**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
  - \( \vec{l}_1 + \vec{l}_2 + \vec{l}_3 + \cdots = \vec{L} \)
  - \( \vec{s}_1 + \vec{s}_2 + \vec{s}_3 + \cdots = \vec{S} \)

- 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 \( H_{\text{SO}} \), 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

\[
\begin{align*}
\vec{L} &= \sum_{i} \vec{l}_i \\
\vec{S} &= \sum_{i} \vec{s}_i
\end{align*}
\]

- 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:
  \[ H_{\text{CF}} \gg H_{\text{res}} \quad \text{and} \quad H_{\text{CF}} \gg H_{\text{SO}} \]

- But then, there are two possibilities:
  - \( H_{\text{res}} > H_{\text{SO}} \)
  - \( H_{\text{SO}} > H_{\text{res}} \)

- 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.
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 $J$. 

\[
H_{SO} > H_{\text{res}}
\]
• 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:
  - \( H_{CF} \psi_{CF} = E_{CF} \psi_{CF} \)
  - \( \Rightarrow |\psi_{CF}\rangle = |n_1 l_1, n_2 l_2, \ldots, n_N l_N \rangle \)
  - 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 characterized by the quantum numbers \( L \) and \( S \)
  - \( 2S+1 \) \( L \)
  - Eigenvector: \( |\psi_{CF}\rangle = |\gamma L S M_L M_S \rangle \)
  - (\( \gamma \): 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 :
  - \( nl_1, n'l_2 \quad (n \neq n') \)
  - \( \begin{cases} 
  L = |l_1 - l_2|, |l_1 - l_2| + 1, \ldots, l_1 + l_2 \\
  S = |s_1 - s_2|, |s_1 - s_2| + 1, \ldots, s_1 + s_2 
  \end{cases} \)
  - \( (s_1 = s_2 = \frac{1}{2}) \Rightarrow S = 0 \) 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 :
    - \( ^1\text{P} \), \( ^1\text{D} \), \( ^1\text{F} \), \( ^3\text{P} \), \( ^3\text{D} \), \( ^3\text{F} \)

• 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 : \( ^1\text{S} \), \( ^1\text{D} \), \( ^3\text{P} \)
  - (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 : \( ^2\text{P} \), \( ^2\text{D} \), \( ^4\text{S} \)
<table>
<thead>
<tr>
<th>Electron configuration</th>
<th>Terms</th>
</tr>
</thead>
<tbody>
<tr>
<td>$ns$</td>
<td>$^2S$</td>
</tr>
<tr>
<td>$ns^2$</td>
<td>$^1S$</td>
</tr>
<tr>
<td>$np^2$, $np^5$</td>
<td>$^2P$</td>
</tr>
<tr>
<td>$np^2$, $np^4$</td>
<td>$^1S$, $^1D$, $^3P$</td>
</tr>
<tr>
<td>$np^3$</td>
<td>$^2P$, $^2D$</td>
</tr>
<tr>
<td>$np^6$</td>
<td>$^1S$</td>
</tr>
<tr>
<td>$nd$, $nd^9$</td>
<td>$^2D$</td>
</tr>
<tr>
<td>$nd^2$, $nd^8$</td>
<td>$^1S$, $^1D$, $^1G$, $^3P$, $^3F$</td>
</tr>
<tr>
<td>$nd^3$, $nd^7$</td>
<td>$^2P$, $^2D$, $^2F$, $^2G$, $^2H$, $^4P$, $^4F$</td>
</tr>
<tr>
<td>$nd^4$, $nd^6$</td>
<td>$^3P$, $^3D$, $^3F$, $^3G$, $^3H$, $^5D$</td>
</tr>
<tr>
<td>$nd^5$</td>
<td>$^2S$, $^2P$, $^2D$, $^2F$, $^2G$, $^2H$, $^2I$, $^4P$, $^4D$, $^4F$, $^4G$, $^6S$</td>
</tr>
<tr>
<td>$nd^{10}$</td>
<td>$^1S$</td>
</tr>
</tbody>
</table>
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:
  - $2S+1L$, corresponding to the ket:
  - $\ket{\gamma L S M_L M_S}$

- We now have to find the corrections given by:
  - $\braket{\gamma L S M_L M_S | H_{SO} | \gamma L S M_L M_S}$

