Character Tables: Procedure for Derivation

- delineate symmetry elements, classes
- # of I.R.'s = # of Classes
- dimensions of I.R.'s:

$$\sum_i [\chi_i(E)]^2 = h$$

- orthogonality and normalization of I.R.'s

$$\sum_R [\chi_i(R)]^2 = h \quad ; \quad \sum_R \chi_i(R)\chi_j(R) = 0 \text{ when } i \neq j$$

- Mulliken Symbols
- bases for I.R.'s, linear and bilinear forms

Derivation of Character Tables; Examples

★ C_{2v} - easy!

★ C_{4v}- an example with a 2-dim. I.R.

★ D_{3h} vs. D_{3d}

★ O_h- Divide and Conquer

- ★ $O_h = O \times C_i$

A Crucial Practical Relationship

- ⋆ Any reducible rep. can be put in block-diagonal form by some similarity transformation (i.e., appropriate choice of basis)
- ⋆ Let a_j be the # of times the j^{th} irred. rep. occurs. The character of the red. rep. is then:

$$\chi(R) = \sum_j a_j \chi_j(R)$$

- ⋆ A formula for a_i is: $$a_i = \frac{1}{h} \sum_R \chi(R) \chi_i(R)$$

Examples

- ⋆ Find the characters of the reducible representation obtained using the four hydrogen 1s orbitals of methane as a basis — then find the irred. reps. spanned by this rep.
- ⋆ Follow the same procedure using the twelve CO π* orbitals of $Cr(CO)_6$ as a basis.
- ⋆ Follow the same procedure using the six CO stretching vibrations of $Cr(CO)_6$ as a basis.

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	–1	–1		
E	2	–1	2	0	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	–1	1	–1	(R_x, R_y, R_z)	
T_2	3	0	–1	–1	1	(x, y, z)	(xy, xz, yz)

O_h	E	$8C_3$	$3C_2$ $(=C_4^2)$	$6C_4$	$6C_2$	i	$8S_6$	$3\sigma_h$	$6S_4$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_{2g}	1	1	1	–1	–1	1	1	1	–1	–1		
E_g	2	–1	2	0	0	2	–1	2	0	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_{1g}	3	0	–1	1	–1	3	0	–1	1	–1	(R_x, R_y, R_z)	
T_{2g}	3	0	–1	–1	1	3	0	–1	–1	1		(xy, xz, yz)
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	2	0	0	–2	1	–2	0	0		
T_{1u}	3	0	–1	1	–1	–3	0	1	–1	1	(x, y, z)	
T_{2u}	3	0	–1	–1	1	–3	0	1	1	–1		