Chapter 5 - LS coupling scheme

For a large number of atoms, the best representation of the wave function has the orbital angular momenta coupled to a total L, $\vec{L} = \vec{l_1} + \vec{l_2} + ...$, and the spins to a total spin, $\vec{S} = \vec{S_1} + \vec{S_2} + ...$. The total L is then coupled to the total S to give $\vec{J} = \vec{L} + \vec{S}$

For nonrelativistic approx, $\vec{L}^2, \vec{S}^2, \vec{J}^2, J_z$ are all conserved

Before getting to properties of energies and Zeeman effect, I want to look at the behavior of matrix elements.

Wigner-Eckart Theorem

For a state of total angular momentum, the matrix elements are proportional to the corresponding angular momentum

Examples

$\langle \alpha J M_J | L_{3x} | \alpha' J' M_J' \rangle = C_{\alpha J, \alpha' J'} \langle J M_J | J_x | J' M_J' \rangle \Rightarrow = 0$ unless $J = J'$, $M_J = M_J' \pm 1$

$\langle \alpha J M_J | L_{1z} | \alpha' J' M_J' \rangle = D_{\alpha J, \alpha' J'} \langle J M_J | J_z | J' M_J' \rangle \Rightarrow = 0$ unless $J = J'$, $M_J = M_J'$

Example $l_1 = 2, l_2 = 1$

$$\underset{LHS}{|L, M\rangle} = \underset{RHS}{|m_1, m_2\rangle} + ... \qquad \vec{L} = \vec{l_1} + \vec{l_2}$$

$|3,3\rangle = |2,1\rangle$

$|3,2\rangle = \frac{1}{\sqrt{3}}|2,0\rangle + \sqrt{\frac{2}{3}}|1,1\rangle$

$|3,1\rangle = \frac{1}{\sqrt{15}}|2,-1\rangle + \sqrt{\frac{8}{15}}|1,0\rangle + \sqrt{\frac{2}{5}}|0,1\rangle$

$|3,0\rangle = \frac{1}{\sqrt{5}}|1,-1\rangle + \sqrt{\frac{3}{5}}|0,0\rangle + \sqrt{\frac{1}{5}}|-1,1\rangle$

$|2,2\rangle = \sqrt{\frac{2}{3}}|2,0\rangle - \frac{1}{\sqrt{3}}|1,1\rangle$

$|2,1\rangle = \sqrt{\frac{1}{3}}|2,-1\rangle + \frac{1}{\sqrt{6}}|1,0\rangle - \frac{1}{\sqrt{2}}|0,1\rangle$

$|2,0\rangle = \sqrt{\frac{1}{2}}|1,-1\rangle - \frac{1}{\sqrt{2}}|-1,1\rangle$

⎤ From C.G. Coeffs

$\frac{1}{\hbar}\langle 3,3|L_{1z}|3,3\rangle = 2 \cdot 1 = \frac{2}{3} \cdot 3$

$\frac{1}{\hbar}\langle 3,2|L_{1z}|3,2\rangle = \frac{1}{3}2 + \frac{2}{3}1 = \frac{2}{3} \cdot 2$

$\frac{1}{\hbar}\langle 3,1|L_{1z}|3,1\rangle = \frac{1}{15}2 + \frac{8}{15} \cdot 1 + \frac{2}{5}0 = \frac{2}{3} \cdot 1$

$\frac{1}{\hbar}\langle 3,0)L_{1z}|3,0\rangle = \frac{1}{5}1 + \frac{3}{5}0 + \frac{1}{5}(-1) = \frac{2}{3} \cdot 0$

$\frac{1}{\hbar}\langle 2,2|L_{1z}|2,2\rangle = \frac{2}{3}2 + \frac{1}{3}1 = \frac{5}{6} \cdot 2$

$\frac{1}{\hbar}\langle 2,1|L_{1z}|2,1\rangle = \frac{1}{3}2 + \frac{1}{6}1 + \frac{1}{20}0 = \frac{5}{6} \cdot 1$

$\frac{1}{\hbar}\langle 2,0|L_{1z}|2,0\rangle = \frac{1}{2}1 + \frac{1}{2}(-1) = \frac{5}{6} \cdot 0$

$\frac{1}{\hbar}\langle 3,3|L_{2z}|3,3\rangle = 1 \cdot 1 = \frac{1}{3} \cdot 3$

$\frac{1}{\hbar}\langle 3,2|L_{2z}|3,2\rangle = \frac{1}{3} \cdot 0 + \frac{2}{3} \cdot 1 = \frac{1}{3} \cdot 2$

