

Example of S-O coupling - an electron has total angular momentum state  $|j, m_j\rangle$ , with  $j=l+1/2$  and  $j=l-1/2$  values allowed.

E.g. (d electron)  $l=2, s=1/2$  i.e.  $j=5/2, 3/2$  states are allowed.

S-O coupling in terms of angular momentum q.n.:

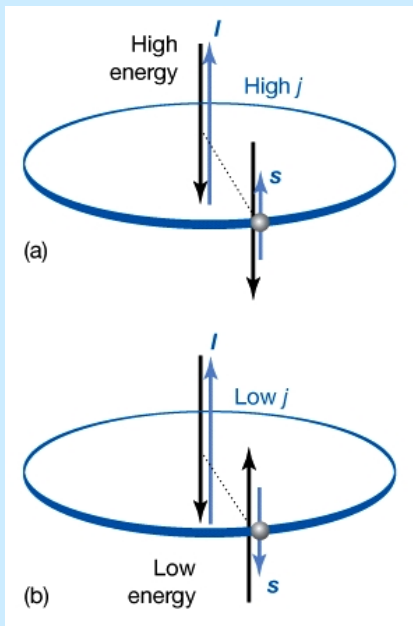
$$E \propto \underset{\substack{\uparrow \\ \text{"moment"}}}{s} \cdot \underset{\substack{\uparrow \\ \text{"field"}}}{l}$$

$$j \cdot j = (l + s) \cdot (l + s)$$

$$= l \cdot l + s \cdot s + 2s \cdot l$$

$$\text{i.e. } s \cdot l = \frac{1}{2} \{ j^2 - l^2 - s^2 \}$$

$$\text{i.e. } \hat{s} \cdot \hat{l} = \frac{1}{2} \{ \hat{j}^2 - \hat{l}^2 - \hat{s}^2 \}$$



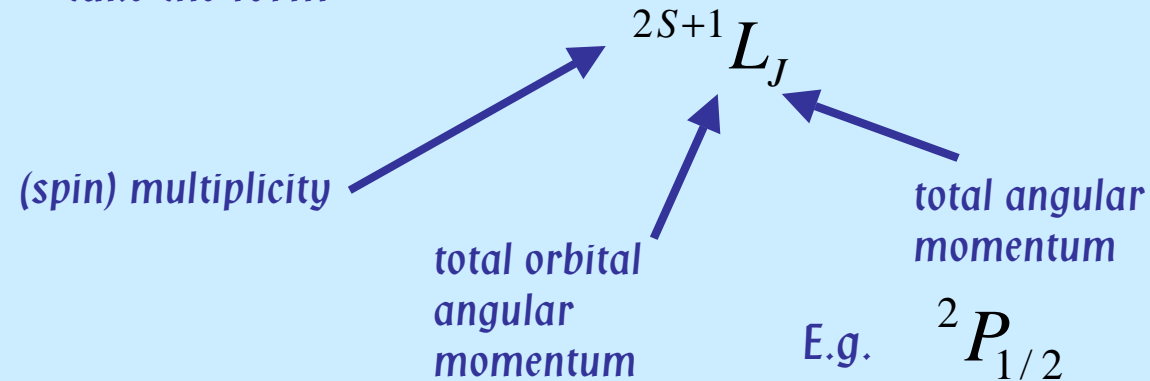
and so

$$\langle j, l, s | \hat{s} \cdot \hat{l} | j, l, s \rangle = \frac{1}{2} \langle j, l, s | \hat{j}^2 - \hat{l}^2 - \hat{s}^2 | j, l, s \rangle$$

$$= \frac{1}{2} \{ j(j+1) - l(l+1) - s(s+1) \}$$

## Term symbols:

These describe the state of a many-electron atom, and take the form



Multiplicity and total angular momentum depend on the Clebsch-Gordan series: this determines the values available for the total momentum when individual momenta are combined (vector coupling).

E.g.  $L = l_1 + l_2, l_1 + l_2 - 1, \dots, |l_1 - l_2|$

(non-negative)

$L = 0$  corresponds to  $S$

$L = 1$  corresponds to  $P$

$L = 2$  corresponds to  $D$  (etc.)

