5. For a two-electron atom, the spin-orbit plus spin-other-orbit interactions are

$$H_{SO} = \frac{\mu}{mc}\Big\{\Big[\underset{\sim}{\mathcal{E}}_1 \times \underset{\sim}{p}_1 + \frac{2e}{r_{12}^{\,2}} \underset{\sim}{r}_{12} \times \underset{\sim}{p}_2\Big] \cdot \underset{\sim}{s}_1$$

$$+ \Big[\underset{\sim}{\mathcal{E}}_2 \times \underset{\sim}{p}_2 + \frac{2e}{r_{12}^{\,2}} \underset{\sim}{r}_{21} \times \underset{\sim}{p}_1\Big] \cdot s_2\Big\}$$

where $\underset{\sim}{\mathcal{E}}_i = -\nabla_i \left\{ \frac{Ze}{r_1} + \frac{Ze}{r_2} - \frac{e}{r_{12}} \right\}$, $\mu = \frac{e\hbar}{2mc}$, $\underset{\sim}{r}_{12} = \underset{\sim}{r}_1 - \underset{\sim}{r}_2$

and the magnetic spin-spin interaction is

$$H_{SS} = \frac{4\mu^2}{r_{12}^{\,3}} \left\{ \underset{\sim}{s}_1 \cdot \underset{\sim}{s}_2 - \frac{3(\underset{\sim}{s}_1 \cdot \underset{\sim}{r}_{12})(s_2 \cdot \underset{\sim}{r}_{12})}{r_{12}^{\,2}} \right\}.$$

H_{SO} is a product of 1st. rank tensors while H_{SS} can be written as a product of 2'nd. rank tensors as

$$H_{SS} = -4\mu^2 \underset{\sim}{\mathcal{L}} \cdot \underset{\sim}{\mathcal{S}}$$

with $\mathcal{S}_2^{\,m} = \sqrt{\frac{2\pi}{15}} (\underset{\sim}{s}_1 \cdot \nabla_r)(\underset{\sim}{s}_2 \cdot \nabla_r)\, \mathcal{Y}_2^{\,m}(\hat{r})$

and $\mathcal{L}_2^{\,m} = \sqrt{\frac{8\pi}{15}}\, \mathcal{Y}_2^{\,m}(\hat{r}_{12})$. $\qquad (\mathcal{Y}_\ell^{\,m} = r^\ell Y_\ell^{\,m})$

The perturbation $H_{SO} + H_{SS}$ is responsible for splitting the $1s2p\ ^3P$ states into three fine-structure components labelled by $J = 0, 1, 2$ with energies

$$E_J = E_0 + \langle 2\ ^3P, JM | H_{SO} + H_{SS} | 2\ ^3P, JM \rangle.$$

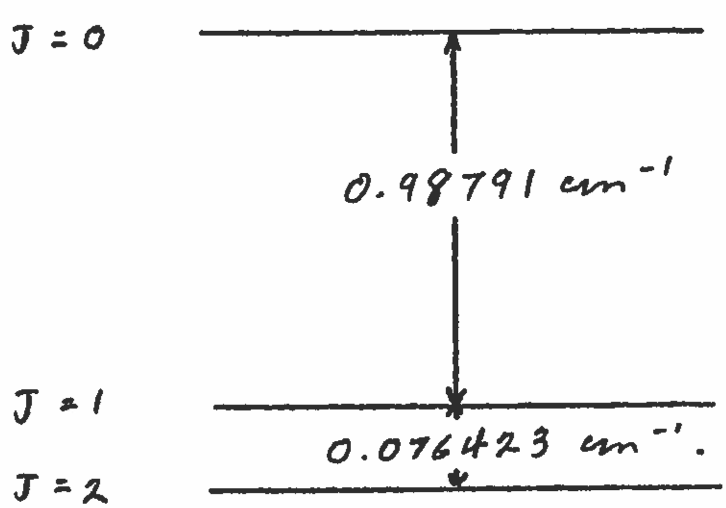
a/ Prove that the matrix element

$$\langle 2\,{}^3P, J'M' \mid H_{so} + H_{ss} \mid 2\,{}^3P, J\,M \rangle$$

vanishes unless $J' = J$, $M' = M$ and that the value is independent of M for a given J.

b/ Evaluate the ratios of matrix elements of H_{so} and H_{ss} for the states $J = 0, 1, 2$.

c/ The $1s2p\ {}^3P$ splitting is observed experimentally to be



Use the above information to obtain numerical values for the matrix elements

$$\langle 2\,{}^3P, 2 \mid H_{so} \mid 2\,{}^3P, 2 \rangle$$

and $\langle 2\,{}^3P, 2 \mid H_{ss} \mid 2\,{}^3P, 2 \rangle$.

