Systematic Reduction of Irreducible Representations

- For complex molecules with a large dimension reducible representation, identification of the component irreducible representations and their quantitative contributions is not straight forward.
- Fortunately, reducing such a representation for a group of finite order can be carried out systematically using the following equation

$$n_i = \frac{1}{h} \sum_c g_c \chi_i \chi_r$$

n_i : number of times the irreducible representation *i* occurs in the reducible representation

h : order of the group

c : class of operations

g_c : number of operations in the class

χ_i : character of the irreducible representation for the operations of the class

χ_r : character of the reducible representation for the operations of the class

- The work of carrying out a systematic reduction is better organized by using the tabular method, rather than writing out the individual equations for each irreducible representation

Tabular Method

- To carry out the reduction, construct a work sheet with rows for each species, columns for each product $g_c \chi_i \chi_r$, a column for the sum of all $g_c \chi_i \chi_r$ products for each species (Σ), and a final column for $n_i = \Sigma\, g_c \chi_i \chi_r / h$.
- Sample reducible representation worksheet for the T_d point group given the reducible representation Γ_r

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
Γ_r	8	-1	4	-2	0	Σ	$\Sigma/24$
A_1							
A_2							
E							
T_1							
T_2							

- Products $g_c \chi_i \chi_r$ T_d :

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
T_1	3	0	-1	1	-1
T_2	3	0	-1	-1	1

Character table for T_d
(without last column for vector transformations and direct products)

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
Γ_r	8	-1	4	-2	0	Σ	$\Sigma/24$
A_1	8	-8	12	-12	0	0	0
A_2	8	-8	12	12	0	24	1
E	16	8	24	0	0	48	2
T_1	24	0	-12	-12	0	0	0
T_2	24	0	-12	12	0	24	1

Thus $\Gamma_i = A_2 + 2E + T_2$

- Checking our solution $\Gamma_i = A_2 + 2E + T_2$

$$d = 1 + 2(2) + 3 = 8 = d_r$$

- Does Γ_r compute ?

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
T_1	3	0	-1	1	-1
T_2	3	0	-1	-1	1

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
E	2	-1	2	0	0
T_2	3	0	-1	-1	1
Γ_r	8	-1	4	-2	0

Trouble Shooting

- The sum across a row is not divisible by the order *h*.
  - An error has been made in one or more of the products, probably while changing signs or multiplying from one row to the next; e.g.,

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
Γ_r	8	-1	4	-2	0	Σ	Σ/24
A_1	8	-8	12	-12	0	0	0
A_2	8	$\boxed{8}$	12	12	0	40	

  - An error was made in generating the original reducible representation; e.g.,

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
Γ_r	8	-1	4	$\boxed{-1}$	0	Σ	Σ/24
A_1	8	-8	12	-6	0	6	

  - You forgot to multiply by the number of operations in the class when generating the first row; e.g.,

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
Γ_r	8	-1	4	-2	0	Σ	Σ/24
A_1	8	-8	12	-2	0	10	

Trouble Shooting *(contd.)*

- The sum of the dimensions of the found irreducible representations does not equal the dimension of the reducible representation.
  - One or more of the lines for individual species is faulty in a way that happens to be divisible by *h*; e.g.,

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
Γ_r	8	-1	4	-2	0	Σ	$\Sigma/24$
A_1	8	-8	12	-12	0	0	0
A_2	8	-8	12	12	0	24	1
E	16	8	24	0	0	48	2
T_1	24	0	-12	-12	0	0	0
T_2	24	0	$\boxed{12}$	12	0	48	2

