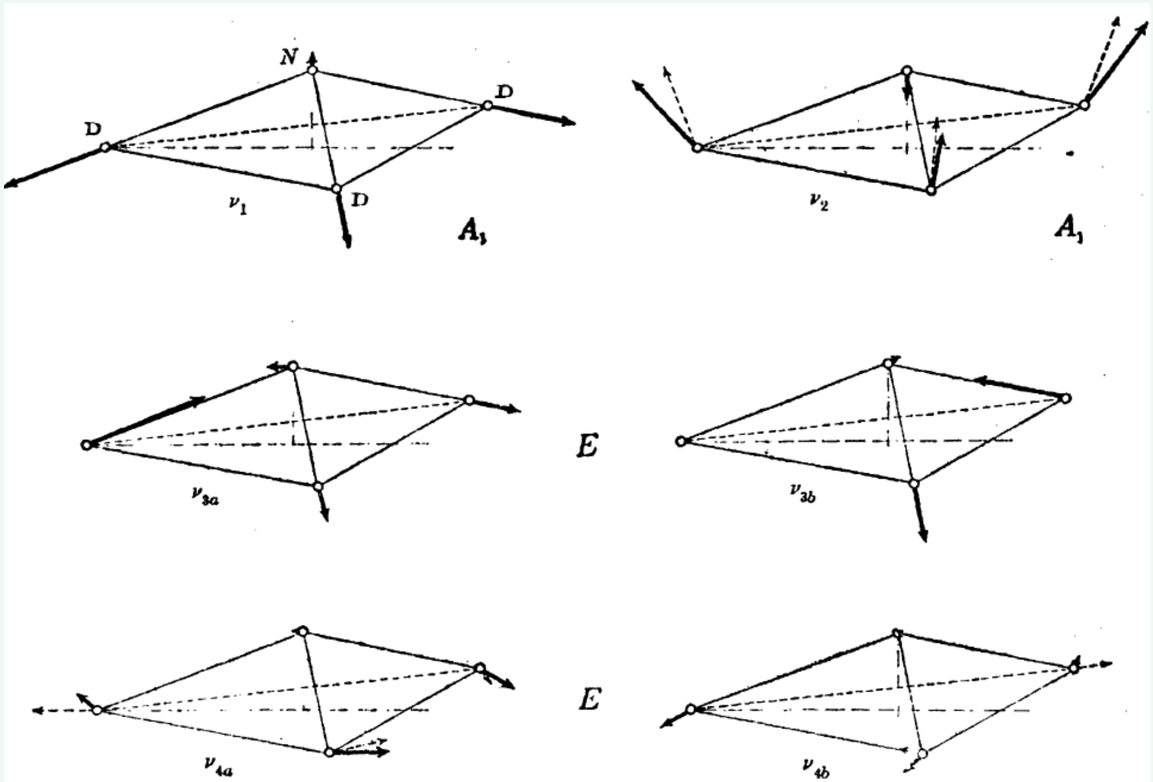
Introduction to Group Theory, part 2

- vibrational modes of pyramidal XY_3 (C_{3v}) molecules
- further example: $P(4)$ and the point group T_d
- notation of point groups (Schoenflies and international)
- direct product of matrices and groups
- example of $D_{3h} = C_{3v} \times C_{1h}$
- notation for the representations
- symmetry operations on functions of coordinates
- basis functions

Molecular vibrations - Herzberg II, pyramidal XY_3 (C_{3v});

3N-6=6 vibrations allowed in both Raman and IR, two doubly degenerate



Molecule	Observed frequencies (cm^{-1})			
	ν_1	ν_2	ν_3	ν_4
NH_3	3337	950[45]	3414	1628
ND_3	2419	749[45]	2555	1191
PH_3	2327	991[45]	2421	1121
PD_3	1694	730[45]	—	806

