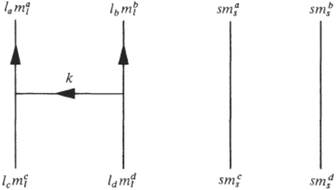
Last time
The Coulomb interaction

$$\langle ab \mid \frac{1}{r_{12}} \mid cd \rangle = \sum_k \int \int P_a(r_1)\, P_b(r_2)\, \frac{r_<^k}{r_>^{k+1}} P_c(r_1)\, P_d(r_2)\, dr_1 dr_2$$
$$\times (-1)^k \langle \ell_a \mid\mid \mathbf{C}^k \mid\mid \ell_c \rangle \langle \ell_b \mid\mid \mathbf{C}^k \mid\mid \ell_d \rangle$$

$\times$

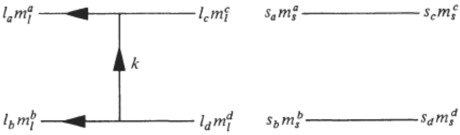


- Reduced Matrix Elements: $\ell_a + k + \ell_c = \text{even}$
- Rule: the internal m/q quantum numbers are summed over.
- Typically the diagrams can be evaluated analytically.

Last time

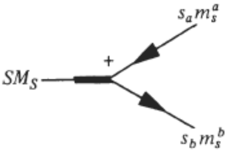
LS-terms for two electron configurations

$$\sum_k X(k, l_a l_b l_c l_d) R^k(ab, cd)$$

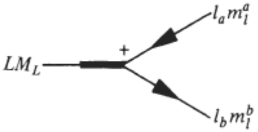


Couple them!

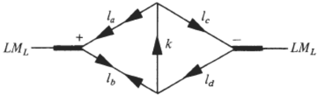
$$\sum_{m_s^a m_s^b}$$



$$\sum_{m_l^a m_l^b}$$



Gives (for L)



$$= (-1)^{k+\ell_a+\ell_c+2\ell_a+L+\ell_a+\ell_b} \begin{Bmatrix} L & \ell_a & \ell_b \\ k & \ell_d & \ell_c \end{Bmatrix}$$

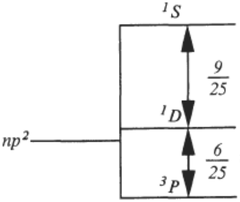
Example np^2

$$\langle \left\{ np^2 \right\} LM_L SM_s \mid \frac{1}{r_{12}} \mid \left\{ np^2 \right\} LM_l SM_S \rangle = \sum_k R^k \left(np^2, np^2 \right)$$

$$(-1)^k \langle p \mid\mid \mathbf{C}^k \mid\mid p \rangle^2 \left\{ \begin{array}{ccc} L & 1 & 1 \\ k & 1 & 1 \end{array} \right\} (-1)^{k+L}$$

- $k =$ even, $L = 0, 1, 2$
- if $k = 0 \rightarrow R^0 \left(np^2, np^2 \right)$ regardless of L
- if $k = 2$ different angular factors

$$\langle \{np^2\}^1 S \mid \frac{1}{r_{12}} \mid \{np^2\}^1 S\rangle = R^0\left(np^2, np^2\right) + \frac{2}{5}R^2\left(np^2, np^2\right)$$
$$\langle \{np^2\}^1 D \mid \frac{1}{r_{12}} \mid \{np^2\}^1 D\rangle = R^0\left(np^2, np^2\right) + \frac{1}{25}R^2\left(np^2, np^2\right)$$
$$\langle \{np^2\}^3 P \mid \frac{1}{r_{12}} \mid \{np^2\}^3 P\rangle = R^0\left(np^2, np^2\right) - \frac{1}{5}R^2\left(np^2, np^2\right)$$



- Remember Hund's rules?

Friedrich Hund ~1925

So far we coupled

- two angular momenta and encountered $3j$-symbols
- three angular momenta and encountered $6j$-symbols

When do we need to couple more angular momenta?

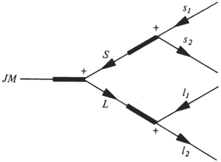
- couple all ℓ:s to $\mathbf{L}$, and all s:s to $\mathbf{S}$ and then $\mathbf{J} = \mathbf{L} + \mathbf{S}$
- or couple each ℓ_i and s_i to j_i and then the j:s to $\mathbf{J}$

What is the relation between **SL** and **jj** coupling?