$\frac{1}{\hbar}\langle 3,1|L_{2z}|3,1\rangle = \frac{1}{15}(-1) + \frac{8}{15}0 + \frac{2}{5}1 = \frac{1}{3} \cdot 1$

$\frac{1}{\hbar}\langle 3,0|L_{2z}|3,0\rangle = \frac{1}{5}(-1) + \frac{3}{5}0 + \frac{1}{5}1 = \frac{1}{3} \cdot 0$

$\frac{1}{\hbar}\langle 2,2|L_{2z}|2,2\rangle = \frac{2}{3}0 + \frac{1}{3}1 = \frac{1}{6} \cdot 2$

$\frac{1}{\hbar}\langle 2,1|L_{2z}|2,2\rangle = \frac{1}{3}(-1) + \frac{1}{6}0 + \frac{1}{2}1 = \frac{1}{6} \cdot 1$

$\frac{1}{\hbar}\langle 2,0|L_{2z}|2,0\rangle = \frac{1}{2}(-1) + \frac{1}{2}1 = \frac{1}{6} \cdot 0$

For all of these cases

$$\frac{1}{\hbar}\langle LM|L_{1z}|LM\rangle = C_{L,L_1 L_2} M$$

$$\frac{1}{\hbar}\langle LM|L_{2z}|LM\rangle = D_{L,L_1 L_2} M$$

If this angular momentum coupling is a good approximation, then there are implications for energy spacings of different J.

$$H_{so} = \left(\beta_1\, \vec{S}_1\cdot\vec{L}_1 + \beta_2\, \vec{S}_2\cdot\vec{L}_2 + \ldots \right)/\hbar^2$$

When find the energy

$$\langle LSJM_J | H_{so} | LSJM_J\rangle = \left(C_1\beta_1\, \langle LSJM_J | \vec{S}\cdot\vec{L} | LSJM_J\rangle \right.$$
$$\left. + C_2\beta_2\, \langle LSJM_J | \vec{S}\cdot\vec{L} | LSJM_J\rangle + \ldots \right)/\hbar^2$$

$$= \beta_{LS}\langle LSJM_J | \vec{S}\cdot\vec{L} | LSJM_J\rangle/\hbar^2 = \tfrac{1}{2}\beta_{LS}\left[J(J+1) - L(L+1) - S(S+1)\right]$$

Example ^3P_J $E_{J=2} - E_{J=1} = 2\left(E_{J=1} - E_{J=0}\right)$

Carbon

	$E_{J=2} - E_{J=1}$	$E_{J=1} - E_{J=0}$
$2s^2 2p^2\ {}^3P$	$= 27\ \text{cm}^{-1}$	$= 16.4\ \text{cm}^{-1}$
$2s^2 2p3s\ {}^3P$	$= 40.5\ \text{cm}^{-1}$	$= 19.2\ \text{cm}^{-1}$
$2s^2 2p3p\ {}^3P$	$= 20.5\ \text{cm}^{-1}$	$= 12.4\ \text{cm}^{-1}$

^3D_J $E_{J=3} - E_{J=2} = 1.5\left(E_{J=2} - E_{J=1}\right)$

	$E_{J=3} - E_{J=2}$	$E_{J=2} - E_{J=1}$
$2s\,2p^3\ {}^3D$	$= -4\ \text{cm}^{-1}$	$= 1\ \text{cm}^{-1}$
$2s^2 2p3p\ {}^3D$	$= 33.4\ \text{cm}^{-1}$	$= 21.1\ \text{cm}^{-1}$
$2s^2 2p3d\ {}^3D$	$= 10.6\ \text{cm}^{-1}$	$= 14.1\ \text{cm}^{-1}$

As can be seen, sometimes works OK and sometimes fails completely.

Why?

Other interactions: spin-other orbit (for example $\vec{S}_1\cdot\vec{L}_2$), spin-spin (for example $\vec{S}_1\cdot\vec{S}_2$), orbit-orbit (for example $\vec{L}_1\cdot\vec{L}_2$)

Another possibility is the original assumption fails: LS coupling is not a good approximation. However, just because the interval rule fails, does not mean LS coupling is a bad approx.

