magnetic hyperfine interaction

in free atoms

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magnetic hyperfine interaction in free atoms

or

coupling of angular momenta : from L-S to I-J

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coupling of angular momenta: L-S

We'll remind first what you saw in earlier courses on the coupling of orbital and spin angular momenta in an atom:

The problem: "**For a given shell (n,l), how do a given number of electrons occupy the available orbitals?**"

Example: C (n=2, l=1), 2 p-electrons

There are 6 different orbitals (m_l=-1,0,+1 and this for either spin), hence 6x6=36 possibilities to put these 2 electrons. Which of those 36 possibilities has the lowest energy (and will therefore be found as the ground state in Nature)?

Hund's rules provide you with an algorithm to find this ground state
(no mathematical justification – these rules were originally derived from experimental trends)

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coupling of angular momenta: L-S

1st Hund's rule

Only configurations where the total S is maximal should be considered further.

S is found as the absolute value of the sum of all m_S values

Our example: only states with S=1 (twice m_S=+1/2 or twice m_S=-1/2) should be considered further.

2nd Hund's rule

Within the previous set, only configurations where the total L is maximal should be considered further.

L is found as the absolute value of the sum of all m_L values

Our example: states with S=1 cannot contain 2 electrons in the same m_L orbital. Hence, the maximal L is L=1 (two electrons in m_L=+1,0, or in m_L=-1,0)

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coupling of angular momenta: L-S

How many of our 36 states are left if we restrict ourselves to S=1 and L=1?

Two ways to count:

First way :

S=1 can have three different orientations (2S+1=3; m_S=-1,0,+1)
L=1 can have three different orientations (2L+1=3; m_L=-1,0,+1)

➔ 3x3=9 out of 36

Second way:

Angular momenta coupling rules: S=1 and L=1 can couple to J=L+S,..,|L-S| = 2,1,0
Each J-value has 2J+1 orientations: 5, 3, 1

➔ 5+3+1=9 out of 36

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coupling of angular momenta: L-S

Which of the remaining (9) states is the ground state?

- If there is no interaction between L and S, all these states are degenerate.
- If there is interaction (spin-orbit coupling), some will have a lower energy than others

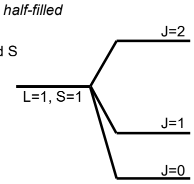
3rd Hund's rule

Of the remaining states, those with the lowest energy are the ones with

- *J minimal if the shell is less than half-filled*
- *J maximal if the shell is more than half-filled*

Physical picture: mutual orientation of L and S

Example: 2 electrons in a p-shell is less than half-filled
➔ J=0 has the lowest energy.



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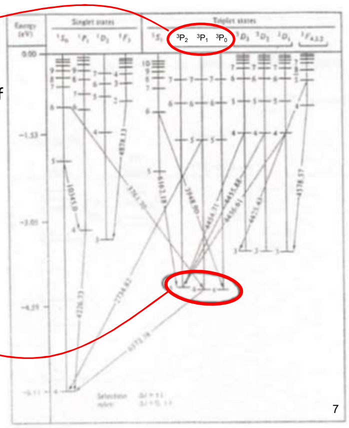
P ⇒ L=1
3 ⇒ S=1

3 different orientations of L w.r.t. S:
J = 2, 1, 0

Energy of the entire atom slightly depends on the value of J



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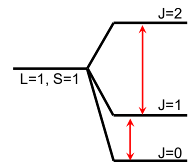
coupling of angular momenta: L-S

Landé's interval rule:

$$\frac{E_J - E_{J-1}}{E_{J-1} - E_{J-2}} = \frac{J}{J-1}$$



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coupling of angular momenta: I-J

A nucleus with spin I has 2I+1 possible orientations.
An electron cloud with total angular momentum J has 2J+1 possible orientations.

If there is no interaction between I and J, all these (2I+1)x(2J+1) possibilities have the same energy.

I is related to the nuclear magnetic moment (dipole moment for the current-current case)
Each J state provides a specific magnetic hyperfine field (dipole field for the current-current case)

➔ I and J do interact
➔ which mutual orientation of I and J corresponds to the lowest energy?

We will discuss this in terms of a new total angular momentum F:

$$F = I+J, I+J-1, \ldots, |I-J|$$

Each value of F corresponds to a different mutual orientation of I and J.
For a given F, different values of m_F correspond to a rotation of the atom as a whole (mutual orientation is unaffected).

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coupling of angular momenta: I-J

nuclear magnetic moment operator

$$\hat{\boldsymbol{\mu}}_I = \frac{\mu}{I\hbar}\hat{\boldsymbol{I}}$$

experimentally known – the 'size' of the nuclear magnetic moment (scalar).

