

## *Character Tables: Procedure for Derivation*

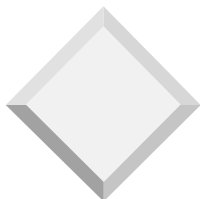
- delineate symmetry elements, classes
- # of I.R.'s = # of Classes
- dimensions of I.R.'s:

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

- 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*

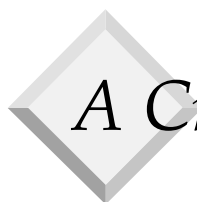
★  $C_{2v}$  - easy!

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

★  $D_{3h}$  vs.  $D_{3d}$

★  $O_h$  - Divide and Conquer

$$\star O_h = O \times C_i$$

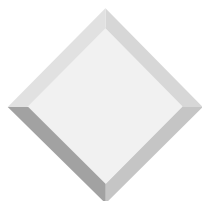


## *A Crucial Practical Relationship*

- ★ 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  $j^{\text{th}}$  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  $\pi^*$  orbitals of  $\text{Cr}(\text{CO})_6$  as a basis.
- ★ Follow the same procedure using the six CO stretching vibrations of  $\text{Cr}(\text{CO})_6$  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	$(x, y, z)$	$(xy, xz, yz)$

$O_h$	$E$	$8C_3$	$3C_2$ ( $=C_4$ )	$6C_4$	$6C_2$	$i$	$8S_6$	$3\sigma_h$	$6S_4$	$6\sigma_d$		
$A_{1g}$	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		