- Problem:
  - $H_{SO}$ is not diagonal in this representation
  - $([H_{SO}, L_z] \neq 0 \text{ and } [H_{SO}, S_z] \neq 0)$

Change of basis

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

$$\ket{L S J M_J} = \sum_{M_L, M_S} C(LSJM_J; M_LM_S) \ket{\gamma L S M_L M_S}$$

- The coefficients $C(LSJM_J; M_LM_S)$ are the “Clebsch-Gordan coefficients”
Finding the fine-structure levels

- \( \vec{J} = \vec{L} + \vec{S} \)
- addition of angular momenta
  \[
  \begin{cases}
  J = |L - S|, |L - S| + 1, \ldots, L + S \\
  M_J = -J, -J + 1, \ldots, J
  \end{cases}
  \]
- For every atomic term, there are \((2S + 1)\) fine-structure levels
  - (or \((2L + 1)\) if \(L < S\))
- example 1:
  - configuration: \(npnp'\)
    - \(3D \Rightarrow J = 3, 2, 1 \Rightarrow 3D_1, 3D_2, 3D_3\)
    - \(1D \Rightarrow J = 2 \Rightarrow 1D_2\)
    - \(3P \Rightarrow J = 2, 1, 0 \Rightarrow 3P_0, 3P_1, 3P_2\)
    - \(1P \Rightarrow J = 1 \Rightarrow 1P_1\)
    - \(3S \Rightarrow J = 1 \Rightarrow 3S_1\)
    - \(1S \Rightarrow J = 0 \Rightarrow 1S_0\)
Figure 8.7 The splitting of the configuration \( np \, n'p \) by the electrostatic perturbation \( H_1 \) and the spin–orbit perturbation \( H_2 \).
• 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

\[ H_{SO} = \beta_{LS} \vec{L} \cdot \vec{S} \]

- here, \( \beta_{LS} \) is a constant typical for the term \( |\gamma LS\rangle \)

\[
E_{SO} = \langle \gamma LSJM | H_{SO} | \gamma LSJM \rangle = \beta_{LS} \langle LSJM | \vec{L} \cdot \vec{S} | LSJM \rangle = \beta_{LS} \frac{1}{2} \langle LSJM | J^2 - L^2 - S^2 | LSJM \rangle = \beta_{LS} \frac{1}{2} [J(J+1) - L(L+1) - S(S+1)]
\]

- Separation between two fine-structure levels

\[
E(J) - E(J-1) = \beta_{LS} \frac{1}{2} \{ [J(J+1) - L(L+1) - S(S+1)] - [(J-1)J - L(L+1) - S(S+1)] \} = \beta_{LS} \frac{1}{2} [J^2 + J - J^2 + J] = \beta_{LS} \frac{1}{2} J
\]

- “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

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

- In this case, we have to begin with the SO-coupling for the individual electrons:
  - we form:
    - \( \vec{j}_1 = \vec{l}_1 + \vec{s}_1 \), \( \vec{j}_2 = \vec{l}_2 + \vec{s}_2 \) \ldots , \( \vec{j}_N = \vec{l}_N + \vec{s}_N \)

- 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 \( \begin{cases} s_1 = 1/2 \\ s_2 = 1/2 \end{cases} \)
\( j_i = |l_i - s_i|, |l_i - s_i| - 1, \ldots, l_i + s_i \)

- \( \Rightarrow j_1 = 1/2 \) 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 \( J \)

- \( J = |j_1 - j_2|, |j_1 - j_2| - 1, \ldots, j_1 + j_2 \)

\[
\left( \frac{1}{2}, \frac{1}{2} \right) \Rightarrow J = 1, 0 \Rightarrow \begin{cases} 
\left( \frac{1}{2}, \frac{1}{2} \right)_0 \\
\left( \frac{1}{2}, \frac{1}{2} \right)_1 
\end{cases}
\]

\[
\left( \frac{1}{2}, \frac{3}{2} \right) \Rightarrow J = 2, 1 \Rightarrow \begin{cases} 
\left( \frac{1}{2}, \frac{3}{2} \right)_1 \\
\left( \frac{1}{2}, \frac{3}{2} \right)_2 
\end{cases}
\]
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

\[ \text{Figure 8.10} \quad \text{The splitting of levels in the first excited } ^1P \text{ and } ^3P \text{ terms of the carbon sequence.} \]

• In the case of C, the Landé rule holds