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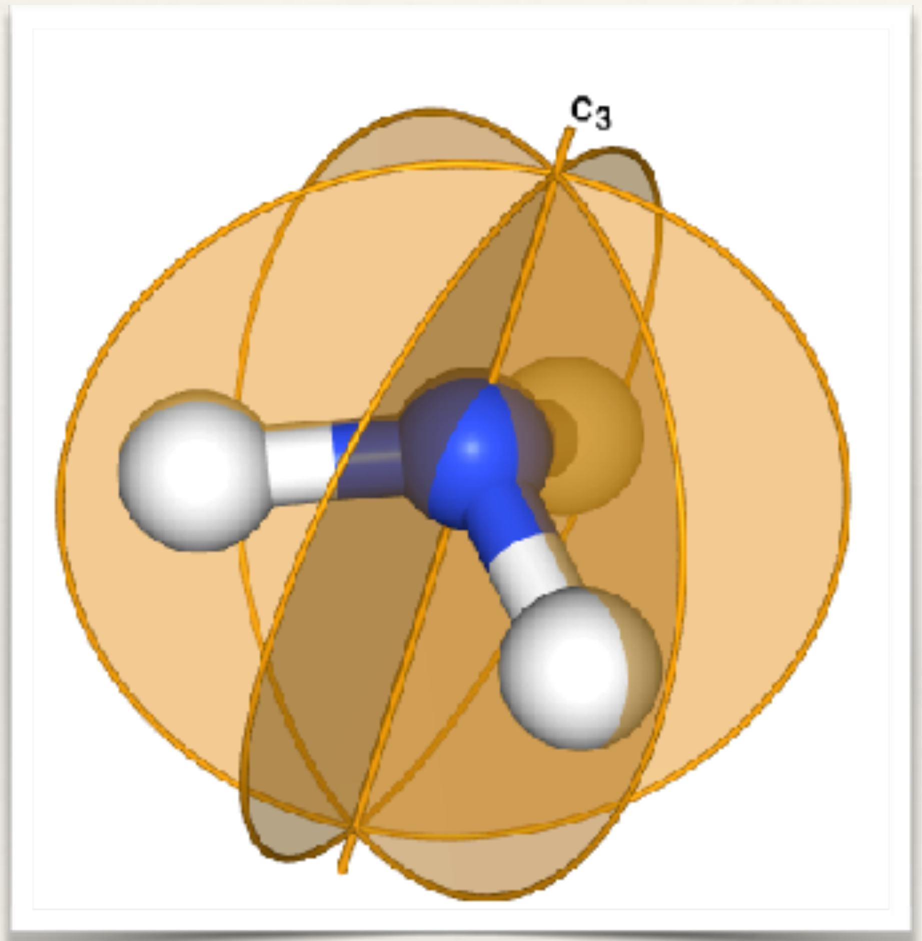
Introduction to the representation theory of molecular symmetry groups

Pere Alemany
Universitat de Barcelona

How do we use group theory in practical applications?



We know now how to detect symmetry in a molecular structure, to determine its point symmetry group, and to find all the structure of this group (multiplication table, subgroups, conjugacy classes , …)

But how do we use this knowledge in practical applications?

$C_{3v} = \{E, C_3, C_3^2, \boldsymbol{\sigma}_1, \boldsymbol{\sigma}_2, \boldsymbol{\sigma}_3]$

Group actions

If G is a group with identity element e, and X is a set, then a (left) **group action** α of G on X is a function

$$\alpha\colon G \times X \to X$$

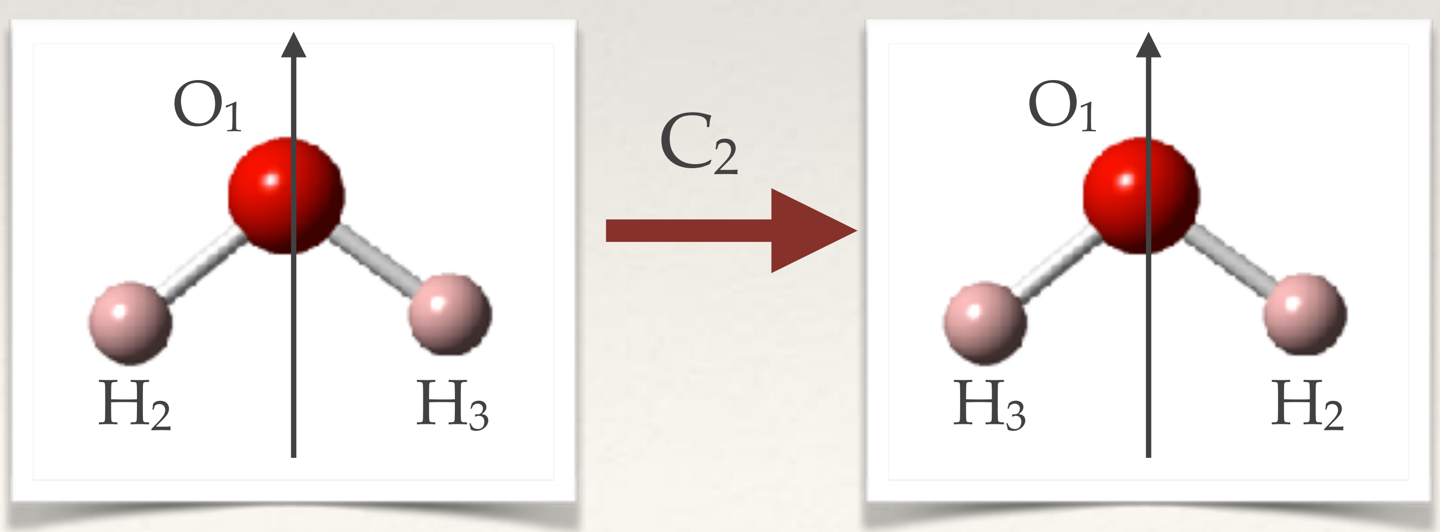
that satisfies:

$\alpha(e,x) = x$	Identity
$\alpha(g, \alpha(h,x)) = \alpha(gh, x)$	Compatibility with the operation in G

We use the notation $\alpha(g,x) = gx$ when the action is clear from the context

$X = \{O_1, H_2, H_3\}$

$G = \{E, C_2, \sigma_1, \sigma_2\}$



$C_2O_1 = O_1$

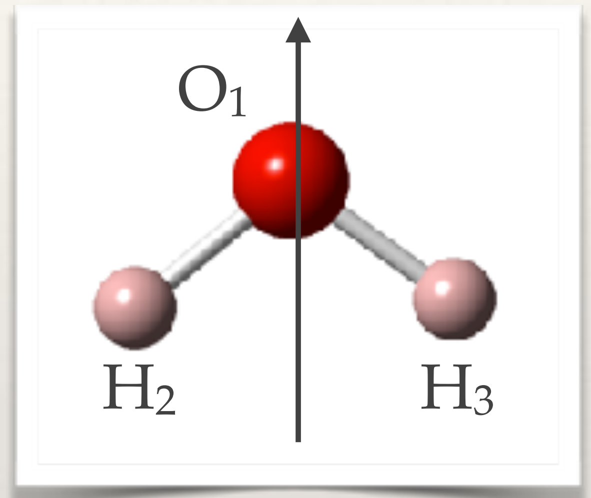
$C_2H_2 = H_3$

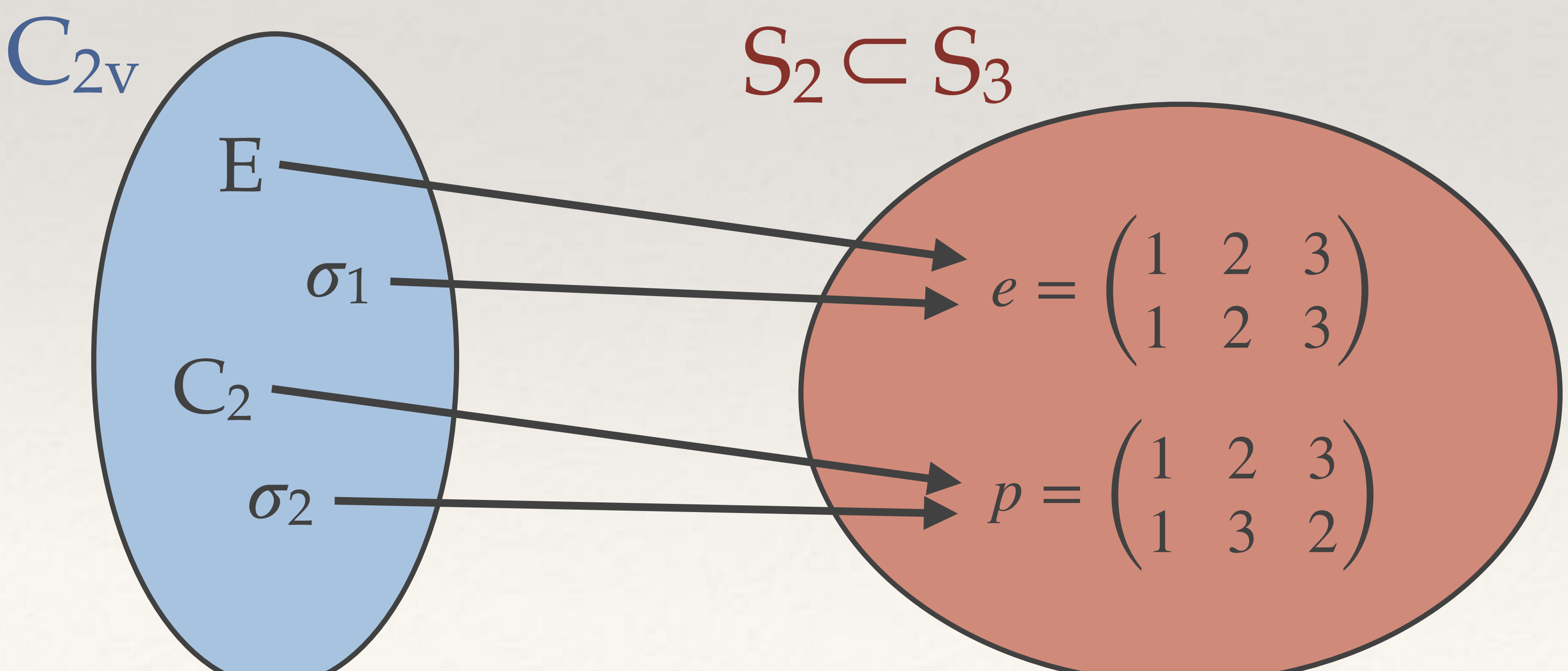
$C_2H_3 = H_2$

Permutation representation

By considering the effect of the action on the set X we can “represent” the molecular symmetry group by a group of permutations

$$X = \{O_1, H_2, H_3\}$$
$$G = \{E, C_2, \sigma_1, \sigma_2\}$$



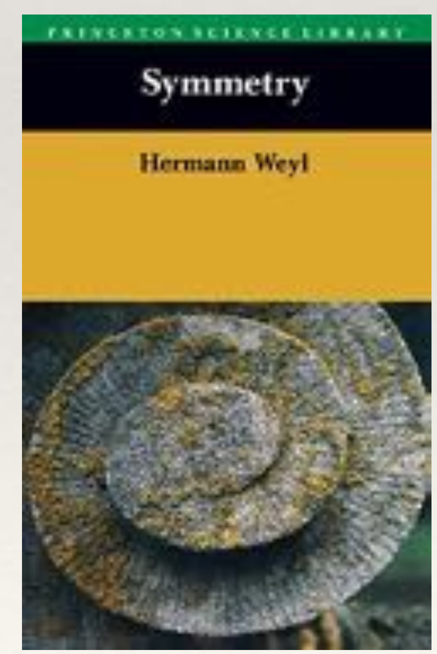


A permutation representation is a **homomorphism** between a group of symmetry operations and a group of permutations