Magnetic hyperfine field operator:

$$\hat{\boldsymbol{B}}_J = \frac{B_J}{J\hbar}\hat{\boldsymbol{J}}$$

Let us consider this for the time being as known (experimentally or computable).

The perturbing hamiltonian H_1:

$$\begin{aligned} \hat{H}_{jj} &= -\hat{\boldsymbol{\mu}}_I \cdot \hat{\boldsymbol{B}}(\mathbf{0}) \\ &= -\frac{\mu B_J}{\hbar^2 IJ}\hat{\boldsymbol{I}} \cdot \hat{\boldsymbol{J}} \\ &= -\frac{\mu B_J}{2\hbar^2 IJ}(\hat{F}^2 - \hat{I}^2 - \hat{J}^2) \end{aligned}$$

Use $\hat{\boldsymbol{F}}^2 = \hat{F}^2 = (\hat{\boldsymbol{I}} + \hat{\boldsymbol{J}})^2 = \hat{I}^2 + \hat{J}^2 + 2\hat{\boldsymbol{I}} \cdot \hat{\boldsymbol{J}}$

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coupling of angular momenta: I-J

Apply perturbation theory

The states of the unperturbed system are the |F> (direct product of |I> and |J>)

The perturbing hamiltonian is likely to lift degeneracies
➔ perturbation theory for the degenrate case

Fortunately the |F> states are orthonormal already (property of angular momentum eigenstates)

$$\begin{bmatrix} \langle 0|\hat{H}_{jj}|0\rangle & \langle 1|\hat{H}_{jj}|0\rangle & \langle 2|\hat{H}_{jj}|0\rangle & \langle 3|\hat{H}_{jj}|0\rangle \\ \langle 0|\hat{H}_{jj}|1\rangle & \langle 1|\hat{H}_{jj}|1\rangle & \langle 2|\hat{H}_{jj}|1\rangle & \langle 3|\hat{H}_{jj}|1\rangle \\ \langle 0|\hat{H}_{jj}|2\rangle & \langle 1|\hat{H}_{jj}|2\rangle & \langle 2|\hat{H}_{jj}|2\rangle & \langle 3|\hat{H}_{jj}|2\rangle \\ \langle 0|\hat{H}_{jj}|3\rangle & \langle 1|\hat{H}_{jj}|3\rangle & \langle 2|\hat{H}_{jj}|3\rangle & \langle 3|\hat{H}_{jj}|3\rangle \end{bmatrix}$$

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coupling of angular momenta: I-J

Only diagonal matrix elements will survive:

$$\begin{aligned} <F|\hat{H}_{jj}|F> &= -\frac{\mu B_J}{2\hbar^2 IJ} <F|\hat{F}^2 - \hat{I}^2 - \hat{J}^2|F> \\ &= -\frac{\mu B_J}{2\hbar^2 IJ}\hbar^2 \underbrace{(F(F+1) - I(I+1) - J(J+1))}_{C} \\ &= -\frac{1}{2}aC \end{aligned}$$

Hence, no diagonalization needed, the matrix is already diagonal and the eigenvalues (=energy corrections) can be read right away :

$$-\frac{1}{2}a \begin{bmatrix} C_{00} & 0 & 0 & 0 \\ 0 & C_{11} & 0 & 0 \\ 0 & 0 & C_{22} & 0 \\ 0 & 0 & 0 & C_{33} \end{bmatrix}$$

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coupling of angular momenta: I-J

Energy difference between two subsequent transitions (cfr. Landé interval rule):

$$\frac{E_F - E_{F-1}}{E_{F-1} - E_{F-2}} = \frac{F(F+1) - (F-1)F}{(F-1)F - (F-2)(F-1)} = \frac{F}{F-1}$$

Level scheme :

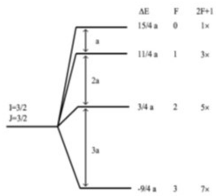

Fig. 5.1. *Magnetic hyperfine splitting for an atom with nuclear spin $I = 3/2$ and electronic spin $J = 3/2$. The energy of the total system depends on how I and J are oriented with respect to each other, which is given by the new total spin F. The picture uses a correct scale. The right column gives the degeneracy of each level. The hyperfine variant of the Landé interval rule is illustrated as well.*

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coupling of angular momenta: I-J

This formalism applies to

- free atoms or free ions *[rigorously]*
- atoms in ionic compounds (salts) *[qualitatively]*

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