E.g. A  $2p^1 3p^1$  configuration can lead to  $L=1+1 = 2$  (D),  $L=1+1-1 = 1$  (P), and  $L = 1 - 1 = 0$  (S) terms, which differ in energy due to the spatial interactions of the electrons.

For shells which are  $>1/2$  filled equivalent states are obtained by considering the “holes”.

For  $S$  again we have  $S = s_1 + s_2, s_1 + s_2 - 1, \dots, |s_1 - s_2|$

E.g A single electron has  $S=1/2$  so  $2S+1=2$  (doublet)

Two electrons yield  $S=1$   $2S+1=3$  (triplet) and

$S=0$   $2S+1=1$  (singlet).

**Multiplicity** ( $2S+1$ ) is the number of  $M_S$  states for a given  $S$ .

**Total angular momentum  $J$**  is calculated in one of two ways:

(1) L-S (Russell-Saunders) coupling -- A (or Z) small

First couple  $l$  to give  $L$  and  $s$  to give  $S$ , then couple  $L$  and  $S$  to give  $J$ .

$$J = L + S, L + S - 1, \dots, |L - S|$$

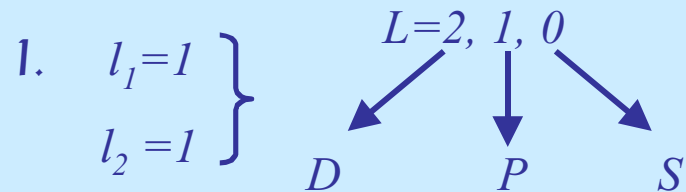
(2) A (or Z) large -- jj-coupling

$$J = j_1 + j_2, j_1 + j_2 - 1, \dots, |j_1 - j_2|$$

These two schemes can be connected via a correlation diagram, and L-S labels can be used to label states that are better described by jj-coupling.

Equivalent electrons lead to a complication, due to the Pauli exclusion principle.

Example:  $p^2$  (This is e.g. the ground state of carbon.)



2.  $S=1, 0 \longrightarrow {}^3D, {}^1D \quad {}^3P, {}^1P \quad {}^3S, {}^1S$

3.  $J=L+S, L+S-1, L+S-2, \dots, |L-S| \longrightarrow {}^3D_3, {}^3D_2, {}^3D_1, {}^1D_2, {}^3P_2, {}^3P_1, {}^3P_0, {}^1P_1, {}^3S_1, {}^1S_0$

However,



Implies  $M_L=+2$ . This implies  $m_l=+1$  for each electron. Hence the electrons cannot both be  $\alpha$  electrons. Hence the  ${}^3D_3$  state is excluded by the Pauli principle. Etc.  
(Check which other states are excluded.)

## Equivalent electrons: method of microstates

$p^2$

Notation:  $(m_{l_1}, m_{l_2})$  with macron (overbar) if electron has  $\beta$  spin, i.e.  $(m_{l_1}, \bar{m}_{l_2})$ .  
Here  $m_l = 1, 0, -1$ .

1. List all possible states, omitting those (such as  $(1, 1)$ ) that are Pauli-forbidden.

$$\left\{ \begin{array}{lll} (1, \bar{1}) & (1, \bar{0}) & (1, \bar{-1}) \\ (0, \bar{1}) & (0, \bar{0}) & (0, \bar{-1}) \\ (-1, \bar{1}) & (-1, \bar{0}) & (-1, \bar{-1}) \end{array} \right\} (\alpha, \beta)$$

$$\begin{array}{lll} (1, 0) & (0, -1) & (1, -1) \\ (\bar{1}, \bar{0}) & (\bar{0}, \bar{-1}) & (\bar{1}, \bar{-1}) \end{array} \quad \begin{array}{l} (\alpha, \alpha) \\ (\beta, \beta) \end{array}$$

2. Note values of  $M_L, M_S$  associated with these, and construct table.

$M_L \backslash M_S$	+1	0	-1
+2		$(1, \bar{1})$	
+1	$(1, 0)$	$(1, \bar{0})(0, \bar{1})$	$(\bar{1}, \bar{0})$
0	$(1, -1)$	$(1, \bar{-1})(0, \bar{0})(-1, \bar{1})$	$(\bar{1}, \bar{-1})$
-1	$(0, -1)$	$(0, \bar{-1})(-1, \bar{0})$	$(\bar{0}, \bar{-1})$
-2		$(-1, \bar{-1})$	

3. Group microstates into  $L$  and  $S$  values. E.g. The presence of  $(1, \bar{1})$  on its own implies that there is an  $L=2, S=0$  state ( $^1D$ ). We can cross off (any) five states with  $M_S=0$  and  $M_L=+2, +1, 0, -1, -2$ .