Modern definition of symmetry

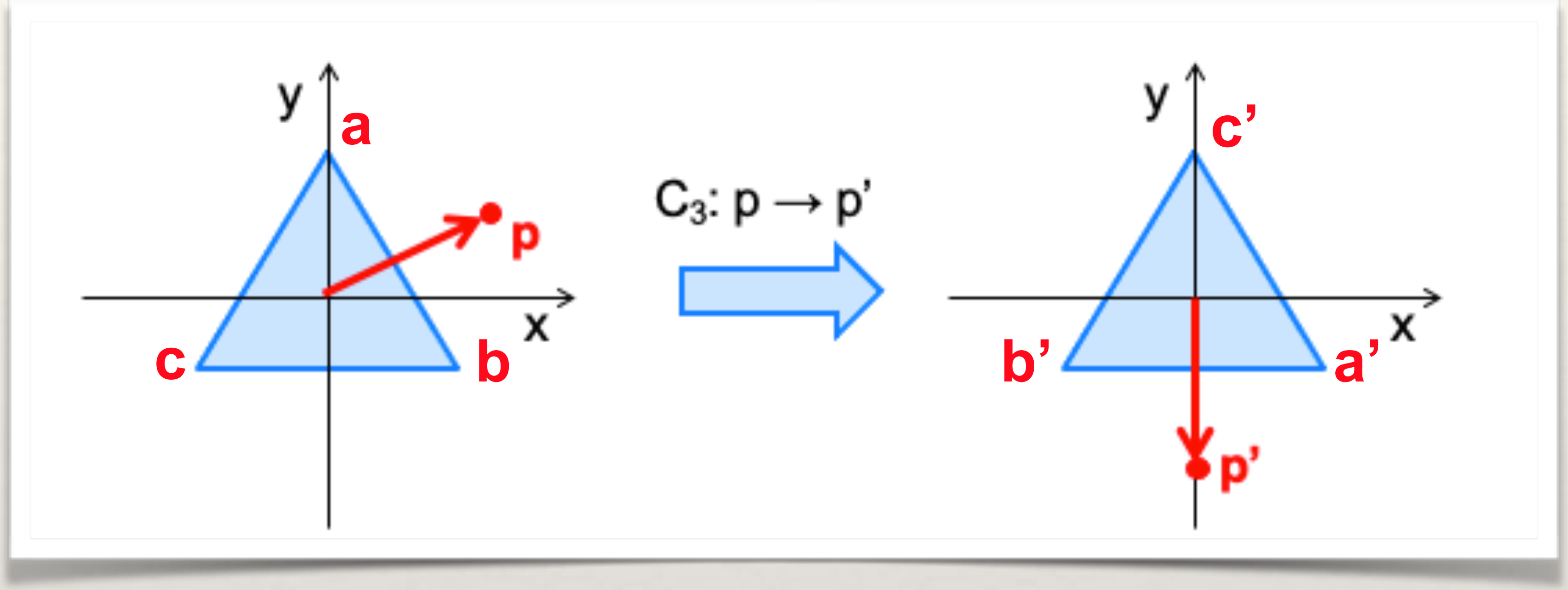
Hermann Weyl, 1885 - 1955

Given a spatial configuration $\mathfrak{F}$, those **automorphisms of space** which leave $\mathfrak{F}$ unchanged **form a group** Γ, and this group describes exactly the symmetry possessed by $\mathfrak{F}$.



Linear representations

An **automorphism** in Euclidean space is a function T: $\mathbb{R}^3 \rightarrow \mathbb{R}^3$



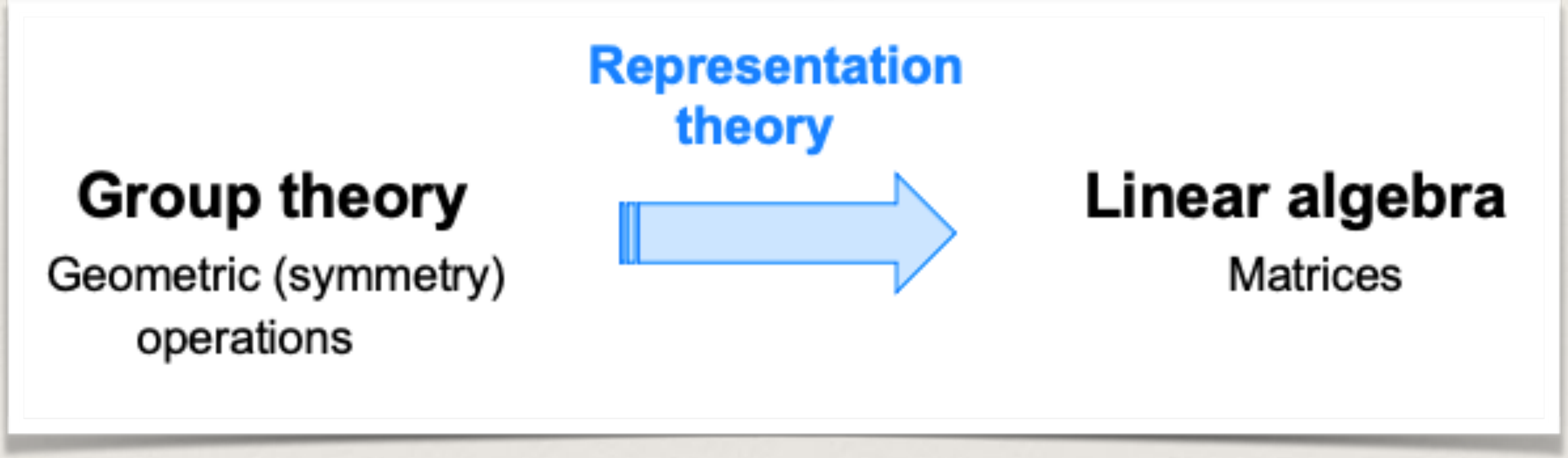
The action of a symmetry group on an object can be represented by the group of automorphisms of $\mathbb{R}^3$ leaving the object unchanged. The endomorphism:

$$\Gamma : G \rightarrow GL(\mathbb{R}^3)$$

where $GL(\mathbb{R}^3)$ is the general linear group (the group of all linear automorphisms of $\mathbb{R}^3$) is called a **linear representation** of G in $\mathbb{R}^3$

Why are linear representations useful?

Representation theory allows us to study the action of an abstract group by analyzing the properties of a set of matrices under matrix multiplication



Its relevance in chemistry stems from the fact that in quantum mechanics states are represented by elements of a special vector space (Hilbert space) and observables by linear operators on that space

Vector spaces

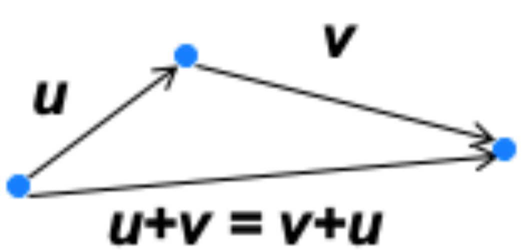
A vector space over a field F is a set V, with two operations + and · (vector addition and multiplication with a scalar) such that:

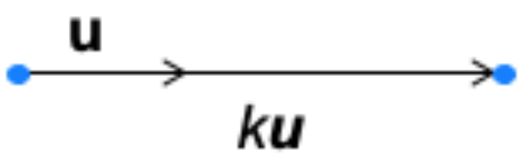
1. V is a commutative group under +
2. For any $k \in$ F and $\mathbf{v} \in$ V the product $k\mathbf{v} \in$ V with:
    - $k (\mathbf{u} + \mathbf{v}) = k\mathbf{u} + k\mathbf{b}$
    - $(k + l) \mathbf{v} = k\mathbf{v} + l\mathbf{v}$
    - $k (l\mathbf{v}) = (kl) \mathbf{v}$
    - $1\text{v} = \text{v}$

The elements of V are called vectors and those of the field F scalars. We write **0** for the neutral element of V under addition.

Examples of vector spaces

Translations with the sequential performance as addition





Set of polynomials with real coefficients

$$k(a_0 + a_1x + a_2x^2 + \ldots + a_nx^n) = ka_0 + ka_1x + ka_2x^2 + \ldots + ka_nx^n$$

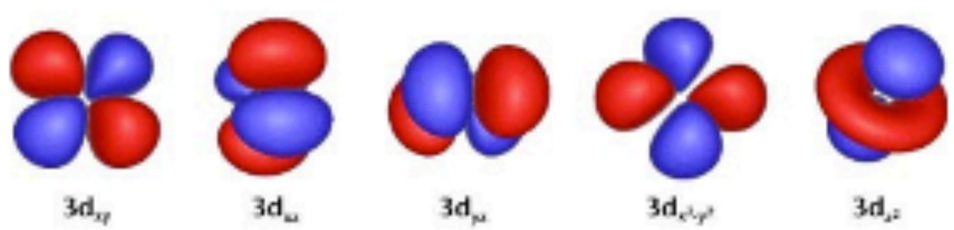
Set of *n*-tuples of real numbers R^n

$$\boldsymbol{u} = (a_1, a_2, a_3, \ldots, a_n)$$

$$(a_1, \ldots, a_n) + (b_1, \ldots, b_n) = (a_1+b_1, \ldots, a_n+b_n)$$

$$k(a_1, \ldots, a_n) = (ka_1, \ldots, ka_n)$$

Set of *d*-type hydrogenic orbitals



Since they are degenerate, any linear combination

$$\varphi = c_1(xy)+c_2(xz)+c_3(yz)+c_4(x^2-y^2) +c_5(z^2)$$

is also a solution of the Schrödinger equation with the same energy

Linear combinations of vectors

Let S = $\{\mathbf{v}_1, \mathbf{v}_2, \ldots, \mathbf{v}_n\}$ be a set of vectors in V. A combination of the type $\mathbf{w} = k_1\mathbf{v}_1+k_2\mathbf{v}_2+\ldots+k_n\mathbf{v}_n$ is called a **linear combination**.

