Spin-Orbit Coupling and Double Groups

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Spin-orbit term in **H** induces coupling of orbital and spin angular momenta to give total angular momentum:

$$\vec{\mathrm{J}} = \vec{\mathrm{L}} + \vec{\mathrm{S}}$$

-splits Russell-Saunders multiplets into their components labeled by the J quantum number.

- recall:

$$\chi(D_L(\alpha)) = \frac{\sin\left[\frac{(2L+1)\alpha}{2}\right]}{\sin\left(\frac{\alpha}{2}\right)}$$

- A deeper analysis shows that this result is related to commutation relations for **L** operators.

Since **S** and **J** obey the same relations:

$$\Rightarrow \chi(D_J(\alpha)) = \frac{\sin\left[\frac{(2J+1)\alpha}{2}\right]}{\sin\left(\frac{\alpha}{2}\right)}$$

Since **L** ≡ integer and **S** ≡ integer or ½-integer

Means **J** can be an integer or ½-integer

no problem   problem

Consider a proper rotation through an angle α + 2π

$$\chi(D_J(\alpha+2\pi)) = \frac{\sin\left[\frac{(2J+1)\alpha}{2} + (2J+1)\pi\right]}{\sin\left[\frac{(\alpha+2\pi)}{2}\right]}$$

$$\because \sin(A+B) = \sin(A)\cos(B) + \cos(A)\sin(B)$$

$$= \frac{\sin\left[\frac{(2J+1)\alpha}{2}\right]\cos[(2J+1)\pi]}{-\sin\left(\frac{\alpha}{2}\right)} \qquad = (-1)^{2J}\chi[D_J(\alpha)]$$

$\therefore$ **J** ≡ integer $\chi[D_J(\alpha+2\pi)] = \chi[D_J(\alpha)]$ as expected

However, when **J** ≡ ½-integer (odd # of electrons)

$$\chi[D_J(\alpha+2\pi)] = -\chi[D_J(\alpha)]$$

This behaviour arises because state functions are spinors (orbital x spin function) and not vectors.

Need a new operator: $\overline{E} = R(2\pi, n) \neq E = R(0, n)$

Adding $\overline{E}$ to the group G = {R} gives a **double group** $\overline{G}$

with elements $\{R\} + \overline{E}\{R\}$

Characters of the matrix representatives of D_J for half-integral J

For $R(\alpha, \zeta)$, $\chi_J(\alpha) = \dfrac{\sin(J+\frac{1}{2})\alpha}{\sin\frac{1}{2}\alpha}$

For $\bar{R}(\alpha, \zeta) = \bar{E}R(\alpha, \zeta)$, $\chi_J(\alpha + 2\pi) = (-1)^{2J}\chi_J(\alpha)$

	E	C_2	C_3	C_4
α	0	π	$\frac{2}{3}\pi$	$\frac{\pi}{2}$
D_J	$2J+1$	0	1 $(J = \frac{1}{2}, \frac{7}{2}, \ldots)$ -1 $(J = \frac{3}{2}, \frac{9}{2}, \ldots)$ 0 $(J = \frac{5}{2}, \frac{11}{2}, \ldots)$	$\sqrt{2}$ $(J = \frac{1}{2}, \frac{9}{2}, \ldots)$ 0 $(J = \frac{3}{2}, \frac{7}{2}, \ldots)$ $-\sqrt{2}$ $(J = \frac{5}{2}, \frac{13}{2}, \ldots)$
$J = \frac{1}{2}$	2	0	1	$\sqrt{2}$
$J = \frac{3}{2}$	4	0	-1	0
$J = \frac{5}{2}$	6	0	0	$-\sqrt{2}$

What about Improper Rotations?

If $i \in G,\ i\psi^j = \pm\psi^j$

and $\chi\left(D_J^{\pm}(IR)\right) = \pm\chi\left(D_J^{\pm}(R)\right)$ IR here means improper rotation

If $i \notin G, \chi(D_J(IR)) = \chi(D_J(R))$

These rules hold for **J** integer or ½-integer, and so for **L** and **S** also.

Note: $\overline{G}$ contains 2 x # elements of G (hence the name), but not necessarily 2 x # classes

The number of new classes in $\overline{G}$ are given by **Opechewski's Rules**

1.) $\overline{C}_{2n} = \overline{E}C_{2n}$ and C_{2n} are in the same class iff there is another C_2 axis with a rotation axis perpendicular to n

2.) $\overline{C}_n = \overline{E}C_n$ are always in different classes if $n \neq 2$

3.) for $n > 2$, C_n^k and C_n^{-k} are in the same class, and so are $\overline{C}_n^k$ and $\overline{C}_n^{-k}$

Let $$\chi_J(\alpha) = \frac{\sin\left[\frac{(2J+1)\alpha}{2}\right]}{\sin\left(\frac{\alpha}{2}\right)} = \chi_J[R(\alpha,n)]$$

$$\chi_J(\alpha + 2\pi) = (-1)^{2J}\chi_J(\alpha) = \chi[\overline{R}(\alpha,n)]$$

Equations work for integer and ½-integer **J**-values

Note: the characters of the new classes $\overline{C}_k$ of $\overline{G}$ are for integer **J** the same as those of the classes C_k of G, but for ½-integer **J** have the same magnitude but opposite sign.

The new representations for $\overline{G}$ by ½-integer **J** are called **spinor representations**

Labels for D_J representations

1.) Bethe’s notation: Γ_j where j ≡ the number of integer values necessary to label all the spinor represntations.