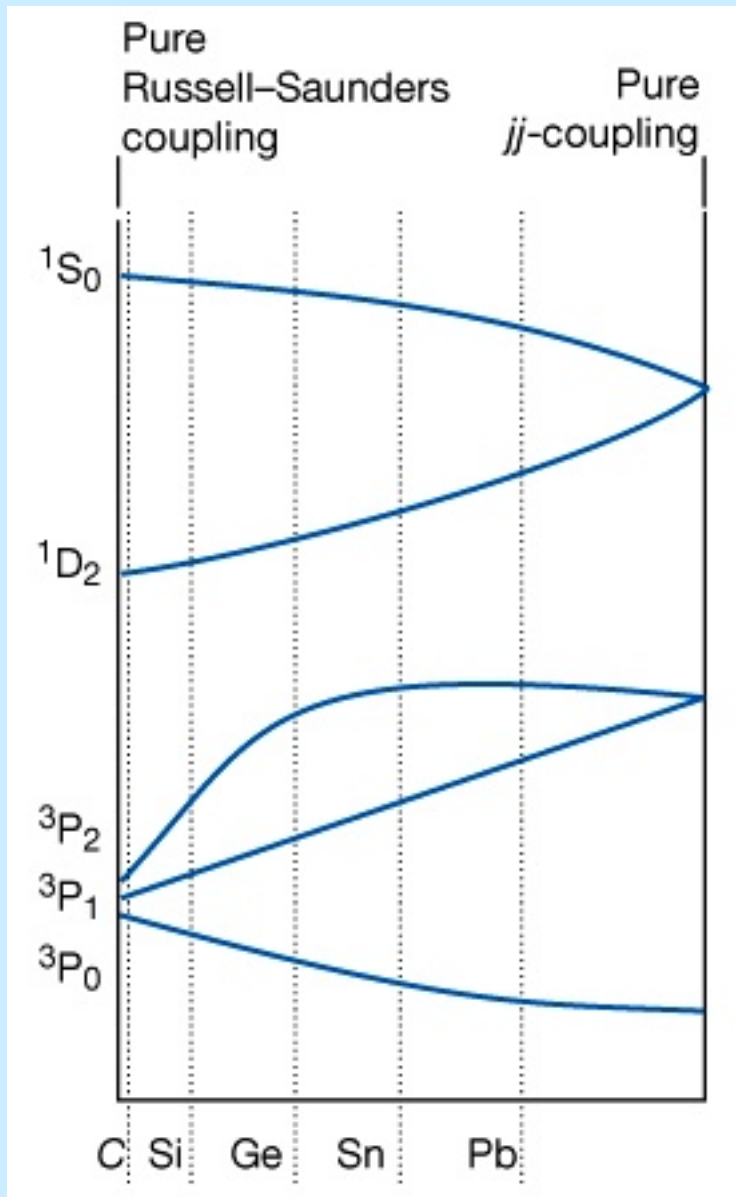
(This is simply a bookkeeping method, and so it does not matter which states we cross off.)

Next, we notice that we have a  $^3P$  state, so we can cross off nine states with  $M_L=+1, 0, -1$  and  $M_S=+1, 0, -1$ .