$$d = 1 + 2(2) + 2(3) = 11 \neq d_r$$

Reducing Representations with Imaginary Characters

- Certain groups *(C_n , $n \geq 3$; C_{nh}* , n ≥ 3; S_{2n} ; T ; T_h) have irreducible representations that contain the imaginary integer i = $(-1)^{1/2}$.
- Imaginary irreducible representations are always shown as complex conjugate pairs on successive lines of the character table and are given a shared Mulliken symbol designation of a doubly-degenerate representation (e.g., *E*).
- Both representations of a complex-conjugate pair are individual non-degenerate representations in their own right.
- For real physical problems, if one imaginary representation is contained in the reducible representation for a property, then the complex conjugate for that representation must also be present in equal number.
- For convenience, complex conjugate pairs of representations are often added together to give a real-character representation, which is a reducible representation with $d_r = 2$.
- We will always designate such combined real-character representations with braces around the Mulliken symbol of the complex conjugate pair; e.g., *{E}.*
- ***If a combined real-character representation is used with the standard reduction formula, the result given for the number of occurrences of the combined representataion (n_i) will be twice its true value.***
- If using the standard reduction formula, divide the result for any combined real-character representation of a complex-conjugate pair by 2.

- For example, let us test the reducible representation in C_{4h} $\Gamma_r = 2B_g + \{E_g\} + A_u$
- First we must generate the complete set of characters for Γ_r according to the C_{4h} character table

C_{4h}	E	C_4	C_2	C_4^3	i	S_4^3	σ_h	S_4
B_g	1	-1	1	-1	1	-1	1	-1
B_g	1	-1	1	-1	1	-1	1	-1
$\{E_g\}$	2	0	-2	0	2	0	-2	0
A_u	1	1	1	1	-1	-1	-1	-1
Γ_r	5	-1	1	-1	3	-3	-1	-3

- Using the tabular method we then carry out a systematic reduction by generating a worksheet:

C_{4h}	E	C_4	C_2	C_4^3	i	S_4^3	σ_h	S_4			
Γ_r	5	-1	1	-1	3	-3	-1	-3	Σ	$\Sigma/8$	
A_g	5	-1	1	-1	3	-3	-1	-3	0	0	
B_g	5	1	1	1	3	3	-1	3	16	2	
$\{E_g\}$	10	0	-2	0	6	0	2	0	16	2	☞ 1
A_u	5	-1	1	-1	-3	3	1	3	8	1	
B_u	5	1	1	1	-3	-3	1	-3	0	0	
$\{E_u\}$	10	0	-2	0	-6	0	-2	0	0	0	☞ 0

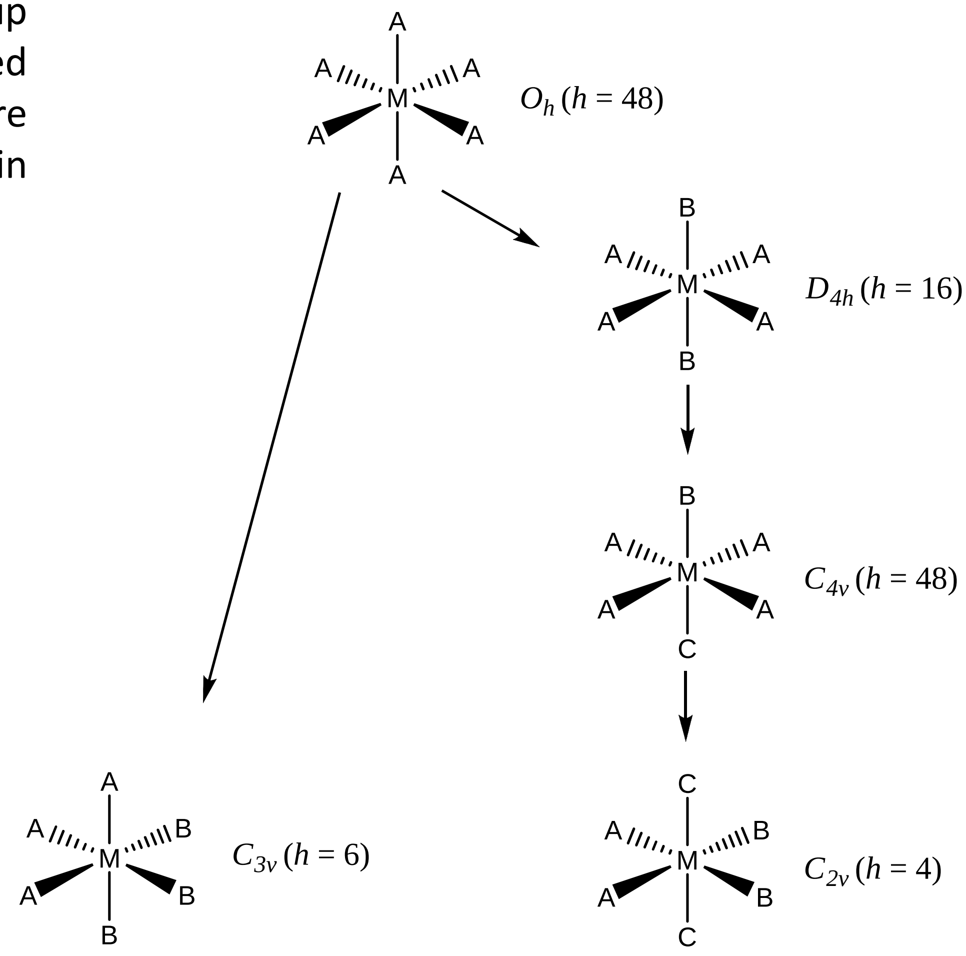
- Dividing the complex contribution by 2 we correctly obtain $\Gamma_r = 2B_g + \{E_g\} + A_u$