d/ Using the vector coupling coefficients, write out explicitly the nine 1s2p $^3P_{J,M}$ eigenfunctions in terms of products of eigenfunctions of L and S. ($\underset{\sim}{J} = \underset{\sim}{L} + \underset{\sim}{S}$)

$$\langle j_1 m_1 1 m_2 | j_1 1 j m \rangle$$

$j =$	$m_2 = 1$	$m_2 = 0$	$m_2 = -1$
j_1+1	$\left(\frac{(j_1+m)(j_1+m+1)}{(2j_1+1)(2j_1+2)}\right)^{1/2}$	$\left(\frac{(j_1-m+1)(j_1+m+1)}{(2j_1+1)(j_1+1)}\right)^{1/2}$	$\left(\frac{(j_1-m)(j_1-m+1)}{(2j_1+1)(2j_1+2)}\right)^{1/2}$
j_1	$-\left(\frac{(j_1+m)(j_1-m+1)}{2j_1(j_1+1)}\right)^{1/2}$	$\frac{m}{[j_1(j_1+1)]^{1/2}}$	$\left(\frac{(j_1-m)(j_1+m+1)}{2j_1(j_1+1)}\right)^{1/2}$
j_1-1	$\left(\frac{(j_1-m)(j_1-m+1)}{2j_1(2j_1+1)}\right)^{1/2}$	$-\left(\frac{(j_1-m)(j_1+m)}{j_1(2j_1+1)}\right)^{1/2}$	$\left(\frac{(j_1+m+1)(j_1+m)}{2j_1(2j_1+1)}\right)^{1/2}$

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

$$\begin{Bmatrix} a & b & c \\ 2 & c & b \end{Bmatrix}$$

$$= (-1)^s \frac{2[3X(X-1) - 4b(b+1)c(c+1)]}{[(2b-1)2b(2b+1)(2b+2)(2b+3)\cdot(2c-1)2c(2c+1)(2c+2)(2c+3)]}$$

where $s = a+b+c$

$X = b(b+1) + c(c+1) - a(a+1)$.

Matrix Elements of Tensor Operators.

- Evaluate $\langle \alpha J M | T_{kq} | \alpha' J' M' \rangle$.

- Regard T_{kq} as an angular momentum eigenvector since it has the same transformation properties under rotations.

- Then $T_{kq} | \alpha' J' M' \rangle$ is analagous to a simple product-type eigenfunction which transforms according to the reducible rep. $\mathcal{D}^{(k)} \times \mathcal{D}^{(J')}$. The transformation to irreducible reps. is

$$| \beta K Q \rangle = \sum_{q M'} T_{kq} | \alpha' J' M' \rangle \langle J' k M' q | K Q \rangle$$

The inverse transformation is

$$T_{kq} | \alpha' J' M' \rangle = \sum_{KQ} | \beta K Q \rangle \langle J' k M' q | K Q \rangle$$

Multiplying through by $\langle \alpha J M |$ picks out the term with $K = J$, $Q = M$ by orthogonality of angular momentum eigenfunctions.

$$\therefore \langle \alpha J M | T_{kq} | \alpha' J' M' \rangle = \sum_{KQ} \langle \alpha J M | \beta K Q \rangle \langle J' k M' q | \cancel{JM} \; KQ \rangle$$

$$= \langle \alpha J M | \beta J M \rangle \langle J' k M' q | \cancel{KQ} \; JM \rangle$$

The transformation coefficients from the $\alpha J M$ to the $\beta J M$ representation are independent of M.

ie $| \beta J M \rangle = \sum_{\alpha} | \alpha J M \rangle \langle \alpha J M | \beta J M \rangle \quad \times J_+$.

- Since $\langle \alpha J M | \beta J M \rangle$ depends only on $\alpha, J, \underbrace{\alpha', J' \text{ and } T_k}_{\beta}$, the notation

$$\langle \alpha J M | \beta J M \rangle = (-1)^{2k} \langle \alpha J \| T_k \| \alpha' J' \rangle$$

reduced matrix element.

