1. Historical introduction

2. The Schrödinger equation for one-particle problems

3. **Mathematical tools for quantum chemistry**

4. The postulates of quantum mechanics

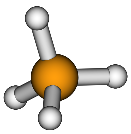
5. Atoms and the 'periodic' table of chemical elements

6. Diatomic molecules

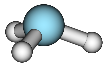
7. Ten-electron systems from the second row

8. More complicated molecules

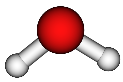
Definition of the geometrical structure of a molecule



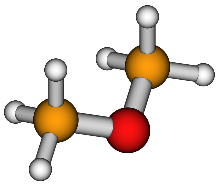
Methane
CH_4



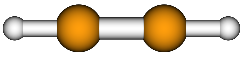
Ammonia
NH_3



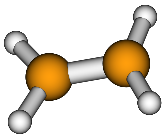
Water
H_2O



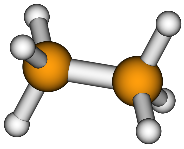
Dimethyl
ether
C_2H_6O



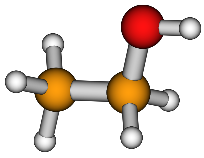
Ethyne
C_2H_2



Ethene
C_2H_4



Ethane
C_2H_6



Ethanol
C_2H_6O

The definition of molecular structure requires knowledge about type (i.e. charge number Z) and position (x, y, z) of the nuclei.

Only the relative position of the nuclei is important (translation and rigid rotation are excluded).

Two frequently used systems of coordinates are
(i) cartesian coordinates, and
(ii) Z matrix coordinates.

The Z matrix definition uses a (suitably chosen) sequence of spherical coordinate systems, and gives values for radius r, polar distance θ and azimuthal angle φ.

A position vector $\boldsymbol{R}_K$, pointing from the origin of the coordinate system to the atomic nucleus, is thus known for each nucleus K.

Coordinates for ethanol, C_2H_5OH:

Cartesian coordinates: $3N$ data for an N-atomic molecule

```
C     0.000000     0.000000     0.000000
C     0.000000     0.000000     1.450000
H     1.026719     0.000000     1.813000
H     0.513360    -0.889165    -0.363000
H    -0.513360     0.889165     1.813000
H    -1.026719     0.000000    -0.363000
H    -0.513360    -0.889165     1.813000
O     0.659967     1.143095    -0.466667
H     0.659967     1.143095    -1.413667
```

Z **matrix**: $3N-6$ data for a non-linear N-atomic molecule

```
zmat angstroms
 c
 c   1 cc2
 h   2 hc3        1 hcc3
 h   1 hc4        2 hcc4        3 dih4
 h   2 hc5        1 hcc5        4 dih5
 h   1 hc6        2 hcc6        3 dih6
 h   2 hc7        1 hcc7        4 dih7
 o   1 oc8        2 occ8        3 dih8
 h   8 ho9        1 hoc9        2 dih9
variables
cc2          1.450000
hc3          1.089000
hcc3         109.471
...
constants
oc8          1.400000
...
end
```

In our typical representations for molecules (crystals, etc.) only the nuclear coordinates have some significance (we ignore, for the moment, the nuclear motion). Everything else, like balls, sticks, ribbons, etc. is merely an eye-guide, though a very useful one.

Operators

Operators $\hat{O}$ represent mathematical instructions, or operations. These operations can be applied to suitably chosen mathematical objects, to yield new mathematical objects of the same or different kind.

Operators can be divided into classes, depending on the number of objects required for their application:

1. Unary operators require a single mathematical object:

$$\hat{O}(a) = z$$

Examples:

- f in $f(x)$, e.g. $f = (\ )^2$, $f = \sin()$, $f = \exp()$
- Important unary operators are linear operators $\hat{L}$:

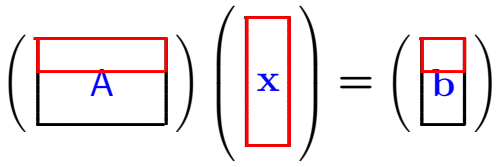
$$\hat{L}(x + y) = \hat{L}x + \hat{L}y$$

- $\hat{L} = \dfrac{\mathrm{d}}{\mathrm{d}x}$ in $f'(x) = \dfrac{\mathrm{d}f}{\mathrm{d}x}$

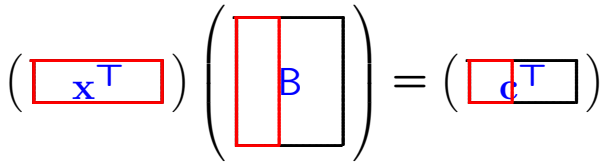
- $\hat{L} = \int \mathrm{d}x$ in $\int \mathrm{d}x\, f(x) = \int f(x)\, \mathrm{d}x$

- the matrices in matrix-vector products:

$\mathsf{A}_{(n\times m)}\, \mathbf{x}_{(m\times 1)} = \mathbf{b}_{(n\times 1)}$



$\mathbf{x}^{\mathsf{T}}_{(1\times m)}\, \mathsf{B}_{(m\times k)} = \mathbf{c}^{\mathsf{T}}_{(1\times k)}$



2. Binary operators require an ordered pair of objects:

$$\hat{O}(a, b) = z$$

Examples:

- '$+$' and '$\cdot$' in $a + b$ and $a \cdot b = a\, b$

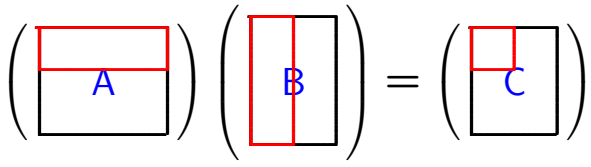
- scalar product and vector product in $\mathbb{R}^3$:

$$\mathbf{a} \cdot \mathbf{b} = a\, b\, \cos(\vartheta) = \mathbf{b} \cdot \mathbf{a} \qquad a = |\mathbf{a}|\,,\ b = |\mathbf{b}|\,,\ \vartheta = \measuredangle(\mathbf{a}, \mathbf{b})$$

$$\mathbf{a} \times \mathbf{b} = a\, b\, \sin(\vartheta)\, \mathbf{n} = -\mathbf{b} \times \mathbf{a} \qquad \mathbf{n} \cdot \mathbf{a} = 0\,,\ \mathbf{n} \cdot \mathbf{b} = 0\,,\ |\mathbf{n}| = 1$$

- matrix multiplication:

$$\begin{aligned} &\mathsf{A}_{(n\times m)} \cdot \mathsf{B}_{(m\times k)} \\ &= \mathsf{A}_{(n\times m)}\, \mathsf{B}_{(m\times k)} = \mathsf{C}_{(n\times k)} \end{aligned}$$