2.) Mulliken-Herzberg notation: IRs are labelled E, G, H, … according to their dimensionality 2, 4, 6, with a subscripts J which corresponds to the representation D_J in which the IR **first occurs**

Example: $\bar{O}$

$\bar{O} = \{O\} + \bar{E}\{O\}$

	O	E	$8C_3$	$3C_2$ ($3\bar{C}_2$)	$6C_4$	$6C_2'$ ($6\bar{C}_2'$)	$\bar{E}$	$8\bar{C}_3$	$6\bar{C}_4$		
Γ_1	A_1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
Γ_2	A_2	1	1	1	−1	−1	1	1	−1		
Γ_3	E	2	−1	2	0	0	2	−1	0		$(x^2-y^2, 2z^2-x^2-y^2)$
Γ_4	T_1	3	0	−1	1	−1	3	0	1	$(x, y, z)(R_x, R_y, R_z)$	
Γ_5	T_2	3	0	−1	−1	1	3	0	−1		(xy, xz, yz)
Γ_6	$E_{1/2}$	2	1	0	$\sqrt{2}$	0	−2	−1	$-\sqrt{2}$		
Γ_7	$E_{5/2}$	2	1	0	$-\sqrt{2}$	0	−2	−1	$\sqrt{2}$		
Γ_8	$G_{3/2}$	4	−1	0	0	0	−4	1	0		
	$D_{5/2}$	6	0	0	$-\sqrt{2}$	0	−6	0	$\sqrt{2}$		
	$D_{7/2}$	8	1	0	0	0	−8	−1	0		
	$\ldots\Gamma_7) + D_{7/2}$	4	−1	0	0	0	−4	1	0		

Dimensions of the new representations:

$$1^2 + 1^2 + 2^2 + 3^2 + 3^2 + \ell_6^2 + \ell_7^2 + \ell_8^2 = 48$$

$$\ell_6 = 2,\ \ell_7 = 2,\ \ell_8 = 4$$

$D_{1/2}$: $\sum_T |\chi_i|^2 = 1(4) + 8(1) + 6(2) + 1(4) + 8(1) + 6(2) = 48 = \bar{g}$ ∴ $D_{1/2}$ is an IR, Γ_6 or $E_{1/2}$

$D_{3/2}$: $\sum_T |\chi_i(T)|^2 = 1(16) + 8(1) + 1(16) + 8(1) = 48 = \bar{g}$ ∴ $D_{3/2}$ is an IR, $G_{3/2}$ or Γ_8.

$D_{5/2}$: $\sum_T |\chi_i(T)|^2 = 1(36) + 6(2) + 1(36) + 6(2) = 96 > \bar{g}$ ∴ reducible

$$a_{\Gamma_6} = \frac{1}{48}[1(2)(6) + 6(\sqrt{2})(-\sqrt{2}) + 1(-2)(-6) + 6(-\sqrt{2})(\sqrt{2})] = 0$$

$$a_{\Gamma_8} = \frac{1}{48}[1(4)(6) + 1(-4)(-6)] = \frac{48}{48} = 1$$

[illegible]

Reduction of $D_{7/2}$:

$$a_{\Gamma_6} = \frac{1}{48}[16 + 8 + 16 + 8] = 1$$

$$a_{\Gamma_7} = \frac{1}{48}[16 + 8 + 16 + 8] = 1$$

∴ $D_{7/2} = \Gamma_6 \oplus \Gamma_7 \oplus \Gamma_8$

All new representations generated by half-integer J are at least 2-fold degenerate in any electrostatic field ≡ **Kramer's Theorem**
Further splittings are possible in a magnetic field.

For inversion symmetry:

1.) Bethe's notation: $\Gamma_j^{\pm}$ even (gerade) / odd (ungerade)

2.) Mulliken-Herzberg notation: use superscripts g and u.

Weak Crystal Fields

Means weaker than $\hat{H}_{\vec{L}\cdot\vec{S}}$.
Therefore a weak crystal field acts on the components of the Russell-Saunders multiplets.

Depending on their degeneracy these components may undergo further splittings in a weak crystal field.

Example: In O the following splittings:

$$D_{3/2} = \Gamma_8$$
$$D_{5/2} = \Gamma_7 \oplus \Gamma_8$$
$$D_{7/2} = \Gamma_6 \oplus \Gamma_7 \oplus \Gamma_8$$
$$D_{9/2} = \Gamma_6 \oplus 2\Gamma_8$$

Selected spin-orbit components

{Γ_j that given in Table}

Question:

Examine the effect of spin-orbit coupling on the states that result from an intermediate-field of O symmetry on the Russell-Saunders multiplet ^4F.

Correlate these states with those produced by a weak crystal field of O symmetry on the components produced by spin-orbit coupling on the ^4F multiplet.

Answer:

^4F implies L =3 in an intermediate field $\Rightarrow A_2 \oplus T_1 \oplus T_2 = \Gamma_2 \oplus \Gamma_4 \oplus \Gamma_5$

To examine the effect of spin-orbit coupling on the intermediate field use $\psi = \phi^i \chi^j$ where ϕ^i forms a basis for Γ^i and χ^j forms a basis for Γ^j. This means $\psi = \phi^i \chi^j$ forms a basis for the direct product $\Gamma^i \otimes \Gamma^j$

$$\because 2S+1=4 \Rightarrow S=\frac{3}{2} \qquad \therefore \Gamma^j \equiv D_{3/2} \equiv \Gamma_8$$

$$\therefore \Gamma_8 \otimes \Gamma_2 = \Gamma_8$$
$$\Gamma_8 \otimes \Gamma_4 = \Gamma_6 \oplus \Gamma_7 \oplus 2\Gamma_8$$
$$\Gamma_8 \otimes \Gamma_5 = \Gamma_6 \oplus \Gamma_7 \oplus 2\Gamma_8$$

Final correlation diagram on the next slide:

Splitting of the ^4F state in weak and intermediate fields of cubic symmetry.