Matrix Elements of Tensor Products.

- Suppose we have a tensor product

$$T_{KQ}(R_{k_1}, S_{k_2}) = \sum_{q_1 q_2} R_{k_1 q_1} S_{k_2 q_2} \langle k_1 k_2 q_1 q_2 | KQ \rangle .$$

Since $\langle JM | T_{KQ} | J'M' \rangle = (-1)^{2K} \langle J \| T_K \| J' \rangle \langle JM | J' K M' Q \rangle$

multiply by $\sum_{M'Q} \langle JM | J' K M' Q \rangle$

$$\therefore \langle J \| T_K \| J' \rangle = \sum_{M'Q} (-1)^{2K} \langle JM | T_{KQ} | J'M' \rangle \langle JM | J' K M' Q \rangle$$

Insert $\sum_{J''M''} | J'' M'' \rangle \langle J'' M'' |$ into expansion of T_{KQ}.

$$\Rightarrow \langle J \| T_K \| J' \rangle = \sum_{\substack{q_1 q_2 M' M'' Q \\ J''}} (-1)^{2K} \langle JM | J' K M' Q \rangle$$

$$\langle KQ | k_1 k_2 q_1 q_2 \rangle \langle JM | R_{k_1 q_1} | J'' M'' \rangle \langle J'' M'' | S_{k_2 q_2} | J' M' \rangle$$

$$= \sum_{\substack{q_1 q_2 M' M'' Q \\ J''}} (-1)^{2(K + k_1 + k_2)} \langle JM | J' K M' Q \rangle \langle KQ | k_1 k_2 q_1 q_2 \rangle$$

$$\langle JM | J'' k_1 M'' q_1 \rangle \langle J'' M'' | J' k_2 M' q_2 \rangle$$

$$\langle J \| R_{k_1} \| J'' \rangle \langle J'' \| S_{k_2} \| J' \rangle$$

The summations are proportional to the 6-j symbol.

Case I, $(k_1, k_2) \to K \qquad (K, J') \to J$

Case II, $(k_2, J') \to J'' \qquad (J'', k_1) \to J$

The transformation coefs. are proportional to $\langle k_1, (k_2 J') J''; J | (k_1 k_2) K, J'; J \rangle$

$$\therefore \langle J \| T_K \| J' \rangle = \sum_{J''} (2K+1)^{1/2} (2J''+1)^{1/2} (-1)^{K+J'+J}$$
$$\times \begin{Bmatrix} k_1 & k_2 & K \\ J' & J & J'' \end{Bmatrix} \langle J \| R_{k_1} \| J'' \rangle \langle J'' \| S_{k_2} \| J' \rangle$$

$$\begin{Bmatrix} k_1 & k_2 & K \\ J' & J & J'' \end{Bmatrix} = (-1)^{k_1+k_2+J'+J} W(k_1\, k_2\, J J';\, K J'')$$

$$\therefore (-1)^{K+J'+J} \begin{Bmatrix} k_1 & k_2 & K \\ J' & J & J'' \end{Bmatrix} = (-1)^{k_1+k_2+K+2J'+2J} W(k_1\, k_2\, J J';\, K J'')$$

$$= (-1)^{k_1+k_2-K} W(\qquad\qquad)$$

since $(-1)^{2K+2J'+2J} = 1$.

We have said nothing about the nature of R_k and S_k. e.g. $|J'\rangle$ could be composed of two parts with "R" acting on one and S_k acting on the other.

The case $K=0$ corresponds to the scalar product of two tensors.

$$T_{00}(R_k S_k) = \frac{(-1)^{-k}}{\sqrt{2k+1}} \vec{R}_k \cdot \vec{S}_k$$

Then

$$\langle J \| R_k \cdot S_k \| J' \rangle = \sum_{J''} (-1)^{-J+J''} \left(\frac{2J''+1}{2J+1} \right)^{1/2} \langle J \| R_k \| J'' \rangle \langle J'' \| S_k \| J' \rangle$$

since $\begin{Bmatrix} j_3 & j_3 & 0 \\ j_2 & j_2 & j_1 \end{Bmatrix} = \dfrac{(-1)^{j_1+j_2+j_3}}{[(2j_2+1)(2j_3+1)]^{1/2}}$

Extension to Composite Systems.