3. Ternary operators require an ordered triple of objects:

$$\hat{O}(a, b, c) = z$$

Examples:

- triple scalar product in $\mathbb{R}^3$:

$$\mathbf{a}\cdot(\mathbf{b}\times\mathbf{c}) = \begin{vmatrix} a_1 & a_2 & a_3 \\ b_1 & b_2 & b_3 \\ c_1 & c_2 & c_3 \end{vmatrix}$$

- triple vector product in $\mathbb{R}^3$:

$$\mathbf{a}\times(\mathbf{b}\times\mathbf{c}) = \lambda\,\mathbf{b} - \mu\,\mathbf{c}, \quad \lambda = \mathbf{a}\cdot\mathbf{c}, \quad \mu = \mathbf{a}\cdot\mathbf{b}$$

Groups

Given one set of elements $S = \{a, b, \ldots\}$ and one binary operation $\circ$.

A **group** $G = (S, \circ)$ is formed, if the following axioms hold:

1. closure: $a \circ b = c$ with $a, b, c \in G$
2. existence of a neutral element e: $e \circ a = a \circ e = a$
3. existence of inverse elements a^{-1}: $a^{-1} \circ a = a \circ a^{-1} = e$
4. associative law: $a \circ (b \circ c) = (a \circ b) \circ c$

Subgroup:
A subset of group elements, which constitutes a group (according to the criteria given above).

Order of the group:
The number of elements in the group is known as the order $g = |G|$ of the group ($g \in \mathbb{N}$, or $g = \infty$ for continuous groups).

Abelian groups:
If, in addition to the criteria given above, the commutative law $a \circ b = b \circ a$ holds (i.e. **all** elements of the group commute), the group is called a commutative (or Abelian*) group.

Some well-known examples for Abelian groups:

$$\begin{aligned} \text{integers}: &\quad (\mathbb{Z}, +) \\ \text{real numbers}: &\quad (\mathbb{R}, +)\,, \quad (\mathbb{R} \setminus \{0\}, \cdot) \end{aligned}$$

(the order g is denumerably infinite in the first case, the last two cases represent continuous groups)

Generators of a finite group:
A subset of group elements from which **all** group elements can be formed (usually, there are several possible choices for a set of generators).

*N. H. Abel (1802-1829)

Permutation groups

The permutations of n objects form a group. The rule of combination (binary operation) is 'subsequent application'.

This group is the permutation group, or symmetric group $\mathcal{S}_n$, which has order $g = n!$.

When the objects are simply the first n positive integers, a general notation for a permutation is

$$P_k = \begin{pmatrix} 1 & 2 & 3 & 4 & \dots & n \\ i_1 & i_2 & i_3 & i_4 & \dots & i_n \end{pmatrix}, \quad i_j \neq i_l\,, \quad 1 \leq k \leq n! \tag{74}$$

The neutral element in a permutation group is the 'identity permutation', which leaves all n objects at their places:

$$P_1 = \begin{pmatrix} 1 & 2 & 3 & 4 & \dots & n \\ 1 & 2 & 3 & 4 & \dots & n \end{pmatrix} = e \tag{75}$$

The next-to-trivial permutations are the permutations of pairs, or transpositions, e.g.

$$P_2 = \begin{pmatrix} 1 & 2 & 3 & 4 & \dots & n \\ 2 & 1 & 3 & 4 & \dots & n \end{pmatrix} \tag{76}$$

Another permutation, which involves already three objects, is

$$P_3 = \begin{pmatrix} 1 & 2 & 3 & 4 & \dots & n \\ 2 & 3 & 1 & 4 & \dots & n \end{pmatrix} \tag{77}$$

A shorter notation for the permutations is the notation with so-called cycles. This gives for our examples

$$P_1 = \begin{pmatrix} 1 & 2 & 3 & 4 & \dots & n \\ 1 & 2 & 3 & 4 & \dots & n \end{pmatrix} = (1)(2)(3)(4)\dots(n) = e \tag{78}$$

$$P_2 = \begin{pmatrix} 1 & 2 & 3 & 4 & \dots & n \\ 2 & 1 & 3 & 4 & \dots & n \end{pmatrix} = (12)(3)(4)\dots(n) \tag{79}$$

$$P_3 = \begin{pmatrix} 1 & 2 & 3 & 4 & \dots & n \\ 2 & 3 & 1 & 4 & \dots & n \end{pmatrix} = (123)(4)\dots(n) \tag{80}$$

Cycles of length 1 are usually omitted.

A subset of the transpositions (ij) can be taken as generators for the permutation groups, i.e. all permutations can be expressed by a sequence of transpositions. Depending on the number of transpositions involved, the permutations can be separated in **even and odd permutations**. The former require an even number of transpositions, the latter require an odd number.

Some examples for $n = 3$:

$$e = \begin{pmatrix} 1 & 2 & 3 \\ 1 & 2 & 3 \end{pmatrix} = (1)(2)(3) \qquad 0 \quad \text{(even)}$$

$$\begin{pmatrix} 1 & 2 & 3 \\ 2 & 1 & 3 \end{pmatrix} = (12) \qquad 1 \quad \text{(odd)}$$

$$\begin{pmatrix} 1 & 2 & 3 \\ 2 & 3 & 1 \end{pmatrix} = (123) = (23)(13) \qquad 2 \quad \text{(even)}$$

$$\begin{pmatrix} 1 & 2 & 3 \\ 3 & 1 & 2 \end{pmatrix} = (132) = (13)(23) \qquad 2 \quad \text{(even)}$$

Note: Start at the rightmost cycle, and work from right to left!

Permutations and functions

Given two functions, depending on the position coordinates of two particles:

$$\Psi_a(1,2) = f(\boldsymbol{r}_1)g(\boldsymbol{r}_2) - g(\boldsymbol{r}_1)f(\boldsymbol{r}_2) \tag{81}$$
$$\Psi_s(1,2) = f(\boldsymbol{r}_1)g(\boldsymbol{r}_2) + g(\boldsymbol{r}_1)f(\boldsymbol{r}_2) \tag{82}$$

How are these functions affected by the permutation $\widehat{P} = (12)$, i.e. the interchange of the particles (or particle coordinates)?

$$(12)\Psi_a(1,2) = \Psi_a(2,1) = f(\boldsymbol{r}_2)g(\boldsymbol{r}_1) - g(\boldsymbol{r}_2)f(\boldsymbol{r}_1) = -\Psi_a(1,2) \tag{83}$$
$$(12)\Psi_s(1,2) = \Psi_s(2,1) = f(\boldsymbol{r}_2)g(\boldsymbol{r}_1) + g(\boldsymbol{r}_2)f(\boldsymbol{r}_1) = +\Psi_s(1,2) \tag{84}$$

Thus, $\Psi_a(1,2)$ changes sign, or in other words, it is **antisymmetric** under this operation 'transposition of 1 and 2', whereas $\Psi_s(1,2)$ is not changed, in other words, it is **symmetric** under this operation.

