THE ROLE OF GROUP THEORY IN MAGNETIC RESONANCE

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In handling calculations in the field of magnetic resonance spectroscopy group theoretical methods enable an exceedingly important generalised approach to be carried out in calculating magnetic resonance data for a vast range of models using a few readily determined parameters.

1. Symmetry coupling coefficient

Two ket vectors which transform as the irreducible representation Γ_1 and Γ_2 of a particular group couple to yield a ket vector $|\Gamma_3 c\rangle$ which transforms as the Γ_3 irreducible representation of the group where Γ_3 occurs in the direct product $\Gamma_1\Gamma_2$. The expression relating the ket vector $|\Gamma_3 c\rangle$ to the basic ket vectors $|\Gamma_1 a\rangle$ and $|\Gamma_2 b\rangle$ is given by the coupling relation

$$|\Gamma_1\Gamma_2\Gamma_3 c\rangle = \sum_{a,b} \langle\Gamma_1\Gamma_2 ab|\Gamma_1\Gamma_2\Gamma_3 c\rangle |\Gamma_1 a\rangle|\Gamma_2 b\rangle$$

where $\langle\Gamma_1\Gamma_2 ab|\Gamma_1\Gamma_2\Gamma_3 c\rangle$ are the symmetry coupling coefficient.

Two simple methods have been used for calculating these symmetry coupling coefficients for single and double groups: the first is to consider the transformation properties of the direct product under the generators of the group, and the other is to define the irreducible representation vectors in terms of the $|JM\rangle$ ket vectors and to use the Wigner coefficients to determine the direct products. Both methods give the same results and it is only in the construction of the V symmetry coefficients that the difference in approach becomes significant. (For details see (1-3) and the appropriate references given in those papers).

I shall define the V coefficients as follows

$$V\begin{pmatrix} \Gamma_1 & \Gamma_2 & \gamma\Gamma_3 \\ a & b & -(c) \end{pmatrix} = (-1)^{2\Gamma_2+\Gamma_3-c} \lambda(\Gamma_3)^{-\frac{1}{2}} \langle\Gamma_1\Gamma_2 ab|\Gamma_1\Gamma_2\gamma\Gamma_3 c\rangle .$$

Here Γ_2 and Γ_3 in the exponent refer to the values J_2 and J_3 of the coupling, c is the component value of the specific component of the irreducible representation Γ_3 of dimension $\lambda(\Gamma_3)$.

The V symmetry coupling coefficients are related to the 3Γ symmetry coupling coefficient as

$$\begin{pmatrix} \Gamma_1 & \Gamma_2 & \gamma\Gamma_3 \\ a & b & c \end{pmatrix} = (-1)^{\Gamma_1+\Gamma_2+\Gamma_3} V\begin{pmatrix} \Gamma_1 & \Gamma_2 & \gamma\Gamma_3 \\ a & b & c \end{pmatrix} .$$

In defining the V coefficients we need to examine the meaning of $-(c)$. Now

$$V\begin{pmatrix} \Gamma_1 & \Gamma_2 & \gamma\Gamma_3 \\ a & b & -(c) \end{pmatrix} = (-1)^{k_3} V\begin{pmatrix} \Gamma_1 & \Gamma_2 & \gamma\Gamma_3' \\ a & b & c' \end{pmatrix}$$

where $k_3 = 0$ or 1. Since we define sets of irreducible representation vectors which transform as $|\Gamma_3 c\rangle$ as

$$|J\gamma\Gamma_3 c\rangle = \sum_M C(JM\gamma\Gamma_3 c)|JM\rangle$$

it follows that

$$|J\gamma\Gamma_3 -(c)\rangle = \sum_M C(JM\gamma\Gamma_3 c)|J - M\rangle$$

$$= (-1)^{k_3}|J\gamma\Gamma_3' c'\rangle .$$

In the octahedral and icosahedral double groups, O* and K* respectively, $\Gamma_3' = \Gamma_3$ in all cases. (This is not the case for the double groups (1) C_n^*, D_n^* and T*.)