FIG. 45. **Normal vibrations of the ND_3 molecule.**—The vibrations are drawn to scale for ND_3 (see p. 177) in oblique projection. (For NH_3 the large mass ratio of N to H would not have allowed the displacement vectors of N to be drawn to the same scale as those of H). Both components of the degenerate vibrations are shown. The broken-line arrows in ν_2 and ν_4 give the symmetry coordinates of Fig. 58 (see p. 155). They are added so that the form of the vibrations can be more clearly visualized. In ν_{3b} there is a very small displacement (too small to show in the scale of the diagram) of the left D nucleus parallel to the line connecting the two other D nuclei (see also the discussion of Fig. 60 on p. 171). It should be noted that ν_{3a} and ν_{4a} are symmetric, ν_{3b} and ν_{4b} antisymmetric with respect to the plane of symmetry through the left D nucleus, that is, the plane of the paper.

Example - T_d

Symmetry operations of a regular tetrahedron (zincblende structures):

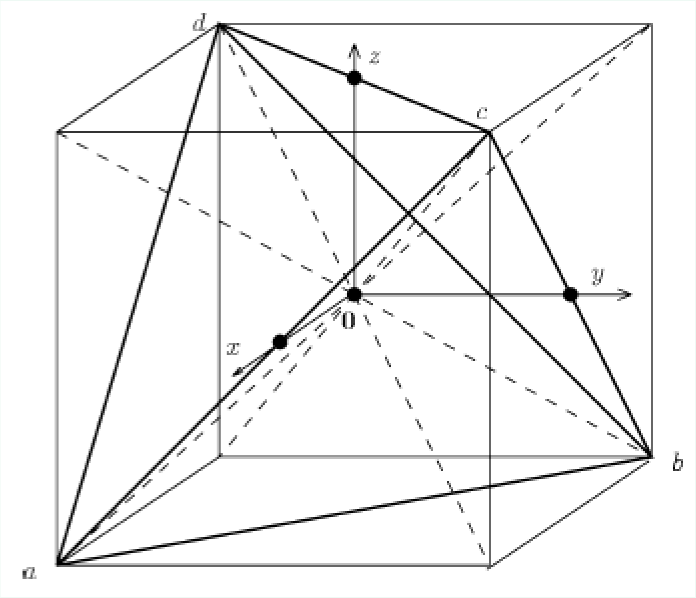
identity E,

eight C_3 axes about diagonals (dashed lines),

three C_2 axes about x,y,z,

six S_4 axes about x,y,z, corresponding to
the rotations of $\pm\pi/2$

six σ_d reflections (diagonal planes)



the group T_d of the order of 24,

isomorphic with $P(4)$,

5 classes, the character table is a 5x5 matrix

Example - T_d

Character tables for the point group T_d ($\bar{4}3m$) from two sources:

Inui, Tanabe, Onodera, Group theory and its applications in physics, Springer 1976

T_d		E	$6IC_4$	$3C_2$	$6\sigma_d$	$8C_3$
A_1	Γ_1	1	1	1	1	1
A_2	Γ_2	1	−1	1	−1	1
E	Γ_3	2	0	2	0	−1
T_1	Γ_4	3	1	−1	−1	0
T_2	Γ_5	3	−1	−1	1	0

M.S. Dresselhaus, G. Dresselhaus, A. Jorio, Group theory, Applications to the physics of Condensed Matter, Springer 2008

	E	$8C_3$	$3C_2$	$6\sigma_d$	$6S_4$
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

Example - T_d

Character tables for the point group T_d and (isomorphic) permutation group $P(4)$ from Dress_2008. Try to understand the notation used for the elements of classes of $P(4)$, and their link to the symmetry operations of T_d.

Note the different labels of the irreducible representations.