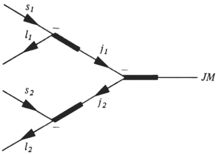
$$
\begin{aligned}
&| \, \{(s_1\ell_1)\, j_1\, (s_2\ell_2)\, j_2\}\, JM\rangle = \\
&\sum_{LS} | \, \{(s_1 s_2)\, S\, (\ell_1\ell_2)\, L\}\, JM\rangle \\
&\times\langle\{(s_1 s_2)\, S\, (\ell_1\ell_2)\, L\}\, JM\rangle \mid \{(s_1\ell_1)\, j_1\, (s_2\ell_2)\, j_2\}\, JM\rangle
\end{aligned}
$$

or vice versa!

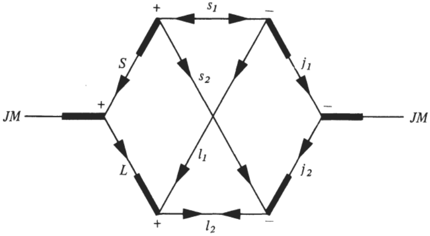
$\langle (s_1 s_2)S, (l_1 l_2)L, JM | =$



$| (s_1 l_1)j_1, (s_2 l_2)j_2, JM \rangle =$

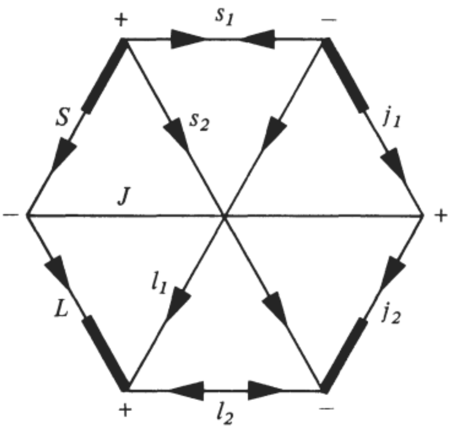


$=$



Coupling of Angular Momenta

sum over all M:s → join the lose ends!



Note! All arrows can be removed!

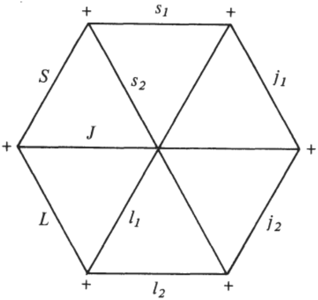
Coupling of Angular Momenta

$$\langle \{(s_1 s_2)\, S\, (\ell_1 \ell_2)\, L\}\, JM \rangle \mid \{(s_1 \ell_1)\, j_1\, (s_2 \ell_2)\, j_2\}\, JM\rangle =$$

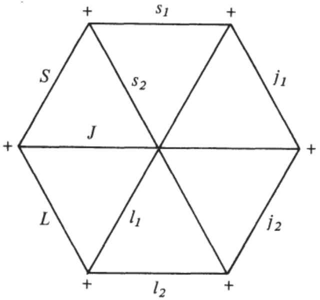
$$(-1)^R \sqrt{(2L+1)\,(2S+1)\,(2j_1+1)\,(2j_2+1)} \times$$

$$(R = s_1 + s_2 + \ell_1 + \ell_2 + j_1 + j_2 + L + S + J)$$

Changing all corners to $+ \to (-1)^R$.



Coupling of Angular Momenta



$$= \left\{ \begin{matrix} s_1 & s_2 & S \\ \ell_1 & \ell_2 & L \\ j_1 & j_2 & J \end{matrix} \right\}$$

- 9-j symbol

- can be calculated from the product of six $3-j$ symbols summed over all m:s (see Lindgren and Morrison 3.71)
- more practical: from the product of three $6-j$ symbols (Edmonds 6.4.3)
- all rows, all columns triangular condition
- odd permutations $\rightarrow (-1)^R$, **LS** versus **SL**?
- rows and columns can be interchanged

Example

$$| \, (1s2p) \ ^1P_{J=1}\rangle \qquad | \left(1s2p_{1/2}\right) \ J=0,1\rangle$$

$$| \, (1s2p)^3 \, P_{J=0,1,2}\rangle \qquad | \left(1s2p_{3/2}\right) J=1,2\rangle$$

$$| \, (1s2p) \ ^{1,3}P_{J=1}\rangle = c_1 \, | \left(1s2p_{1/2}\right) \ J=1\rangle + c_2 \, | \left(1s2p_{3/2}\right) \ J=1\rangle$$

$$| \, (1s2p) \ ^1P_{J=1}\rangle = \sqrt{\frac{1}{3}} \, | \left(1s2p_{1/2}\right) \ J=1\rangle + \sqrt{\frac{2}{3}} \, | \left(1s2p_{3/2}\right) \ J=1\rangle$$

$$| \, (1s2p) \ ^3P_{J=1}\rangle = \sqrt{\frac{2}{3}} \, | \left(1s2p_{1/2}\right) \ J=1\rangle - \sqrt{\frac{1}{3}} \, | \left(1s2p_{3/2}\right) \ J=1\rangle$$

- Remember this is just the angular momentum coupling!