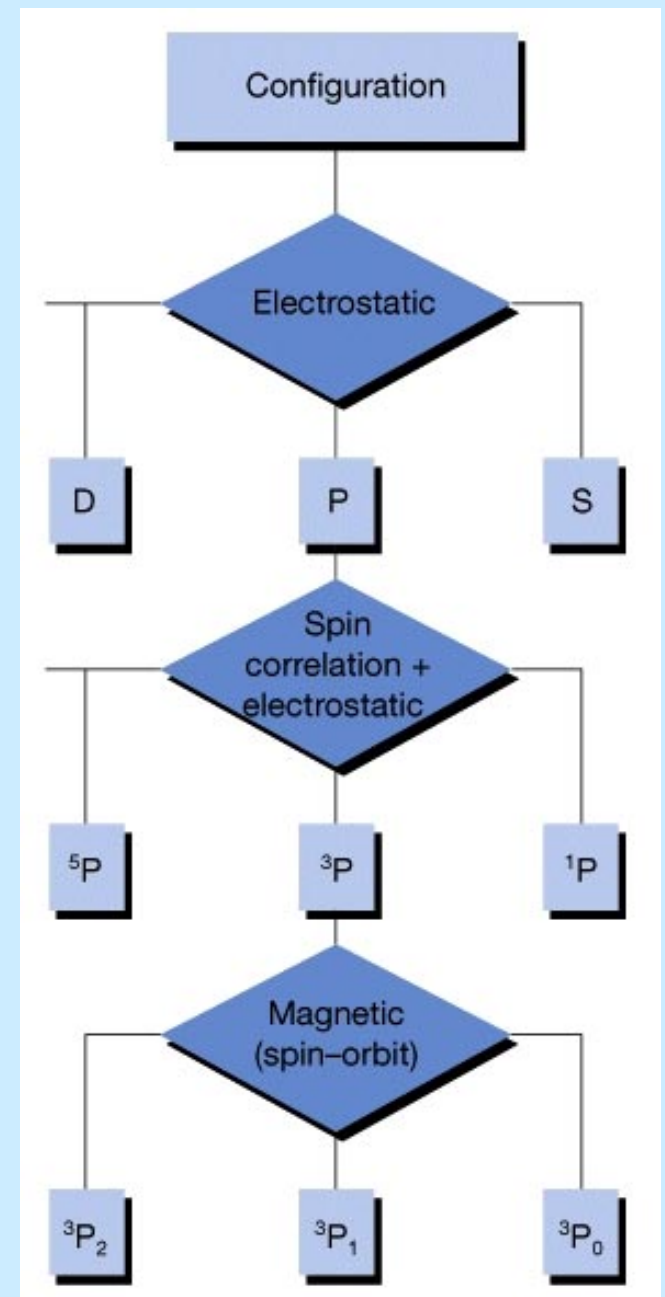
This leaves only  $M_L=0, M_S=0$ , which corresponds to  $L=0, S=0$ , a  $^1S$  state.

Hence we have three states:  $^1D$ ,  $^3P$ , and  $^1S$ . With the appropriate  $J$  values, these generate the allowed terms for the  $p^2$  configuration.

## Correlation diagram



## Summary of interactions



## Transitions and selection rules

Initial and final states may be denoted by the appropriate term symbols

E.g. Na doublet:  $3p^1 \ ^2P_{3/2} \rightarrow 3s^1 \ ^2S_{1/2}$  (Convention: upper state on left. Absorption transitions use left-pointing arrow.)  
 $3p^1 \ ^2P_{1/2} \rightarrow 3s^1 \ ^2S_{1/2}$

Selection rules (conservation of angular momentum in transitions):

$$\Delta S = 0 \quad \Delta L = 0, \pm 1 \quad \Delta l = \pm 1 \quad \Delta J = 0, \pm 1$$



(photon has no direct interaction with spin)



(but no transitions between J=0 states)

## Specification of Coupled States

An angular momentum state (orbital, spin, or general) can be fully described using its quantum numbers, as  $|j, m_j\rangle$ .

Consider two such one-particle states,  $|j_1, m_{j1}\rangle$  and  $|j_2, m_{j2}\rangle$ . What are the limitations if we are to consider the combined state as  $|j_1, m_{j1}; j_2, m_{j2}\rangle$ ? (We need to consider which operators commute and which do not.)

Is it legitimate to write  $|j_1, m_{j1}; j_2, m_{j2}\rangle$ ? I.e. can we consider these four quantum numbers simultaneously? Answer: since  $j_1$  commutes with  $j_{z1}$  and  $j_2$  commutes with  $j_{z2}$ , and since  $j1$  and  $j2$  are independent, all four quantum numbers **can** be considered simultaneously.