S is **linearly independent** iff

$$k_1\mathbf{v}_1+k_2\mathbf{v}_2+\ldots+k_n\mathbf{v}_n = \mathbf{0} \quad \text{implies} \quad k_1 = k_2 = \ldots = k_n = 0$$

A linearly independent set of vectors B $=\{\mathbf{e}_1, \mathbf{e}_2, \ldots, \mathbf{e}_n\}$ that span the whole space is called a basis of V. Any vector in V is expressed as a unique linear combination $\mathbf{w} = k_1\mathbf{e}_1+k_2\mathbf{e}_2+\ldots+k_n\mathbf{e}_n$ of the basis vectors.

Bases are not unique, but they have, however, the same number n of independent vectors and n is called the dimension of V.

Expression of a vector in a basis

Vectors are uniquely defined entities but changing the basis we may change the mode of describing them. In order to avoid confusions we will introduce a new notation:

$\mathbf{v}$, $\mathbf{u}$, $\mathbf{w}$ vectors in $\mathbb{R}^n$
$v_1, v_2, \ldots, v_n$ components of a vector
$\mathbf{e}_1, \mathbf{e}_2, \ldots, \mathbf{e}_n$ basis set for $\mathbb{R}^n$

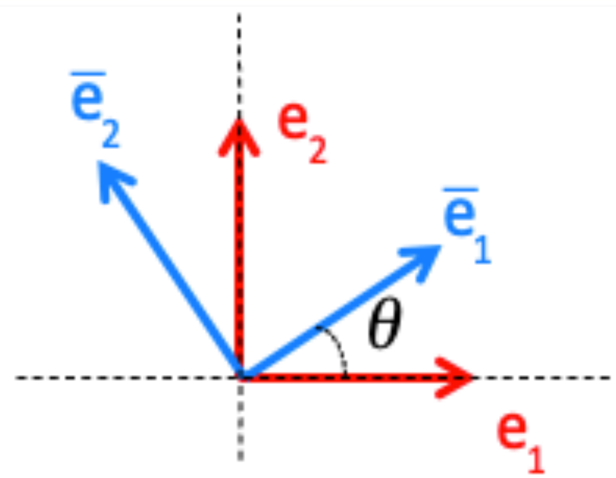
$$\mathbf{v} = \mathbf{e}_1 v_1 + \ \ldots \ + \mathbf{e}_n v_n = \sum_{i=1}^{n} \mathbf{e}_i v_i$$

$$\mathbf{v} = \begin{pmatrix} \mathbf{e}_1 & \mathbf{e}_2 & \ldots & \mathbf{e}_n \end{pmatrix} \begin{pmatrix} v_1 \\ v_2 \\ \vdots \\ v_n \end{pmatrix} = \mathbf{e}\,\mathbf{v}$$

row matrix of vectors

column matrix of components

Basis change: effect on vectors

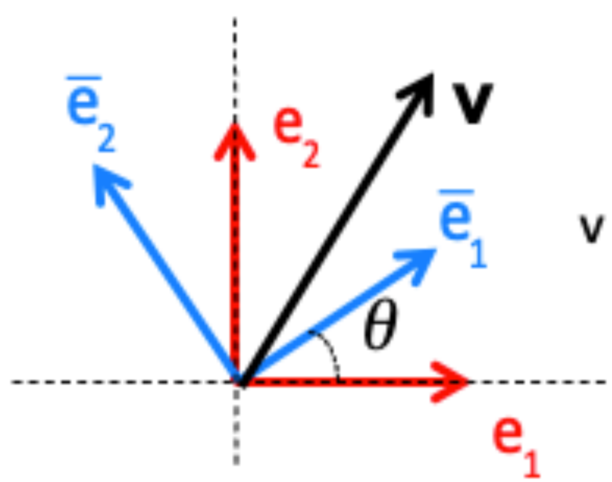


$$\bar{e}_1 = \cos\theta \cdot e_1 + \sin\theta \cdot e_2$$

$$\bar{e}_2 = -\sin\theta \cdot e_1 + \cos\theta \cdot e_2$$

$$(\bar{e}_1\ \bar{e}_2) = (e_1\ e_2)\underbrace{\begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix}}_{\mathbf{T}}$$

$$(e_1\ e_2) = (\bar{e}_1\ \bar{e}_2)\underbrace{\begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix}}_{\mathbf{T}^{-1}}$$



$$v = \underbrace{(e_1\ e_2)\begin{pmatrix} v_1 \\ v_2 \end{pmatrix}}_{\mathbf{e}\,\mathbf{v}} = \underbrace{(\bar{e}_1\ \bar{e}_2)\begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix}\begin{pmatrix} v_1 \\ v_2 \end{pmatrix}}_{\bar{\mathbf{e}}\,\mathbf{T}^{-1}\,\mathbf{v}} = \underbrace{(\bar{e}_1\ \bar{e}_2)\begin{pmatrix} \bar{v}_1 \\ \bar{v}_2 \end{pmatrix}}_{\bar{\mathbf{e}}\,\bar{\mathbf{v}}}$$

Linear transformations

If U and V are vector spaces over a field F, a function $h : U \rightarrow V$ is a homomorphism if it satisfies the following conditions:

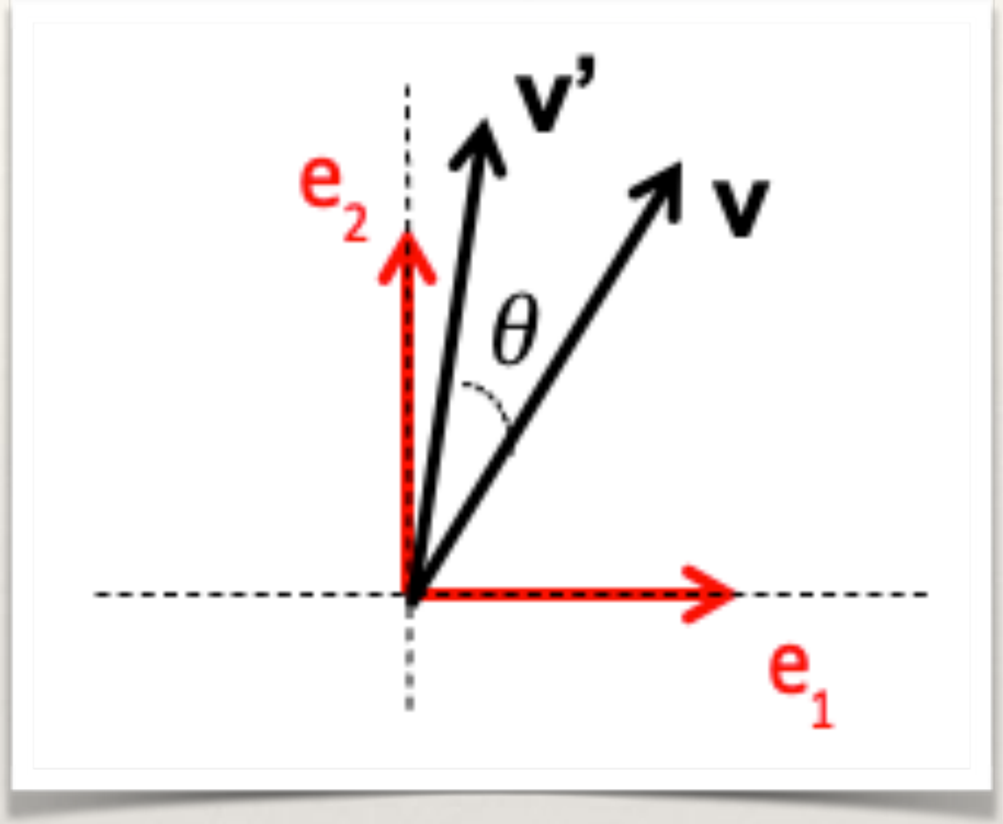
$$h(\mathbf{a}+\mathbf{b}) = h(\mathbf{a}) + h(\mathbf{b})$$
$$h(k\mathbf{a}) = k \cdot h(\mathbf{a})$$

A homomorphism between vector spaces is called a linear transformation, When V = U the map is called a linear operator or an endomorphism of V. An endomorphism that is also an isomorphism, is called an automorphism.

The set of automorphisms of a vector space *Aut*(V) with the sequential composition as operation has the structure of a group called the general linear group of V, written as GL(V).

Effect of a linear transformation

A linear transformation h: V → V sends each vector **v** into another vector **v′** = h(**v**).



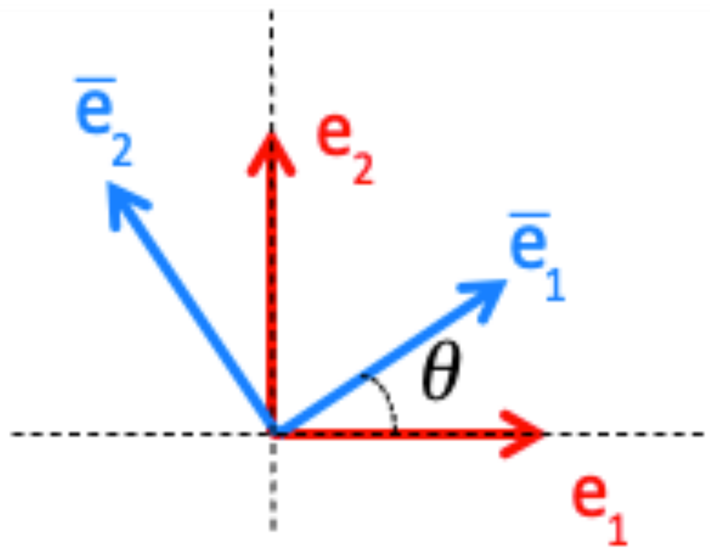
The effect of the transformation on the components of **v** is described by a square matrix: **v′** = **T v**

$$\begin{pmatrix} v'_1 \\ v'_2 \end{pmatrix} = \begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} v_1 \\ v_2 \end{pmatrix}$$