Example from a real ion

He-like neon (Z=10), Dirac based calculation.

$$E_1 = -60.1294 \text{ a.u. } 0.55 \mid \left(1s2p_{1/2}\right) \; J=1\rangle + 0.826 \mid \left(1s2p_{3/2}\right) \; J=1\rangle$$
$$E_2 = -60.3935 \text{ a.u. } 0.828 \mid \left(1s2p_{1/2}\right) \; J=1\rangle - 0.56 \mid \left(1s2p_{3/2}\right) \; J=1\rangle$$

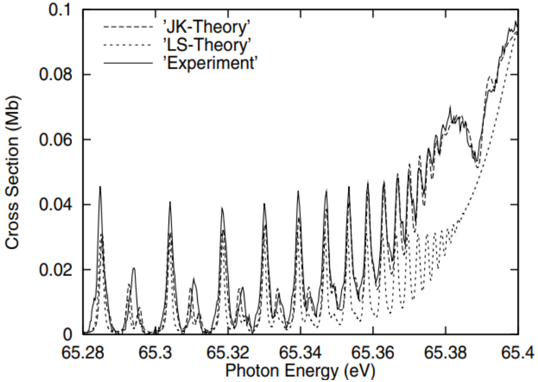
while $\sqrt{1/3} \approx 0.58$, $\sqrt{2/3} \approx 0.82$?

- Not pure LS-coupling
- The higher energy state 99.94% ${}^1P$, 0.06% ${}^3P$
- The lower energy state 99.94% ${}^3P$, 0.06% ${}^1P$
- Still approximately LS.
- what happens when Z increases?

Why do we get singlet-triplet mixing?

- the singlet-triplet splitting is determined by the Coulomb interaction ($\sim Z$)
- the mixing is determined by the spin-orbit interaction $\rightarrow$ (slightly) different *radial* wave functions for $2p_{1/2}$, $2p_{3/2}$
- increases with Z: spin-orbit interaction $\sim Z^4$
- Rydberg states ($n_2 \gg n_1$): Coulomb interaction decreases. Inner electron spin-orbit interaction remains $\rightarrow$ intermediate-coupling regime.

LS-coupling can fail even for helium!



Fluorescence cross section, Gorzyka et al prl85,1202.

series limit ($n \to \infty$) 65.4 eV

$1s^2 + \Omega \to 2\ell n\ell' \to 1s^2 + \Omega$ Pure LS coupling $\to \Delta S = 0$

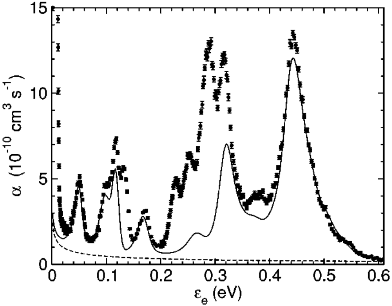
Another example

Electron ion recombination (autoionization backwards) through resonances

$$F^{6+}\left(1s^2 2s\right) + e^- \rightarrow F^{5+}\left(1s^2 2pn\ell\right)$$

$(2p_{3/2}\,6p_{1/2})_1$	^3P 60%
$(2p_{3/2}\,6p_{1/2})_2$	^3P 92%
$(2p_{1/2}\,6d_{3/2})_2$	^3F 79%
$(2p_{1/2}\,6d_{5/2})_3$	^3F 93%
$(2p_{3/2}\,6p_{3/2})_2$	^1D 93%
$(2p_{1/2}\,6d_{5/2})_2$	^1D 68%
$(2p_{3/2}\,6d_{5/2})_4$	^3F 100%
$(2p_{1/2}\,6d_{3/2})_1$	^3D 84%
$(2p_{3/2}\,6d_{3/2})_2$	^3D 58%
$(2p_{1/2}\,6f_{5/2})_3$	^3G 57%
$(2p_{1/2}\,6f_{7/2})_4$	^3F 46%
$(2p_{1/2}\,6f_{7/2})_3$	^3F 50%

and many more..



Solid line: allowed in LS-coupling

E.g. $\{2p6p\}$ P cannot autoionize in LS-coupling.

Intermediate (jK) coupling

- Coupling scheme for Rydberg states as

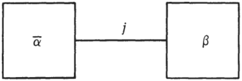
$$2\ell n\ell',\ \ n \gg 2$$

- Couple ℓ and s to j for the inner electron
- Couple ℓ' of the outer electron to j of the inner: Form K
- couple K and s of the outer to the final J.

