Systematic Reduction

A reducible representation of finite order can be systematically reduced into its component irreducible representations by applying the following equation for each and every species (irreducible representation) of the group:

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

n_i number of times the *i*th irreducible representation contributes to the reducible representation

h group order

c class

g_c number of operations in the class c

χ_i character of the irreducible representation for the class c

χ_r character for the reducible representation for the class c

☞ 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 $g_i\chi_i\chi_r$, a column for the sum of all $g_i\chi_i\chi$ products for each species (Σ), and a final column for $n_i = \Sigma\, g_i\chi_i\chi/h$.

Sample reducible representation worksheet:

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							

Character table for T_d (without last column for vector transformations):

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	

Filled-In Work Sheet for Sample Representation

Sample reducible representation worksheet, filled in:

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

Character table for T_d (without last column for vector transformations):

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

Result:

$$\Gamma_r = A_2 + 2E + T_2$$

☞ Carrying out the work this way involves simply multiplying or changing signs of the results in one row to get the results for the next.

Checking the Result

$$\Gamma_r = A_2 + 2E + T_2$$

Dimension check: $d = 1 + (2)(2) + 3 = 8 = d_r$

Sum check:

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	$\Sigma/24$
A_1	8	-8	12	-12	0	0	0
A_2	8	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	-1	0	Σ	$\Sigma/24$
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	$\Sigma/24$
A_1	8	-8	12	-2	0	10	

Trouble Shooting

✔ 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	12	12	0	48	2

$$d = 1 + (2)(2) + (2)(3) = 11 \neq 8 = d_r$$

Practice Reduction Worksheet

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
Γ	18	0	-2	4	-2	4	Σ	Σ/h
A_1'								
A_2'								
E'								
A_1''								
A_2''								
E''								

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_2'	1	1	−1	1	1	−1	R_z	
E'	2	−1	0	2	−1	0	(x, y)	$(x^2 - y^2, xy)$
A_1''	1	1	1	−1	−1	−1		
A_2''	1	1	−1	−1	−1	1	z	
E''	2	−1	0	−2	1	0	(R_x, R_y)	(xz, yz)

Practice Reduction Worksheet - Solution

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	Σ	Σ/h
Γ	18	0	-2	4	-2	4		
A_1'	18	0	-6	4	-4	12	24	2
A_2'	18	0	6	4	-4	-12	12	1
E'	36	0	0	8	4	0	48	4
A_1''	18	0	-6	-4	4	-12	0	0
A_2''	18	0	6	-4	4	12	36	3
E''	36	0	0	-8	-4	0	24	2

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_2'	1	1	−1	1	1	−1	R_z	
E'	2	−1	0	2	−1	0	(x, y)	$(x^2 - y^2, xy)$
A_1''	1	1	1	−1	−1	−1		
A_2''	1	1	−1	−1	−1	1	z	
E''	2	−1	0	−2	1	0	(R_x, R_y)	(xz, yz)

$$\Gamma = 2A_1' + A_2' + 4E' + 3A_2'' + 2E''$$

Dimension check: $d_r = 2 + 1 + (4)(2) + 3 + (2)(2) = 18$ ✔

Reducing Representations with Imaginary Characters

- Certain groups (C_n, $n \geq 3$; C_{nh}, $n \geq 3$; S_{2n}; T; T_h) have irreducible representations that contain the imaginary integer $i = \sqrt{-1}$.

- 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.

Example of Combining Complex Conjugate Pairs - C_{4h}

C_{4h}	E	C_4	C_2	C_4^3	i	S_4^3	σ_h	S_4
A_g	1	1	1	1	1	1	1	1
B_g	1	-1	1	-1	1	-1	1	-1
E_g^a	1	i	-1	$-i$	1	i	-1	$-i$
E_g^b	1	$-i$	-1	i	1	$-i$	-1	i
A_u	1	1	1	1	-1	-1	-1	-1
B_u	1	-1	1	-1	-1	1	-1	1
E_u^a	1	i	-1	$-i$	-1	$-i$	1	i
E_u^b	1	$-i$	-1	i	-1	i	1	$-i$

C_{4h}	E	C_4	C_2	C_4^3	i	S_4^3	σ_h	S_4
A_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
B_u	1	-1	1	-1	-1	1	-1	1
$\{E_u\}$	2	0	-2	0	-2	0	2	0

Example of Reducing a Representation in a Group With Imaginary Irreducible Representations

C_{4h}	E	C_4	C_2	C_4^3	i	S_4^3	σ_h	S_4
A_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
B_u	1	-1	1	-1	-1	1	-1	1
$\{E_u\}$	2	0	-2	0	-2	0	2	0

Generating a test representation in C_{4h}:

$$\Gamma_r = 2B_g + \{E_g\} + A_u$$

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

Reduction Work Sheet for Example Γ_r

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	Σ/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

Result: $\Gamma_r = 2B_g + \{E_g\} + A_u$ *q.e.d.*

C_{4h}	E	C_4	C_2	$C_4^{\,3}$	i	$S_4^{\,3}$	σ_h	S_4
A_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
B_u	1	-1	1	-1	-1	1	-1	1
$\{E_u\}$	2	0	-2	0	-2	0	2	0

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.

