

Lecture 19 Title: $j-j$ coupling

Page-1

It is seen that for heavier atoms, the nuclear charge causes the spin-orbit interactions to be strong enough the force between the individual l and s .

For large Z atoms, the electron-electron repulsion becomes weaker than the spin-orbit interaction of the individual electrons.

In this case, the $L-S$ coupling scheme can not explain the observed transitions from these atoms.

The calculated energy levels from $L-S$ coupling scheme fails to predict energy levels for these atoms.

In the lecture, we will describe the $j-j$ coupling scheme that describes the observed transitions from these heavy atoms.

In previous lectures, we have described the Hamiltonian as

$$H = \underbrace{-\frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N U(r_i)}_{\text{Central field}} + \underbrace{\sum_{i < j}^N \frac{e^2}{r_{ij}} - \left\langle \sum_{i < j}^N \frac{e^2}{r_{ij}} \right\rangle}_{\text{electron-electron repulsion}} + \underbrace{A_{so} \vec{L} \cdot \vec{S}}_{\text{spin-orbit interaction}}$$

Here, the first term is the central field term, second is the nonspherical part of the electron electron repulsion and the third part is the spin-orbit interaction.

Since for the low Z-atoms, the electron-electron repulsion is greater, it is treated as perturbation before the spin orbit interaction.

For High Z atoms, the electron-electron repulsion is lower, it should be treated as perturbation after the spin orbit interaction.

Thus the Hamiltonian becomes,

$$H = -\frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \frac{Z e^2}{r_i} + \underbrace{A_{so} \vec{l}_i \cdot \vec{s}_i}_{\text{spin-orbit interaction}} + \underbrace{\sum_{i < j}^N \frac{e^2}{r_{ij}}}_{\text{electron-electron repulsion}}$$

This is known as j-j coupling

In this coupling scheme, Hamiltonian is

$$H = -\frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \frac{Ze^2}{r_i} + \underbrace{A_{so} \vec{l}_i \cdot \vec{s}_i}_{\text{spin-orbit interaction}} + \underbrace{\sum_{i < j}^N \frac{e^2}{r_{ij}}}_{\text{electron-electron repulsion}}$$

Due to the spin orbit interaction, the spin and orbital angular momenta of the individual electron get coupled as shown in the figure-20.1.

$$\vec{j} = \vec{l} + \vec{s}$$

$$j^2 = l^2 + s^2 + 2\vec{l} \cdot \vec{s}$$

$$\vec{l} \cdot \vec{s} = \frac{1}{2} [j^2 - l^2 - s^2]$$

Thus at this level, j, m_j are the good quantum numbers. Hence to calculate the energy for this perturbation, we have

$$\begin{aligned} \Delta E_{so} &= \langle jm_j | A_{so} \vec{l} \cdot \vec{s} | jm_j \rangle \\ &= \frac{A_{so}}{2} \langle jm_j | j^2 - l^2 - s^2 | jm_j \rangle \\ &= \frac{A_{so}}{2} [j(j+1) - l(l+1) - s(s+1)] \end{aligned}$$

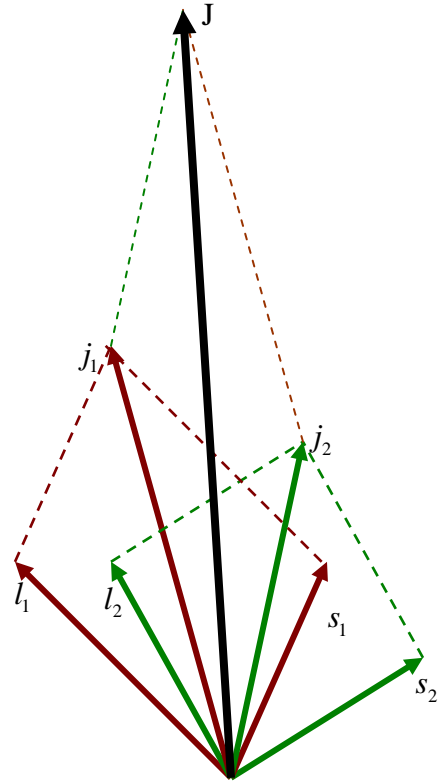


Figure-19.1

Page-4

When the electron-electron interaction takes place the individual coupled angular momenta get coupled to get the total angular momentum J .

So for two electron system,

$$\vec{J} = \vec{j}_1 + \vec{j}_2$$

$$J^2 = j_1^2 + j_2^2 + 2\vec{j}_1 \cdot \vec{j}_2$$

$$\vec{j}_1 \cdot \vec{j}_2 = \frac{1}{2} [J^2 - j_1^2 - j_2^2]$$

This interaction energy then

$$\begin{aligned} \Delta E_{ee} &= \langle Jm_J | A_{ee} \vec{j}_1 \cdot \vec{j}_2 | Jm_J \rangle \\ &= \frac{A_{ee}}{2} \langle Jm_J | J^2 - j_1^2 - j_2^2 | Jm_J \rangle \\ &= \frac{A_{ee}}{2} [J(J+1) - j_1(j_1+1) - j_2(j_2+1)] \end{aligned}$$

Page-5

Now, let us take some examples.