The function $\Psi_a(1,2)$ can be written in the form of a determinant:

$$\Psi_a(1,2) = \begin{vmatrix} f(\boldsymbol{r}_1) & f(\boldsymbol{r}_2) \\ g(\boldsymbol{r}_1) & g(\boldsymbol{r}_2) \end{vmatrix} = \begin{vmatrix} f(\boldsymbol{r}_1) & g(\boldsymbol{r}_1) \\ f(\boldsymbol{r}_2) & g(\boldsymbol{r}_2) \end{vmatrix} \tag{85}$$

Such a 'determinant representation' is always possible for a totally antisymmetric many-particle wave function, if it is approximated by products of single-particle functions.

Real- or complex-valued single-particle functions, which are square integrable, i.e. $\int f^*(\boldsymbol{r})\, f(\boldsymbol{r})\, \mathrm{d}\boldsymbol{r} = N^2 < \infty$, are called '**orbitals**'. Single-particle functions which include the spin coordinate, i.e. $f(\boldsymbol{x})$ with $\boldsymbol{x} = (\boldsymbol{r}, \sigma)$, are called '**spin orbitals**'. A determinant built from spin orbitals is known as **Slater**† **determinant**.

† J. C. Slater (1900-1976)

A Slater determinant for three particles ($n = 3$):

$$\Psi(1,2,3) = N \begin{vmatrix} \phi_1(\boldsymbol{x}_1) & \phi_1(\boldsymbol{x}_2) & \phi_1(\boldsymbol{x}_3) \\ \phi_2(\boldsymbol{x}_1) & \phi_2(\boldsymbol{x}_2) & \phi_2(\boldsymbol{x}_3) \\ \phi_3(\boldsymbol{x}_1) & \phi_3(\boldsymbol{x}_2) & \phi_3(\boldsymbol{x}_3) \end{vmatrix} \tag{86}$$

N denotes a normalization constant. The choice $\phi_1(\boldsymbol{x}) = 1s(\boldsymbol{r})\alpha(\sigma)$, $\phi_2(\boldsymbol{x}) = 1s(\boldsymbol{r})\beta(\sigma)$, and $\phi_3(\boldsymbol{x}) = 2s(\boldsymbol{r})\alpha(\sigma)$ for the spin orbitals yields a valid approximate state function for the ground state of the Li atom, $1s^2\ 2s^1\ {}^2S$.

Note that 'every particle uses every function', i.e. there is no relation or association between the coordinates (of a particle) and the single-particle functions which have these coordinates as arguments.

A Li atom in the ground state 'has an occupied $2s$ orbital', but there is no '$2s$ electron'.

Symmetry groups (point groups, space groups)

A set of symmetry operations (covering operations, which may be applied to a rigid body in 3-dimensional space, e.g. a molecule with fixed structure) constitutes a symmetry group. The rule of combination (binary operation) is 'subsequent application'.

Symmetry groups are, in general, non-Abelian groups, i.e. the sequence of application of symmetry operations is important.

At least one point remains fixed in space under all point group symmetry operations, while space groups include also translations as symmetry operations.

Operation (in connection with symmetry groups):
A transformation of coordinates, or alternatively a transformation of a molecule to a new position.

Symmetry operation:
An operation (not necessarily a physically feasible one) that carries a molecule into a new position which is indistinguishable from (or equivalent to) the original position.

Proper operations:
Pure rotations about a specified axis (these are physically feasible).

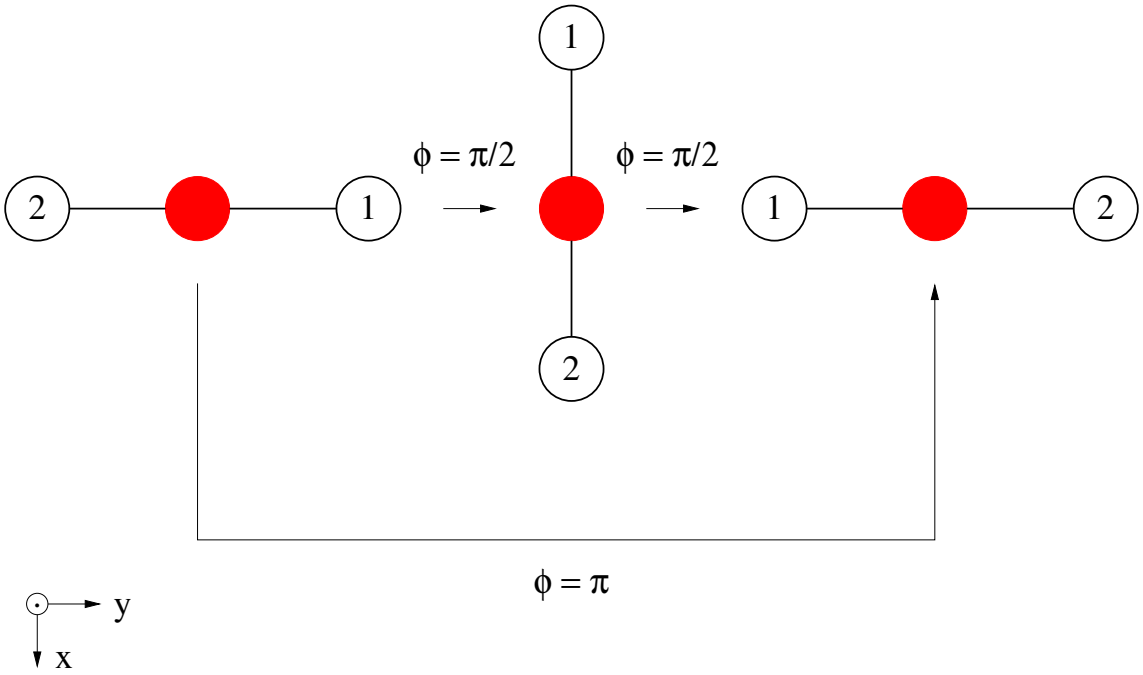
Improper operations:
These may be regarded as rotations-reflections (or alternatively rotations-inversions, these are **not** physically feasible).

Symmetry element:
A geometrical entity (point, line or plane) related to a symmetry operation.