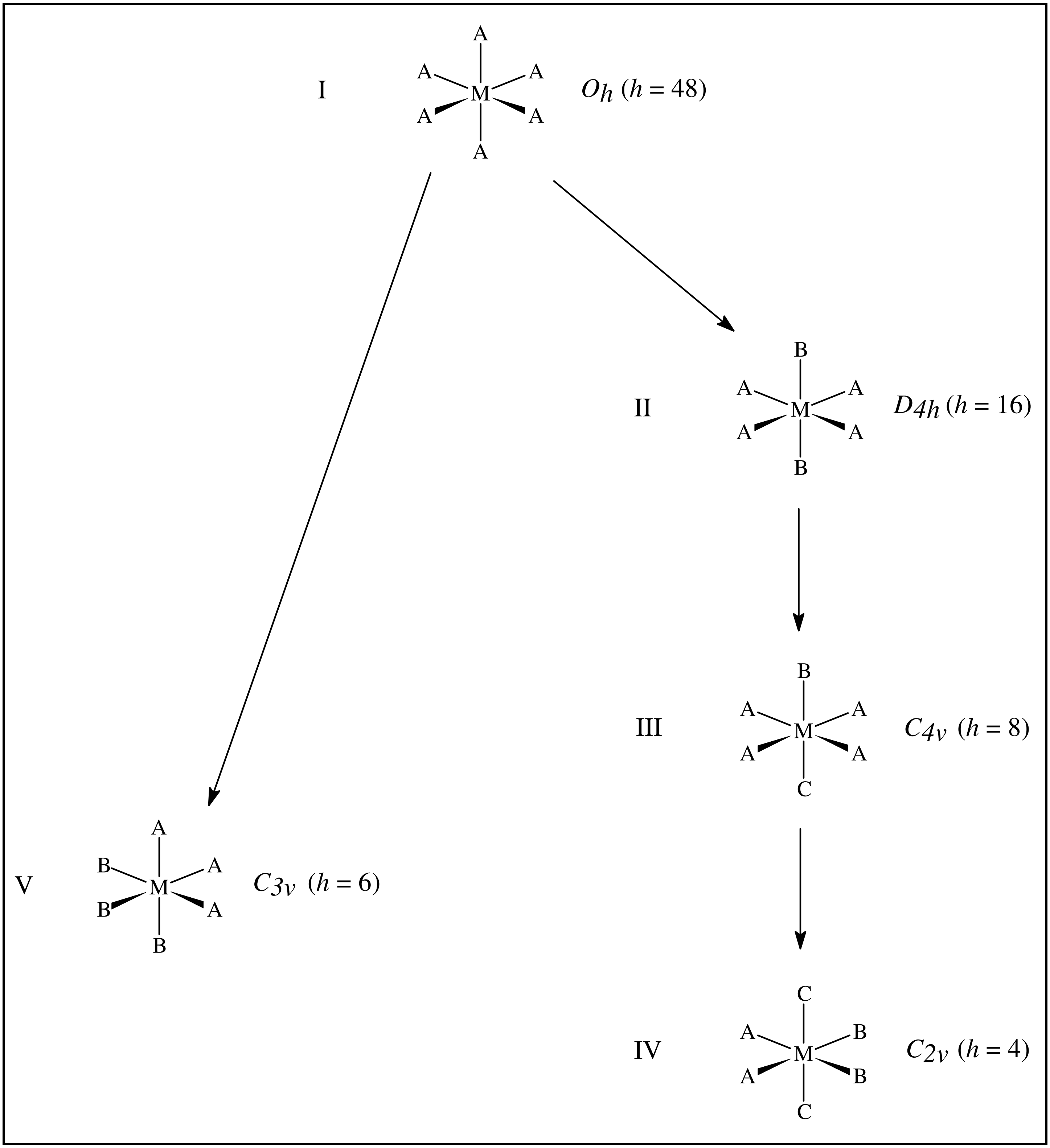
●If the new structure belongs to a higher-order group of which the old structure's point group is a subgroup, then *ascent* in symmetry has occurred.

•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.