The electronic configuration $1p2p$ (non equivalent electrons)

$$l_1 = 1, \quad s_1 = \frac{1}{2}, \quad j_1 = \frac{3}{2}, \frac{1}{2}$$

$$l_2 = 1, \quad s_2 = \frac{1}{2}, \quad j_2 = \frac{3}{2}, \frac{1}{2}$$

Now, the notation for the coupling states are $\{j_1, j_2\}_J$

$$\left\{\frac{3}{2}, \frac{3}{2}\right\}_{3,2,1,0} \quad \left\{\frac{3}{2}, \frac{1}{2}\right\}_{2,1} \quad \left\{\frac{1}{2}, \frac{3}{2}\right\}_{2,1} \quad \left\{\frac{1}{2}, \frac{1}{2}\right\}_{1,0}$$

The J states are degenerate in this level of consideration

Next when the electron-electron interaction takes place all these level will be splitted.

$$\left\{\frac{3}{2}, \frac{3}{2}\right\}_3, \quad \left\{\frac{3}{2}, \frac{3}{2}\right\}_2, \quad \left\{\frac{3}{2}, \frac{3}{2}\right\}_1, \quad \left\{\frac{3}{2}, \frac{3}{2}\right\}_0$$

$$\left\{\frac{3}{2}, \frac{1}{2}\right\}_2, \quad \left\{\frac{3}{2}, \frac{1}{2}\right\}_1$$

$$\left\{\frac{1}{2}, \frac{3}{2}\right\}_2, \quad \left\{\frac{1}{2}, \frac{3}{2}\right\}_1$$

$$\left\{\frac{1}{2}, \frac{1}{2}\right\}_1, \quad \left\{\frac{1}{2}, \frac{1}{2}\right\}_0$$

For the equivalent electrons such as p^2 configuration.

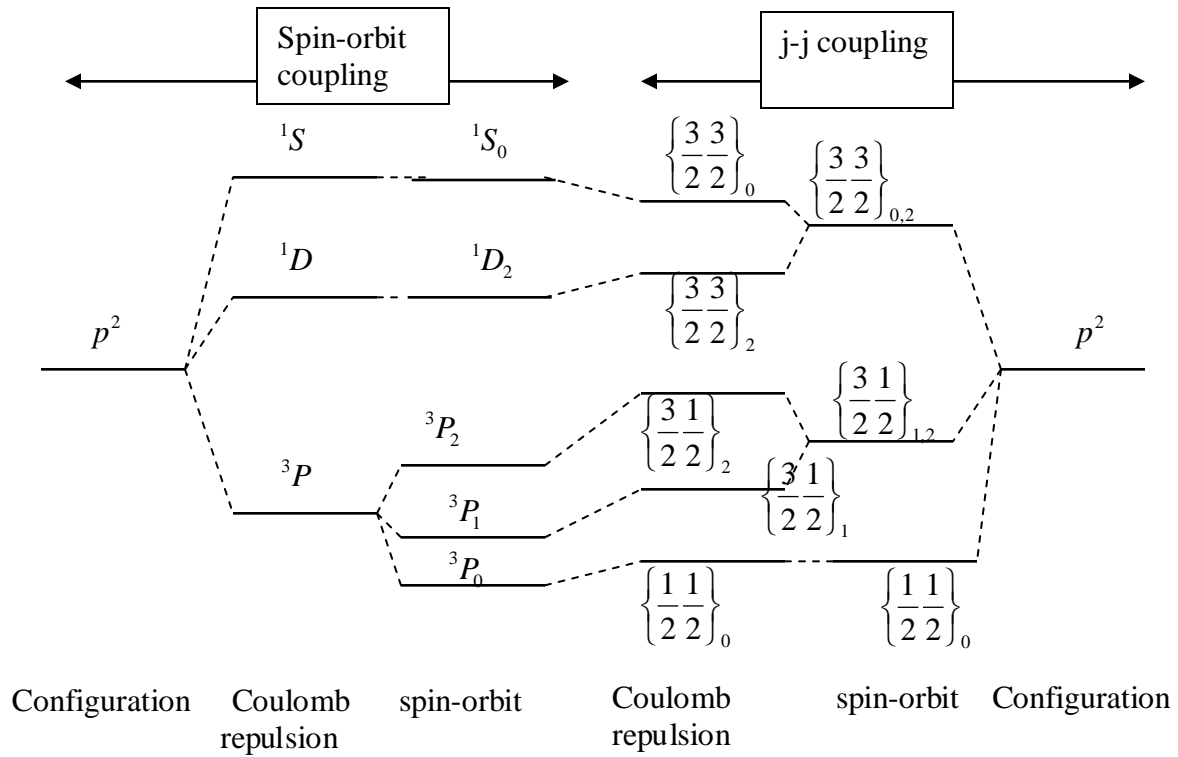
The rules are

1. When $j_1 \neq j_2$, the value of J in $\{j_1, j_2\}_J$ is found by the rules for the coupling of angular momentum
2. When $j_1 = j_2$, the allowed values in $\{j_1, j_2\}_J$ are given by $J = 2j - 1, 2j - 3, \dots$

So for p^2 , the possible states in j-j coupling are

$$\left\{\frac{3}{2}, \frac{3}{2}\right\}_{2,0}, \quad \left\{\frac{3}{2}, \frac{1}{2}\right\}_{2,1}, \quad \left\{\frac{1}{2}, \frac{1}{2}\right\}_0$$

In the following the comparison of the levels between the L-S coupling scheme and the j-j coupling scheme is given. It is to be noted that although the total number of final states are same, but their relative energies are different.



Page-7

In this lecture we understood that for heavier atoms the L-S coupling scheme is not valid.

In this case we have to consider j-j coupling scheme.

The relative energies of the final states for these two schemes are different, but the total number of splitted levels is same.

Since the equivalent electrons are in the same values of n and l , the electrostatic interaction is expected to be larger than spin-orbit interaction. In this case L-S coupling is favoured.

It is for nonequivalent, j-j coupling is important

There are many situations where neither L-S nor j-j coupling are valid approximation. In this case both have to be treated simultaneously as perturbation. This coupling scheme is known as intermediate coupling.