Consider $\langle j_1 j_2 J \| T_k(1) \| j_1' j_2' J' \rangle$

where $T_k(1)$ acts only on part 1 of system.
e.g. orbit and spin parts. $j_2 = j_2'$

Proceeding as before,

$\langle j_1 j_2 J M | T_{kq} | j_1' j_2' J' M' \rangle = (-1)^{2k} \langle J \| T_{kq} \| J' \rangle \times \langle J M | J' k M' q \rangle$

Multiply by $\sum_{M'q} \langle J M | J' k M' q \rangle$

$$\langle j_1 j_2 J \| T_k(1) \| j_1' j_2' J' \rangle$$

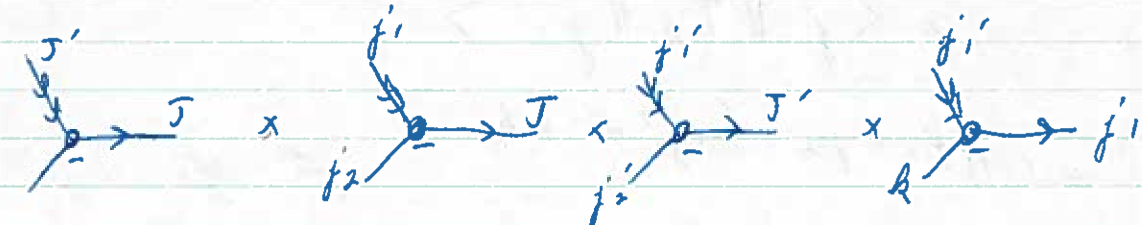
$$= \sum_q (-1)^{2k} \langle J M | J' k M' q \rangle \langle j_1 j_2 J M | T_{kq} | j_1' j_2' J' M' \rangle$$

$$= \sum_{\substack{M'q\, m_1 m_2 \\ m_1' m_2'}} \langle J M | J' k M' q \rangle \langle j_1 j_2 m_1 m_2 | J M \rangle$$

$$\times \langle j_1' j_2' m_1' m_2' | J' M' \rangle \langle j_1 m_1 | j_1' k m_1' q \rangle$$

$$\times \langle j_1 \| T_k \| j_1' \rangle \, \delta(j_2 j_2')$$

$= (2J'+1)^{1/2} (2j_1+1)^{1/2}$



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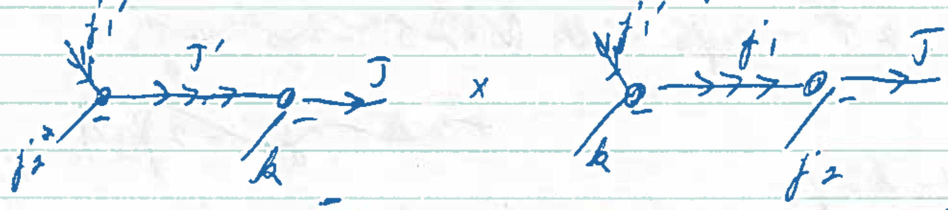