Group-Subgroup Relationships Among Substituted Octahedral Molecules



Characters of Group-Subgroup Related Representations

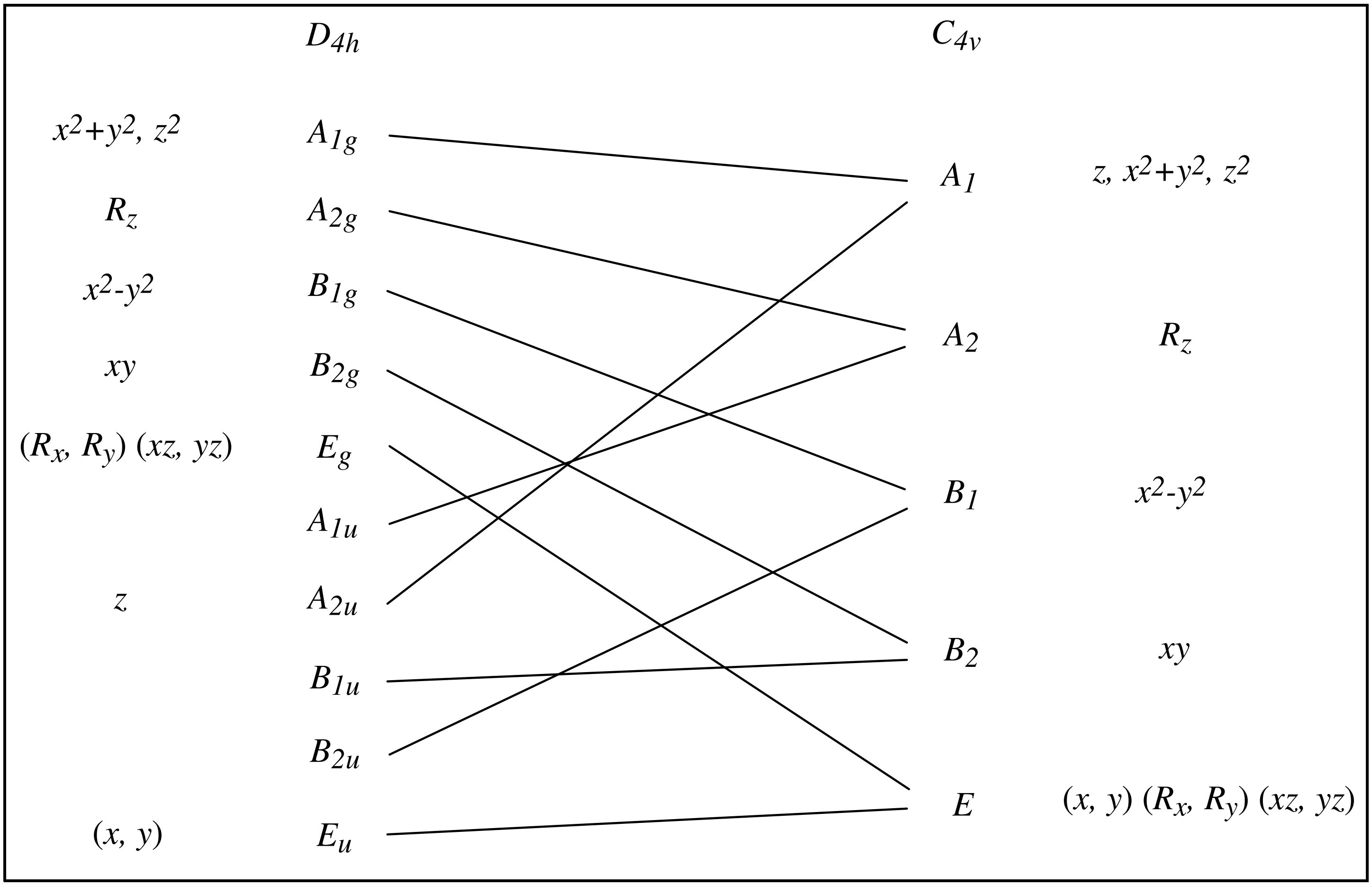
●Groups that have a group-subgroup relationship have related representations whose characters are the same for the shared operations in the two groups.

●Between a group and any of its subgroups, representations arising from the same vector basis will have the same $\chi(r)$ 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 split 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.