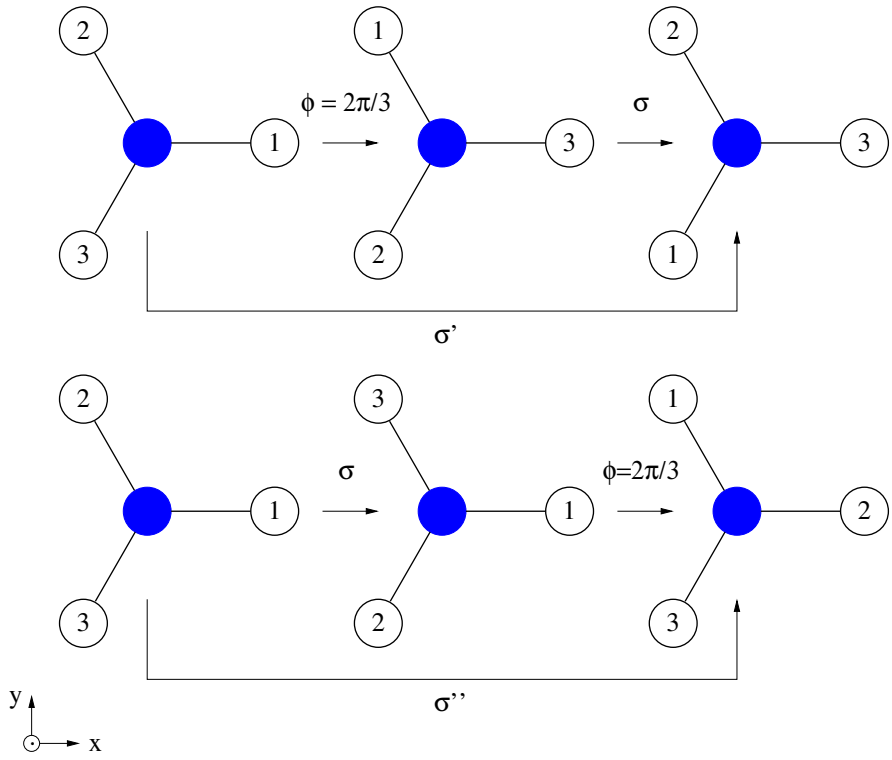
Symmetry element		Symmetry	Definition of
Symbol[a]	Name	operations	symmetry operations
—	—	$\widehat{E}$	Identity (neutral element)
		Proper symmetry operations	
C_n	n-fold rotation axis (usually assumed to be in the z direction)	$\widehat{C}_n^k$	Rotation through $\phi = k \cdot 2\pi/n$, $1 \leq k \leq n$, about the principal axis
C_2', C_2''	2-fold rotation axis perpendicular to the principal C_n axis	$\widehat{C}_2'$, $\widehat{C}_2''$	Rotation through $\phi = \pi$ about the axis
		Improper symmetry operations	
S_n	n-fold rotation-reflection axis	$\widehat{S}_n^k$	Rotation through $\phi = k \cdot 2\pi/n$, combined with reflection k times in a plane normal to the axis, n even: $1 \leq k \leq n$, n odd: $1 \leq k \leq 2n$
i $(= S_2)$	inversion center	$\widehat{i}$ $(= \widehat{S}_2)$	Inversion through the origin
σ $(= S_1)$	mirror plane	$\widehat{\sigma}$ $(= \widehat{S}_1)$	Reflection in a plane
σ_v, σ_h, σ_d	(vertical, horizontal, dihedral planes)	$\widehat{\sigma}_v$, $\widehat{\sigma}_h$, $\widehat{\sigma}_d$	

[a]Notation due to A. Schoenflies (1853-1928)

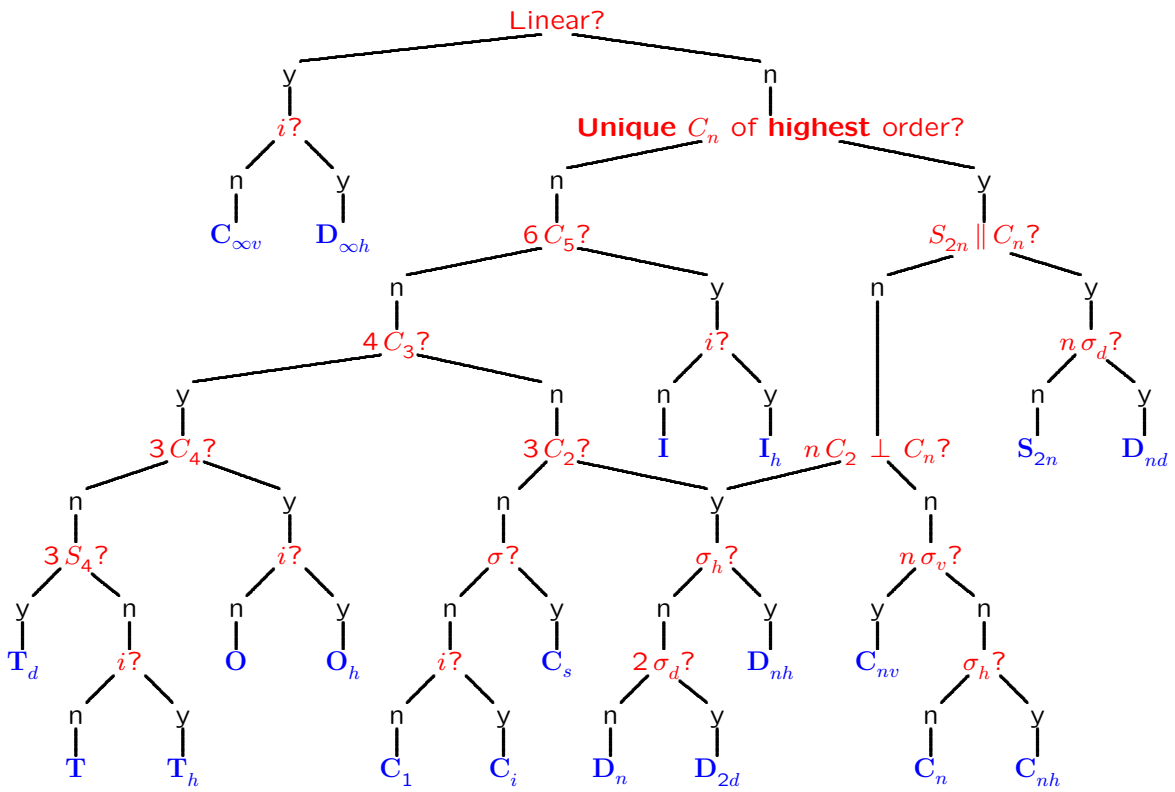
The symmetry operation $\hat{C}_2$ and the water molecule