Counterclockwise rotation by θ around the origin

Transformation matrices

The transformation matrix is fully determined by looking at the effect of the transformation on a set of basis vectors



$$\bar{e}_1 = \cos\theta \cdot e_1 + \sin\theta \cdot e_2$$

$$\bar{e}_2 = -\sin\theta \cdot e_1 + \cos\theta \cdot e_2$$

$$\left(\bar{e}_1 \; \bar{e}_2\right) = \left(e_1 \; e_2\right) \underbrace{\begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix}}_{\mathbf{T}}$$

$$\left(e_1 \; e_2\right) = \left(\bar{e}_1 \; \bar{e}_2\right) \underbrace{\begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix}}_{\mathbf{T}^{-1}}$$

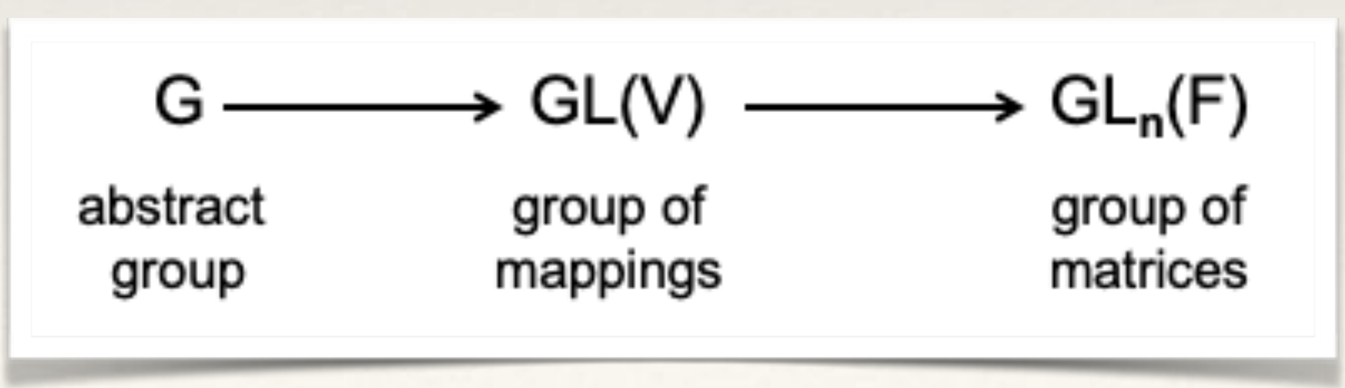
Matrix representations of groups

The effect of a linear transformation is completely determined by its effect upon *n* independent basis vectors:

$$\mathbf{e} \rightarrow \bar{\mathbf{e}} = \mathbf{e}\mathbf{R} \quad \Rightarrow \quad \mathbf{v} \rightarrow \mathbf{v}' = \mathbf{R}\,\mathbf{v}$$

This is a one-to-one association between the mapping a matrix (the actual matrix depends on the basis choice). For a whole set of mappings {A, B, … } each one will have its corresponding matrix {**A**, **B**, … }.

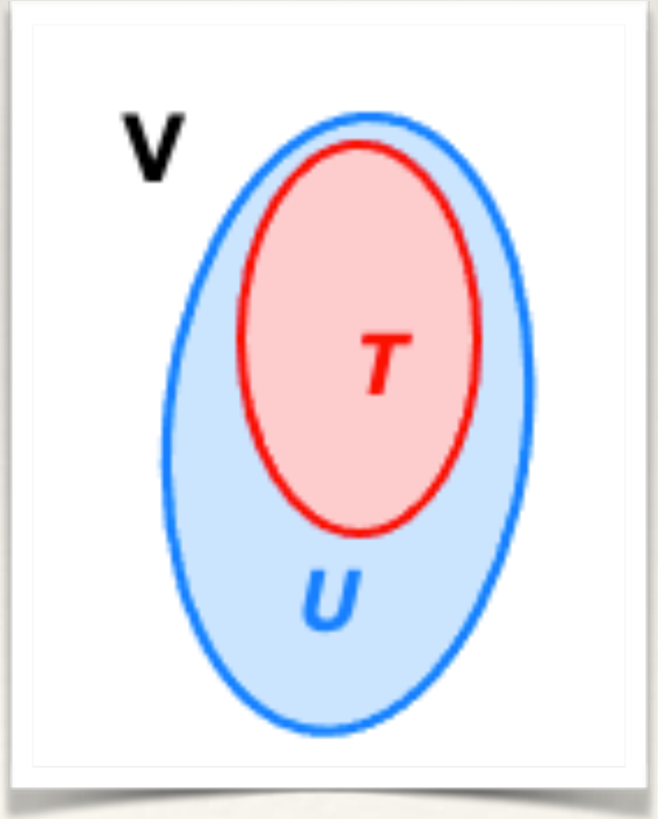
A **matrix representation** of a finite group G on a vector space V over a field F is a group homomorphism from G to $GL_n(F)$, the group of n x n invertible matrices with entries in F.



Decomposition of vector spaces

Let T and U be subspaces of V. The **sum** of T and U, denoted by T+U, is the set of all vectors **t**+**u** where **t** ∈ T and **u** ∈ U

If V = T + U and T ∩ U = {**0**}, then V is said to be the **direct sum** of T and U, written as T⊕U



V = T⊕U iff every vector **v** ∈ V can be written, in a **unique manner**, as a sum **v** = **t** + **u** where **t** ∈ T and **u** ∈ U

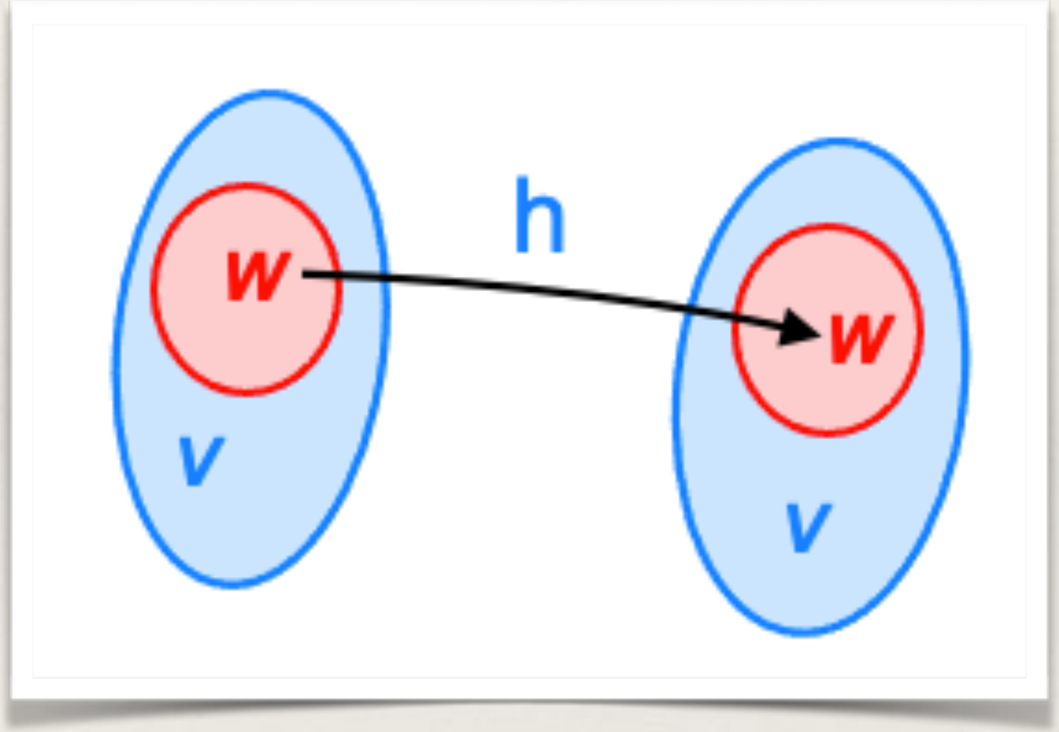
Example:

XY = sp {(1,0,0), (0,1,0)} and Z = sp {(0,0,1)}

$$\mathbb{R}^3 = XY \oplus Z$$

Invariant subspaces

A subspace W of a vector space V is said to be invariant under a linear transformation $h : V \to V$ if $h(\mathbf{w})$ is contained in W for any $\mathbf{w} \in W$



Example

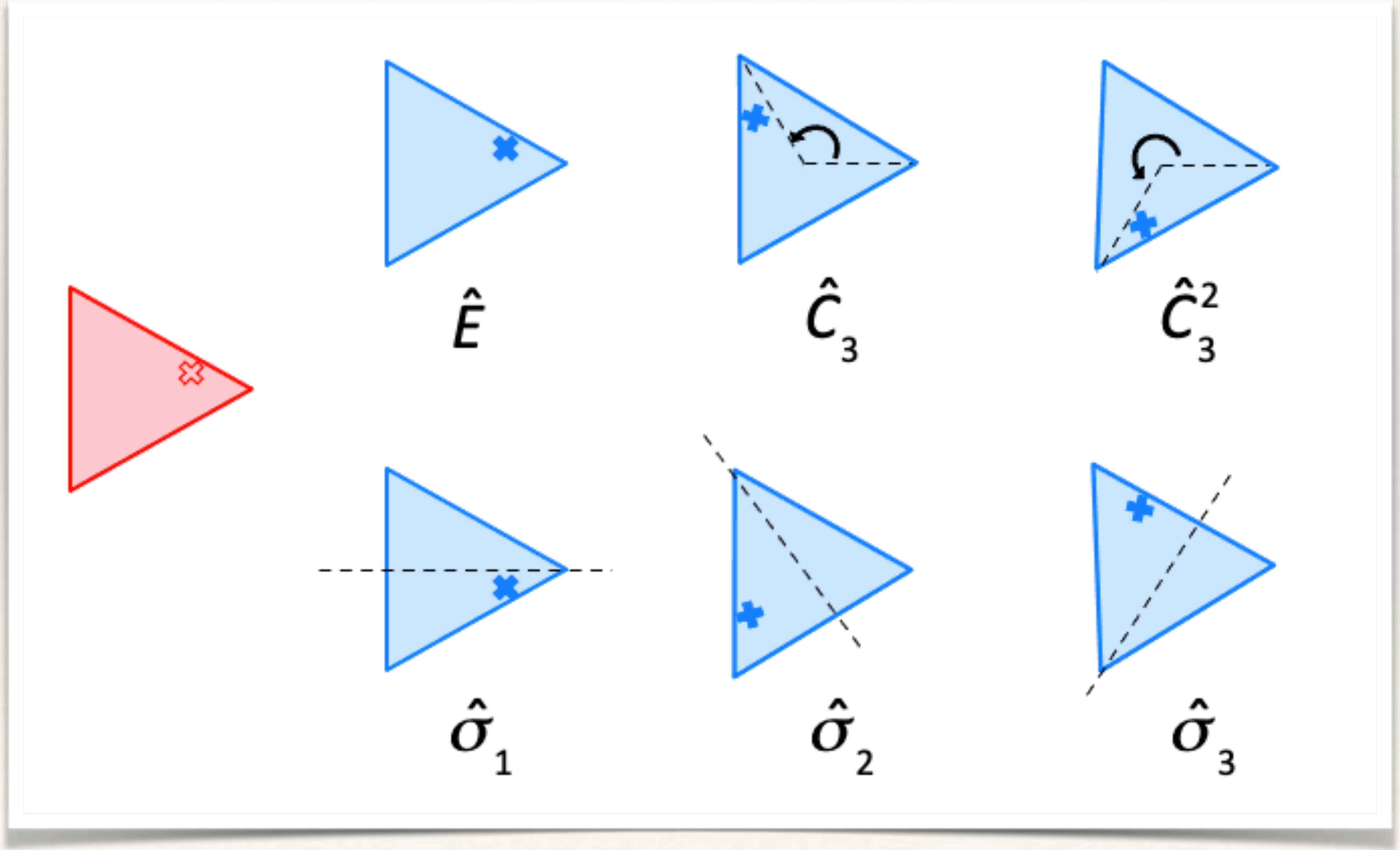
Consider a C_n rotation around the z axis in $\mathbb{R}^3$