	E	$8C_3$	$3C_2$	$6\sigma_d$	$6S_4$
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

$P(4)$	(1^4)	$8(3,1)$	$3(2^2)$	$6(2,1^2)$	$6(4)$
Γ_1^s	1	1	1	1	1
Γ_1^a	1	1	1	-1	-1
Γ_2	2	-1	2	0	0
Γ_3	3	0	-1	1	-1
$\Gamma_{3'}$	3	0	-1	-1	1

<u>(Crystallographic) point groups</u> – two main naming conventions:
Schoenflies and “international” (Hermann-Maguin)

Translation symmetry restricts the n-fold rotation axis C_n to n=1,2,3,4, and 6.

Schoenfliess	international
C_n	1,2,3,4,6
σ (mirror reflection)	m
S_n (rotatory inversion axis)	$\bar{1}, \bar{3}, \bar{4}, \bar{6}$

the symbol m for the mirror plane does not distinguish between vertical, horizontal, and diagonal planes; instead,

n/m   means a horizontal plane perpendicular to the n-fold axis,

nm   means a horizontal plane containing the n-fold axis.

Point groups – two main naming conventions for 32 crystallographic point groups

Crystal system	Schönflies symbol	International symbol (abbreviated)
Cubic	O_h	$\frac{4}{m}\bar{3}\frac{2}{m}$ (m3m)
	O	432
	T_d	$\bar{4}3m$
	T_h	$\frac{2}{m}\bar{3}$ (m3)
	T	23
Tetragonal	D_{4h}	$\frac{4}{m}\frac{2}{m}\frac{2}{m}$ (4/mmm)
	D_4	422
	D_{2d}	$\bar{4}2m$
	C_{4v}	4mm
	C_{4h}	$\frac{4}{m}$ (4/m)
	S_4	$\bar{4}$
	C_4	4
Orthorhombic	D_{2h}	$\frac{2}{m}\frac{2}{m}\frac{2}{m}$ (mmm)
	D_2	222
	C_{2v}	2mm

Point groups – two main naming conventions for 32 crystallographic point groups

Crystal system	Schönflies symbol	International symbol (abbreviated)
Hexagonal	D_{6h}	$\frac{6}{m}\frac{2}{m}\frac{2}{m}$ (6/mmm)
	D_6	622
	D_{3h}	$\bar{6}m2$
	C_{6v}	6mm
	C_{6h}	$\frac{6}{m}$ (6/m)
	C_{3h}	$\bar{6}$
	C_6	6
Trigonal	D_{3d}	$\bar{3}\frac{2}{m}$ ($\bar{3}m$)
	D_3	32
	C_{3v}	3m
	$C_{3i}(S_6)$	$\bar{3}$
	C_3	3
Monoclinic	C_{2h}	$\frac{2}{m}$ (2/m)
	$C_{1h}(C_s)$	m
	C_2	2
Triclinic	C_i	$\bar{1}$
	C_1	1

Direct product of matrices

Let A and B be a matrices of $l_{Ac}\, l_{Ar}$ and $l_{Bc}\, l_{Br}$ elements:

A_{ij} , i=1,...,l_{Ar} , j=1,...,l_{Ac} , and B_{km} , k=1,...,l_{Br}, m=1,...,l_{Bc} .

The matrix $C=A\times B$, called the direct product, consists of $l_{Ar}\, l_{Ac}\, l_{Br}\, l_{Bc}$ elements of all products $A_{ij}\, B_{km} = C_{ik,jm}$. An alternative symbol for the direct product is $C=A\otimes B$.

The ordering in rectangular arrays is convenient for dealing with matrices.

The pair ik labels the rows, the pair jm labels the columns of the rectangular array of $l_{Ar}l_{Br}$ rows and $l_{Ac}l_{Bc}$ columns of C.

A convenient definition of multiplication of the direct-product matrices results from the requirement of the representation of "transformations" by successive multiplications of the matrices:

$A''=A'A$ represents the operation A succeeded by the operation A';

similarly $B''=B'B$, and $C''=C'C=A'A\times B'B$. The elements of the direct product are

$$(C'C)_{ik,jm} = \sum_p \sum_q A'_{ip} A_{pj} B'_{kq} B_{qm} = \sum_p \sum_q A'_{ip} B'_{kq} A_{pj} B_{qm} = \sum_p \sum_q C'_{ik,pq} C_{pq,jm},$$

which is the usual "row-times-column" multiplication of the matrices C' and C.