Symmetry operations and the ammonia molecule

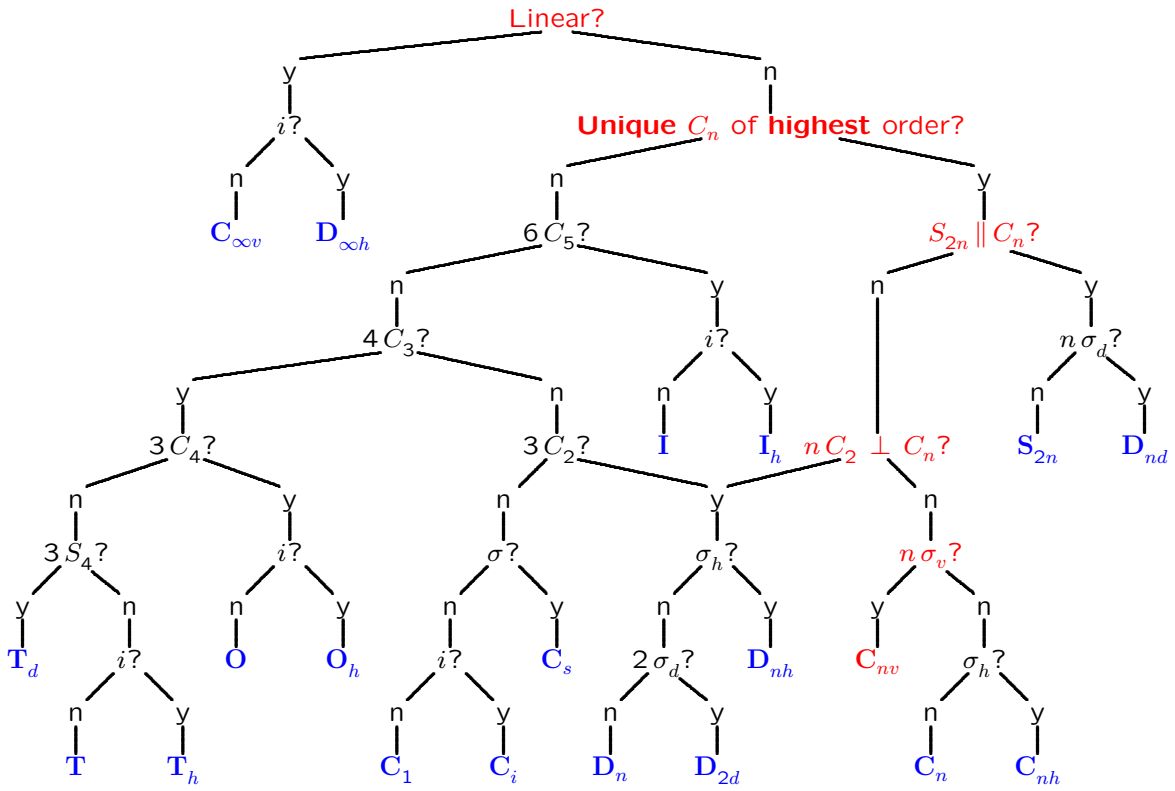


An algorithm to determine the point group from symmetry elements[‡]



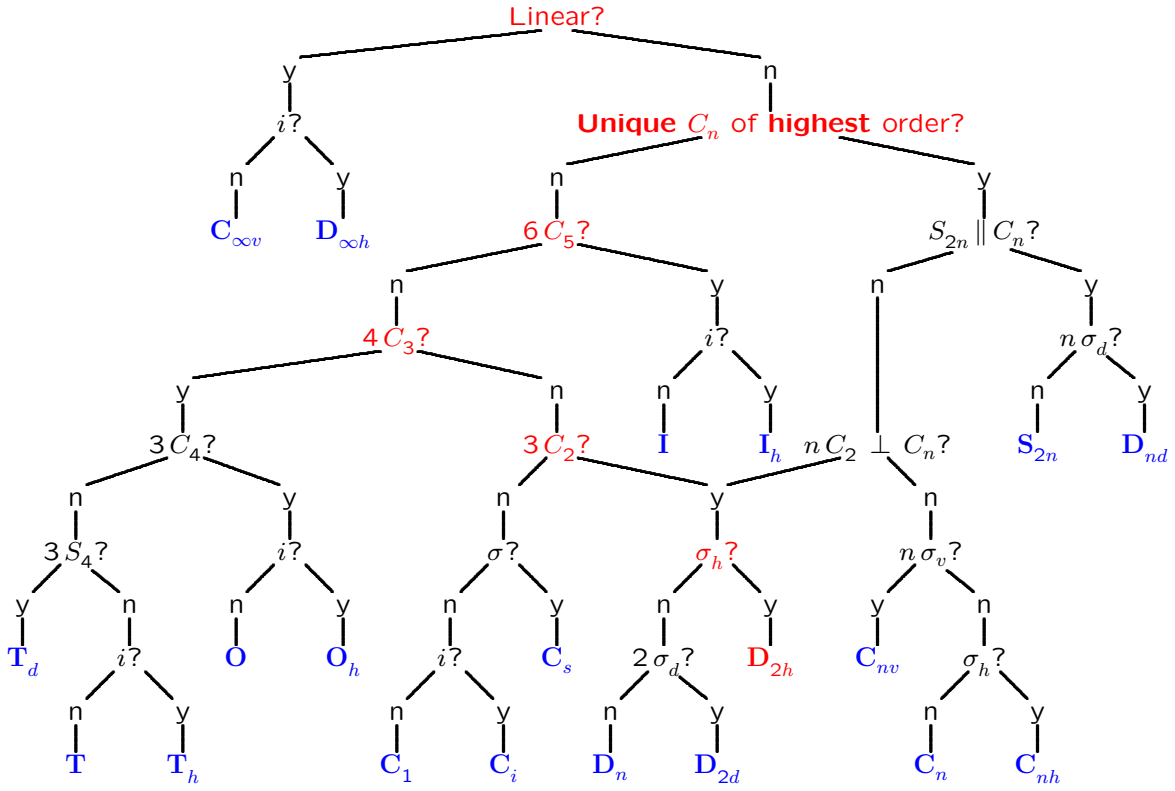
[‡]J. A. Salthouse, M. J. Ware: Point group character tables and related data. Cambridge, 1972.

Determination of point groups $\mathbf{C}_{nv}$[‡] (Examples: H_2O [$n = 2$], NH_3 [$n = 3$])



[‡]J. A. Salthouse, M. J. Ware: Point group character tables and related data. Cambridge, 1972.