Any vector (0,0,z) will be carried to (0,0,z) by the rotation, while any vector (x,y,0) will be carried to a (x′,y′,0) vector

In this case, $W_1 = \{ (0,0,z) \}$ and $W_2 = \{ (x,y,0) \}$ are invariant subspaces of $\mathbb{R}^3$ under the C_n rotation

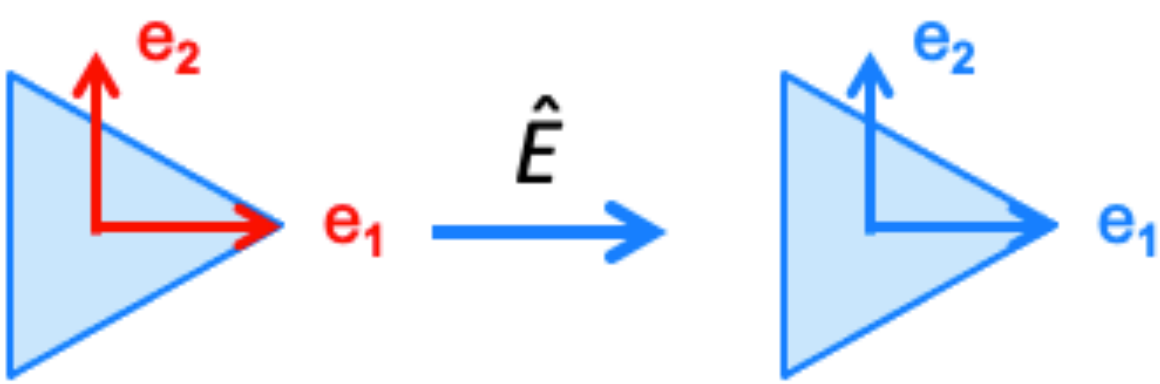
Constructing representations for C_{3v} in $\mathbb{R}^2$

Let us consider a 2-D equilateral triangle and the transformations that bring it to self-coincidence

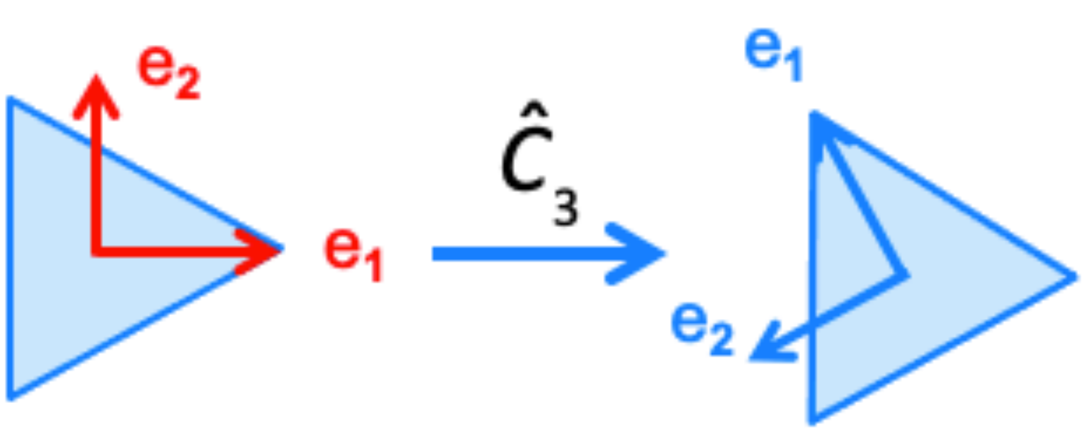


Transformation matrices

Now we look at the effect of these operations on a basis for $\mathbb{R}^2$:



$$(e_1\ e_2) = (e_1\ e_2)\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$



$$(e_1\ e_2) = (e_1\ e_2)\begin{pmatrix} \cos(120^\circ) & -\sin(120^\circ) \\ \sin(120^\circ) & \cos(120^\circ) \end{pmatrix}$$

$$= (e_1\ e_2)\begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix}$$

A 2-dimensional representation for C_{3v}

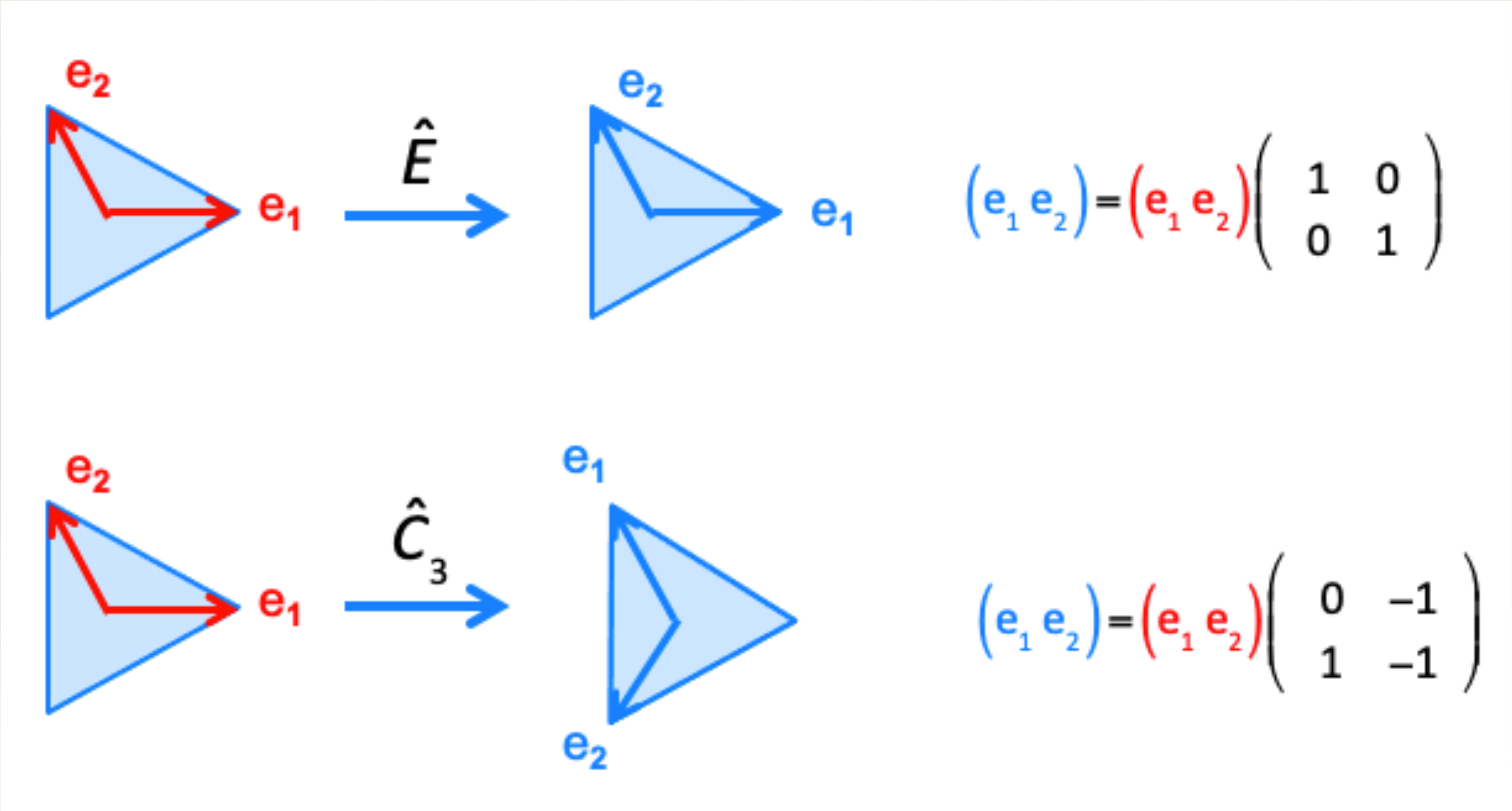
Working out all the matrices associated with the symmetry operations
In the group we find:

$$\hat{E} \rightarrow \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad \hat{C}_3 \rightarrow \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \qquad \hat{C}_3^2 \rightarrow \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$$

$$\hat{\sigma}_1 \rightarrow \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \qquad \hat{\sigma}_2 \rightarrow \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix} \qquad \hat{\sigma}_3 \rightarrow \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$$

Effect of basis changes on representations

Let's take a look at the representation that we obtain for another basis of $\mathbb{R}^2$:



2-D representations for C_{3v}

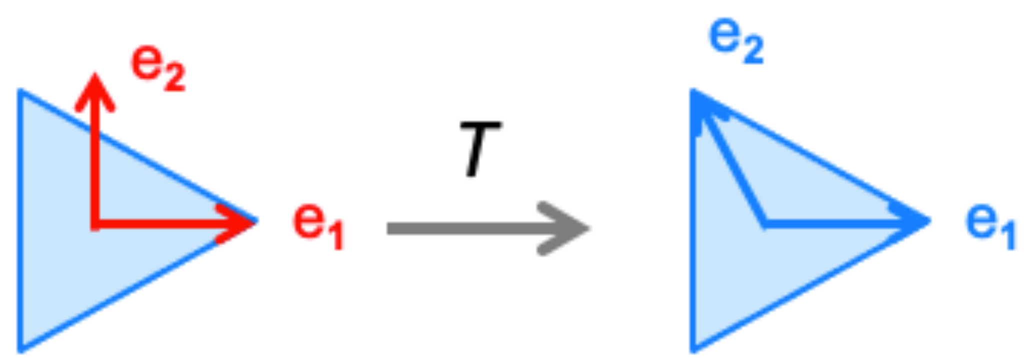
Using different basis sets for $\mathbb{R}^2$ we arrive to two different 2-dim matrix representations for C_{3v}:

$\hat{E}$	$\hat{C}_3$	$\hat{C}_3^2$	$\hat{\sigma}_1$	$\hat{\sigma}_2$	$\hat{\sigma}_3$
$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix}$	$\begin{pmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & 1/2 \end{pmatrix}$	$\begin{pmatrix} -1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & 1/2 \end{pmatrix}$
$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ 1 & -1 \end{pmatrix}$	$\begin{pmatrix} -1 & 1 \\ -1 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & -1 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ -1 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$

Both sets form a group with matrix multiplication that represents the C_{3v} symmetry group in $\mathbb{R}^2$. Are they really different representations? Or do they just contain the same information in a different format?

