Quantum Chemistry Supplementary Subject
GROUP THEORY PROBLEMS 4

1. From the character table for the point group O, derive the following relations:

$$T_1 \otimes A_1 = T_1 \qquad T_1 \otimes A_2 = T_2$$
$$T_1 \otimes E = T_1 \oplus T_2 \qquad T_1 \otimes T_1 = A_1 \oplus E \oplus T_1 \oplus T_2 \qquad T_1 \otimes T_2 = A_2 \oplus E \oplus T_1 \oplus T_2$$

2. Consider the matrix elements $\int \psi_i \hat{\boldsymbol{\mu}} \psi_j \mathrm{d}\tau$, where ψ_i and ψ_j are functions that belong to two different irreps of the group O. Using the results of Q1, explain why the only non-vanishing matrix elements are those that correspond to the transitions:

$$T_1 \leftarrow A_1 \qquad T_2 \leftarrow A_2$$
$$T_1, T_2 \leftarrow E \qquad A_1, E, T_1, T_2 \leftarrow T_1 \qquad A_2, E, T_1, T_2 \leftarrow T_2$$

3. Determine the term symbols for the terms of the excited [He]$2p3d$ configuration of Be.

4. What are the terms arising from a $t_{2g}e_g$ electronic configuration in an octahedral (O_h) environment?

5. Show why the diagonal entries of a direct product table always contains the totally-symmetric irrep (TSIR) once, while off-diagonal entries never contain it.

   You might want to use the following three results:

   (a) The little orthogonality theorem states that

   $$\sum_R \chi^{(l)}(R)\chi^{(l')}(R) = h\delta_{ll'}$$

   where the sum is over all symmetry elements R (i.e. not over the classes).

   (b) The number of times that irrep l occurs in the reduction of Γ is given by

   $$a_l = \frac{1}{h}\sum_R \chi^{(l)}(R)\chi^{\Gamma}(R).$$

   (c) The direct product of two irreps gives a new representation Γ with characters that satisfy

   $$\chi^{(l)}(R)\chi^{(l')}(R) = \chi^{\Gamma}(R).$$

6. This is a harder problem. In the point group R_3 there are infinitely-many irreps, whose dimensions are $(2j+1)$ for integer $j \geq 0$. The character of the $(2j+1)$-dimensional irrep under a rotation around any axis by φ is

$$\chi^{(j)}(\varphi) = \sum_{m=-j}^{j} \mathrm{e}^{im\varphi}. \tag{1}$$

The irrep itself is denoted $\Gamma^{(j)}$.

In this problem you will show that

$$\Gamma^{(j_1)} \otimes \Gamma^{(j_2)} = \Gamma^{(j_1+j_2)} \oplus \Gamma^{(j_1+j_2-1)} \oplus \cdots \oplus \Gamma^{(|j_1-j_2|)}, \tag{2}$$

which is the Clebsch-Gordan series that you have encountered in quantum mechanics lectures. The connection can be made concrete using the fact that the infinitesimal rotation operators of R_3 obey the same commutation relations as the angular momentum operators.

There are two steps to the calculation.

(a) Show that

$$\chi^{(j)}(\varphi) = \frac{\sin(j+\frac{1}{2})\varphi}{\sin\frac{1}{2}\varphi}. \tag{3}$$

To do this, note that the series in (1) is a geometric series with initial term $\mathrm{e}^{-ij\varphi}$ and constant ratio $\mathrm{e}^{i\varphi}$. Use the formula for a geometric series and then multiply top and bottom by $\mathrm{e}^{-i\varphi/2}$.

(b) Now use (1) and (3) to write

$$\chi^{(j_1)}(\varphi)\chi^{(j_2)}(\varphi) = \frac{\mathrm{e}^{i(j_1+1/2)\varphi} - \mathrm{e}^{-i(j_1+1/2)\varphi}}{2i\sin\frac{1}{2}\varphi} \sum_{m=-j_2}^{j_2} \mathrm{e}^{im\varphi},$$

where j_1 can be assumed to be $\geq j_2$. You can then bring all the terms inside the sum. By arguing that m can be replaced by $-m$ in the sum (explain why!), show that

$$\chi^{(j_1)}(\varphi)\chi^{(j_2)}(\varphi) = \sum_{j=j_1-j_2}^{j_1+j_2} \frac{\sin(j+\frac{1}{2})\varphi}{\sin\frac{1}{2}\varphi}$$

and hence obtain (2).

Notice that the derivation you've just been through would work also if j is half an odd integer (which makes sense, as you already know that the Clebsch-Gordan series holds for spin angular momenta too!). To understand this properly requires the introduction of a new group called $SU(2)$, and is therefore a story for another day…