The V symmetry coupling coefficients possess three basic properties:

(a) it is unchanged by an even permutation of the columns

(b) it is changed by an odd permutation of the columns by the factor $(-1)^{\Gamma_1+\Gamma_2+\Gamma_3}$

(c) for a change of sign of a, b and c the V coefficient is changed by the factor $(-1)^{\Gamma_1+\Gamma_2+\Gamma_3}$

$$V\begin{pmatrix}\Gamma_1 & \Gamma_2 & \Gamma_3 \\ a & b & c\end{pmatrix} = (-1)^{\Gamma_1+\Gamma_2+\Gamma_3} \; V\begin{pmatrix}\Gamma_1 & \Gamma_2 & \Gamma_3 \\ -(a) & -(b) & -(c)\end{pmatrix}$$

$$= (-1)^{k_1+k_2+k_3}(-1)^{\Gamma_1+\Gamma_2+\Gamma_3} \; V\begin{pmatrix}\Gamma_1' & \Gamma_2' & \Gamma_3' \\ a' & b' & c'\end{pmatrix},$$

These properties greatly reduce the number of V symmetry coefficients that need to be evaluated.

2. Symmetry reduced matrix elements

The evaluation of matrix elements can very simply be carried out through the application of the Wigner-Eckart theorem which in group theoretical notation is given by

$$\langle \Gamma_7 g|0(\Gamma_4 d)|\Gamma_3 c\rangle$$

$$= \sum_J\left[(-1)^{\Gamma_7-g} \; V\begin{pmatrix}\Gamma_7 & \Gamma_3 & J\Gamma_4 \\ -(g) & c & d\end{pmatrix}\langle \Gamma_7||J\Gamma_4||\Gamma_3\rangle\right].$$

[1]

Here J is required if the derived product of $\Gamma_7 \times \Gamma_3$ contains Γ_4 more than once.

3. The definitions of the irreducible representations.

The definitions of the irreducible representations for the octahedral and the icosahedral double groups are given in references (4) and (5) respectively.

4. A d-electron problem

The hamiltonian representing a crystal field interaction of octahedral symmetry may be written as

$$\mathcal{H} = \left\{\frac{\sqrt{7}}{2\sqrt{3}} Y_{40}(\theta,\phi) + \frac{\sqrt{5}}{2\sqrt{6}} Y_{44}(\theta,\phi) + \frac{\sqrt{5}}{2\sqrt{6}} Y_{4-4}(\theta,\phi)\right\}\frac{2(21\pi)^{\frac{1}{2}}}{5}\Delta.$$

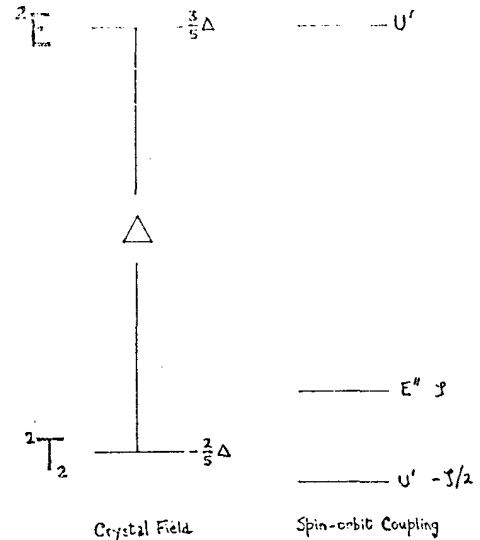The energy level diagram for a d-electron in such a potential field is shown in Fig. 1.

FIGURE 1

We shall next add a crystal field component of the form

$$\mathcal{H} = -Y_{20}(\theta,\phi)\frac{14\sqrt{\pi}}{\sqrt{5}}\delta$$

where the distortion is along the z-axis. We may rotate this distortion so that it is along any axis, namely,

$$\mathcal{H} = -D(\alpha,\beta,\gamma)Y_{20}(\theta,\phi)\frac{14\sqrt{\pi}}{\sqrt{5}}\delta$$

$$= -\left[\frac{\sqrt{3}}{2\sqrt{2}} \sin^2\beta\left\{e^{-i2\alpha} Y_{22}(\theta,\phi) + e^{i2\alpha} Y_{2-2}(\theta,\phi)\right\}\right.$$

$$+ \frac{\sqrt{3}}{\sqrt{2}} \sin\beta\cos\beta\left\{-e^{-i\alpha} Y_{21}(\theta,\phi) + e^{i\alpha} Y_{2-1}(\theta,\phi)\right\}$$

$$\left.+ \frac{1}{2} (3\cos^2\beta - 1) Y_{20}(\theta,\phi)\right]\frac{14\sqrt{\pi}}{\sqrt{5}}\delta.$$

[2]

$D(\alpha,\beta,\gamma)$ refers to a rotation operator (6).