Relation between representations

Since we have built two 2D representations for C_{3v} just by changing the basis, they must be obviously related. For the basis change we have:



$$e = e\,T$$

$$\begin{pmatrix} e_1 & e_2 \end{pmatrix} = \begin{pmatrix} e_1 & e_2 \end{pmatrix} \begin{pmatrix} 1 & -1/2 \\ 0 & \sqrt{3}/2 \end{pmatrix}$$

$$e = e\,T^{-1}$$

$$\begin{pmatrix} e_1 & e_2 \end{pmatrix} = \begin{pmatrix} e_1 & e_2 \end{pmatrix} \begin{pmatrix} 1 & \sqrt{3}/3 \\ 0 & 2\sqrt{3}/3 \end{pmatrix}$$

And for the symmetry operation R:

$$e' = e\,R$$

$$e' = e\,R$$

$$\longrightarrow \quad e' = e'\,T = e\,R\,T = e\,T^{-1}\,R\,T \quad \longrightarrow$$

$$\boxed{\begin{aligned} R &= T^{-1}\,R\,T \\ R &= T\,R\,T^{-1} \end{aligned}}$$

For example, for C_3 we find

$$\begin{pmatrix} 0 & -1 \\ 1 & -1 \end{pmatrix} = \begin{pmatrix} 1 & \sqrt{3}/3 \\ 0 & 2\sqrt{3}/3 \end{pmatrix} \begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix} \begin{pmatrix} 1 & -1/2 \\ 0 & \sqrt{3}/2 \end{pmatrix}$$

Similarity transformations

If a matrix **Q** exists such that:

$$\mathbf{Q}^{-1}\mathbf{A}\mathbf{Q} = \mathbf{B}$$

then **A** and **B** are said to be related by a similarity transformation and:

$$\det(\mathbf{A}) = \det(\mathbf{B})$$
$$\lambda\text{'s of } \mathbf{A} = \lambda\text{'s of } \mathbf{B}$$
$$\mathrm{Tr}(\mathbf{A}) = \mathrm{Tr}(\mathbf{B})$$

If for a set $\mathbf{A}' = \mathbf{Q}^{-1}\mathbf{A}\mathbf{Q}$, $\mathbf{B}' = \mathbf{Q}^{-1}\mathbf{B}\mathbf{Q}$, $\mathbf{C}' = \mathbf{Q}^{-1}\mathbf{C}\mathbf{Q}$ … then any relation between **A**, **B**, **C**, … is also satisfied between **A′**, **B′**, **C′**, …

Equivalent representations

Two matrix representations that are related by a similarity transformation are said to be **equivalent**

R	$\hat{E}$	$\hat{C}_3$	$\hat{C}_3^2$	$\hat{\sigma}_1$	$\hat{\sigma}_2$	$\hat{\sigma}_3$
D(R)	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix}$	$\begin{pmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & 1/2 \end{pmatrix}$	$\begin{pmatrix} -1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & 1/2 \end{pmatrix}$
D'(R)	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ 1 & -1 \end{pmatrix}$	$\begin{pmatrix} -1 & 1 \\ -1 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & -1 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ -1 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$
det D(R)	1	1	1	-1	-1	-1
Tr D(R)	2	-1	-1	0	0	0

Using determinants as matrix representations

Since

$$\det(\mathbf{AB}) = \det(\mathbf{A})\,\det(\mathbf{B})$$

the determinants of a matrix representation {**A**, **B**, … } of a finite group satisfy also the multiplication table of the group they form a 1-D representation (1x1 matrices) of the group:

	$\hat{E}$	$\hat{C}_3$	$\hat{C}_3^2$	$\hat{\sigma}_1$	$\hat{\sigma}_2$	$\hat{\sigma}_3$
$D_1(R)$	1	1	1	-1	-1	-1
$D_2(R)$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ 1 & -1 \end{pmatrix}$	$\begin{pmatrix} -1 & 1 \\ -1 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & -1 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ -1 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$

The trivial representation

Since 1 x 1 = 1, all groups have a trivial 1-D representation, called the totally symmetric representation, that associates 1 to each element in the group:

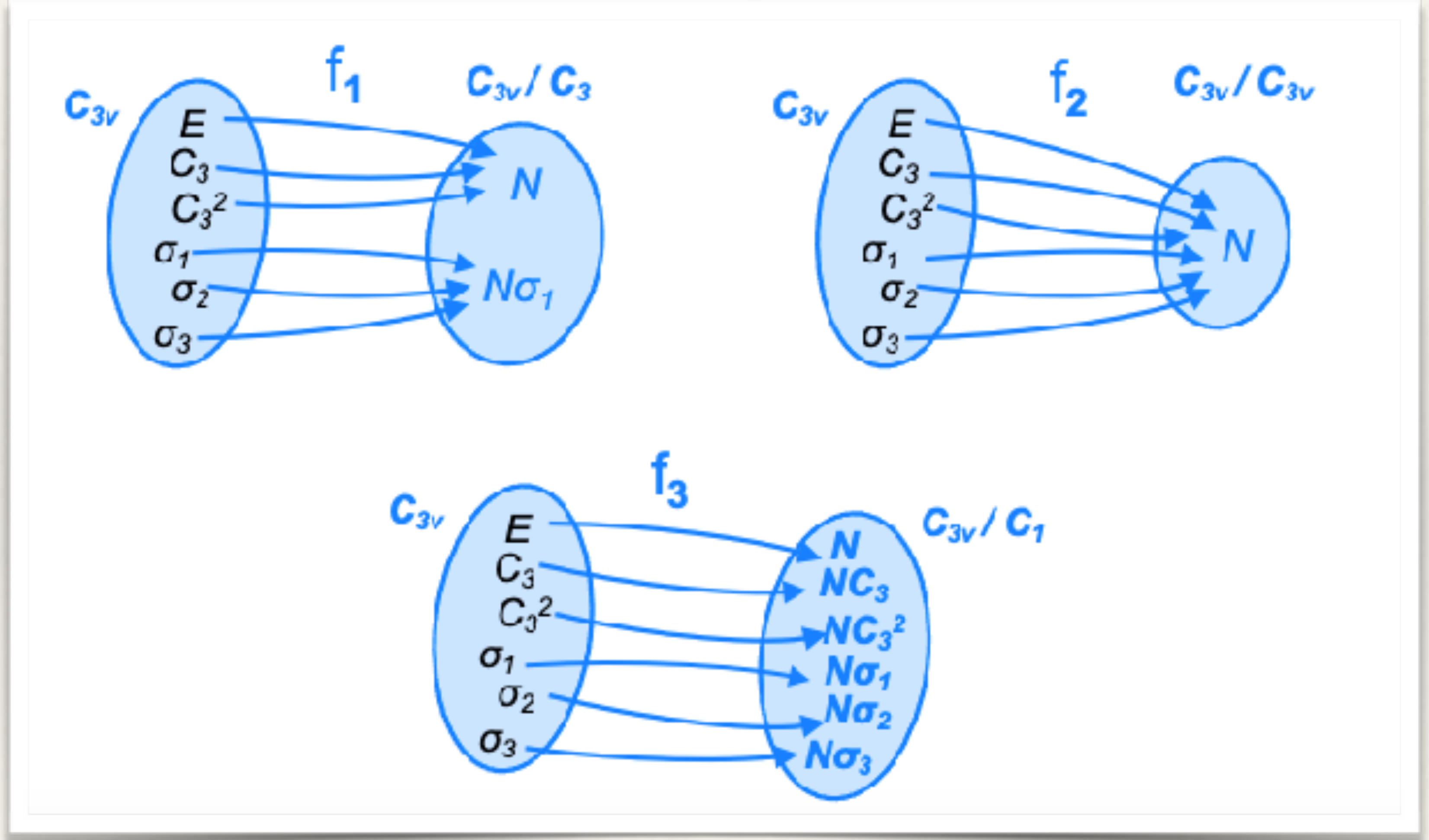
	$\hat{E}$	$\hat{C}_3$	$\hat{C}_3^2$	$\hat{\sigma}_1$	$\hat{\sigma}_2$	$\hat{\sigma}_3$
$D'_1(R)$	1	1	1	1	1	1

We can build n-D versions of the trivial representation using the *n*×*n* identity matrix, but all contain the same information:

$D^{TS}_3(R)$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$

Representations and the FHT

C_{3v} has 3 normal subgroups and the FHT states that there are only three possible different homomorphic images of C_{3v}

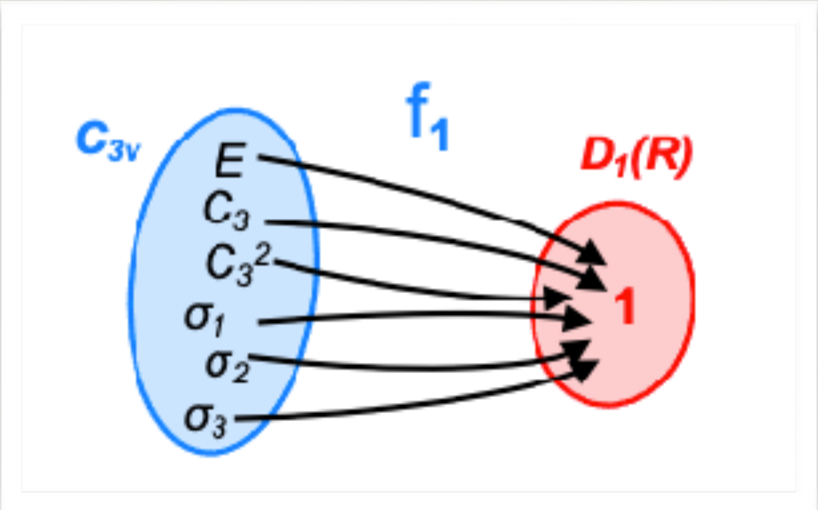


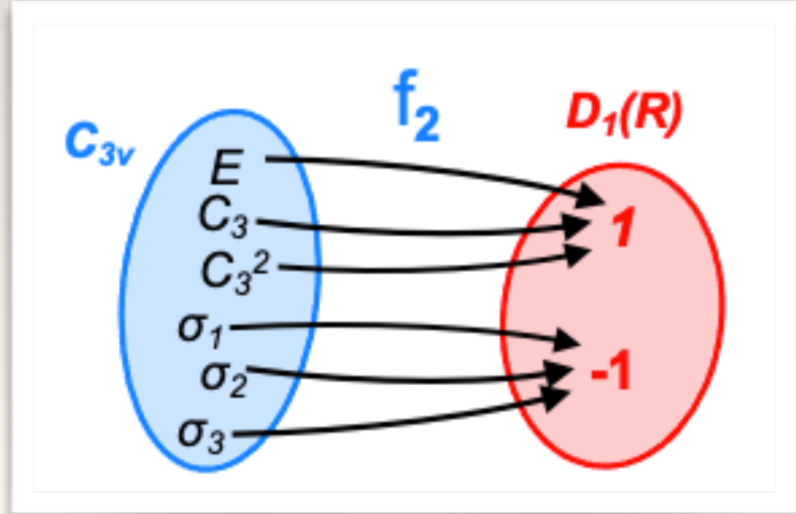
Since representations are group homomorphisms, there are only 3 really different representations for C_{3v}