Group-Subgroup Relationships

- When a structural change occurs, there is often a group-subgroup relationship between the original and new structures.
- If the new structure belongs to a point group that is a subgroup of the point group of the original structure, then descent in symmetry has occurred.
- Descent in symmetry may cause formerly degenerate properties to become distinct non-degenerate properties.
- If the new structure belongs to a higher-order group of which the old structure's point group is a subgroup, then ascent in symmetry has occurred.
- Ascent in symmetry may cause formerly distinct non-degenerate properties to become degenerate.
- Observing changes in degeneracy (e.g., splitting or coalescing of bands in spectra) can be revealing of structure changes.
- Knowledge of group-subgroup relationships can simplify the work of group theory applications by solving the problem in a smaller-order subgroup and correlating the results to the true group.

O_h Subgroups

- Groups that have a group-subgroup relationship have related representations whose characters are the same for the shared operations in the two groups.



Group-Subgroup Relationships

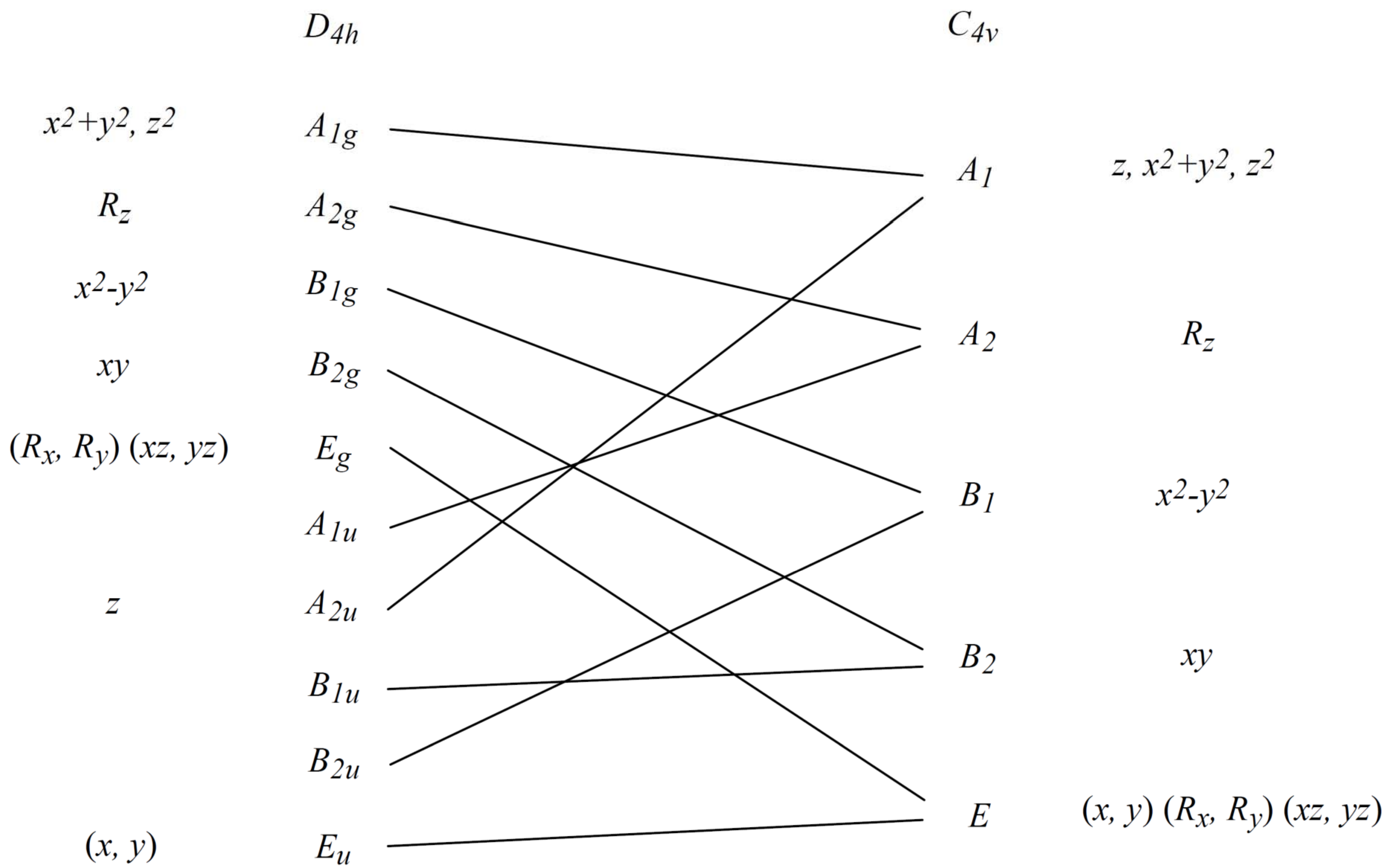
- Between a group and any of its subgroups, representations arising from the same vector basis will have the same *χ(r)* values for all operations that occur in both groups.

