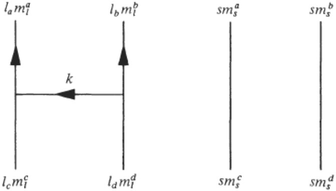
$$\langle ab \mid \frac{1}{r_{12}} \mid cd \rangle = \sum_k \int \int P_a(r_1) P_b(r_2) \frac{r_<^k}{r_>^{k+1}} P_c(r_1) P_d(r_2) dr_1 dr_2$$

$$\times (-1)^k \langle \ell_a \mid\mid \mathbf{C}^k \mid\mid \ell_c \rangle \langle \ell_b \mid\mid \mathbf{C}^k \mid\mid \ell_d \rangle$$

$\times$

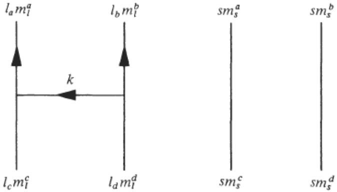


- Reduced Matrix Elements: $\ell_a + k + \ell_c = \mathrm{even}$
- Rule: the internal m/q quantum numbers are summed over.
- Typically the diagrams can -eventually- be evaluated analytically.

The Coulomb interaction

$$\langle ab \mid \frac{1}{r_{12}} \mid cd \rangle = \sum_k R^k\,(ab, cd)\,X\,(k, \ell_a, \ell_b, \ell_c, \ell_d)$$

$\times$

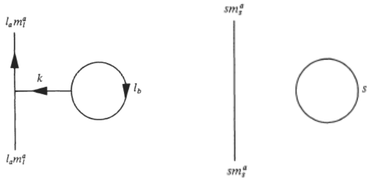


Example: What is the total interaction of one electron a with all the electron in a filled shell? (we call them b)

$$\sum_{m_\ell^b}\sum_{m_s^b}\left(\langle ab \mid \frac{1}{r_{12}} \mid ab\rangle - \langle ba \mid \frac{1}{r_{12}} \mid ab\rangle\right)$$

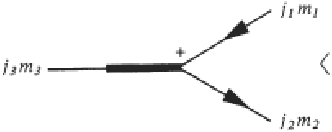
First term:

$$\sum_k R^k\left(ab,ab\right)X\left(k,\ell_a,\ell_b,\ell_a,\ell_b\right)\times$$



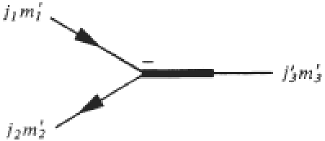
- Rule: the internal m/q quantum numbers are summed over.

$$\langle (j_1 j_2) j_3 m_3 | = \sum_{m_1 m_2}$$



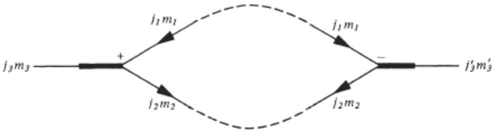
$$\langle j_1 m_1, j_2 m_2 |$$

$$|(j_1 j_2) j_3' m_3' \rangle = \sum_{m_1' m_2'} | j_1 m_1', j_2 m_2' \rangle$$



$$\langle (j_1 j_2) j_3 m_3 | (j_1 j_2) j_3' m_3' \rangle$$

$$= \sum_{m_1 m_2}$$

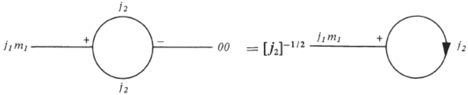


$$= \delta\left(j_3, j_3'\right) \delta\left(m_3, m_3'\right)$$

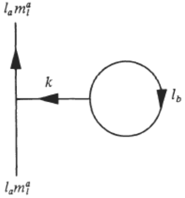
$$j_3' = 0 \rightarrow j_3 = 0$$

$$= \begin{pmatrix} j_2 & 0 & j_1 \\ m_2 & 0 & m_1 \end{pmatrix} = \delta\left(j_1, j_2\right) \delta\left(-m_1, m_2\right) \left(-1\right)^{j_1 - m_1} \frac{1}{\sqrt{2j_1 + 1}} =$$

$$\times \frac{1}{\sqrt{2j_1 + 1}}$$



$$= \delta(j_1, 0) \rightarrow \qquad \sqrt{2j_2 + 1}\,\delta\left(j_1, 0\right)$$