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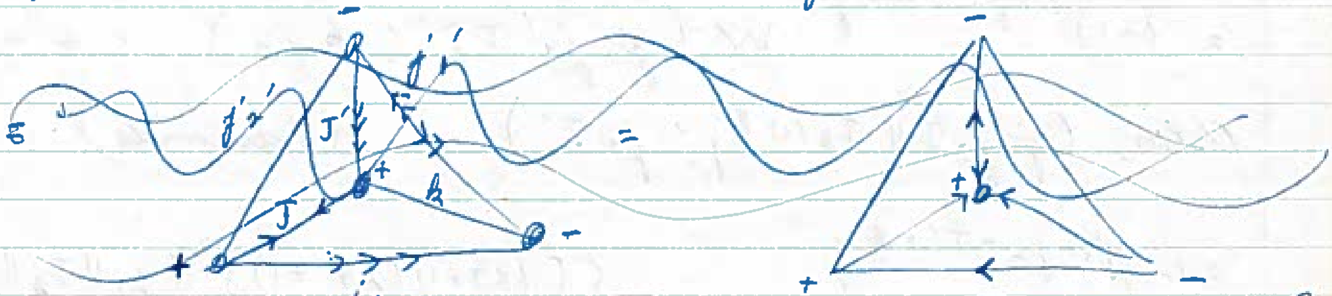
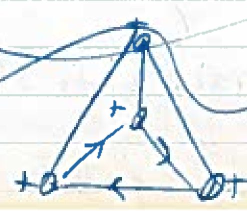
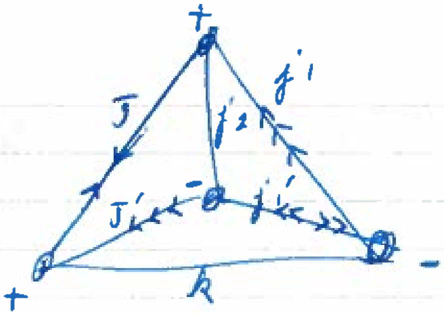


$= (-1)^{j_1'+j_2'+J'+j_1'+j_1+k+2k}$



$= (-1)^{3j_1'+j_1+j_2+J'-k}$

$$= (2J'+1)^{1/2}(2j_1'+1)^{1/2}$$



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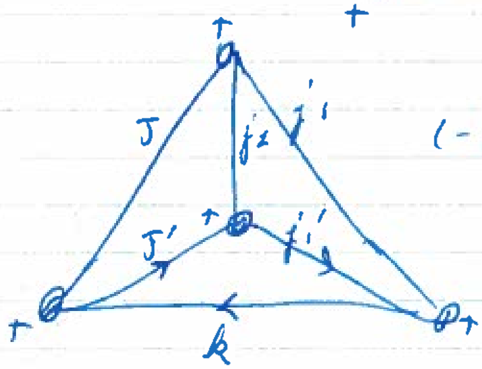


$$(-1)^{j_1+j_2+J'+k}(2J'+1)^{1/2}(2j_1'+1)^{1/2}$$

$$\therefore \langle j_1 j_2 J \| T_k(1) \| j_1' j_2 J' \rangle$$

$$= (-1)^{j_1+j_2+J'+k} \begin{Bmatrix} j_1 & J & j_2 \\ J' & j_1' & k \end{Bmatrix} (2J'+1)^{1/2}(2j_1'+1)^{1/2}$$

$$\times \langle j_1 \| T_k \| j_1' \rangle$$

$$= (-1)^{2j_1+j_2+J+j_1'+2J'+k \; -2J-2J \; -2j_1-2J'-2j_2-2k}$$

$$= (-1)^{J+j_1'-k-j_2} \, W(j_1 j_1' J J'; k j_2) \; \cdots$$

Also, $(j_1 j_2 J \| T_k(1) \| j_1' j_2 J')$ (Edmonds)

$$= (-1)^{j_1+j_2+J'+k} \Big\{ \quad \Big\} [(2J+1)(2J'+1)]^{1/2} (j_1 \| T_k \| j_1')$$

and $(j_1 j_2 J \| T_k(2) \| j_1 j_2' J') = (-1)^{j_1+j_2'+J+k} \begin{Bmatrix} j_2 & J & j_1 \\ J' & j_2' & k \end{Bmatrix}$

$$\times [(2J+1)(2J'+1)]^{1/2} (j_2 \| T_k \| j_2')$$

$W(l_1 l_1' l_2 l_2'; k l) = (-1)^{l_1+l_1'+l_2+l_2'} \times \begin{Bmatrix} l_1 & l_1' & k \\ l_2' & l_2 & l \end{Bmatrix}$