The rectangular array of the elements of $E \times B$ might be visualized as follows:

$$A \times B = \begin{bmatrix} A_{11}B & A_{12}B & \dots & A_{1l_{Ac}}B \\ A_{21}B & A_{22}B & \dots & A_{2l_{Ac}}B \\ . & & & \\ A_{l_{Ar}1}B & A_{l_{Ar}2}B & \dots & A_{l_{Ar}l_{Ac}}B \end{bmatrix},$$

where B is the rectangular block

$$B = \begin{bmatrix} B_{11} & B_{12} & \dots & B_{1l_{Bc}} \\ B_{21} & B_{22} & \dots & B_{2l_{Bc}} \\ . & & & \\ B_{l_{Br}1} & B_{l_{Br}2} & \dots & B_{l_{Br}l_{Bc}} \end{bmatrix}.$$

Direct product of groups

Two groups,

$\boldsymbol{G}_A$ with the elements A_i , i=1,...,n_A , and

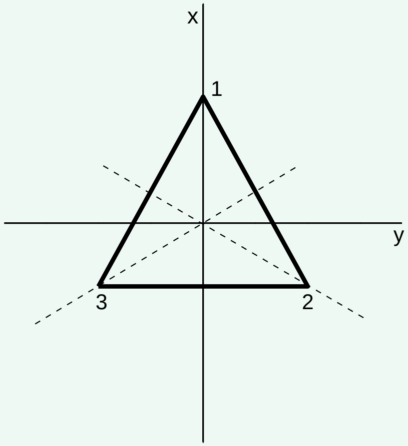
$\boldsymbol{G}_B$ with the elements B_j , j=1,...,n_B , such that $A_iB_j=B_jA_i$ for all of their elements,

form the direct product group $\boldsymbol{G}_A\times\boldsymbol{G}_B$ consisting of all A_iB_j.

The four group axioms are evidently fulfilled:

1. $A_iB_jA_kB_l = (A_iA_k)(B_jB_l)$,
2. the unit element is E_AE_B,
3. the inverse element of is $A_i^{-1}B_j^{-1}$, since $A_i^{-1}B_j^{-1}A_iB_j=E_AE_B$,
4. the multiplication is associative.

If $\boldsymbol{G}_A$ and $\boldsymbol{G}_B$ have no common elements (except possibly for the identity), the order of $\boldsymbol{G}_A\times\boldsymbol{G}_B$ is n_An_B.



Direct product of groups – example

The symmetry operations of an equilateral triangle (Schoenflies notation)

form the point group C_{3v} $\{E, 3\sigma_v, 2C_3\}$ if the upper and lower faces are distinguishable; if this asymmetry is removed, there is another symmetry operation:
σ_h , the mirror reflection in the horizontal plane.
Since $\sigma_h\sigma_h = E$, the group C_{1h} $\{E,\sigma_h\}$ is a cyclic group of order 2.

The horizontal reflection σ_h commutes with any element of C_{3v}, and the complete symmetry of the equilateral triangle is described by the group
$D_{3h} = C_{3v} \times C_{1h}$ with the 12 elements
$\{E, \sigma_1, \sigma_2, \sigma_3, C_3, C_3^2, \sigma_h, \sigma_h\sigma_1, \sigma_h\sigma_2, \sigma_h\sigma_3, \sigma_hC_3, \sigma_hC_3^2\}$.