Determination of the point group $\mathbf{D}_{2h}$[‡] (Example: C_2H_4)



[‡]J. A. Salthouse, M. J. Ware: Point group character tables and related data. Cambridge, 1972.

Point group symbol	Generating operations	Symmetry elements	Order g	Comments
$\mathbf{C}_1$	$\widehat{E}$	none	1	no symmetry
$\mathbf{C}_s$	$\widehat{\sigma}$	σ	2	$\mathbf{C}_s = \mathbf{C}_{1h} = \mathbf{C}_{1v} = \mathbf{S}_1$
$\mathbf{C}_i$	$\widehat{i}$	i	2	$\mathbf{C}_i = \mathbf{S}_2$
$\mathbf{C}_n$	$\widehat{C}_n$	C_n	n	
$\mathbf{S}_{2n}$	$\widehat{S}_{2n}$	C_n, S_{2n}	$2n$	
$\mathbf{C}_{nh}$	$\widehat{C}_n$, $\widehat{\sigma}_h$	C_n, σ_h, S_n	$2n$	if n odd: $\mathbf{C}_{nh} = \mathbf{S}_n$
$\mathbf{C}_{nv}$	$\widehat{C}_n$, $\widehat{\sigma}_v$	C_n, $n\,\sigma_v$	$2n$	n-gonal regular pyramid
$\mathbf{D}_n$	$\widehat{C}_n$, $\widehat{C}'_2$	C_n, $n\,C'_2$	$2n$	
$\mathbf{D}_{nh}$	$\widehat{C}_n$, $\widehat{C}'_2$, $\widehat{\sigma}_h$	C_n, $n\,C'_2$, S_n, σ_h, $n\,\sigma_v$	$4n$	n-gonal archimedian prism
$\mathbf{D}_{nd}$	$\widehat{C}_n$, $\widehat{C}'_2$, $\widehat{\sigma}_d$	C_n, $n\,C'_2$, $n\,\sigma_d$, S_{2n}	$4n$	n-gonal archimedian antiprism
$\mathbf{C}_{\infty v}$	$\widehat{C}^{(z)}_\infty$, $\widehat{\sigma}_v$	C_∞, $\infty\,\sigma_v$	∞	
$\mathbf{D}_{\infty h}$	$\widehat{C}^{(z)}_\infty$, $\widehat{C}'_2$, $\widehat{\sigma}_h$	C_∞, $\infty\,\sigma_v$, S_∞, $\infty\,C'_2$	∞	
$\mathbf{T}$	$\widehat{C}^{(xyz)}_3$, $\widehat{C}^{(z)}_2$	$4\,C_3$, $3\,C_2$	12	
$\mathbf{T}_h$	$\widehat{C}^{(xyz)}_3$, $\widehat{C}^{(z)}_2$, $\widehat{i}$	$4\,C_3$, $3\,C_2$, $4\,S_6$, $3\,\sigma_v$	24	
$\mathbf{T}_d$	$\widehat{C}^{(xyz)}_3$, $\widehat{S}^{(z)}_4$	$4\,C_3$, $3\,C_2$, $3\,S_4$, $6\,\sigma_d$	24	regular tetrahedron
$\mathbf{O}$	$\widehat{C}^{(xyz)}_3$, $\widehat{C}^{(z)}_4$	$4\,C_3$, $3\,C_4$, $6\,C_2$	24	
$\mathbf{O}_h$	$\widehat{C}^{(xyz)}_3$, $\widehat{C}^{(z)}_4$, $\widehat{i}$	$4\,C_3$, $3\,C_4$, $6\,C_2$, $3\,S_4$, $4\,S_6$, $3\,\sigma_h$, $6\,\sigma_d$	48	regular octahedron
$\mathbf{I}$	$\widehat{C}^{(\mathrm{ico})}_3$, $\widehat{C}^{(z)}_5$	$6\,C_5$, $10\,C_3$, $15\,C_2$	60	
$\mathbf{I}_h$	$\widehat{C}^{(\mathrm{ico})}_3$, $\widehat{C}^{(z)}_5$, $\widehat{i}$	$6\,C_5$, $10\,C_3$, $15\,C_2$, $12\,S_{10}$, $10\,S_6$, $15\,\sigma$	120	regular icosahedron
$\mathbf{K}$	$\widehat{C}_\infty$	$\infty\,C_\infty$	∞	
$\mathbf{K}_h$	$\widehat{C}_\infty$, $\widehat{i}$	$\infty\,C_\infty$, $\infty\,S_\infty$	∞	sphere

Transformation of vectors in $\mathbb{R}^3$

Introduce a suitable basis to describe the (active) rotation of a position vector $\boldsymbol{r}$ around an axis through the origin in direction of the unit vector $\boldsymbol{n}$ by an angle ϕ into a new position vector $\boldsymbol{r}' = \hat{R}(\phi\boldsymbol{n})\,\boldsymbol{r}$:

1. The component of $\boldsymbol{r}$ parallel to $\boldsymbol{n}$:

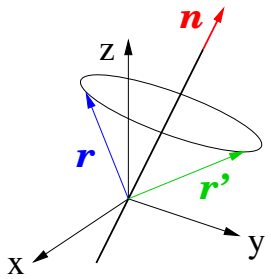
$$\boldsymbol{r}_\parallel = (\boldsymbol{n}\cdot\boldsymbol{r})\,\boldsymbol{n} = \boldsymbol{n}\,(\boldsymbol{n}\cdot\boldsymbol{r})$$

2. The orthogonal complement to $\boldsymbol{r}_\parallel$:

$$\boldsymbol{r}_\perp = \boldsymbol{r} - \boldsymbol{r}_\parallel$$

3. The vector normal to the plane spanned by $\boldsymbol{n}$ and $\boldsymbol{r}$:

$$\boldsymbol{n}\times\boldsymbol{r} = \boldsymbol{n}\times(\boldsymbol{r}_\parallel + \boldsymbol{r}_\perp) = \boldsymbol{n}\times\boldsymbol{r}_\perp$$



$$\boldsymbol{n} = \begin{pmatrix} n_1 \\ n_2 \\ n_3 \end{pmatrix}$$

$$|\boldsymbol{n}| = 1$$

The new position vector $\boldsymbol{r}'$, which results from the action of the operation $\hat{R}(\phi\boldsymbol{n})$ on the old position vector $\boldsymbol{r}$, is now representable as a linear combination of these basis vectors:

$$\begin{aligned}\boldsymbol{r}' = \hat{R}(\phi\boldsymbol{n})\,\boldsymbol{r} &= a\,\boldsymbol{r}_\perp + b\,\boldsymbol{n}\times\boldsymbol{r} + c\,\boldsymbol{r}_\parallel \\ &= a\,\boldsymbol{r} + b\,\boldsymbol{n}\times\boldsymbol{r} + (c-a)\,(\boldsymbol{n}\cdot\boldsymbol{r})\,\boldsymbol{n} \\ &= (a + b\,\boldsymbol{n}\times + (c-a)\,\boldsymbol{n}\,\boldsymbol{n}\cdot)\,\boldsymbol{r}\end{aligned}$$

with $a = \cos(\phi)$, $b = \sin(\phi)$, and $c = +1$ for pure rotations (or $c = -1$ for rotations-reflections).

