Representation Reduction for Molecular Orbitals

To determine the linear combination of irreducible representations that comprise a reducible representation, we need only treat rows of the character table as vectors and take the dot product of the reducible vector with every irreducible vector and normalize by the order of the group.

To demonstrate, we repeat the example from class. The character table for O_h is reproduced below, the representation we wish to decompose is appended to the end of the table:

	E	$\mathbf{8}C_3$	$\mathbf{6}C_2$	$\mathbf{6}C_4$	$\mathbf{3}C_2 = (C_4)^2$	i	$\mathbf{6}S_4$	$\mathbf{8}S_6$	$\mathbf{3}\sigma_h$	$\mathbf{6}\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	−1	−1	1	1	−1	1	1	−1
E_g	2	−1	0	0	2	2	0	−1	2	0
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1
A_{2u}	1	1	−1	−1	1	−1	1	−1	−1	1
E_u	2	−1	0	0	2	−2	0	1	−2	0
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1
T_{2u}	3	0	1	−1	−1	−3	1	0	1	−1
Γ_{red}	7	1	1	3	3	1	1	1	5	3

Note that some of the symmetry elements have coefficients (bolded in table) in front of them indicating that they are in a class of several elements with the same character. This is just a shorthand to make the table smaller. We therefore will multiply by the coefficient when we take the dot product.

Then $A_{1g} \cdot \Gamma_{red} = \langle 1, \mathbf{8}\cdot 1, \mathbf{6}\cdot 1, \mathbf{6}\cdot 1, \mathbf{3}\cdot 1, 1, \mathbf{6}\cdot 1, \mathbf{8}\cdot 1, \mathbf{3}\cdot 1, \mathbf{6}\cdot 1\rangle \cdot \langle 7, 1, 1, 3, 3, 1, 1, 1, 5, 3\rangle = 96$.

The order of the group is 48, so the coefficient of A_{1g} is 2. Taking this dot product with the rest of the irreducible representations (and normalizing) yields:

A_{1g}	2
A_{2g}	0
E_g	1
T_{1g}	0
T_{2g}	0
A_{1u}	0
A_{2u}	0
E_u	0
T_{1u}	1
T_{2u}	0

Thus the representation $\Gamma_{red} = 2A_{1g} + E_g + T_{1u}$.

Representation Reduction for Vibrational Modes

The same method works for vibrational modes except it is required that we multiply the entries of our reducible representation by the "character contribution" of whatever symmetry action we are performing (in case you were wondering, the character contribution is the trace of the matrix representation of that symmetry element, but that's not really important).

The character contributions are:

E	3
C_2	-1
C_3	0
C_4	1
C_5	$\frac{1+\sqrt{5}}{2}$
C_6	2
σ	1
i	-3
S_3	-2
S_4	-1
S_6	0
C_n	$1 + 2\cos(\frac{2\pi}{n})$
S_n	$-1 + 2\cos(\frac{2\pi}{n})$

Then Γ_{red} becomes $\Gamma'_{red} = \langle 21, 0, -1, 3, -3, -3, -1, 0, 5, 3\rangle$

Repeating the dot product (and normalizing) with this representation gives the following:

A_{1g}	1
A_{2g}	0
E_g	1
T_{1g}	1
T_{2g}	1
A_{1u}	0
A_{2u}	0
E_u	0
T_{1u}	3
T_{2u}	1

However, we care only about the vibrational modes so we may throw out the T_{1g} and one of the T_{1u}s, because they correspond to a molecular rotation and molecular translation, respectively, as opposed to a vibration. Thus the vibrational modes of this representation are: $\Gamma'_{red} = A_{1g} + E_g + T_{2g} + 2T_{1u} + T_{2u}$.