels, classified by J
- $J = |j_1 - j_2|, |j_1 - j_2| - 1, \dots, j_1 + j_2$

$$\left(\frac{1}{2}, \frac{1}{2}\right) \Rightarrow J = 1, 0 \Rightarrow \left\{ \begin{array}{l} \left(\frac{1}{2}, \frac{1}{2}\right)_0 \\ \left(\frac{1}{2}, \frac{1}{2}\right)_1 \end{array} \right.$$

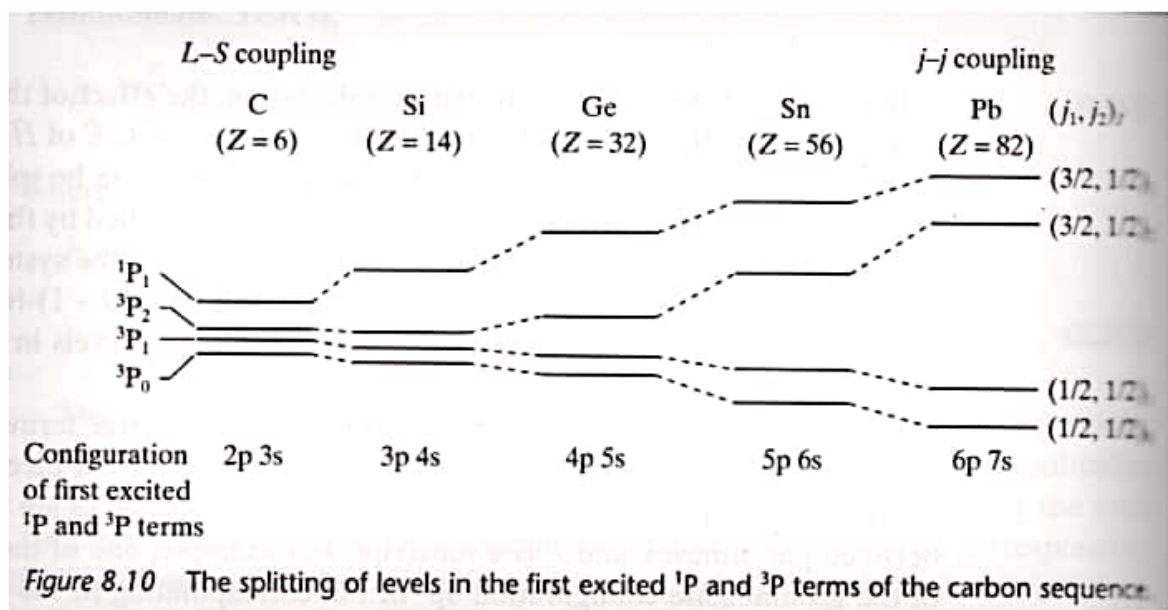
$$\left(\frac{1}{2}, \frac{3}{2}\right) \Rightarrow J = 2, 1 \Rightarrow \left\{ \begin{array}{l} \left(\frac{1}{2}, \frac{3}{2}\right)_1 \\ \left(\frac{1}{2}, \frac{3}{2}\right)_2 \end{array} \right.$$

Comparison between coupling schemes

- For light atoms, LS -coupling dominates, since the SO -term is small
- For heavy atoms, the situation is often intermediate between LS and jj



- As example, take the isoelectronic sequence of np^2 atoms
 - C, Si, Ge, Sn, Pb
 - Look at the splittings in the first excited states (1P and 3P)
 - C has almost pure LS -coupling
 - Pb is well described by jj -coupling
 - The others are intermediate
 - This can be seen by studying spectra



- In the case of C, the Landé rule holds