In group theoretical notation we may write [2] as

$$D(\alpha,\beta,\gamma)|E\theta> = \frac{\sqrt{3}}{2} \sin^2\beta \cos 2\alpha |E\epsilon>$$

$$-\frac{\sqrt{3}}{2} i \sin^2\beta \sin 2\alpha |T_2 0>$$

$$+\frac{\sqrt{3}}{\sqrt{2}} \sin\beta \cos\beta \ \bar{e}^{i\alpha}|T_2 -1>$$

$$+\frac{\sqrt{3}}{\sqrt{2}} \sin\beta \cos\beta \ e^{i\alpha}|T_2 1>$$

$$+ \frac{1}{2} (3 \cos^2\beta - 1)| E\theta>.$$

[3]

Therefore the distortion crystal field matrix element may be written as

$$<\Gamma_7 g|D(\alpha,\beta,\gamma)E\theta|\Gamma_3 c>.$$

As an example, we shall evaluate one matrix element

$$<U'\kappa'|D(\alpha,\beta,\gamma)E\theta|U'\lambda'>$$

noting that $U' \times U' = A_1 + A_2 + E + 2T_1 + 2T_2$.

Using [3] and [1] we have

$$<U'\kappa'|D(\alpha,\beta,\gamma)E\theta|U'\lambda'>$$

$$= \frac{\sqrt{3}}{\sqrt{2}} \sin\beta \cos\beta \ e^{-i\alpha} \left\{ V \begin{pmatrix} U' & U' & T_2 \\ \nu' & \lambda' & -1 \end{pmatrix} <U'||T_2||U'> \right.$$

$$\left. + V \begin{pmatrix} U' & U' & 3T_2 \\ \nu' & \lambda' & -1 \end{pmatrix} <U'||3T_2||U'> \right\}$$

$$= \frac{1}{4} \sin\beta \cos\beta \ e^{-i\alpha} \left\{ 2<U'||T_2||U'> - <U'||3T_2||U'> \right\}.$$

Since in this problem the wave functions transform as U' or E" all the matrix elements may be expressed in terms of five reduced matrix elements $<U'||E||U'>$, $<U'||T_2||U'>$, $<U'||3T_2||U'>$, $<U'||E||E">$ and $<U'||T_2||E">$.

Up to now we have not needed to define the U' and E" wavefunctions. To evaluate the five reduced matrix elements we need to determine at least five matrix elements for a specific system. We choose the U' and E" wavefunctions from the $^2T_2$ level for the single d-electron in a crystal field of octahedral symmetry.

For example, since

$$|T_2 E'U'\kappa'> = \frac{\sqrt{2}}{\sqrt{3}} |T_2 0>|E'\beta'> + \frac{1}{\sqrt{3}} |T_2 -1>|E'\alpha'>$$

and $$|T_2 E'E''\beta''> = - \frac{1}{\sqrt{3}} |T_2 0>|E'\beta'> + \frac{\sqrt{2}}{\sqrt{3}} |T_2 - 1>|E'\alpha'>$$

and $$<T_2 0|V|T_2 0> = (3 \cos^2\beta -1) \delta$$

$$<T_2 - 1|V|T_2 - 1> = \frac{-1}{2} (3 \cos^2\beta - 1)\delta$$

it follows that

$$<U'\kappa'|V|U'\kappa'> = \frac{1}{2}(3 \cos^2\beta - 1) \delta$$

and $$<U'\kappa'|V|E''\beta''> = - \frac{1}{\sqrt{2}} (3 \cos^2\beta - 1) \delta$$

$$\therefore \ <U'||E||U'> = 2\sqrt{2} \ \delta$$

and $$<U'||E||E''> - 2\sqrt{2} \ \delta.$$

The other reduced matrix elements are

$$<U'||T_2||U'> = 2\sqrt{3}\delta$$

$$<U'||3T_2||U'> = 0$$

and $$<U'||T_2||E''> = -2\sqrt{3} \ \delta.$$

The spin-orbit coupling matrix elements are as follows:

$$\langle U'c'|\zeta\underline{\ell}.\underline{s}|U'c'\rangle = -\zeta/2$$

and $\langle E''c''|\zeta\underline{\ell}.\underline{s}|E''c''\rangle = \zeta.$

From these matrix elements the energy level pattern may be determined when the crystal field distortion is parallel to any specific directions defined by the angles α and β. As an illustration the angle dependence of the energy separation of the three doublets is plotted when $\alpha = \pi/4$ and when β varies from 0^0 to 90^0, namely, in the plane containing the z-axis, the C_3 rotation axis and the C'_2 rotation axis.