Compare $2s\,2p^3\ {}^3D$ (96%) with $2s^2 2p3d\ {}^3D_3$ is 75% $^3D_3$ and 23% $^3F_3$

        LS approx good   LS approx not good

One common way LS coupling fails is when N-1 electrons have a large spin-orbit splitting and other electron is excited and has ~0 spin orbit. Probably what's happening $2s^2 2p\, 3d\; ^3D_3$

Example two electrons   Si: $3s^2\, 3p\, 4f$
In LS coupling, should have $^1D_2,\; ^3D_{1,2,3},\; ^1F_3,\; ^3F_{2,3,4},\; ^1G_4,\; ^3G_{3,4,5}$
Instead have:

$3s^2\left(\left(3p\,(^2P_{1/2})\,4f\right)_{5/2}\, \tfrac{1}{2}\right)$	J=3	58 774.368 cm^{-1}	J=2	58 775.451 cm^{-1}
$\left(\left(3p\,(^2P_{1/2})\,4f\right)_{7/2}\, \tfrac{1}{2}\right)$	J=3	58 786.860 cm^{-1}	J=4	58 775.451 cm^{-1}
$3s^2\left(\left(3p\,(^2P_{3/2})\,4f\right)_{7/2}\, \tfrac{1}{2}\right)$	J=3	59 034.988 cm^{-1}	J=4	59 037.043 cm^{-1}
$\left(\left(3p\,(^2P_{3/2})\,4f\right)_{5/2}\, \tfrac{1}{2}\right)$	J=3	59 109.959 cm^{-1}	J=2	59 110.892 cm^{-1}
$\left(\left(3p\,(^2P_{3/2})\,4f\right)_{9/2}\, \tfrac{1}{2}\right)$	J=5	59 128.40 cm^{-1}	J=4	59 131.912 cm^{-1}
$\left(\left(3p\,(^2P_{3/2})\,4f\right)_{3/2}\, \tfrac{1}{2}\right)$	J=1	59 190.46 cm^{-1}	J=2	59 191.072 cm^{-1}

Number of states   1 (J=1), 3 (J=2), 4 (J=3), 3 (J=4), 1 (J=5)

Another common coupling scheme is jj.
Example
$3s^2\left(3p\,(^2P_{3/2})\; 4f\,(^2F_{5/2})\right)$ J=1, 2, 3, 4

In all cases, if there is no nuclear spin and no external fields, J is a conserved quantity. This means the specific representation can be flawed (for example $3s^2 3p\, 4f\; ^3D_3$) but the J is good (in this example J=3).

There are important trends in how LS coupling breaks down. These can be used to advantage.

Example Sr $5s^2$ 0 $5s5p$ $^3P_0$ 14317.507 cm^{-1}
                                    $^3P_1$ 14504.334 cm^{-1} $5s5p$ $^1P_1$ 21 698.452 cm^{-1}
                                    $^3P_2$ 14898.545 cm^{-1}

$^3P_1$ and $^1P_1$ mix. This allows laser excitation to $^3P_1$. Small radiative lifetime $\sim 21\,\mu s$ $\Rightarrow$ $\Gamma = 2\pi\ 7.6\ kHz$

Takes advantage of 2 states with same J and parity can mix.

The Zeeman effect for the electrons (ignore effects from nuclear spin which is in the ext chapter). If the magnetic field is weak (how to determine?), the energy splittings from magnetic field s are simple.

$$H_{ZE} = \mu_B B (L_z + g_s S_z)/\hbar \qquad\qquad g_s \cong 2$$

From page 1, we know the energy should be proportional to M_J

$$E_{ZE} = g_J \mu_B B M_J$$

If LS coupling is a good approx $\quad g_J = \dfrac{3}{2} + \dfrac{S(S+1) - L(L+1)}{2J(J+1)}$
(uses $g_s = 2$)

Examples
C	$2s^2 2p^2$ ^3P	$J=1,2$	$g_J = 1.501\ldots$	formula $= \frac{3}{2}$
C	$2s^2 2p^2$ $^1P_1$		$g_J = 0.97$	formula $= 1$
All singlets		$g_J = 1$		
Pg 1	$^3D_3$	$1\frac{2}{3} + g_s\frac{1}{3} = \frac{4}{3}$		formula $= \frac{4}{3}$
Pg 1	$^3D_2$	$1\frac{5}{6} + g_s\frac{1}{6} = \frac{7}{6}$		formula $= \frac{7}{6}$
All $L = S$		$g_J = \frac{3}{2}$		

This has implications for the spectra in a B-field. For singlet $\longleftrightarrow$ singlet or if $L=S \longleftrightarrow L=S$, the g_J doesn't change $\Rightarrow$ $\Delta M_J = 0$ $\quad \Delta E = 0$, $\quad \Delta M_J = \pm 1 \rightarrow \pm g_J \mu_B B$