In the more general case, ~~ar~~ T_K is a tensor product $T_K(R_{k_1}(1) S_{k_2}(2))$ with R acting on j_1 and ~~A~~ S acting on j_2. This can be viewed as the recoupling of 4 angular momenta.

$$\langle j_1 j_2 J \| T_K(k_1 k_2) \| j_1' j_2' J' \rangle$$

$$= [(2J'+1)(2K+1)\overset{(2J+1)}{\cancel{(2j_1+1)(2j_2+1)}}]^{1/2}$$

$$\times \begin{Bmatrix} J & J' & K \\ j_1 & j_1' & k_1 \\ j_2 & j_2' & k_2 \end{Bmatrix} \langle j_1 \| R_{k_1} \| j_1' \rangle \langle j_2 \| S_{k_2} \| j_2' \rangle$$

Represents recoupling from row scheme to column scheme.

The case $K=0$ is particularly useful and simple since $9j \to 6j$.

$$\langle j_1 j_2 J | R_k(1) \cdot S_k(2) | j_1' j_2' J' \rangle = \cancel{[(2j_1+1)(2j_2+1)]^{1/2}}$$

$$\delta(J,J')(-1)^{J+j_1'+j_2} \cancel{W(j_1 j_1' j_2 j_2'; kJ)} \begin{Bmatrix} J' & j_2 & j_1 \\ k & j_1' & j_2' \end{Bmatrix}$$

$$\langle j_1 \| R_k \| j_1' \rangle \langle j_2 \| S_k \| j_2' \rangle .$$

An example is the scalar product of two spherical harmonics. Here we know the reduced matrix elements

$$\langle l_1 l_2 L \| C_k(1) \cdot C_k(2) \| l_1' l_2' L' \rangle = \delta(L,L')(-1)^{L+k}$$

$$[(2l_1+1)(2l_2+1)(2l_1'+1)(2l_2'+1)]^{1/2} \times \underbrace{W(l_1 l_1' l_2 l_2'; k l)}_{(-1)^{l_1+l_1'+l_2+l_2'} \begin{Bmatrix} l_1 & l_1' & k \\ l_2' & l_2 & l \end{Bmatrix}}$$

$$\begin{pmatrix} k & l_1 & l_1' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} k & l_2 & l_2' \\ 0 & 0 & 0 \end{pmatrix} .$$

Fractional Parentage + Seniority.

The foregoing methods become very complex for systems containing many electrons outside closed shells.

- For one-electron operators, the fractional parentage method is very useful.

General Form

Suppose $|\alpha(n), JM\rangle$ is an antisymmetrized n-electron wave function constructed from products of 1-electron orbitals

e.g. suppose we have 3 orbitals u v w.

$$|\alpha(3), JM\rangle = \frac{1}{\sqrt{3!}} \sum_P (-1)^P u(1) v(2) w(3)$$

$$= \frac{1}{\sqrt{3!}} \begin{vmatrix} u(1) & v(1) & w(1) \\ u(2) & v(2) & w(2) \\ u(3) & v(3) & w(3) \end{vmatrix}$$

$$= \frac{1}{\sqrt{3!}} \left[u(1) \{ v(2) w(3) - w(2) v(3) \} + \cdots \right.$$

It is clearly not possible to write $|\alpha(3), JM\rangle$ as a simple product of, say, $w(3)$ with

$$|\alpha(2), J_P M_P\rangle = \frac{1}{\sqrt{2!}} \left(u(1) v(2) - v(1) u(2) \right)$$

but it is possible to write $|\alpha(3), JM\rangle$ as a linear combination of such products with one of $u(3)$, $v(3)$ or $w(3)$ as the third orbital.
In general,

$$|\alpha(n), JM\rangle = \sum_{\substack{\alpha_P J_P \\ a j}} |\alpha_P(n-1) J_P, aj; JM\rangle \langle \alpha_P(n-1) J_P, aj | \} \alpha(n) J\rangle$$

Matrix Element of $\vec{L}_1$ in the $(l_1 l_2)$ ~~LM~~ Scheme.