The energy pattern is shown in Fig.2 where $\zeta = 3 \, \delta/10$.
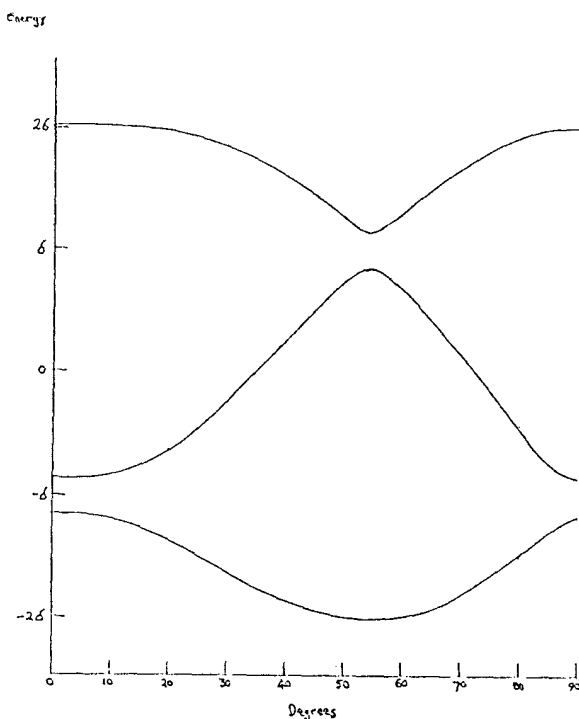

FIGURE 2

5. An f-electron Problem

Next we shall consider the case when an f-electron is in a crystal field environment of approximately octahedral symmetry. In this case since the spin-orbit coupling is usually much larger than the crystal field interaction the energy level diagram is as shown in Fig. 3.
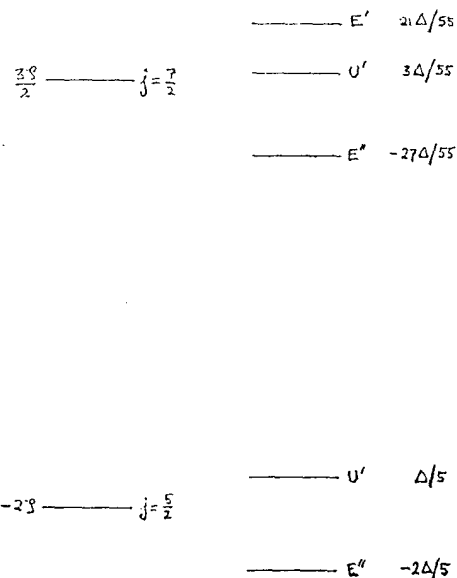

FIGURE 3

As an illustration we shall only consider the crystal field distortion within the 5/2 U' level. The matrix elements in the form of the symmetry reduced matrix elements are as before. In this case the reduced matrix elements are

$$\langle U'||E||U'\rangle = \frac{16\sqrt{2}}{5}\delta$$

$$\langle U'||T_2||U'\rangle = -\frac{4\sqrt{3}}{5}\delta$$

$$\langle U'||3T_2||U'\rangle = 0.$$

The crystal field distortion will split the U' level into two doublets the separation depending on the direction of the distortion. If we wish to determine the g-values for the two doublets we next need consider the magnetic field interaction. This is given by the hamiltonian

$$\mathcal{H} = \mu_B(\underline{\ell} + 2\underline{s}) . \underline{B}$$

$$\mathcal{H} = \mu_B \{(\ell_x + 2s_x)B_x + (\ell_y + 2s_y)B_y + (\ell_z + 2s_z)B_z\}.$$