Characters for shared operations in D_{4h} and C_{4v}

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	C_{4v}
A_{1g}	1	1	1						1	1	A_1
A_{2g}	1	1	1						-1	-1	A_2
B_{1g}	1	-1	1						1	-1	B_1
B_{2g}	1	-1	1						-1	1	B_2
E_g	2	0	-2						0	0	E
A_{1u}	1	1	1						-1	-1	A_2
A_{2u}	1	1	1						1	1	A_1
B_{1u}	1	-1	1						-1	1	B_2
B_{2u}	1	-1	1						1	-1	B_1
E_u	2	0	-2						0	0	E

Correlation diagram for D_{4h} and C_{4v}

- Those species in both groups that are not associated with a listed unit vector transformation share a vector basis that is simply not one of those routinely listed.



Lifting Degeneracies

- Degenerate representations may be spit into lower-order representations (non-degenerate or a mixture of double and non-degenerate representations) in a subgroup that is too small to have higher-order degeneracies.

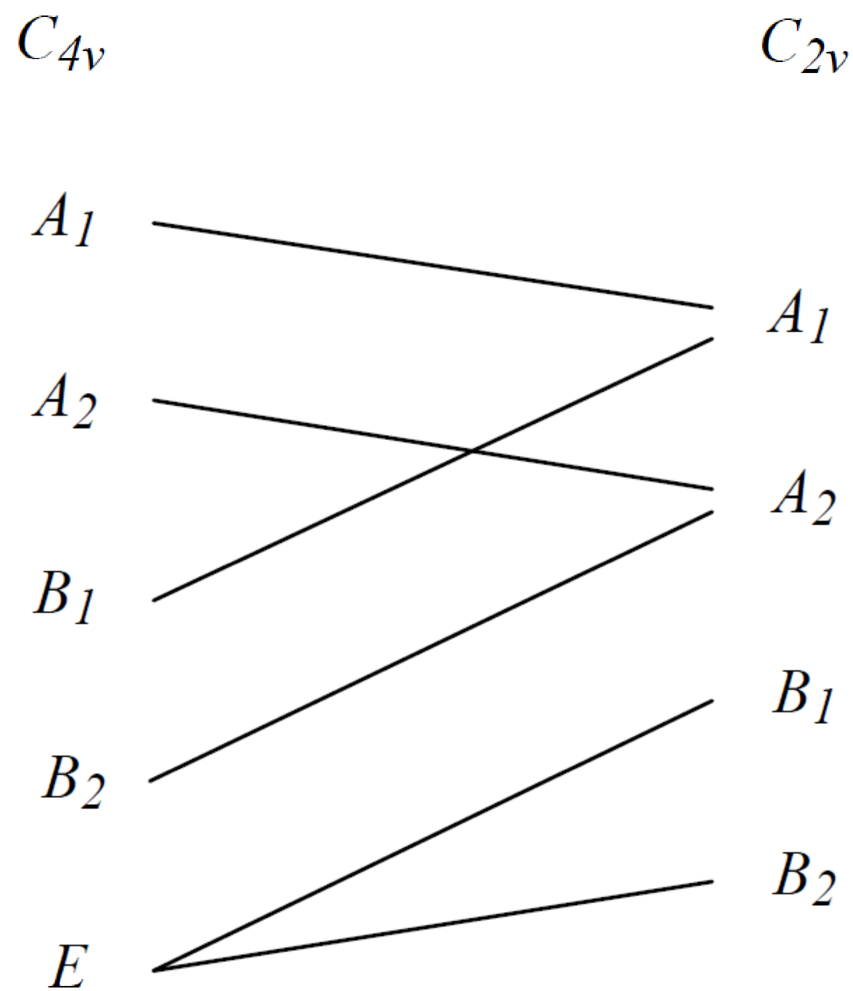
Characters for shared operations in C_{4v} and C_{2v}

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$	
	E		C_2	σ_v, σ_v'		C_{2v}
A_1	1		1	1		A_1
A_2	1		1	-1		A_2
B_1	1		1	1		A_1
B_2	1		1	-1		A_2
E	2		-2	0		$B_1 + B_2$

- The characters of E in C_{4v} form a reducible representation in C_{2v} , Γ_E , which reduces to $B_1 + B_2$.

C_{2v}	E	C_2	σ_v	σ_v'
B_1	1	-1	1	-1
B_2	1	-1	-1	1
E	2	-2	0	0

Correlation diagram for C_{4v} and C_{2v}



Reducing Representations of $C_{\infty v}$ *and* $D_{\infty h}$