Then $\langle \alpha J M | T_{kq} | \alpha' J' M' \rangle$

$$= (-1)^{2k} \langle J' k\, M' q | J M \rangle \langle \alpha J \| T_k \| \alpha' J' \rangle$$

$$= (-1)^{2k} (-1)^{-J'+k-M} (2J+1)^{1/2} \begin{pmatrix} J' & k & J \\ M' & q & -M \end{pmatrix} \langle \alpha J \| T_k \| \alpha' J' \rangle$$

$$= (-1)^{J-M} \begin{pmatrix} J & k & J' \\ -M & q & M' \end{pmatrix} (2J+1)^{1/2} \langle \alpha J \| T_k \| \alpha' J' \rangle$$

Edmonds absorbs the factor of $(2J+1)^{1/2}$ into the reduced matrix element by defining

$$(\alpha J \| T_k \| \alpha' J') = (2J+1)^{1/2} \langle \alpha J \| T_k \| \alpha' J' \rangle$$

so that

$$\langle \alpha J M | T_{kq} | \alpha' J' M' \rangle = (-1)^{J-M} \begin{pmatrix} J & k & J' \\ -M & q & M' \end{pmatrix} (\alpha J \| T_k \| \alpha' J')$$

<u>Evaluation of the Reduced Matrix Element.</u>

- If the full matrix element is known for one particular set of values of M, q, M', then the reduced matrix element can be calculated through the relation

$$(\alpha J \| T_k \| \alpha' J') = \frac{\langle \alpha J M | T_{kq} | \alpha' J' M' \rangle}{(-1)^{J-M} \begin{pmatrix} J & k & J' \\ -M & q & M' \end{pmatrix}}$$

For example, consider the matrix elements for the electric dipole transitions of hydrogen. - say ~~[illegible]~~ 4f - 3d. In general, we have to calculate

$\langle nlm | \hat{e}\cdot\vec{r} | n'l'm'\rangle$

$= \langle nlm | r_q | n'l'm'\rangle$ if $\hat{e} = (-1)^q \hat{e}_{-q}$; $q = \pm 1, 0$.

$= \int_0^\infty R^*_{nl}(r)\, r\, R_{n'l'}(r)\, r^2 dr \qquad r_q = r\, C_1^q(\theta,\phi)$

$$\times \underbrace{\langle lm | C_1^q | l'm'\rangle}_{\text{angular integral}}$$

$$\langle lm | C_1^q | l'm'\rangle = \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta\, Y_l^{m*}\, C_1^q\, Y_{l'}^{m'}$$

Consider first products of spherical harmonics of the form $C_k^q(\theta,\phi)\, C_{l'}^{m'}(\theta,\phi)$ with fixed k and l'. They can be coupled to form irreducible tensors $T_K^Q(\theta,\phi)$.

$$T_{K,Q}(\theta,\phi) = \sum_{q,m'} \langle k\, l'\, q\, m' | KQ\rangle\, C_k^q\, C_{l'}^{m'}(\theta,\phi)$$
$$= A_K\, C_K^Q(\theta,\phi)$$

A_K must be independent of Q since otherwise the $T_{K,Q}$ wouldn't transform among themselves in the right way. It can be evaluated by setting $\theta = 0$, since $C_K^Q(0,\phi) = \delta_{0,Q}$

ie $A_K \cdot 1 = \langle k\, l'\, 0\, 0 | K\, 0\rangle \cdot 1 \cdot 1$

- Applying the inverse transformation yields

$$C_k^q(\theta,\phi)\, C_{l'}^{m'}(\theta,\phi) = \sum_{K,Q} \langle k\, l'\, q\, m' | KQ\rangle \langle k\, l'\, 0\, 0 | K\, 0\rangle$$
$$\times\, C_K^Q(\theta,\phi)$$

or $C_k^q(\theta,\phi)\, Y_{l'}^{m'}(\theta,\phi) = \dfrac{(2l'+1)^{1/2}}{(2K+1)^{1/2}} \sum_{K,Q} \langle \quad \rangle \langle \quad \rangle\, Y_K^Q(\theta,\phi)$

Multiplying by a particular $Y_\ell^{m*}(\theta,\phi)$ and integrating yields

$$\langle \ell m | C_k^q | \ell' m' \rangle = \frac{(2\ell'+1)^{1/2}}{(2\ell+1)^{1/2}} \langle k \ell' q m' | k\ell' \ell m \rangle \times \langle k \ell' 0 0 | k\ell' \ell 0 \rangle$$

$$= \frac{(2\ell'+1)^{1/2}}{(2\ell+1)^{1/2}} (2\ell+1)(-1)^{2(\ell'-k)+m} \begin{pmatrix} \ell & k & \ell' \\ -m & q & m' \end{pmatrix} \begin{pmatrix} \ell & k & \ell' \\ 0 & 0 & 0 \end{pmatrix}$$

$$= [(2\ell'+1)(2\ell+1)]^{1/2} (-1)^m \begin{pmatrix} \ell & k & \ell' \\ -m & q & m' \end{pmatrix} \begin{pmatrix} \ell & k & \ell' \\ 0 & 0 & 0 \end{pmatrix}$$

comparing with

$$\langle \ell m | C_k^q | \ell' m' \rangle = (-1)^{\ell-m} \begin{pmatrix} \ell & k & \ell' \\ -m & q & m' \end{pmatrix} (\ell \| C_k \| \ell')$$

we see that

$$(\ell \| C_k \| \ell') = (-1)^\ell \underbrace{[(2\ell'+1)(2\ell+1)]^{1/2}}_{\{\ell', \ell\}^{1/2}} \begin{pmatrix} \ell & k & \ell' \\ 0 & 0 & 0 \end{pmatrix}$$