Direct product of groups – example of $D_{3h} = C_{3v} \times C_{1h}$, the multiplication table

simpler notation of $P(3)$: $\sigma_1 \equiv A, \sigma_2 \equiv B, \sigma_3 \equiv C, C_3 \equiv D, C_3^2 \equiv F$; further, $\sigma_h \equiv S$:

right left	E	A	B	C	D	F
E	E	A	B	C	D	F
A	A	E	D	F	B	C
B	B	F	E	D	C	A
C	C	D	F	E	A	B
D	D	C	A	B	F	E
F	F	B	C	A	E	D

	E	S
E	E	S
S	S	E

right left	E	A	B	C	D	F	S	SA	SB	SC	SD	SF
E	E	A	B	C	D	F				?		
A	A	E	D	F	B	C						
B	B	F	E	D	C	A		?				
C	C	D	F	E	A	B						?
...												

Direct product of groups – example of $D_{3h} = C_{3v} \times C_{1h}$, classes, irreducible reps

six classes:

$\{E\}, \{\sigma_1, \sigma_2, \sigma_3\},\{C_3,C_3^2\},$

$\{\sigma_h\},\{\sigma_h\sigma_1, \sigma_h\sigma_2, \sigma_h\sigma_3\},\{\sigma_h C_3, \sigma_h C_3^2\}$

we are interested in the 6x6 matrix of characters of irreducible representations of the direct product

(character tables from Inui, Tanabe, Onodera, Group theory and its applications in physics, Springer 1976)

Table 4.2. Characters of the irreducible representations of the group C_{3v}

Class:	$\mathscr{C}_1$	$\mathscr{C}_2$	$\mathscr{C}_3$
Element:	E	C_3, C_3^{-1}	$\sigma_1, \sigma_2, \sigma_3$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

Table 4.3. Irreducible representations of the group C_s

	E	σ
A'	1	1
A''	1	-1

Direct product of groups – example of $D_{3h} = C_{3v} \times C_{1h}$, characters of irreps

the 3x3 matrix of characters of D_{3h} is 3x repeated, and the lower diagonal block is of the opposite sign due to the second irreducible representation of C_{1h} , with the character A''=(1,-1)

Table 4.4. Characters of the irreducible representations of the group $D_{3h} = C_{3v} \times C_s$

	E	C_3, C_3^{-1}	$\sigma_1, \sigma_2, \sigma_3$	σ_h	$C_3\sigma_h, C_3^{-1}\sigma_h$	U_1, U_2, U_3
$A_1 \times A' = A'_1$	1	1	1	1	1	1
$A_2 \times A' = A'_2$	1	1	-1	1	1	-1
$E \times A' = E'$	2	-1	0	2	-1	0
$A_1 \times A'' = A''_1$	1	1	1	-1	-1	-1
$A_2 \times A'' = A''_2$	1	1	-1	-1	-1	1
$E \times A'' = E''$	2	-1	0	-2	1	0

Direct product of groups – example of $D_{3h} = C_{3v} \times C_{1h}$, classes, irreducible reps

a different notation for some of the classes

(character tables from M.S. Dresselhaus, G. Dresselhaus, A. Jorio, Group theory, Applications to the physics of Condensed Matter, Springer 2008)

the rows and columns are distinct (in fact, orthogonal) → we can find the correspondence with the previous version of the table (the are identical as far as the characters are concerned)

Table A.14. Character table for group D_{3h} (hexagonal)

$D_{3h} = D_3 \otimes \sigma_h$ $(\bar{6}m2)$			E	σ_h	$2C_3$	$2S_3$	$3C_2'$	$3\sigma_v$
x^2+y^2, z^2		A_1'	1	1	1	1	1	1
	R_z	A_2'	1	1	1	1	-1	-1
		A_1''	1	-1	1	-1	1	-1
	z	A_2''	1	-1	1	-1	-1	1
(x^2-y^2, xy)	(x, y)	E'	2	2	-1	-1	0	0
(xz, yz)	(R_x, R_y)	E''	2	-2	-1	1	0	0

Point groups: notation for the representations

Chemical (Mulliken,1933) notation is common in molecular physics or in lattice dynamics. It uses

A and *B* for one-dimensional representations (*B* if odd under the smallest rotation of the principal axis),

E for two-dimensional representations,

T,*U*,*V*,*W* for the dimensionalities of 3,4,5,6.