For the application of any symmetry operation $\hat{R}$ in a point group to a point $\boldsymbol{r}$ in space we may thus write $\boldsymbol{r}' = \hat{R}_\pm(\phi\boldsymbol{n})\,\boldsymbol{r}$, or $\mathbf{r}' = \mathrm{R}_\pm(\phi\mathbf{n})\,\mathbf{r}$ in matrix-vector notation. Explicitly, with coordinates (or vector components):

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} a+(c-a)n_1^2 & (c-a)n_1n_2 - bn_3 & (c-a)n_1n_3 + bn_2 \\ (c-a)n_1n_2 + bn_3 & a+(c-a)n_2^2 & (c-a)n_2n_3 - bn_1 \\ (c-a)n_1n_3 - bn_2 & (c-a)n_2n_3 + bn_1 & a+(c-a)n_3^2 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \tag{87}$$

With $\phi = 2\pi/n$ and suitably chosen $\mathbf{n}$:

$$\hat{R} = \hat{C}_n \longrightarrow \mathsf{R}_+(\phi\mathbf{n}), \qquad \hat{R} = \hat{S}_n \longrightarrow \mathsf{R}_-(\phi\mathbf{n}) \tag{88}$$

For every point group, the resulting set of matrices $\mathsf{R}_\pm(\phi\mathbf{n})$ forms a group under matrix multiplication, which is isomorphic to the point group.

Transformation of scalar functions

With knowledge about the tranformation of position vectors, $\boldsymbol{r}$, the transformation law for scalar functions of the coordinates, $f(\boldsymbol{r})$, can be derived.

The condition of equality of function values, i.e. the transformed function $\hat{O}_R f$ shall have at the transformed position $\boldsymbol{r}' = \hat{R}\boldsymbol{r}$ the same function value as the original function f at the original position $\boldsymbol{r} = \hat{R}^{-1}\boldsymbol{r}'$, leads to:

$$\hat{O}_R f(\boldsymbol{r}') = f(\boldsymbol{r}) = f(\hat{R}^{-1}\boldsymbol{r}') \qquad \Rightarrow \qquad \hat{O}_R f(\boldsymbol{r}) = f(\hat{R}^{-1}\boldsymbol{r}) \tag{89}$$

since this relation should be valid for every argument $\boldsymbol{r}$ in $\mathbb{R}^3$.

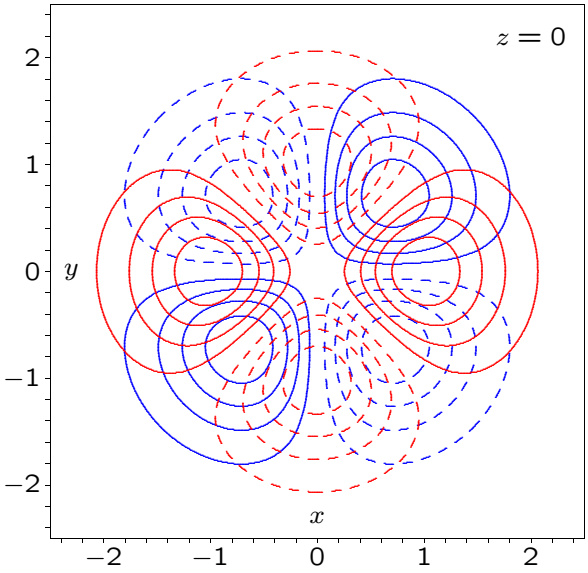
What happens to the function $f(\boldsymbol{r}) = f(x,y,z) = x\,y\,\exp(-r^2)$ under the counterclockwise rotation around the z axis ($\mathbf{n} = (0,0,1)^\mathsf{T}$) through an angle $\phi = \pi/4 = 2\pi/8$?

$$\hat{C}_8 \rightarrow \mathsf{R} = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\hat{C}_8^{-1} \rightarrow \mathsf{R}^{-1} = \begin{pmatrix} \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \\ \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\mathsf{R}^{-1}\mathbf{r} = \mathsf{R}^{-1}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}}(x-y) \\ \frac{1}{\sqrt{2}}(x+y) \\ z \end{pmatrix}$$

$$\begin{aligned} \hat{O}_R f(\mathbf{r}) &= f(\mathsf{R}^{-1}\mathbf{r}) \\ &= f(\frac{1}{\sqrt{2}}(x-y), \frac{1}{\sqrt{2}}(x+y), z) \\ &= \frac{1}{2}(x^2-y^2)\exp(-r^2) \end{aligned}$$



Fields

Given one set of elements $S = \{a, b, \ldots\}$ and two binary operations $\circ$ and $*$.

A **field** $F = (S, \circ, *)$ is formed, if the following axioms hold:

1. $(S, \circ)$ is an Abelian group (with neutral element 0)
2. $(S \setminus \{0\}, *)$ is an Abelian group (with neutral element 1)
3. distributive laws: $a*(b\circ c) = (a*b)\circ(a*c)$, $(a\circ b)*c = (a*c)\circ(b*c)$.

Some well-known examples:

$$\begin{aligned} \text{rational numbers}: &\quad (\mathbb{Q}, +, \cdot) \\ \text{real numbers}: &\quad (\mathbb{R}, +, \cdot) \\ \text{complex numbers}: &\quad (\mathbb{C}, +, \cdot) \end{aligned}$$

Linear vector spaces

Given two sets (in fact not only sets, but algebraic structures):

(1) an abelian group $G = (S, \oplus)$, generated from a set of 'vectors'[§] $S = \{|\,a\,\rangle, |\,b\,\rangle, \ldots, |\,v\,\rangle, \ldots\}$, and a binary operation '$\oplus$' called 'vector addition' (with the 'null vector' $|\,o\,\rangle$ as neutral element),

(2) a field $F = (\mathbb{K}, +, \cdot)$ (usually $\mathbb{K} = \mathbb{R}$ or $\mathbb{K} = \mathbb{C}$) with elements α, β, γ, ..., called 'scalars'.