For other cases, the energy change depends on the M_J
$$\Delta M_J = 0 \qquad \Delta E = \mu_B B (g_{J_f} - g_{J_i}) M_J$$
$$\Delta M_J = \pm 1 \qquad \Delta E = \mu_B B (g_{J_f} - g_{J_i}) M_J \pm \mu_B B g_{J_f}$$

In high precision/QIS situations, the $M_J = 0 \longleftrightarrow M_J = 0$ is insensitive to B. From Chap1.pdf
$$\mu_B/h \cong 14 \text{ GHz/T} = 14 \text{ MHz/(10 gauss)} = 14 \text{ kHz/(0.01 gauss)}$$

What is meant by small B?

Diamagnetic effects for ground state $\sim 15\,kHz\,(B/1T)^2$

$B = 1000\,g \Rightarrow \sim 150\,Hz$, $B = 100\,g \Rightarrow \sim 1.5\,Hz$

At large enough B, the Zeeman terms can cause the J to uncouple

Example Li $1s^2\,2p$ $^2P_{3/2,\,1/2}$ $g_{3/2} = 4/3$ $g_{1/2} = \frac{2}{3}$

$E = \mu_B B\, 2,\ \mu_B B\,\frac{2}{3},\ -\mu_B B\,\frac{2}{3},\ -\mu_B B\, 2$ and $\mu_B B\,\frac{1}{3},\ -\mu_B B\,\frac{1}{3}$

At large B $E = \mu_B B\,(M_L + 2M_s) \Rightarrow$ $\overset{1,\,1/2}{2\mu_B B},\ \overset{1,\,-1/2}{0\mu_B B},\ \overset{0,\,1/2}{\mu_B B},\ \overset{0,-1/2}{-\mu_B B},\ \overset{-1,1/2}{0\mu_B B},\ \overset{-1,-1/2}{-2\mu_B B}$

Why does this happen? The two $M_J = 1/2$ interact and the two $M_J = -1/2$ interact.

Find the Hamiltonian for $M_J = 1/2$

$\langle 3/2,\, 1/2 | H | 3/2,\, 1/2 \rangle = E_{3/2} + \frac{2}{3}\mu_B B$

$\langle 1/2,\, 1/2 | H | 1/2,\, 1/2 \rangle = E_{1/2} + \frac{1}{3}\mu_B B$

$\langle 3/2,\, 1/2 | H | 1/2,\, 1/2 \rangle = \qquad\ \ -\frac{\sqrt{2}}{3}\mu_B B$

$E_\pm = \frac{E_{3/2}+E_{1/2}}{2} + \frac{\mu_B B}{2} \pm \left[\frac{1}{4}\left(E_{3/2} - E_{1/2} + \frac{\mu_B B}{3}\right)^2 + \frac{2}{9}\mu_B^2 B^2 \right]^{1/2}$

Small B $E_\pm \approx \frac{E_{3/2}+E_{1/2}}{2} + \frac{\mu_B B}{2} \pm \left[\frac{E_{3/2}-E_{1/2}}{2} + \frac{\mu_B B}{6} \right] \overset{\checkmark}{=} E_{3/2} + \frac{2}{3}\mu_B B$ and $E_{1/2} + \frac{1}{3}\mu_B B$

large B $E_\pm \approx \frac{E_{3/2}+E_{1/2}}{2} + \frac{\mu_B B}{2} \pm \left(\frac{\mu_B B}{2} + \frac{E_{3/2}-E_{1/2}}{6}\right) \overset{\checkmark}{=} \left(\frac{2}{3}E_{3/2} + \frac{1}{3}E_{1/2}\right) + \mu_B B$ and $\frac{1}{3}E_{3/2} + \frac{2}{3}E_{1/2} + 0\mu_B B$

Example Li $1s^2\,2p$ $\Delta E = E_{3/2} - E_{1/2} = 0.34\,cm^{-1} = 4.2\times10^{-5}\,eV = 10.2\,GHz\,h$

$\mu_B = 14.0\,GHz\,h$ $E_{3/2} = E_{2p} + \frac{1}{3}\Delta E$ $E_{1/2} = E_{2p} - \frac{2}{3}\Delta E$

See plots

As a rough guide, the simple expressions with g_J only work if $\mu_B B \ll |E_J - E_{J'}|$

If you find Zeeman transmission frequency has B^2 dependence, usually due to the breakdown of $\vec{J}$.