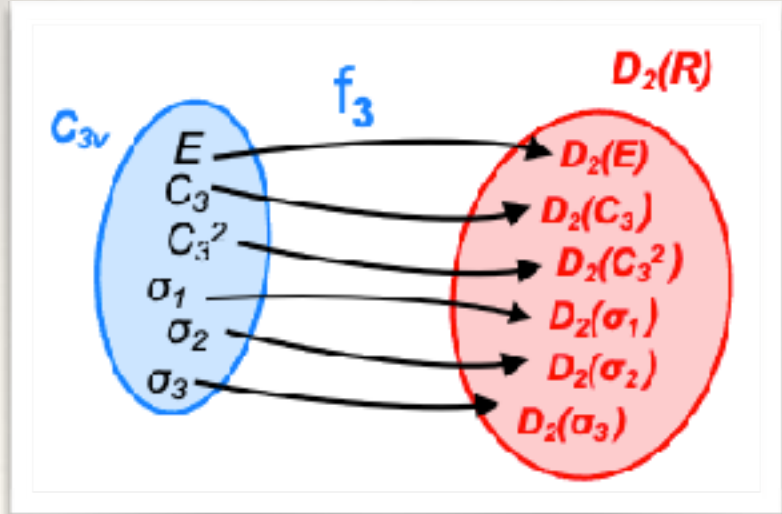
Matrix representations for C_{3v}

The three fundamentally different representations of C_{3v} are:

	$\hat{E}$	$\hat{C}_3$	$\hat{C}_3^2$	$\hat{\sigma}_1$	$\hat{\sigma}_2$	$\hat{\sigma}_3$
$D_1(R)$	1	1	1	1	1	1
$D'_1(R)$	1	1	1	-1	-1	-1
$D_1(R)$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix}$	$\begin{pmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & 1/2 \end{pmatrix}$	$\begin{pmatrix} -1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & 1/2 \end{pmatrix}$



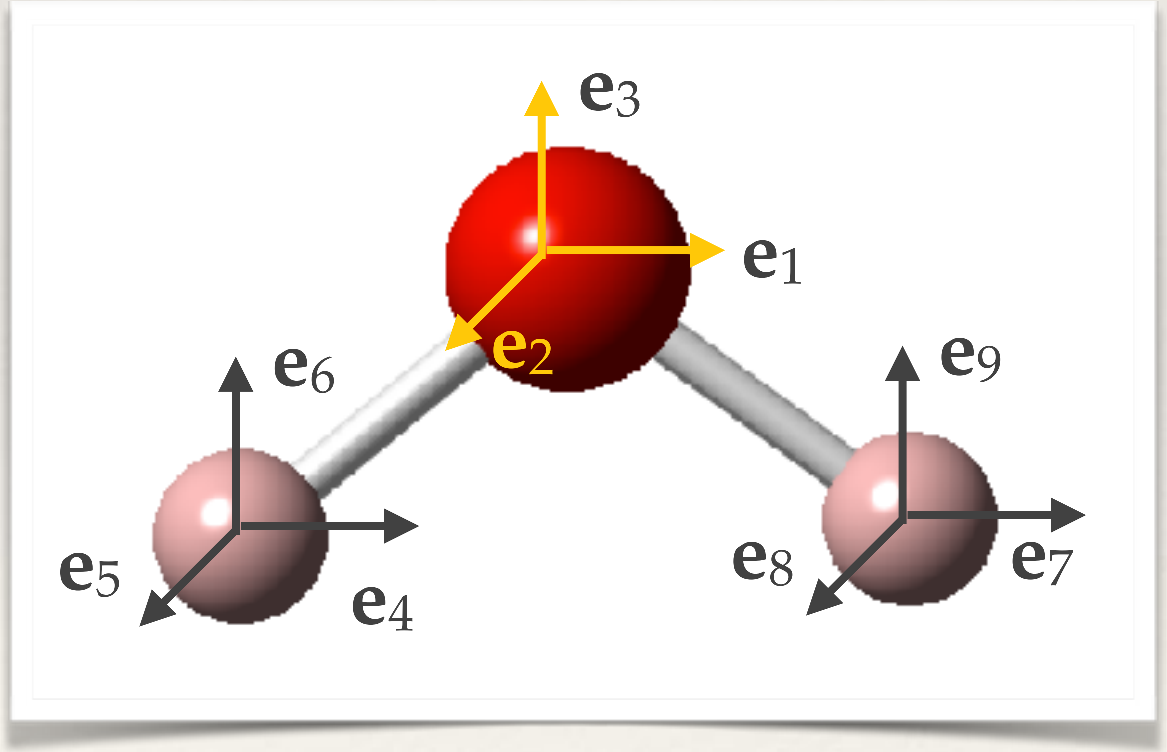




The Γ_{3N} representation for a molecule

Considering a molecular structure with N atoms we can build a 3N-dimensional vector space V whose basis are the elemental $\mathbf{e}_x$, $\mathbf{e}_y$, $\mathbf{e}_z$ cartesian displacements for each of the atoms.

Warning: V is not the same as $\mathbb{R}^{3N}$

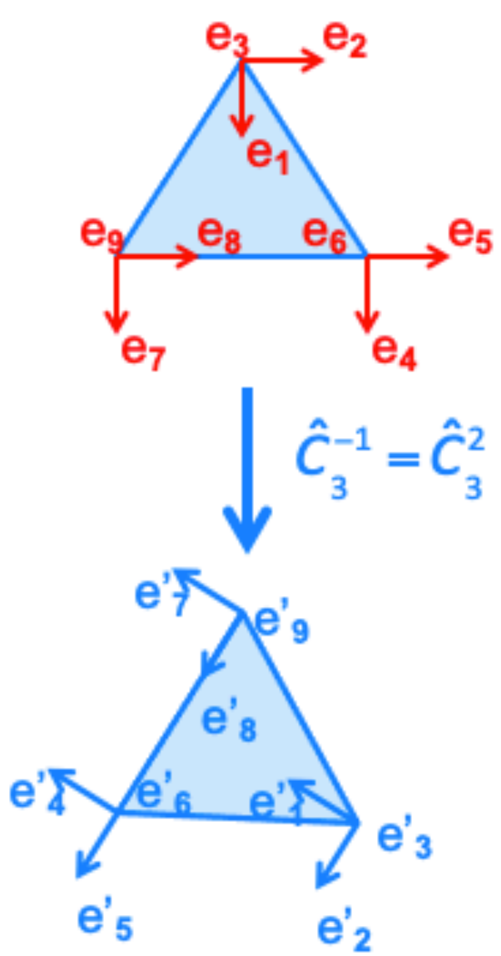


The action of the symmetry group G on V is restricted to linear combinations of displacements on sets of equivalent atoms, partitioning V in invariant subspaces:

$$V = V_O \oplus V_H$$

Building the Γ_{3N} representation

To obtain the Γ_{3N} representation we just need to find out the effects of each operation in G on the basis set $\{e_1, e_2, e_3, \ldots, e_{3N}\}$ and build the corresponding matrices



$$e'_1 = \hat{C}_3^2\, e_1 = -e_4/2 - (\sqrt{3}/2)\, e_5$$
$$e'_2 = \hat{C}_3^2\, e_2 = (\sqrt{3}/2) e_4 - e_5/2$$
$$e'_3 = \hat{C}_3^2\, e_3 = e_6$$
$$e'_4 = \hat{C}_3^2\, e_4 = -e_7/2 - (\sqrt{3}/2)\, e_8$$
$$e'_5 = \hat{C}_3^2\, e_5 = (\sqrt{3}/2) e_7 - e_8/2$$
$$e'_6 = \hat{C}_3^2\, e_6 = e_9$$
$$e'_7 = \hat{C}_3^2\, e_7 = -e_1/2 - (\sqrt{3}/2)\, e_2$$
$$e'_8 = \hat{C}_3^2\, e_8 = (\sqrt{3}/2) e_1 - e_2/2$$
$$e'_9 = \hat{C}_3^2\, e_9 = e_3$$

In this example, the in-plane and the perpendicular displacements form two invariant subspaces that partition V:

$$V = V_{\parallel} \oplus V_{\perp}$$

Building the Γ_{3N} representation

With the relations in the previous slide we can construct the matrix associated with C_3^2 in our 9-D representation

$$\begin{pmatrix} e'_1 & \cdots & e'_9 \end{pmatrix} = \begin{pmatrix} e_1 & \cdots & e_9 \end{pmatrix} \begin{pmatrix} R_{11} & \cdots & R_{19} \\ \vdots & \ddots & \vdots \\ R_{91} & \cdots & R_{99} \end{pmatrix}$$