- The standard reduction equation cannot be used with groups that have $h = \infty$, like $C_{\infty v}$ and $D_{\infty h}$.

  Work-around technique:

  - Set up and solve the problem in a finite subgroup

    e.g., C_{2v} for $C_{\infty v}$, D_{2h} for $D_{\infty h}$.

  - Correlate the results in the subgroup to the true infinite-order group, using either a partial correlation table or by matching shared vectors in the related groups.

  - Complete correlations to an infinite group are not possible, because there are an infinite number of irreducible representations.

  - A partial correlation table is sufficient, because only a limited number of irreducible representations in either $C_{\infty v}$ or $D_{\infty h}$ are related to real physical properties.

Partial correlation tables for $C_{\infty v}$ and $D_{\infty h}$

$C_{\infty v}$	C_{2v}
$A_1 = \Sigma^+$	A_1
$A_2 = \Sigma^-$	A_2
$E_1 = \Pi$	$B_1 + B_2$
$E_2 = \Delta$	$A_1 + A_2$

$D_{\infty h}$	D_{2h}
Σ_g^+	A_g
Σ_g^-	B_{1g}
Π_g	$B_{2g} + B_{3g}$
Δ_g	$A_g + B_{1g}$
Σ_u^+	B_{1u}
Σ_u^-	A_u
Π_u	$B_{2u} + B_{3u}$
Δ_u	$A_u + B_{1u}$

Direct Products of Irreducible Representations

- Any product of irreducible representations is also a representation of the group.

$$\Gamma_a \, \Gamma_b \, \Gamma_c = \Gamma_{abc}$$

- The character $\chi(R)$ for an operation R in a product representation is the product of the characters of R in the component representations.