Physical (Bethe, 1929; Koster, Dimmock, Wheeler and Statz, 1963) notation:

Γ_1, Γ_2, Γ_3,... ; preferred in the recent solid-state literature.

An alternative (Bouckaert, Smoluchowski and Wigner, 1935) is available on occasion; example for T_d:

Mulliken	KDWS	BSW
A_1	Γ_1	Γ_1
A_2	Γ_2	Γ_2
E	Γ_3	Γ_{12}
T_1	Γ_4	Γ_{15}
T_2	Γ_5	Γ_{25}

Point groups: notation for the representations

The Mulliken notation has an additional rule:
if the group contains inversion, the symbol has an additional suffix, either
“g” (gerade) for the even parity under inversion, or
“u” (ungerade) for the odd parity.

The example of the orthorhombic point group $D_{2h}=D_2\times C_I$, $C_I=\{E,I\}$ is a cyclic group of order 2.

D_{2h}		Basis	E	C_{2z}	C_{2y}	C_{2x}	I	σ_z	σ_y	σ_x
A_g	Γ_1^+	x^2, y^2, z^2	1	1	1	1	1	1	1	1
B_{1g}	Γ_2^+	xy	1	1	−1	−1	1	1	−1	−1
B_{2g}	Γ_3^+	xz	1	−1	1	−1	1	−1	1	−1
B_{3g}	Γ_4^+	yz	1	−1	−1	1	1	−1	−1	1
A_u	Γ_1^-	xyz	1	1	1	1	−1	−1	−1	−1
B_{1u}	Γ_2^-	z	1	1	−1	−1	−1	−1	1	1
B_{2u}	Γ_3^-	y	1	−1	1	−1	−1	1	−1	1
B_{3u}	Γ_4^-	x	1	−1	−1	1	−1	1	1	−1

Symmetry operations on functions of coordinates

Consider a rotation by the angle α in the (x,y) plane,

$$\begin{bmatrix} x' \\ y' \end{bmatrix} = \begin{bmatrix} x\cos\alpha - y\sin\alpha \\ x\sin\alpha + y\cos\alpha \end{bmatrix} = R(\alpha)\begin{bmatrix} x \\ y \end{bmatrix}, \quad R(\alpha) = \begin{bmatrix} \cos\alpha & -\sin\alpha \\ \sin\alpha & \cos\alpha \end{bmatrix}, \quad R^{-1}(\alpha) = \begin{bmatrix} \cos\alpha & \sin\alpha \\ -\sin\alpha & \cos\alpha \end{bmatrix}.$$

This transformation of the coordinates transforms also their functions, $f(x,y)$, such as $f_1(x,y)=x$, $f_2(x,y)=x^2+y^2$, $f_3(x,y)=x^2-y^2$, $f_4(x,y)=xy$, $f_5(x,y)=x^3-3xy^2$,...
The transformed function values are given by

$$f'(x',y') = f(x,y),$$

and the transformed function results from the original one by the action of an operator P_R (acting on functions):

$$f' = P_R f, \quad P_R f(x',y') = f(x,y) = f(x'\cos\alpha + y'\sin\alpha, y'\cos\alpha - x'\sin\alpha).$$

The explicit form for the transformed function is therefore

$$P_R f(x,y) = f(x\cos\alpha + y\sin\alpha, y\cos\alpha - x\sin\alpha).$$

Symmetry operations on functions of coordinates

The rotation R_α transforms the complex-valued function $f_{c1}(x,y)=x+iy$ into

$$P_R f_{c1}(x,y) = x\cos\alpha + y\sin\alpha + i(y\cos\alpha - x\sin\alpha) = e^{-i\alpha} f_{c1}(x,y).$$

