3.7: The "Great Orthogonality Theorem"

One thing that is important about irreducible representations is that they are orthogonal. This is the property that makes group theory so very useful in chemistry, because orthogonality makes integrals zero. It's always easier to do the integrals when orthogonality tells us the result will be zero before doing any complicated math!

The **Great Orthogonality Theorem** (GOT) can be stated:

$$\sum_R \left[\Gamma_i(R)_{mn}\right]\left[\Gamma_j(R)_{m'n'}\right]^* = \frac{h}{\sqrt{l_i l_j}}\delta_{ij}\delta_{mm'}\delta_{nn'}$$

(Any theorem with that many subscripts must have something truly useful to say!) In this notation, $\Gamma_i(R)_{mn}$ indicates the row m, column n element of the i^{th} irreducible representation for symmetry operation R. The m and n are needed since not all irreducible representations are made up of just 1 and –1. Many irreducible representations need to use matrices to represent each symmetry element. For these cases, l_i gives the dimension of the matrices used in the Γ_i. In our example of the C_{2v} point group, all irreducible representations have $l = 1$, so the GOT can be stated more simply (for this point group specifically) as

$$\sum_R \left[\Gamma_i(R)\right]\left[\Gamma_j(R)\right]^* = h\delta_{ij}$$

Consider applying this statement to the A_2 and B_1 irreducible representations (Γ_2 and Γ_3) for the C_{2v} point group.

$$\begin{aligned} \sum_R \left[\Gamma_2(R)\right]\left[\Gamma_3(R)\right]^* &= \Gamma_2(E)\Gamma_3(E) + \Gamma_2(C_2)\Gamma_3(C_2) + \Gamma_2(\sigma_v)\Gamma_3(\sigma_v) + \Gamma_2(\sigma_v')\Gamma_3(\sigma_v') \\ &= (1)(1) + (1)(-1) + (-1)(1) + (-1)(-1) \\ &= 1 - 1 - 1 + 1 \\ &= 0 \end{aligned}$$

Similarly, considering using the GOT on just Γ_4 (the B_2 irreproducible representation) yields the following

$$\begin{aligned} \sum_R \left[\Gamma_4(R)\right]\left[\Gamma_4(R)\right]^* &= \Gamma_4(E)\Gamma_4(E) + \Gamma_4(C_2)\Gamma_4(C_2) + \Gamma_4(\sigma_v)\Gamma_4(\sigma_v) + \Gamma_4(\sigma_v')\Gamma_4(\sigma_v') \\ &= (1)(1) + (-1)(-1) + (-1)(-1) + (1)(1) \\ &= 1 + 1 + 1 + 1 \\ &= 4 \end{aligned}$$

Recall that the order of the group (h) is 4 because there are four symmetry elements in the group.

In the case of the C_{3v} point group, there is a 2x2 matrix representation. Consider the upper right member of each of the $\Gamma_3(E)$ matrices (row 1, column 2) and apply the GOT to these elements along with the elements of $\Gamma_1(A_1)$.

$$\begin{aligned} \sum_R \left[\Gamma_1(R)\right]\left[\Gamma_3(R)_{12}\right] &= (1)(0) + (1)(\sqrt{3}/2) + (1)(-\sqrt{3}/2) + (1)(0) + (1)(-\sqrt{3}/2) + (1)(\sqrt{3}/2) \\ &= 0 \end{aligned}$$

Similarly, applying the GOT to the row 1, column 1 elements of $\Gamma_3(E)$ we see

$$\begin{aligned} \sum_R \left[\Gamma_3(R)_{11}\right]\left[\Gamma_3(R)_{11}\right] &= (1)^2 + (-1/2)^2 + (-1/2)^2 + (-1)^2 + (1/2)^2 + (1/2)^2 \\ &= 3 = 6/2 = h/l_3 \end{aligned}$$

Now tell me . . isn't that truly a ***Great* Orthogonality Theorem** ? (Now how much would you pay?) Once we introduce the concept of *character*, we will restate the GOT in terms of class characters.