<u>Exercise</u>: show that $(\ell \| \vec{L} \| \ell')$

$$= \hbar \delta_{\ell,\ell'} [(2\ell+1)(\ell+1)\ell]^{1/2}$$

and $(\tfrac{1}{2} \| \vec{S} \| \tfrac{1}{2}) = \hbar \sqrt{3/2}$

The original matrix element is thus

$$\langle n \ell m | r_q | n' \ell' m' \rangle = (-1)^{\ell-m} \begin{pmatrix} \ell & k & \ell' \\ -m & q & m' \end{pmatrix} (n\ell \| \vec{r} \| n'\ell')$$

where $(n\ell \| \vec{r} \| n'\ell') = \int_0^\infty R_{n\ell}^* \, r \, R_{n'\ell'} \, r^2 dr \times (\ell \| C_1 \| \ell')$

Application to Oscillator Strengths

- The oscillator strength for a transition between states labelled by angular momentum quantum numbers LM and $L'M'$ (or $J\,M_J$ and $J'\,M_J'$ in the coupled representation) is

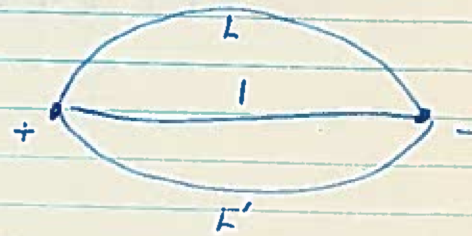
$$f(\gamma L M \to \gamma' L' M') = \frac{2}{3}(E'-E)\sum_{\hat{e}} \left|\langle \gamma' L' M' | \hat{e}\cdot\vec{r} | \gamma L M\rangle\right|^2$$

$$\left(\vec{r} \to \sum_{i=1}^{N} \vec{r}_i \text{ for } N\text{-electron systems}\right)$$

- The averaged oscillator strength $\bar{f}(\gamma L \to \gamma' L')$ is obtained by summing over final states and averaging over initial states.

ie $$\bar{f}(\gamma L \to \gamma' L') = \frac{1}{(2L+1)} \sum_{M_L, M_L'} f(\gamma L M \to \gamma' L' M')$$

$$= \frac{2(E'-E)}{3(2L+1)} \left|(\gamma' L' \| \vec{r} \| \gamma L)\right|^2 \underbrace{\sum_{M_L, q, M_L'} \begin{pmatrix} L' & 1 & L \\ -M' & q & M \end{pmatrix}^2}$$



$= 1$

$$= \frac{2(E'-E)}{3(2L+1)} \left|(\gamma' L' \| \vec{r} \| \gamma L)\right|^2$$

For the 4f-3d transition, we would have to evaluate things like

$$\begin{pmatrix} 3 & 1 & 2 \\ -M & q & M \end{pmatrix}$$

For the case $q = 0$, we can use

$$\begin{pmatrix} a & a+1 & 1 \\ \alpha & -\alpha & 0 \end{pmatrix} = (-1)^{a-\alpha-1}\left[\frac{(a-\alpha+1)(a+\alpha+1)}{(a+1)(2a+1)(2a+3)}\right]^{1/2}$$

Taking $a = 2$, $\alpha = 0$ yields

$$\begin{pmatrix} 3 & 1 & 2 \\ 0 & 0 & 0 \end{pmatrix} = -\left[\frac{3^2}{3\cdot 5\cdot 7}\right]^{1/2} = -\frac{\sqrt{3}}{\sqrt{35}}$$

The angular integral is thus

$$\langle 3\,0|C_1^0|2\,0\rangle = [7\cdot 5]^{1/2}\left(\frac{-\sqrt{3}}{\sqrt{35}}\right)^2$$

$$= \underline{3}\,\sqrt{35}$$

The angular reduced matrix element is

$$(3\|C_1\|2) = -[7\cdot 5]^{1/2}\left(\frac{-\sqrt{3}}{\sqrt{35}}\right) = +\sqrt{3}$$

and the full reduced matrix element is

$$(4,3\|\vec{r}\|3,2) = \sqrt{3} \times \int_0^\infty R^*_{4,3}(r)\, r\, R_{3,2}(r)\, r^2\, dr.$$