- Note minus sign at left vertex, plus at the right. Unimportant if ℓ integer.

$$= \sum_{m_\ell^b} (-1)^{\ell_a - m_a} \begin{pmatrix} \ell_a & 0 & \ell_a \\ -m_a & 0 & m_a \end{pmatrix} \sqrt{2\ell_b + 1} =$$

$$\sqrt{\frac{2\ell_b + 1}{2\ell_a + 1}} \delta(k, 0)$$

Remember what is in front:

$$R^{k=0}(ab, ab) \langle \ell_a || \mathbf{C}^{k=0} || \ell_a \rangle \langle \ell_b || \mathbf{C}^{k=0} || \ell_b \rangle = R^{k=0}(ab, ab) \sqrt{2\ell_a + 1} \sqrt{2\ell_b + 1}$$

Altogether:

$$R^{k=0}(ab, ab)(2\ell_b + 1)$$

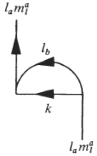
Why? And what about the spin part?

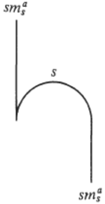
Example: What is the total interaction of one electron a with all the electron in a filled shell? (we call them b)

$$\sum_{m_\ell^b} \sum_{m_s^b} \left(\langle ab \mid \frac{1}{r_{12}} \mid ab \rangle - \langle ba \mid \frac{1}{r_{12}} \mid ab \rangle \right)$$

Second term:

$$-\sum_k R^k\left(ba, ab\right) X\left(k, \ell_b, \ell_a, \ell_a, \ell_b\right) \times$$





$$= \sum_{m_\ell^b} \sum_q (-1)^{2\ell_a + \ell_a + \ell_b + k} \begin{pmatrix} \ell_b & k & \ell_a \\ m_b & q & m_a \end{pmatrix} \begin{pmatrix} \ell_b & k & \ell_a \\ m_b & q & m_a \end{pmatrix} \delta\left(m_s^a, m_s^b\right)$$

$$= \sum_{m_\ell^b} \sum_q (-1)^{2\ell_a+\ell_a+\ell_b+k} \begin{pmatrix} \ell_b & k & \ell_a \\ m_b & q & m_a \end{pmatrix} \begin{pmatrix} \ell_b & k & \ell_a \\ m_b & q & m_a \end{pmatrix} =$$

$$(2.91)\ (-1)^{2\ell_a+\ell_a+\ell_b+k} \frac{1}{2\ell_a+1}$$

- non-relativistically: $\ell_a + \ell_b + k$ =even, ℓ integer $\rightarrow$ no phase
- relativistically: $(-1)^{2j_a+j_a+j_b+k} = (-1)^{j_a-j_b+k}$

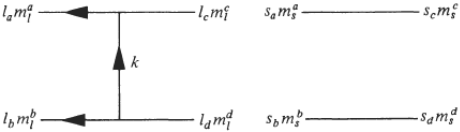
Conclusion

$$\sum_k R^k(ab, cd)\, X(k, \ell_a, \ell_b, \ell_c, \ell_d)$$

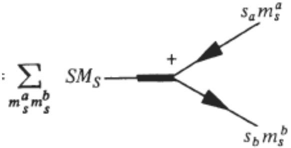
times simple numerical factors.

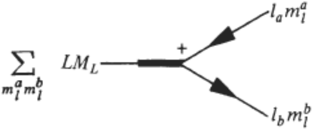
LS-terms for two electron configurations

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

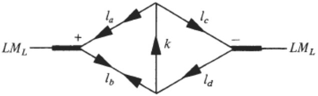


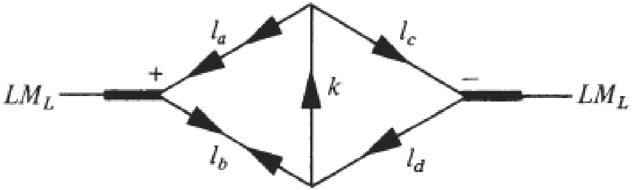
Couple them!