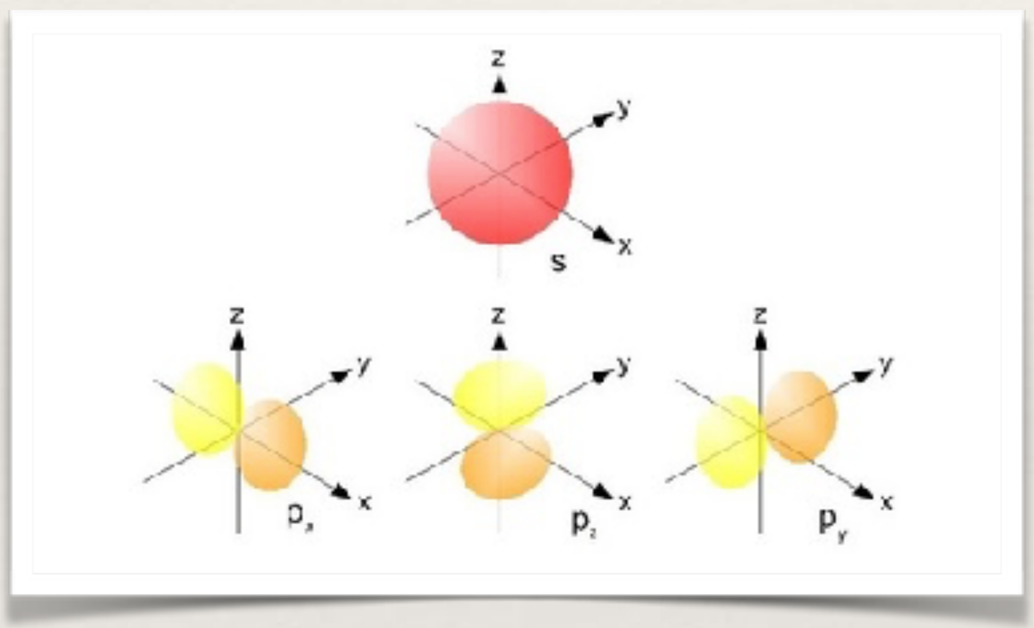
	e'_1 ↓	e'_2 ↓	e'_3 ↓	e'_4 ↓	e'_5 ↓	e'_6 ↓	e'_7 ↓	e'_8 ↓	e'_9 ↓
e_1 →	0	0	0	0	0	0	$-1/2$	$\sqrt{3}/2$	0
e_2 →	0	0	0	0	0	0	$-\sqrt{3}/2$	$-1/2$	0
e_3 →	0	0	0	0	0	0	0	0	1
e_4 →	$-1/2$	$\sqrt{3}/2$	0	0	0	0	0	0	0
e_5 →	$-\sqrt{3}/2$	$-1/2$	0	0	0	0	0	0	0
e_6 →	0	0	1	0	0	0	0	0	0
e_7 →	0	0	0	$-1/2$	$\sqrt{3}/2$	0	0	0	0
e_8 →	0	0	0	$-\sqrt{3}/2$	$-1/2$	0	0	0	0
e_9 →	0	0	0	0	0	1	0	0	0

Since operations in G interchange atoms the matrices in the Γ^{3N} representation are always built from 3x3 blocks.

In most cases we will only need the elements on the diagonal, the trace of the, matrix) so that we need only to look for each operation for atoms that do not change their position.

Obtaining representations from function spaces

Let us consider a C atom at the origin in a cartesian coordinate system and a C_n rotation around the z axis. The valence $2s$ and $2p$ orbitals form a 4-dimensional vector space from which we can obtain a representation.



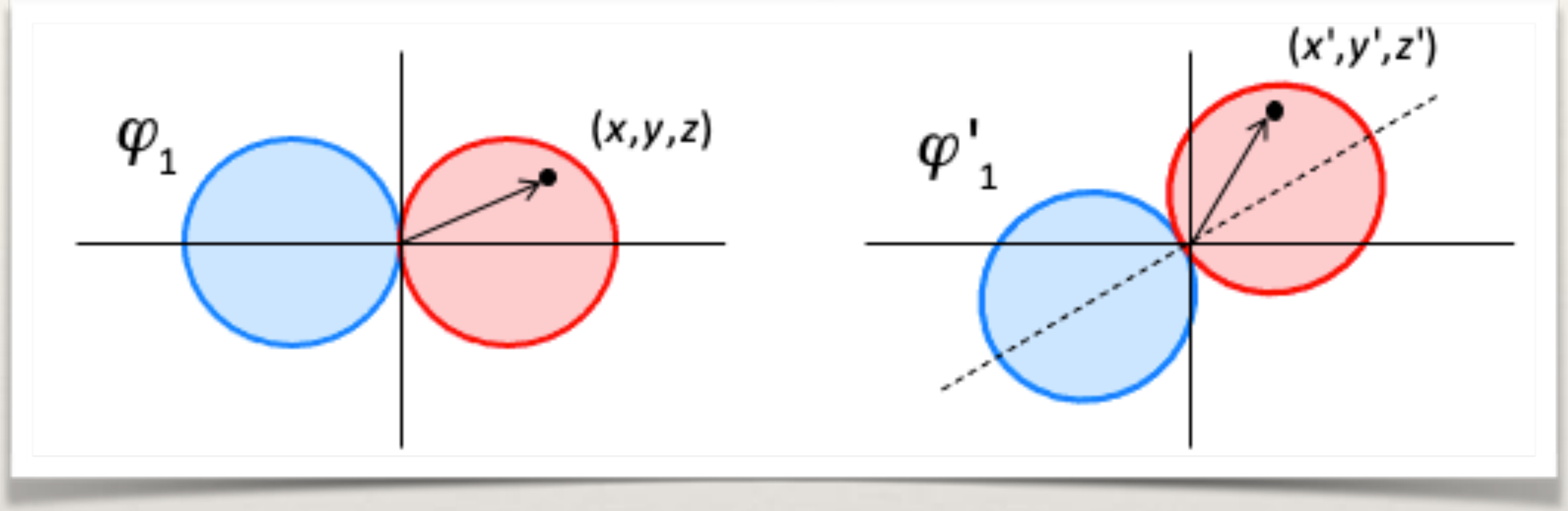
By inspection we can see that the rotation leaves the s and p_z orbitals unchanged and convert the p_x and p_y ones into ap_x+bp_y linear combinations

Since we have a partition $V = V_s \oplus V_{x,y} \oplus V_z$ the matrix for $C_n(z)$ will have a 1 + 2x2 + 1 block form

$$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & a & b & 0 \\ 0 & c & d & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

Effect of symmetry operations on functions

The symmetry operation acts on the full $\mathbb{R}^3$ space, sending each point (x,y,z) to a new point (x′,y′,z′)



The effect of the operation on $\mathbb{R}^3$ induces a new (transformed) function:

$$\hat{R}\,(x,y,z) \rightarrow (x',y',z') \qquad \hat{O}_R \varphi_1(x,y,z) = \varphi'_1(x,y,z)$$

The value of the new function at a given point in old coordinates must be the same as that of the old function at the same point in new coordinates

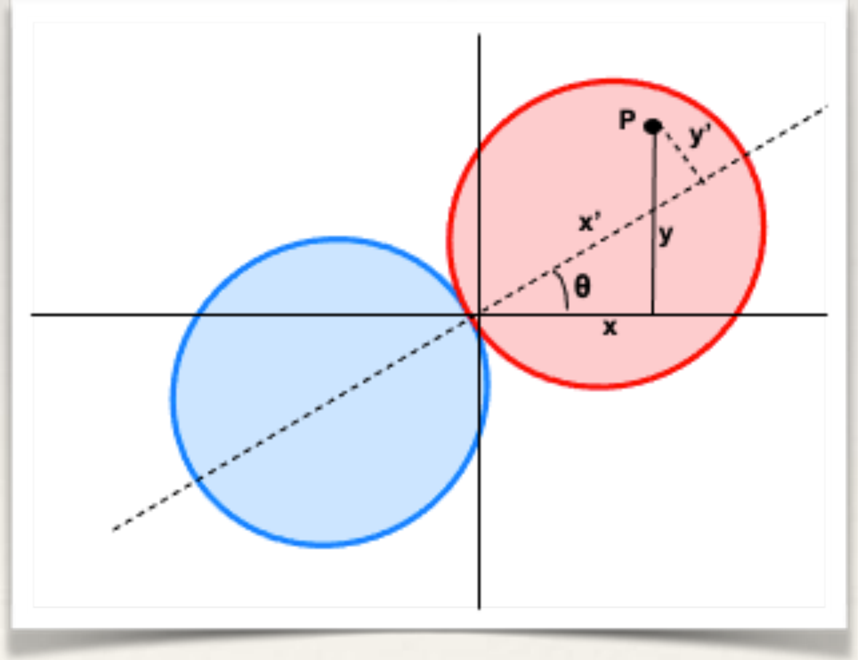
$$\varphi'_1(x,y,z) = \varphi_1(x',y',z')$$

Effect of a $C_n(z)$ rotation on p_x

The mathematical expression for the p orbitals is

$$p_x \to \varphi_1(x,y,z) = x \cdot f(r) \qquad p_y \to \varphi_2(x,y,z) = y \cdot f(r) \qquad p_z \to \varphi_3(x,y,z) = z \cdot f(r)$$

where $r = \sqrt{x^2 + y^2 + z^2}$



Using the relation

$$\varphi'_1(x,y,z) = \varphi_1(x',y',z')$$

we arrive at

$$\varphi'_1(x,y,z) = (x\cos\theta + y\sin\theta) f(r) = x\cos\theta f(r) + y\sin\theta f(r) =$$

$$= \cos\theta \cdot \varphi_1(x,y,z) + \sin\theta \cdot \varphi_2(x,y,z)$$

$C_n(z)$ matrix representation

Repeating the procedure for the other two p-type orbitals we get:

$$\varphi'_1(x,y,z) = \cos\theta \cdot \varphi_1(x,y,z) + \sin\theta \cdot \varphi_2(x,y,z)$$
$$\varphi'_2(x,y,z) = -\sin\theta \cdot \varphi_1(x,y,z) + \cos\theta \cdot \varphi_2(x,y,z)$$
$$\varphi'_3(x,y,z) = \varphi_3(x,y,z)$$

That can be expressed as a matrix equation:

functions $$\begin{pmatrix} \varphi'_1 & \varphi'_2 & \varphi'_3 \end{pmatrix} = \begin{pmatrix} \varphi_1 & \varphi_2 & \varphi_3 \end{pmatrix} \begin{pmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

translations $$\begin{pmatrix} e'_1 & e'_2 & e'_3 \end{pmatrix} = \begin{pmatrix} e_1 & e_2 & e_3 \end{pmatrix} \begin{pmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Matrix representation for C_{3v} using $V = \{p_x, p_y, p_z\}$

Applying the same technique for the other operations in C_{3v} we arrive to the following 3-dim representation:

$$\hat{E}: \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \hat{C}_3: \begin{pmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \hat{C}_3^2: \begin{pmatrix} -1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\hat{\sigma}_1: \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \hat{\sigma}_2: \begin{pmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \hat{\sigma}_3: \begin{pmatrix} -1/2 & \sqrt{3}/2 & 0 \\ \sqrt{3}/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

which is the same as the representation obtained from $V = \mathbb{R}^3$ using the standard orthonormal $\{\mathbf{e}_x, \mathbf{e}_y, \mathbf{e}_z\}$ basis