$l(l+1)$ is the eigenvalue of $L^2 = (\vec{L}_1 + \vec{L}_2)^2$

$$(l_1\, l_2\, l \,\|\, \vec{L}_1 \,\|\, l_1\, l_2\, l) = (-1)^{l_1+l_2+l+1}(2l+1)\begin{Bmatrix} l_1 & l & l_2 \\ l & l_1 & 1 \end{Bmatrix}$$

$$\times \underbrace{[(2l_1+1)(l_1+1)\,l_1]^{1/2}}_{(l_1 \| \vec{L}_1 \| l_1)}$$

Using $\begin{Bmatrix} a & b & c \\ 1 & c & b \end{Bmatrix} = (-1)^{a+b+c+1}\dfrac{2[\,b(b+1)+c(c+1)-a(a+1)\,]}{[\,2b(2b+1)(2b+2)\,2c(2c+1)(2c+2)\,]^{1/2}}$

from Edmonds (or $W(aabb;1c)$ from p. 43 of B. and S.) the above becomes

$$\frac{(l_1\, l_2\, l \,\|\, \vec{L}_1 \,\|\, l_1\, l_2\, l)}{(2l+1)^{1/2}} = \frac{l_1(l_1+1) + l(l+1) - l_2(l_2+1)}{2[\,l(l+1)\,]^{1/2}}$$

This has a simple semiclassical interpretation.

Consider $\dfrac{\vec{L}_1 \cdot \vec{L}}{[\,l(l+1)\,]^{1/2}} \simeq \vec{L}_1 \cdot \hat{L}$

$$\vec{L} - \vec{L}_1 = \vec{L}_2$$

$$\therefore\; L^2 - 2\vec{L}\cdot\vec{L}_1 + L_1^2 = L_2^2$$

$$\therefore\; 2\vec{L}\cdot\vec{L}_1 = L^2 + L_1^2 - L_2^2$$

$$\downarrow$$

$$\frac{L_1^2 + L^2 - L_2^2}{2[\,l(l+1)\,]^{1/2}}$$

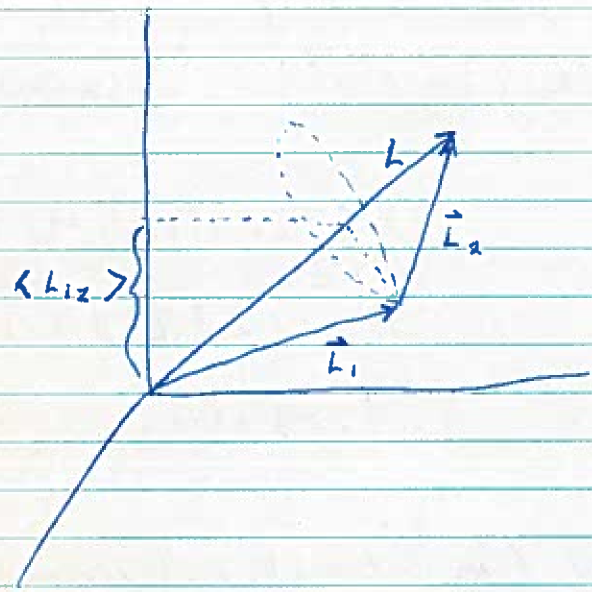
The expectation value is $\dfrac{l_1(l_1+1) + l(l+1) - l_2(l_2+1)}{2[\,l(l+1)\,]^{1/2}}$