Since the magnetic field vector transforms as T_1 the operators $(1_x + 2s_x), (1_y + 2s_y)$ and $(1_z + 2s_z)$ transform as T_{1x}, T_{1y} and T_{1z} where for the octahedral group

$$|T_1x> = \frac{1}{\sqrt{2}}\{|T_1 - 1> - |T_11>\}$$

$$|T_1y> = \frac{i}{\sqrt{2}}\{|T_1 - 1> + |T_11>\}$$

$$|T_1z> = |T_10>.$$

Therefore using [1] the magnetic field matrix elements may be determined in terms of four reduced matrix elements. As an illustration:

$$<U'\kappa'|T_{1x}|U'\lambda'> = <U'||T_1||U'>/2\sqrt{5}$$
$$- <U'||3T_1||U'>/4\sqrt{5}.$$

The reduced matrix elements are evaluated as outlined before and the appropriate values for the f-electron when $j = 5/2$ are

$$<U'||T_1||U'> = \frac{-6\sqrt{15}}{7}$$

$$<U'||3T_1||U'> = \frac{-4\sqrt{15}}{7}$$

$$<U'||T_1||E''> = -<E''||T_1||U'> = \frac{4\sqrt{30}}{7}$$

$$<E''||T_1||E''> = \frac{5\sqrt{6}}{7}.$$

With the knowledge of the magnetic field matrix elements we may determine the g-values. When calculating the g-tensor components, however, it is more appropriate to define

$$\mu_B(\ell_{x'} + 2s_{x'})B_{x'} = \cos\alpha\cos\beta\,\mu_B(\ell_x + 2s_x)B_x + \sin\alpha\cos\beta\,\mu_B(\ell_y + 2s_y)B_y$$
$$- \sin\beta\,\mu_B(\ell_z + 2s_z)B_z$$

$$\mu_B(\ell_{y'} + 2s_{y'})B_{y'} = -\sin\alpha\,\mu_B(\ell_x + 2s_x)B_x + \cos\alpha\,\mu_B(\ell_y + 2s_y)B_y$$

$$\mu_B(\ell_z + 2s_z)B_{z'} = \cos\alpha\sin\beta\,\mu_B(\ell_x + 2s_x)B_x + \sin\alpha\sin\beta\,\mu_B(\ell_y + 2s_y)B_y$$
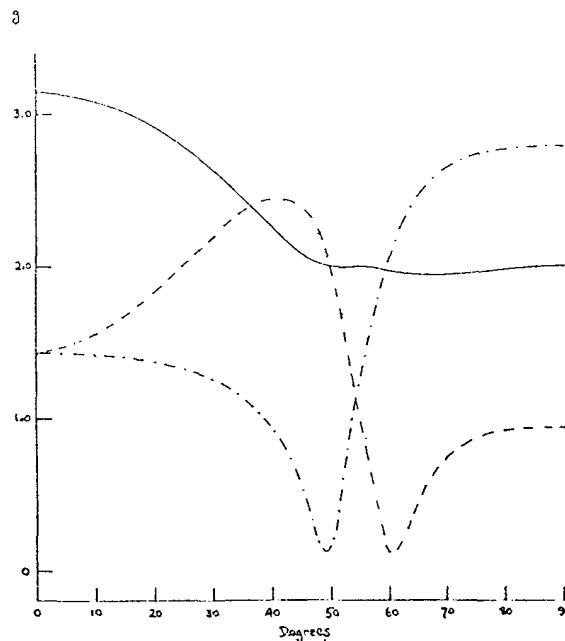$$+ \cos\beta\,\mu_B(\ell_z + 2s_z)B_z.$$

FIGURE 4

The g-value angular dependence in the plane defined when $\gamma = 0$ and $\alpha = \pi/4$ of the two doublets arising from within the level is given in Figs. 4 and 5.
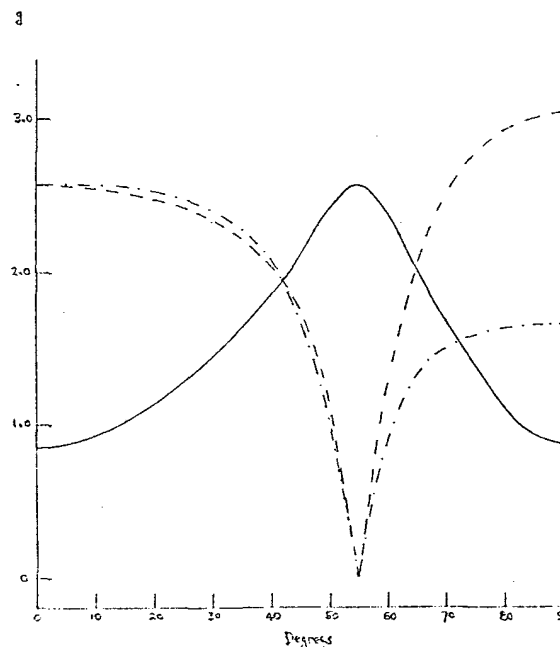

FIGURE 5

From these results it can be seen that the g-tensor is axially symmetric when the distortion is parallel to the four-fold

and the three-fold axes only.

