PG SEMISTR II, UNIT III, SYMMETRY ELEMENTS

BY

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Character Tables

Schoenflies symmetry symbol

D_{3d}	E	$2C_3$	$3C_2$	i	$2S_6$	$3\sigma_d$		
A_{1g}	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	−1	1	1	−1	R_z	
E_g	2	−1	0	2	−1	0	(R_x, R_y)	$(x^2-y^2, xy), (xz, yz)$
A_{1u}	1	1	1	−1	−1	−1		
A_{2u}	1	1	−1	−1	−1	1	z	
E_u	2	−1	0	−2	1	0	(x, y)	

Mulliken symbols

Characters of the irreducible representations

x, y, z
R_x, R_y, R_z

Squares & binary products of the coordinates

Mulliken Symbol Notation

1) **A** or **B**: 1-dimensional representations

   E : 2-dimensional representations

   T : 3-dimensional representations

2) **A** = symmetric with respect to rotation by the C_n axis

   B = anti-symmetric w/respect to rotation by C_n axis

Symmetric = + (positive) character

Anti-symmetric = – (negative) character

3) **Subscripts 1 and 2 associated with A and B symbols indicate whether a C_2 axis ⊥ to the principle axis produces a symmetric (1) or anti-symmetric (2) result.**

D_{3d}	E	$2C_3$	$3C_2$	i	$2S_6$	$3\sigma_d$
A_{1g}	1	1	1	1	1	1
A_{2g}	1	1	−1	1	1	−1

If C_2 axes are absent, then it refers to the effect of vertical mirror planes (e.g., C_{3v})

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	−1
E	2	−1	0

4) **Primes and double primes indicate representations that are symmetric (′) or anti-symmetric (″) with respect to a σ_h mirror plane. They are NOT used when one has an inversion center present (e.g., D_{2nh} or C_{2nh}).**

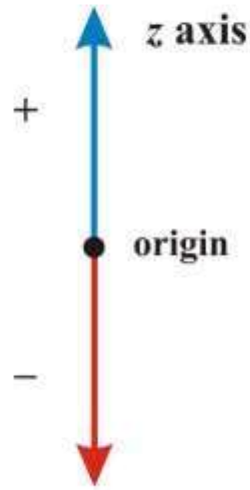
5) **In groups with an inversion center, the subscript "g" ("gerade" meaning even) represents a Mulliken symbol that is symmetric with respect to inversion.**

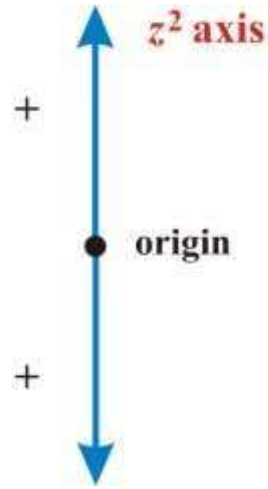
The symbol "u" ("ungerade" meaning uneven) indicates that it is anti-symmetric.

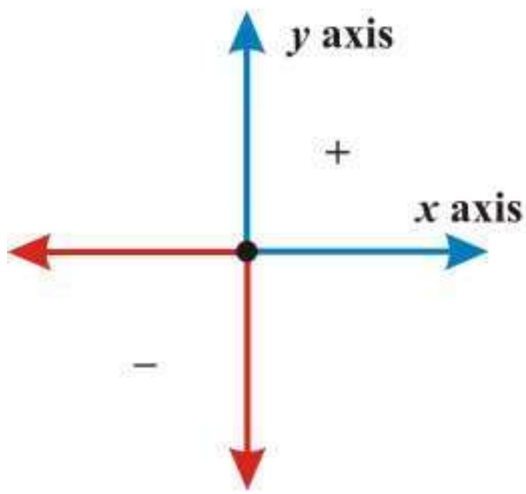
6) **The use of numerical subscripts on E and T symbols follow some fairly complicated rules that will not be discussed here. Consider them to be somewhat arbitrary.**

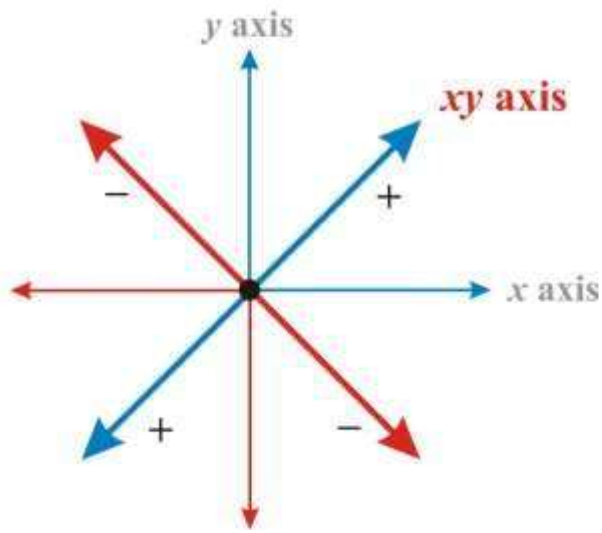
Square and Binary Products

These are higher order "combinations" or products of the primary *x*, *y*, and *z* axes.









The Great Orthogonality Theorem

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

$\Gamma_i(R)_{mn}$	**The element in the *m*th row and *n*th column of the matrix corresponding to the operation R in the *i*th irreducible representation Γ_i.**
$\Gamma_i(R)_{mn}^*$	**complex conjugate used when imaginary or complex #'s are present (otherwise ignored)**
h	**the order of the group**
l_i	**the dimension of the *i*th representation (A = 1, B = 1, E = 2, T = 3)**
δ	**delta functions, = 1 when $i = j$, $m = m'$, or $n = n'$; = 0 otherwise**

The different irreducible representations may be thought of as a series of orthonormal vectors in *h*-space, where *h* is the order of the group.

Because of the presence of the delta functions, the equation = 0 unless $i = j$, $m = m'$, or $n = n'$. Therefore, there is only one case that will play a direct role in our chemical applications:

$$\sum_R [\Gamma_i(R)_{mn}][\Gamma_j(R)_{m'n'}] = 0 \qquad \text{if } i \neq j$$

$$\sum_R [\Gamma_i(R)_{mn}][\Gamma_j(R)_{m'n'}] = 0 \qquad \text{if } m \neq m',\ n \neq n'$$

$$\sum_R [\Gamma_i(R)_{mn}][\Gamma_i(R)_{mn}] = \frac{h}{l_i}$$