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

\[
\mathbf{J} = \mathbf{L} + \mathbf{S}
\]

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

- recall:

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

- A deeper analysis shows that this result is related to commutation relations for \( \mathbf{L} \) operators.

Since \( \mathbf{S} \) and \( \mathbf{J} \) obey the same relations:

\[
\Rightarrow \chi(D_j(\alpha)) = \frac{\sin\left(\frac{(2J+1)\alpha}{2}\right)}{\sin\frac{\alpha}{2}}
\]
Since $\mathbf{L} \equiv \text{integer}$ and $\mathbf{S} \equiv \text{integer or } \frac{1}{2}\text{-integer}$

Means $\mathbf{J}$ can be an integer or $\frac{1}{2}$-integer

\[ \downarrow \quad \downarrow \quad \text{no problem} \quad \text{problem} \]

Consider a proper rotation through an angle $\alpha + 2\pi$

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

\[
\therefore \sin(A + B) = \sin(A)\cos(B) + \cos(A)\sin(B)
\]

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

\[\therefore J \equiv \text{integer} \quad \chi[D_J(\alpha + 2\pi)] = \chi[D_J(\alpha)] \quad \text{as expected}\]

However, when $\mathbf{J} \equiv \frac{1}{2}\text{-integer}$ (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: \( \mathbf{E} = R(2\pi, n) \neq \mathbf{E} = R(0, n) \)

Adding \( \mathbf{E} \) to the group \( G = \{ R \} \) gives a double group \( \overline{G} \) with elements \( \{ R \} + \mathbf{E}\{ R \} \).
What about Improper Rotations?

If \( i \in G, \ i \psi^I = \pm \psi^I \)
and \( \chi(J^I (IR)) = \pm \chi(J^R) \) \ IR here means improper rotation

If \( i \notin G, \chi(J^I (IR)) = \chi(J^R) \)

These rules hold for \( J \) integer or \( \frac{1}{2} \)-integer, and so for \( L \) and \( S \) also.
Note: $\overline{G}$ contains $2 \times \#$ elements of $G$ (hence the name), but not necessarily $2 \times \#$ classes.

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

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

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

$\chi_J(\alpha + 2\pi) = (-1)^J \chi_J(\alpha) = \chi_J[\varepsilon R(\alpha, n)]$

Equations work for integer and $\frac{1}{2}$-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 $\frac{1}{2}$-integer $J$ have the same magnitude but opposite sign.

The new representations for $\overline{G}$ by $\frac{1}{2}$-integer $J$ are called spinor representations.
Labels for D_J representations

1.) Bethe’s notation: \( \Gamma_j \) where \( j \) is the number of integer values necessary to label all the spinor representations.

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

Example: \( \overline{O} \)
All new representations generated by half-integer J are at least 2-fold degenerate in any electrostatic field \( \equiv \text{Kramer’s Theorem} \). 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 \( \hat{H}_{LS} \).

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:

- \( D_{\frac{1}{2}} = \Gamma_8 \)
- \( D_{\frac{3}{2}} = \Gamma_7 \oplus \Gamma_8 \)
- \( D_{\frac{1}{2}} = \Gamma_6 \oplus \Gamma_7 \oplus \Gamma_8 \)
- \( D_{\frac{3}{2}} = \Gamma_6 \oplus 2\Gamma_8 \)

\( \{\Gamma_j\} \) 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 $\psi = \phi \chi$ where $\phi$ forms a basis for $\Gamma_i$ and $\chi$ forms a basis for $\Gamma_j$. This means $\psi = \phi \chi$ forms a basis for the direct product $\Gamma_i \otimes \Gamma_j$

\[ \therefore 2S + 1 \Rightarrow S = \frac{3}{2} \quad \therefore \Gamma_j = D_{\frac{3}{2}} = \Gamma_8 \]

Spin-orbit coupling and double groups

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

Final correlation diagram on the next slide:
Splitting of the $^1F$ state in weak and intermediate fields of cubic symmetry.

$$H_0 + H_{ow} + H_{SL} + H_{CS} \quad H_{SL} + H_{CS} + H_{SF} + H_0$$

weak cubic field \quad intermediate cubic field