With $f_2(x,y)=x^2+y^2$, $f_3(x,y)=x^2-y^2$, $f_4(x,y)=xy$, we obtain the following examples of the transformations:

$$f_2' = x^2 + y^2 = f_2,$$

$$f_4' = -\cos\alpha\sin\alpha(x^2 - y^2) + (\cos^2\alpha - \sin^2\alpha)xy = -\cos\alpha\sin\alpha\, f_3 + (\cos^2\alpha - \sin^2\alpha)\, f_4.$$

Symmetry operations on functions of coordinates

For any transformation R of the 3-dimensional vector $\boldsymbol{r}=(x,y,z)$, $\boldsymbol{r}'=R\boldsymbol{r}$, we obtain the transformed function from the generalized recipe:

$$P_R f(\boldsymbol{r}') = f(\boldsymbol{r}) = f(R^{-1}\boldsymbol{r}'), \text{ i.e.,}$$

$$P_R f(\boldsymbol{r}) = f(R^{-1}\boldsymbol{r}).$$

Two successive operations R and S transform an arbitrary function f in the following way:

$$P_S P_R f(\boldsymbol{r}) = P_S[P_R f(\boldsymbol{r})] = P_S g(\boldsymbol{r}) = g(S^{-1}\boldsymbol{r}) = f(R^{-1}S^{-1}\boldsymbol{r}),$$

where $g=P_R f$.

The combined action of the operation R (applied first) and S is the product SR:

$$P_{SR} f(\boldsymbol{r}) = f[(SR)^{-1}\boldsymbol{r}] = f(R^{-1}S^{-1}\boldsymbol{r}),$$

leading to the identical result as the product $P_S P_R$. Consequently, it is possible to use the same symbol for the operations R and P_R:

$$Rf(\boldsymbol{r}) \equiv f(R^{-1}\boldsymbol{r}).$$

Basis functions of a representation

The set of independent functions f_1, f_2, ..., f_d is called a basis of a d-dimensional representation, formed by the matrices with the elements $D_{kl}(A_i)$, if

$$A_i f_l = \sum_{k=1}^{d} D_{kl}(A_i) f_k \quad \text{for any } A_i \in G.$$

This is the condition of the closure of the set of functions under the operations of the group $\boldsymbol{G}$.

Individual functions of this set are called basis functions, partners, or basis vectors.

The l-th partner results from the linear combination with the coefficients from the l-th column of the set of representation matrices; it belongs to the l-th column.

A (reducible) 3-dimensional representation of $P(3)$ can be used as the following transformation of $f_1=x$, $f_2=y$, $f_3=z$ by the elements of C_{3v}:

E

$$\begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

C_3

$$\begin{bmatrix} z \\ x \\ y \end{bmatrix} = \begin{bmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

C_3^{-1}

$$\begin{bmatrix} y \\ z \\ x \end{bmatrix} = \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

σ_1

$$\begin{bmatrix} y \\ x \\ z \end{bmatrix} = \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

σ_2

$$\begin{bmatrix} x \\ z \\ y \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

σ_3

$$\begin{bmatrix} z \\ y \\ x \end{bmatrix} = \begin{bmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

Its character is $P_3=A_1+E$, it is orthogonal to A_2 (the projection on A_2 vanishes)

	E	$3\sigma_v$	$2C_3$
P_3	3	1	0
A_1	1	1	1
A_2	1	-1	1
E	2	0	-1

The function

$$f_{A_1} = f_1 + f_2 + f_3 = x + y + z$$

remains invariant under all operations of C_{3v};

if forms a basis for the representation A_1, or it transforms as A_1.

Similarly, the functions

$$f_{E1} = (2x - y - z)/\sqrt{6}, \; f_{E2} = (y - z)/\sqrt{2}$$

form the basis for the irreducible representation E.

A basis for the representation A_2 can be obtained from polynomials of the third order:

$$f_{A_2} = x(y^2 - z^2) + y(z^2 - y^2) + z(x^2 - y^2).$$