Compare this with the expectation value of L_{1z}.

$$\langle l_1\, l_2\, l m | L_{1z} | l_1\, l_2\, l m \rangle = (-1)^{l-m}\begin{pmatrix} l & 1 & l \\ -m & 0 & m \end{pmatrix}(l_1\, l_2\, l \| \vec{L}_1 \| l_1\, l_2\, l)$$

$$= \frac{m[\,l_1(l_1+1) + l(l+1) - l_2(l_2+1)\,]}{2\,l(l+1)} = \frac{m}{[\,l(l+1)\,]^{1/2}}\left\langle \frac{\vec{L}_1\cdot\vec{L}}{[\,l(l+1)\,]^{1/2}} \right\rangle$$

$$\simeq \frac{m}{l} \langle \vec{L}_1 \cdot \hat{L} \rangle$$



The Zeeman Effect

.. This result can be used to find a simple formula for the Zeeman splitting of atomic spectra in a weak magnetic field. The interaction Hamiltonian is

$$H^M = \frac{e\mathcal{H}}{2mc}(L_z + 2S_z) \quad \left(\text{actually } g_s = 2(1+\alpha/2\pi+\cdots) \simeq 2.0023\right)$$

for a field in the z-direction. In the absence of external fields, $\vec{L}$ and $\vec{S}$ are coupled to form $\vec{J}$ and H^M acts as a small perturbation. To a first approximation, the energy shifts are given by the diagonal matrix elements

$$\frac{2mc}{e\mathcal{H}} \langle SLJM | H^M | SLJM \rangle$$

$$= (-1)^{J-M} \begin{pmatrix} J & 1 & J \\ -M & 0 & M \end{pmatrix} \left\{ (SLJ \| \vec{L} \| SLJ) + g_s (SLJ \| \vec{S} \| SLJ) \right\}$$

$$= \frac{M}{[(\cancel{2J+1})(J+1)J]^{1/2}} \left\{ \frac{L(L+1)+J(J+1)-S(S+1)}{2\,[J(J+1)]^{1/2}} + g_s\left(\frac{S(S+1)+J(J+1)-L(L+1)}{2\,[J(J+1)]^{1/2}}\right)\right\}$$

$$= \frac{M}{2J(J+1)} \Big\{ L(L+1)+J(J+1)-S(S+1) + g_s[S(S+1)+J(J+1)-L(L+1)] \Big\}$$

$= M$ if $S=0$ or $g_s = 1$ (normal Zeeman effect)

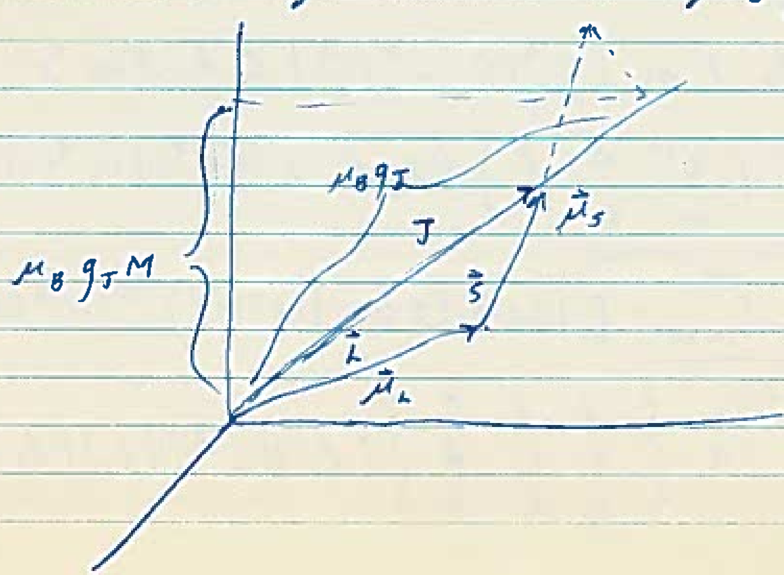
In this case, all the energy splittings have the same size $\frac{e\hbar}{2mc}$ and all transitions with the same ΔM fall on top of one another.