Next question: Is  $\mathbf{j} = \mathbf{j}_1 + \mathbf{j}_2$  an angular momentum?

$$\begin{aligned} [j_x, j_y] &= [j_{1x} + j_{2x}, j_{1y} + j_{2y}] \\ &= [j_{1x}, j_{1y}] + [j_{2x}, j_{1y}] + [j_{1x}, j_{2y}] + [j_{2x}, j_{2y}] \\ &= i\hbar j_{1z} + i\hbar j_{2z} = i\hbar j_z \end{aligned}$$

If so, its components should behave in the same way as the components of  $\mathbf{j}_1$  and  $\mathbf{j}_2$ .

Yes,  $\mathbf{j}$  behaves like an angular momentum.

(If you believe this was obvious, see what happens with  $\mathbf{j}_1 - \mathbf{j}_2$ .)

Similarly, if  $j_1$  and  $j_2$  have been specified, we can still specify  $j$  (since each of  $j_1^2$  and  $j_2^2$  commutes with its components, and since  $j^2$  can be expressed in terms of these components), i.e.  $[j^2, j_1^2] = [j^2, j_2^2] = 0$

E.g. For a 2p electron ( $l=1, s=1/2$ ), we can define the value of the total angular momentum  $j$ .

Since  $j^2$  commutes with  $j_z$  we can specify  $m_j$  as well as  $j$ . However, in this case we cannot specify  $m_{j1}$  or  $m_{j2}$  because e.g.

$$\begin{aligned}
 [j_{1z}, j^2] &= [j_{1z}, j_x^2] + [j_{1z}, j_y^2] + [j_{1z}, j_z^2] \\
 &= [j_{1z}, (j_{1x} + j_{2x})^2] + [j_{1z}, (j_{1y} + j_{2y})^2] + [j_{1z}, (j_{1z} + j_{2z})^2] \\
 &= [j_{1z}, (j_{1x}^2 + 2j_{1x}j_{2x})] + [j_{1z}, (j_{1y}^2 + 2j_{1y}j_{2y})] \\
 &= [j_{1z}, (j_{1x}^2 + j_{1y}^2)] + 2[j_{1z}, j_{1x}]j_{2x} + 2[j_{1z}, j_{1y}]j_{2y} \\
 &= [j_{1z}, (j^2 + j_{1z}^2)] + 2i\hbar j_{1y}j_{2x} - 2i\hbar j_{1x}j_{2y} \\
 &= 2i\hbar(j_{1y}j_{2x} - j_{1x}j_{2y}) \neq 0
 \end{aligned}$$

In other words, if we want to specify the total angular momentum  $j$ , we cannot simultaneously specify  $m_{j1}$  and  $m_{j2}$ .

We have a choice of:

The uncoupled representation  $|j_1 m_{j_1}; j_2 m_{j_2}\rangle$

No information about relative orientations. Total number of states =  $(2j_1+1)(2j_2+1)$ .

or

The coupled representation  $|j_1 j_2; j m_j\rangle$

No information about individual components.

Example:  $m_{j_1} = j_1, m_{j_2} = j_2 \longrightarrow m_j = j_1 + j_2$

$m_{j_1} = j_1 - 1, m_{j_2} = j_2 \longrightarrow m_j = j_1 + j_2 - 1$

$m_{j_1} = j_1, m_{j_2} = j_2 - 1 \longrightarrow m_j = j_1 + j_2 - 1$

...

...

$m_{j_1} = j_1, m_{j_2} = -j_2 \longrightarrow m_j = j_1 - j_2$

One of these corresponds to  $j = j_1 + j_2$  - hence there must be another coupled state for which the **maximum**  $m_j$  is  $j = j_1 + j_2 - 1$ .

This is how the Clebsch-Gordan series ( $j = j_1 + j_2, j_1 + j_2 - 1, \dots, |j_1 - j_2|$ ) is constructed.