$$\chi(R)_a \, \chi(R)_b \, \chi(R)_c = \chi_{abc}(R)$$

- The dimension of a product representation, d_p, is the product of the dimensions of the component representations

$$d_p = \prod_i d_i$$

Relationships of Direct Products

1. *If all the combined irreducible representations are non-degenerate, then the product will be a non-degenerate representation, too.*

   e.g., a partial character table for C_{4v}

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
B_1	1	-1	1	1	-1
B_2	1	-1	1	-1	1
E	2	0	-2	0	0

The direct product B_1 B_2 results in the irreducible representation A_2

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
B_1	1	-1	1	1	-1
B_2	1	-1	1	-1	1
A_2	1	1	1	-1	-1

Relationships of Direct Products

2. *The product of a non-degenerate representation and a degenerate representation is a degenerate representation.*

   e.g., a partial character table for C_{4v}

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
B_1	1	-1	1	1	-1
B_2	1	-1	1	-1	1
E	2	0	-2	0	0

The direct product B_2 E results in the irreducible representation E

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
B_2	1	-1	1	-1	1
E	2	0	-2	0	0
E	2	0	-2	0	0

Relationships of Direct Products

3. *The direct product of any representation with the totally symmetric representation is the representation itself.*

e.g., a partial character table for C_{4v}

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
B_1	1	-1	1	1	-1
B_2	1	-1	1	-1	1
E	2	0	-2	0	0

The direct product A_1 E results in the irreducible representation E

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
A_1	1	1	1	1	1
E	2	0	-2	0	0
E	2	0	-2	0	0

Relationships of Direct Products

4. *The direct product of degenerate representations is a reducible representation.*

e.g., a partial character table for C_{4v}

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
B_1	1	-1	1	1	-1
B_2	1	-1	1	-1	1
E	2	0	-2	0	0

The direct product *E E* results in the reducible representation Γ_p

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
E	2	0	-2	0	0
E	2	0	-2	0	0
Γ_p	4	0	4	0	0

Systematic reduction gives $\Gamma_p = A_1 + A_2 + B_1 + B_2$

Relationships of Direct Products

5. *The direct product of an irreducible representation with itself is or contains the totally symmetric representation.*

e.g., a partial character table for C_{4v}

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
B_1	1	-1	1	1	-1
B_2	1	-1	1	-1	1
E	2	0	-2	0	0

The non-degenerate self product $B_1\,B_1$ results in the totally symmetric representation A_1

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
B_2	1	-1	1	-1	1
B_2	1	-1	1	-1	1
A_1	1	1	1	1	1

The degenerate self product $\Gamma_E\,\Gamma_E = \Gamma_p = A_1 + A_2 + B_1 + B_2$

Relationships of Direct Products

5. *Only the direct product of a representation with itself is or contains the totally symmetric representation. Moreover, the self-product contains the totally symmetric representation only once*

Proof: How many times does the totally symmetric representation occur in any direct product?

$$n_i = \frac{1}{h}\sum_c g_c \chi_i \chi_r$$

where $\chi_i = \chi_A = 1$ for all R of the totally symmetric representation,

$$hn_A = \sum_c g_c \chi_i \chi_r = \sum_c g_c \chi_A \chi_p = \sum_c g_c \chi_p$$

But $\chi_p = \chi_a \chi_b$ for $\Gamma_p = \Gamma_a \Gamma_b$. Also, Γ_a and Γ_b must be orthogonal. Thus,

$$hn_A = \sum_c g_c \chi_p = \sum_c g_c \chi_a \chi_b = h\delta_{ab}$$

$$hn_A = h\delta_{ab}$$

only the self-product contains the totally symmetric representation, and then only once.

Direct Products of Representations with Symmetry or Anti-symmetry to a Specific Operation

In general:

sym × sym = sym

anti-sym × anti-sym = sym

anti-sym × sym = anti-sym

In terms of Mulliken symbols:

$g \times g = g$

$u \times u = g$

$u \times g = u$

‘ × ‘ = ‘

‘’ × ‘’ = ‘

‘’ × ‘ = ‘’