Gives (for L)

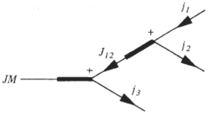




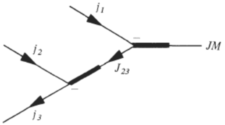
- Sum over m/q internal lines
- Each vertex a $3j$ -symbol.
- How it is connected to coupling of three angular momenta?

$$| j_1, (j_2 j_3)\, J_{23}, J\rangle = \sum_{J_{12}} | (j_1 j_2)\, J_{12} j_3, J\rangle \langle (j_1 j_2)\, J_{12} j_3, J \,|\, j_1, (j_2 j_3)\, J_{23}, J\rangle$$

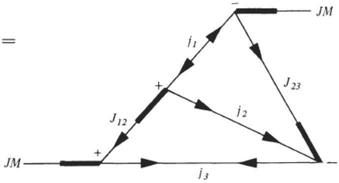
$\langle (j_1 j_2) J_{12}, j_3, JM | =$



$|j_1, (j_2 j_3) J_{23}, JM\rangle =$



$=$



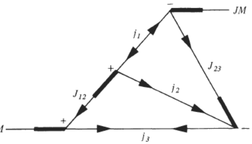
- Join the J-lines $\rightarrow$ $\sum M \rightarrow 2J+1$,remove the thick lines

The 6j Symbol

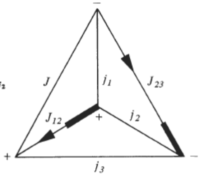
Coupling of three angular momenta

$$\langle (j_1 j_2)\, J_{12} j_3, J \mid j_1, (j_2 j_3)\, J_{23}, J \rangle =$$

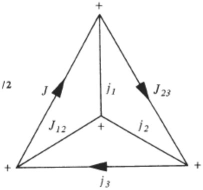
$=$



$= (-1)^{2j_2}$



$= (-1)^{j_1+j_2+j_3+J}\,[J_{12}, J_{23}]^{1/2}$

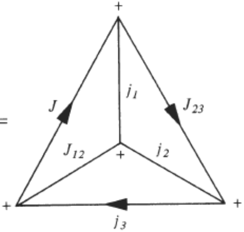


the phase: note that $j_2 + j_3 + J_{23}$ is always an integer

$$(-1)^{2j_2})(-1)^{J+J_{23}+j_3}(-1)^{j_2+J_{23}+j_3}(-1)^{2j_3} =$$

$$(-1)^{j_1+j_2+j_3+J}(-1)^{2(j_2+j_3+J_{23})}$$

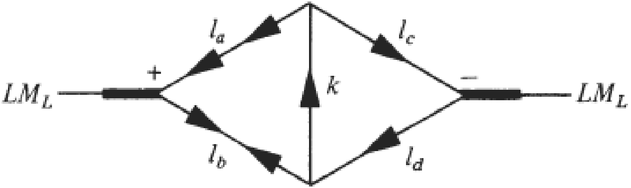
$$\begin{Bmatrix} j_1 & J_{12} & j_2 \\ j_3 & J_{23} & J \end{Bmatrix} =$$



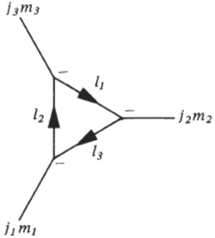
$$\sum_{\text{all } m} \begin{pmatrix} j_1 & J_{12} & j_2 \\ -m_1 & -M_{12} & -m2 \end{pmatrix} \begin{pmatrix} j_1 & J_{23} & J \\ m_1 & -M_{23} & M \end{pmatrix} \begin{pmatrix} J_{12} & J & j_3 \\ M_{12} & -M & m_3 \end{pmatrix}$$

$$\times \begin{pmatrix} j_2 & j_3 & J_{23} \\ m_2 & -m_3 & M_{12} \end{pmatrix} (-1)^{j_1 - m_1 + J_{12} - M_{12} + j_2 - m_2 + j_3 - m_3}$$