In addition the g-values are very sensitive to the direction of the distortion especially near the three-fold axis.

6. f^n-ions in an environment of approximately icosahedral symmetry

In this case we shall proceed as outlined for the f-electron in an environment of approximately octahedral symmetry. The crystal field hamiltonian of icosahedral symmetry may be expressed as:

$$\mathcal{H} = \left\{ \frac{\sqrt{11}}{5} Y_{60}(\theta,\phi) - \frac{\sqrt{7i}}{5}\left[Y_{65}(\theta,\phi) + Y_{6-5}(\theta,\phi)\right]\right\} \frac{6\sqrt{143}\sqrt{\pi}\Delta}{35}$$

[4]

where Δ is the appropriate crystal field parameter such that when spin-orbit coupling is neglected, the splitting of the f^1-system by the crystal field is Δ. The crystal field hamiltonian given by [4] defines the z-axis along the five-fold axis and is the appropriate form for use in group theory methodology.

One method for examining a distortion from icosahedral symmetry is to consider a crystal field distortion component, expressed in terms of spherical harmonics, as

$$\mathcal{H} = a_2 Y_{20}(\theta,\phi) + a_4 Y_{40}(\theta,\phi) + a_6 Y_{60}(\theta,\phi).$$

[5]

To generalise the calculations by using group theoretical symmetry coupling coefficients it is necessary to define that the z-axis is parallel to the five-fold axis and consider the crystal field distortion component at a general angle to the axis system defined by Eq. [4].

The result of rotating the spherical harmonics in the distortion hamiltonian [5] may be expressed in group theoretical notation as:

$$D(\alpha,\beta,0)Y_{J0}(\theta,\phi) = C_J(Aa)|Aa\rangle + C_J(U\kappa)|U\kappa\rangle + C_J^*(U\kappa)|U\nu\rangle$$

$$+ C_J(U\lambda)|U\lambda\rangle + C_J^*(U\lambda)|U\mu\rangle$$

$$+ C_J(V2)|V2\rangle + C_J^*(V2)|V-2\rangle$$

$$+ C_J(V1)|V1\rangle + C_J^*(V1)|V-1\rangle + C_J(V0)|0\rangle$$

where $C_J^*(a)$ is the complex conjugate of $C_J(a)$.

The reduced matrix elements are evaluated as outlined in section 4. These are given for f^n-ions in a recent publication by Golding, Pascual and Hoare (7). In addition the variation of the principal g-values for the three $9/2W'$ – doublets as the direction of the crystal changes are shown when the distortion is in the plane containing a five-fold, a three-fold and a two-fold axes. This work also shows how very sensitive the g-values are to small changes in the direction of the distortion especially near the symmetry axes. Also in (7) some specific results are given for the f^3-ion case and compared with electron paramagnetic resonance, optical and magnetic susceptibility data.

7. Conclusion

The examples I have chosen illustrate how versatile group theoretical methods are in generalising a very wide range of calculations in interpreting data such as magnetic resonance results. It is clear that group theoretical methods give a much greater wealth of information than may be determined from a single calculation such as for a specific f^n system in a pre-determined crystal field environment and will lead to a much greater understanding of the system under investigation.

(1) R.M.Golding and J.D.Newmarch, Molec. Phys. 33, 1301 (1977)
(2) J.D.Newmarch and R.M.Golding, J.Math.Phys. 22, 233 (1981)
(3) J.D.Newmarch and R.M.Golding, J.Math. Phys. 22, 2113 (1981)
(4) R.M.Golding, Molec. Phys. 21, 157 (1971)
5. R.M.Golding, Molec. Phys. 26, 661 (1973)
6. D.M.Brink and G.R.Satchler, Angular Momentum, Claredon Press, Oxford (1968)
7. R.M.Golding, R.O.Pascual and I.C.Hoare, Theoret. Chim. Acta 67, 157 (1985)