- In actual fact, $g_s \simeq 2$ and if $s \neq 0$, transitions with the same ΔM no longer coincide.

- Physically, we can write the total magnetic moment in the form

$$\vec{\mu} = \vec{\mu}_L + \vec{\mu}_s, \quad \vec{\mu}_L = \mu_B \vec{L}, \quad \vec{\mu}_S = \mu_B g_s \vec{S}$$

Then $\langle SLJM | \vec{\mu}\cdot\vec{H} | SLJM \rangle = \mu_B g_J M$



Two-Body Interactions

- The simplest example is the electron-electron interaction

$$\frac{1}{r_{12}} = \frac{1}{[(\vec{r}_1-\vec{r}_2)^2]^{1/2}} = \frac{1}{[r_1^2+r_2^2-2r_1r_2\cos\theta_{12}]^{1/2}}$$

which has the well-known expansion

$$\frac{1}{r_{12}} = \sum_{k=0}^{\infty} \frac{r_<^k}{r_>^{k+1}} P_k(\cos\theta_{12})$$

This is a special case of general expansions of the form

$$V(r_{12}) = \sum_{k=0}^{\infty} V_k(r_1,r_2)\, P_k(\cos\theta_{12})$$

The problem is to evaluate matrix elements of $V(r_{12})$ in a coupled scheme $(l_1 l_2)\, l$.

- Using the spherical harmonic addition theorem,

$$P_k(\cos\theta_{12}) = \sum_{m=-k}^{k} (-1)^k C^k_m(\theta_1,\phi_1)\, C^k_{-m}(\theta_2,\phi_2)$$
$$= C^k(1)\cdot C^k(2) \;,\; = (-1)^{-k}(2k+1)^{1/2}\, T_{00}(C^k, C^k)$$

$$\therefore \langle l_1' l_2' l' m' \,|\, C^k(1)\cdot C^k(2) \,|\, l_1 l_2 l m\rangle$$
$$= \underbrace{(-1)^{l'-m'}\begin{pmatrix} l' & 0 & l \\ -m' & 0 & m\end{pmatrix}}\,(l_1' l_2' l' \| C^k(1)\cdot C^k(2) \| l_1 l_2 l)$$

$$= \frac{\delta_{l,l'}\,\delta_{m,m'}}{(2l+1)^{1/2}}\, [(2l+1)(2\cdot 0+1)(2l+1)]^{1/2}(-1)^{-k}(2k+1)^{1/2}$$
$$\times \begin{Bmatrix} l & l & 0 \\ l_1 & l_1' & k \\ l_2 & l_2' & k \end{Bmatrix} (l_1' \| C^{(k)} \| l_1)(l_2' \| C^{(k)} \| l_2)$$

$$= \delta_{l,l'}\,\delta_{m,m'}\,(2l+1)^{1/2}\,\frac{(-1)^{-k}(2k+1)^{1/2}(-1)^{l_1+l_2'+l+k}}{(2k+1)^{1/2}(2l+1)^{1/2}}\begin{Bmatrix} l & l_2' & l_1' \\ k & l_1 & l_2 \end{Bmatrix}$$

$$\times(-1)^{l_1'+l_2'}\left[(2l_1'+1)(2l_1+1)(2l_2'+1)(2l_2+1)\right]^{1/2}\begin{pmatrix} l_1' & k & l_1 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l_2' & k & \\ 0 & 0 & 0 \end{pmatrix}$$

$$= (-1)^{l_2+l_2'+l}\,\delta_{ll'}\,\delta_{mm'}\begin{Bmatrix} l & l_2' & l_1' \\ k & l_1 & l_2 \end{Bmatrix}$$

$$\times\left[(2l_1'+1)(2l_1+1)(2l_2'+1)(2l_2+1)\right]^{1/2}\begin{pmatrix} l_1 & k & l_1' \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l_2 & k & l_2' \\ 0 & 0 & 0 \end{pmatrix}$$

where $|\alpha_p(n-1)J_p, aj; JM\rangle = \sum_{M_p m} |\alpha_p(n-1)J_p M_p\rangle |ajm\rangle_n$
$\langle J_p j M_p m | J M\rangle$