The relationship between the coupled and uncoupled schemes can be written in terms of a linear combination:

$$|j_1 j_2; j m_j\rangle = \sum_{m_{j_1}, m_{j_2}} C_{j_1 m_{j_1}, j_2 m_{j_2}}^{j m_j} |j_1 m_{j_1}; j_2 m_{j_2}\rangle$$

(vector coupling coefficient, a.k.a. Clebsch-Gordan coefficient)

## Example: Two spins $s=1/2$ .

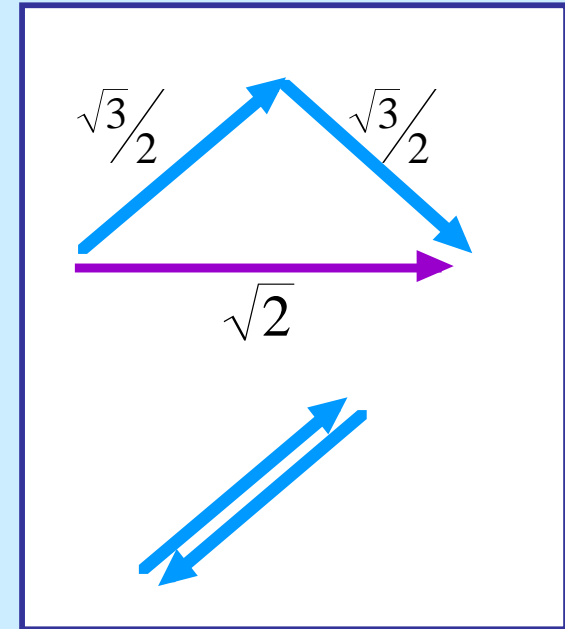
Uncoupled picture:  $\alpha_1\alpha_2, \alpha_1\beta_2, \beta_1\alpha_2, \beta_1\beta_2$ .

Coupled picture:  $S=1$  (triplet)  $\begin{cases} \rightarrow M_S=+1 \\ \rightarrow M_S=0 \\ \rightarrow M_S=-1 \end{cases}$

$S=0$  (singlet)  $\rightarrow M_S=0$

$$S=1/2 \text{ length} = (S(S+1))^{1/2} = \sqrt{3}/2$$

$$S=0 \text{ length} = (S(S+1))^{1/2} = \sqrt{2}$$



NB Spins are truly antiparallel in  $S=0$  state, but only nearly parallel in  $S=1$  state.

In the  $|S, M_S\rangle$  representation

$$\begin{aligned} |1, +1\rangle &= \alpha_1\alpha_2 \\ |1, 0\rangle &= \frac{1}{\sqrt{2}}(\alpha_1\beta_2 + \beta_1\alpha_2) \\ |1, -1\rangle &= \beta_1\beta_2 \\ |0, 0\rangle &= \frac{1}{\sqrt{2}}(\alpha_1\beta_2 - \beta_1\alpha_2) \end{aligned}$$

NB This is a spin-parallel triplet state even though it seems to be composed of opposite spins - it is the sign which implies that the spins are "in phase" with each other.

We can represent this relationship in the form of a table:

$m_{s_1}$	$m_{s_2}$	$ 1,+1\rangle$	$ 1,0\rangle$	$ 0,0\rangle$	$ 1,-1\rangle$
$+\frac{1}{2}$	$+\frac{1}{2}$	1	0	0	0
$+\frac{1}{2}$	$-\frac{1}{2}$	0	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	0
$-\frac{1}{2}$	$+\frac{1}{2}$	0	$\frac{1}{\sqrt{2}}$	$-\frac{1}{\sqrt{2}}$	0
$-\frac{1}{2}$	$-\frac{1}{2}$	0	0	0	1

The Clebsch-Gordan coefficients can be thought of as “overlap integrals” between the uncoupled and coupled representations.

$$\langle j_1 m_{j_1}; j_2 m_{j_2} | j_1 j_2; j m_j \rangle = C_{j_1 m_{j_1}, j_2 m_{j_2}}^{j m_j}$$

I.e. The C-G coefficients give an indication of the extent to which the states in the uncoupled and coupled representations resemble one another.

General expressions for the C-G coefficients exist, but it is usual to look them up in tables. For more than two angular momenta, the C-G coefficients are replaced by the Racah or 6-j coefficients.

## **Calculation of the electronic structure of many-electron atoms**

*No analytic solution of the many-electron atom problem exists.*

*Usually treated using the self-consistent field method (initially proposed by Douglas R. Hartree; corrected by Vladimir Fock: known as Hartree-Fock theory).*

*In the SCF method a set of initial guess orbitals are taken and iteratively optimized by calculating the field experienced by each electron as a result of all the others, refining the orbitals appropriately, and continuing until self-consistency is achieved.*

*Similar methods are used in molecular calculations and we will encounter them in more detail there.*