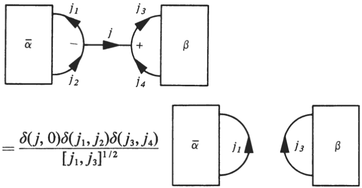
The coupling schemes are just labels

- The accuracy of the calculation is determined by the physical effects included: correlation? relativistic effects?
- a well chosen coupling scheme makes it easier to understand what we see.
- relativistic calculations implies *jj*-coupling. This is never "wrong", but translation to *LS* or *jK* can help the interpretation.

More about graphs

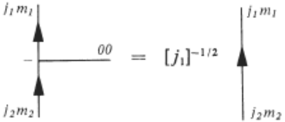


Convenient form:



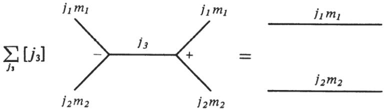
JLV1 (the zero line has been removed as was shown in Chap. 3)

- Two parts connected by *one* line. One of the parts is *closed* (here $\overline{\alpha}$). If $\overline{\alpha}$ has one arrow on each internal line (we call that *normal form*) then $j \equiv 0$
- basic JLV theorem after Jucys, Levinson and Vanagas 1962.

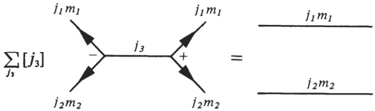


What about two lines?

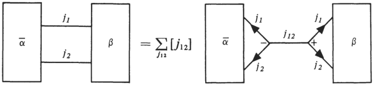
Start from 3.33:



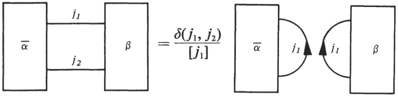
Adding arrows gives:



Put this between $\overline{\alpha}$ and β:



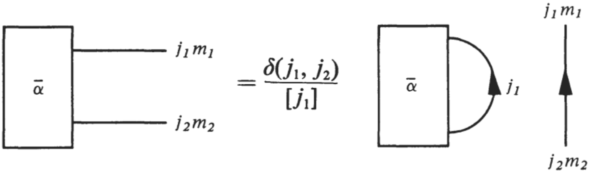
Remove the zero line:



JLV2

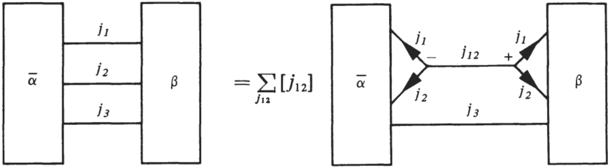
- $j_1 = j_2$

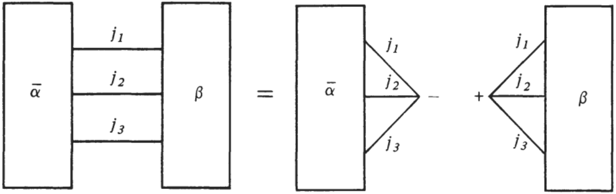
True also if β is empty



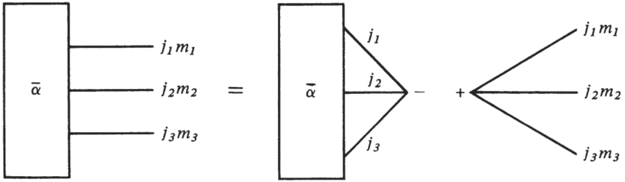
- $j_1 = j_2$
- can be view as a form of conservation of angular momentum
- Possible to continue with three and four lines etc.

Three lines


$\bar{\alpha}$
j_1
j_2
j_3
β
$= \sum_{j_{12}} [j_{12}]$
$\bar{\alpha}$
j_1
j_2
$-$
j_{12}
$+$
j_1
j_2
j_3
β


$\bar{\alpha}$
j_1
j_2
j_3
β
$=$
$\bar{\alpha}$
j_1
j_2
j_3
$-$
$+$
j_1
j_2
j_3
β

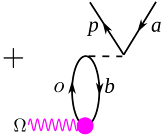
Three lines, no β

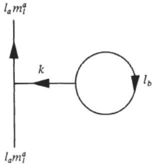


- Wigner Eckarts theorem: m-independent part to the left, 3j-symbol to the right

Examples

One of the RPAE-diagrams





- The dipole operator is a rank one tensor operator. Thus the line connecting o and b must also have angular momentum one

$$\sum_k \frac{r_<^k}{r_>^{k+1}} \mathbf{C}^k(1) \cdot \mathbf{C}^k(2) \rightarrow k = 1 \text{ only}$$

- Interaction with e$^-$ in a closed shell

$$\sum_b^{\text{closed shell}} \langle ab \mid \frac{1}{r_{12}} \mid ab \rangle$$

only $K = 0$ contributes.

- Next time Chapter 5 and the independent particle model.