The sum is over all possible parents x one electron orbitals weighted by the cfp's.

The cfp expansion is useful in calculating matrix elements of one-electron operators.

$$\langle \alpha(n) J \| \underset{\sim}{F}_k \| \alpha'(n) J' \rangle$$

$$= n \sum_{\substack{\alpha_p J_p \\ a\, j \\ a'\, j'}} (-1)^{J_p + k - j - j'} [(2J'+1)(2j+1)]^{1/2} W(jj'JJ'; kJ_p)$$

$$\times \langle aj \| \underset{\sim}{f}_k \| a'j' \rangle \langle \alpha(n) J \{ |\alpha_p(n-1) J_p, aj\rangle \langle \alpha_p(n-1) J_p a'j' | \} \alpha'(n) J' \rangle$$

$$\underset{\sim}{F}_k = \underset{\sim}{f}_k(1) + \underset{\sim}{f}_k(2) + \cdots + \underset{\sim}{f}_k(n)$$

-Since the parent states are orthonormal, only those parents $\alpha_p J_p$ common to both n-particle states contribute.

The above is analagous to

$$\langle j_1 j_2 J \| T_k(1) \| j_1' j_2 J' \rangle$$

$$= (-1)^{J + j_1' - k - j_2} [(2J'+1)(2j_1+1)]^{1/2} W(j_1 j_1' J J'; k J_2)$$

$$\times \langle j_1 \| T_k \| j_1' \rangle$$

summed over all parent states $J_p = j_2$.

Particularly simple results emerge if the electrons are all equivalent. If there are n equivalent electrons all with angular momentum j, then the sum over aj and $a'j'$ reduces to just this one term.

$$\langle \alpha (j^n) J \| \underset{\sim}{F}_k \| \alpha' (j^n) J' \rangle$$

$$= n \langle a j \| \underset{\sim}{f}_k \| a j \rangle$$

$$\times \sum_{\alpha_p J_p} (-1)^{J_p + k - J - j} [(2J'+1)(2j+1)]^{1/2} W(j j J J'; k J_p)$$

$$\times \langle \alpha J \{ | \alpha_p J_p, a j \rangle \langle \alpha_p J_p, a j | \} \alpha' J' \rangle$$

Since the summation is independent of f_k, it follows that for two operators of the same rank k

$$\frac{\langle \alpha (j^n) J \| F_k \| \alpha' (j^n) J' \rangle}{\langle \alpha (j^n) J \| G_k \| \alpha' (j^n) J' \rangle} = \frac{\langle a j \| f_k \| a j \rangle}{\langle a j \| g_k \| a j \rangle}$$

L-S Coupling Scheme

In the L-S coupling scheme, the parents are eigenfunctions of

	Eigenvalue
$(\underset{\sim}{s}_1 + \underset{\sim}{s}_2 + \cdots + \underset{\sim}{s}_{n-1})^2$	$S_p(S_p+1)$
$(\underset{\sim}{l}_1 + \underset{\sim}{l}_2 + \cdots + l_{n-1})^2$	$L_p(L_p+1)$

$$| \alpha (l^n) S L \rangle = \sum_{S_p L_p} | (l^{n-1}) S_p L_p, l; S L \rangle \langle (l^{n-1}) S_p L_p, l; S L | \} \alpha (l^n) S L \rangle$$