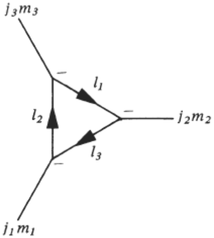
- arrows added on empty lines $\rightarrow$ phases
- note triangular conditions



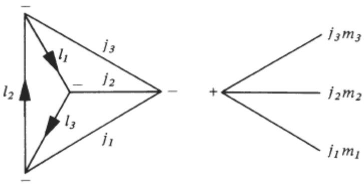
- A triangular shape



$j_3 m_3$
l_1
l_2
$j_2 m_2$
l_3
$j_1 m_1$



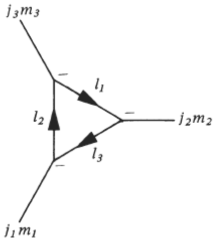
$j_3 m_3$
l_1
l_2
$j_2 m_2$
l_3
$j_1 m_1$

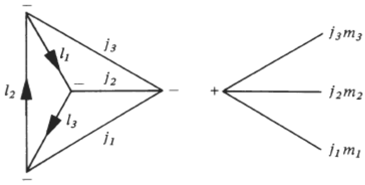


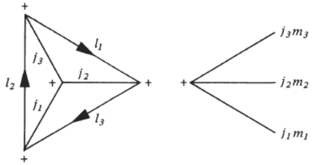
j_3
l_1
j_2
l_2
l_3
j_1
$j_3 m_3$
$j_2 m_2$
$j_1 m_1$

The 6j Symbol

Coupling of three angular momenta

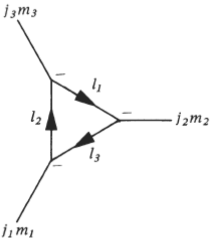


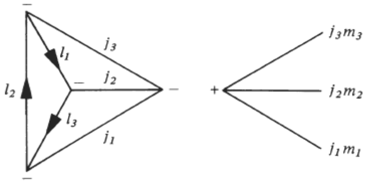


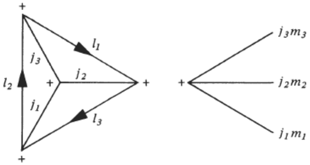


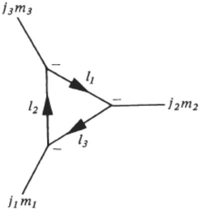
The 6j Symbol

Coupling of three angular momenta

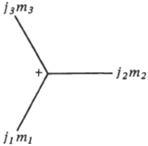




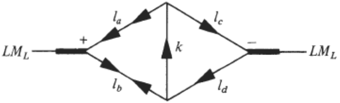




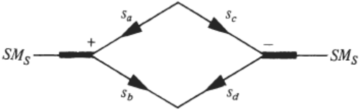
$$= \begin{Bmatrix} j_1 & j_2 & j_3 \\ l_1 & l_2 & l_3 \end{Bmatrix}$$



LS-terms for two electron configurations



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



$$= 1 \qquad (1)$$

$$(-1)^{k+\ell_c+4\ell_a+L+\ell_b} = (-1)^{k+\ell_c+L+\ell_b}$$

- true for both integer and half-integer angular momenta

Example np^2

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

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

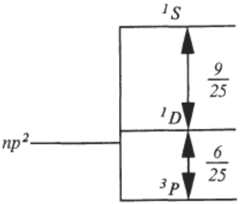
- $k = \text{even}, \ L = 0, 1, 2$
- if $k = 0 \rightarrow R^0 \left(np^2, np^2 \right)$ regardless of L
- if $k = 2$ different angular factors

LS-terms for a two electron configuration

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

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

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



Summary and Outlock

- Couple two angular momenta $\rightarrow 3j$ -symbol (Clebsch-Gordan)
- Couple three angular momenta $\rightarrow 6j$ -symbol (Term splittings)
- Couple four angular momenta $\rightarrow 9j$ -symbol (Translate bweteen LS and jj-coupling). Still todo!
- The angular momentum graphs gives simple numerical factors that can easily be recognized. No explicit summation over m:s necessary!