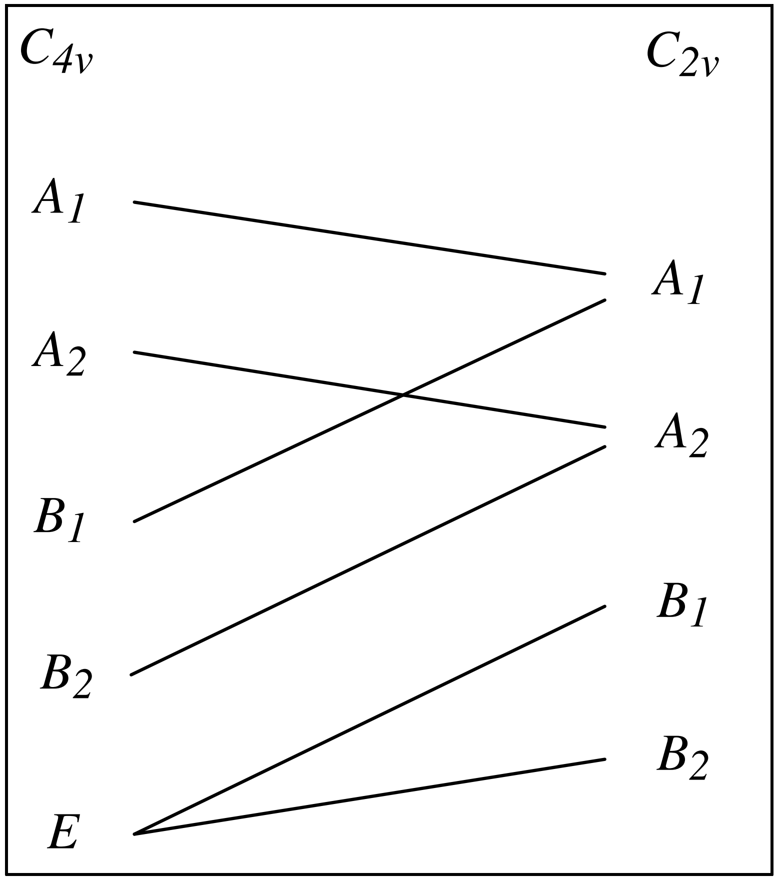
Characters for Shared Operations of C_{4v} and C_{2v}

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 and 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	$A_u + B_{1u}$

Relationships from the Great Orthogonality Theorem

1. The sum of the squares of the dimensions of all the irreducible representations is equal to the order of the group:

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

C_{3v}	E	$2C_3$	$3\sigma_v$	$h = 6$
A_1	1	1	1	$d_i^2 = 1$
A_2	1	1	-1	$d_i^2 = 1$
E	2	-1	0	$d_i^2 = 4$
				$\Sigma d_i^2 = 6$

2. The number of irreducible representations of a group is equal to the number of classes.

3. In a given representation (irreducible or reducible) the characters for all operations belonging to the same class are the same.

Relationships from the
Great Orthogonality Theorem

4. The sum of the squares of the characters in any irreducible representation equals the order of the group:

$$\sum_R [\chi_i(R)]^2 = h = \sum_{R_c} g_c[\chi_i(R_c)]^2$$

C_{3v}	E	$2C_3$	$3\sigma_v$	$h = 6$
A_1	1	1	1	(1)(1) + (2)(1) + (3)(1) = 6
A_2	1	1	-1	(1)(1) + (2)(1) + (3)(1) = 6
E	2	-1	0	(1)(4) + (2)(1) + (3)(0) = 6

5. Any two different irreducible representations are orthogonal:

$$\sum_{R_c} g_c\chi_i(R_c)\chi_j(R_c) = 0$$

C_{3v}	E	$2C_3$	$3\sigma_v$	
A_2	1	1	-1	
E	2	-1	0	$\Sigma g_c\chi_i\chi_j$
$g_c\chi_i\chi_j$	(1)(1)(2) = 2	(2)(1)(-1) = -2	(3)(-1)(0) = 0	2 – 2 + 0 = 0

Relationships from the Great Orthogonality Theorem

Combining points 4 and 5:

$$\sum_{R_c} g_c \chi_i(R_c)\chi_j(R_c) = h\delta_{ij}$$

Kronecker delta function, δ_{ij}:

$\delta_{ij} = 0$ if $i \neq j$

$\delta_{ij} = 1$ if $i = j$

Direct Products of Irreducible Representations

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

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

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

$$\chi_a(R)\chi_b(R)\chi_c(R)\ldots = \chi_{abc\ldots}(R)$$

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 nondegenerate, then the product will be a nondegenerate representation, too.*

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

Example:

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 nondegenerate representation and a degenerate representation is a degenerate representation.*

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

Example:

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.*

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

Example:

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.*

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

Example:

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

By systematic reduction:

$$\Gamma_p = A_1 + A_2 + B_1 + B_2$$

Relationships of Direct Products

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

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

Examples:

Nondegenerate self-product

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

Degenerate self-product (as previously seen)

$$\Gamma_E \Gamma_E = \Gamma_p = A_1 + A_2 + B_1 + B_2$$

Relationships of Direct Products

6. *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?

From the reduction equation, 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,

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

$$\Rightarrow n_A = \delta_{ab}$$

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:

$g \times g = g$

$u \times u = g$

$u \times g = u$

$' \times ' = '$

$'' \times '' = '$

$'' \times ' = ''$