A **linear vector space** V over the field F is formed, if in addition to the above

1. a scalar multiplication (S multiplication) is defined as:

$$\alpha\,|\,a\,\rangle = |\,a\,\rangle\,\alpha = |\,v\,\rangle \in V \tag{90}$$

2. distributive and associative laws hold:

$$\begin{gathered} (\alpha + \beta)\,|\,a\,\rangle = \alpha\,|\,a\,\rangle \oplus \beta\,|\,a\,\rangle \\ \alpha\,(|\,a\,\rangle \oplus |\,b\,\rangle) = \alpha\,|\,a\,\rangle \oplus \alpha\,|\,b\,\rangle \\ (\alpha\,\beta)\,|\,a\,\rangle = \alpha\,(\beta\,|\,a\,\rangle) \end{gathered} \tag{91}$$

[§] These are called 'ket' vectors in the Dirac notation used here.

Usually, the binary operations '$+$' and '$\oplus$' (addition of scalars and vectors, respectively) are not distinguished any further, and only the symbol '$+$' is used to denote both.

For $\mathbb{K} = \mathbb{R}$ the linear vector space V is called a real linear vector space, whereas for $\mathbb{K} = \mathbb{C}$ it is called a complex linear vector space.

These definitions include already, or are easily extended to include:

(a) **linear combinations**, i.e. a weighted sum of an arbitrary finite number l of vectors (the limit $l \to \infty$ requires further study):

$$|\,v\,\rangle = \sum_{i=1}^{l} \alpha_i\,|\,a_i\,\rangle = \sum_{i=1}^{l} |\,a_i\,\rangle\,\alpha_i \tag{92}$$

If, for the special case $|\,v\,\rangle = |\,o\,\rangle$,

$$\sum_{i=1}^{l} \alpha_i\,|\,a_i\,\rangle = |\,o\,\rangle \qquad \Rightarrow \qquad \alpha_i = 0 \quad \text{(for all } i\text{)} \tag{93}$$

i.e. there exists only the trivial solution, then the set of vectors $\{|\,a_i\,\rangle\}$ is called **linearly independent** (and **linearly dependent** otherwise).

(b) a **basis** (or **basis set**), i.e. a set of vectors $\{|\,b_k\,\rangle\}$ which is linearly independent and capable of representing an arbitrary vector $|\,v\,\rangle$ through linear combination:

$$\sum_{k=1}^{n} \beta_k\,|\,b_k\,\rangle = |\,v\,\rangle \qquad \text{for any } |\,v\,\rangle \in V \tag{94}$$

The number $n \geq 1$ ($n \in \mathbb{N}$) of basis vectors is the **dimension** of V. This dimension can be finite ($n < \infty$) or denumerably infinite ($n = \infty$), and even the case of a continuum ($n = \infty$) could be included, if we change the discrete summation in eq. (94) to an integration in a suitable way. For $n = \infty$, however, the convergence of the expansion in eq. (94) cannot be taken for granted. If convergence (pointwise or in the mean) holds for $n = \infty$, the set $\{|\,b_k\,\rangle\}$ is called **complete**.

With any ordered pair of vectors, $(|\,u\,\rangle, |\,v\,\rangle)$, may be associated a **scalar product** $\langle\, u \,|\, v \,\rangle \in \mathbb{K}$[¶]. A scalar product has, in general, the following properties:

- $\langle\, v \,|\, v \,\rangle \in \mathbb{R}$; $\langle\, v \,|\, v \,\rangle \geq 0$; $\langle\, v \,|\, v \,\rangle = 0 \Rightarrow |\,v\,\rangle = |\,o\,\rangle$;
- $\langle\, u \,|\, v \,\rangle = \langle\, v \,|\, u \,\rangle^*$;
- $\langle\, \alpha_1\, u_1 + \alpha_2\, u_2 \,|\, v \,\rangle = \alpha_1{}^* \langle\, u_1 \,|\, v \,\rangle + \alpha_2{}^* \langle\, u_2 \,|\, v \,\rangle$ and $\langle\, u \,|\, \beta_1\, v_1 + \beta_2\, v_2 \,\rangle = \beta_1 \langle\, u \,|\, v_1 \,\rangle + \beta_2 \langle\, u \,|\, v_2 \,\rangle$.

A linear vector space with scalar product is also known as 'inner product space' or 'pre-Hilbert[‖] space'.

A scalar product can be used to define the **length** (or **norm**) of a vector:

$$\|v\| = \sqrt{\langle\, v \,|\, v \,\rangle} \geq 0 \tag{95}$$

in which case the linear vector space turns into a **unitary** space, where the following relations hold:

[¶] This is called a 'bra-c-ket' in the Dirac notation used here.

[‖] D. Hilbert (1862-1943)

- triangle inequality: $\|u + v\| \leq (\|u\| + \|v\|)^2$;
- Cauchy-Schwarz inequality: $|\langle\, u \,|\, v \,\rangle|^2 = \langle\, u \,|\, v \,\rangle \langle\, u \,|\, v \,\rangle^* = \langle\, u \,|\, v \,\rangle \langle\, v \,|\, u \,\rangle \leq \langle\, u \,|\, u \,\rangle \langle\, v \,|\, v \,\rangle$;
- parallelogram equality: $\|u + v\|^2 + \|u - v\|^2 = 2(\|u\|^2 + \|v\|^2)$

A vector $|\,v\,\rangle$ with $\|v\| = 1$ is called 'normalized to unity' (or just '**normalized**').

Two vectors $|\,u\,\rangle$, $|\,v\,\rangle$ with $\langle\, u \,|\, v \,\rangle = 0$ are called 'orthogonal to each other' (or just '**orthogonal**').

A set of vectors $\{|\,v_k\,\rangle\}$ $(k = 1, \ldots, m)$ with

$$\langle\, v_k \,|\, v_l \,\rangle = \delta_{kl} = \begin{cases} 1 & \text{for } k = l \\ 0 & \text{for } k \neq l \end{cases} \tag{96}$$

is called an '**orthonormal**' set.

An orthonormal set of basis vectors, $\{|\,b_k\,\rangle\}$ ($k = 1, \ldots, n$) with $\langle\, b_k \,|\, b_l \,\rangle = \delta_{kl}$, makes the evaluation of the expansion coefficients β_k in a linear combination particularly simple:

$$\langle\, b_k \,|\, b_l \,\rangle = \delta_{kl} \qquad \Rightarrow \qquad |\,v\,\rangle = \sum_{k=1}^{n} |\,b_k\,\rangle\,\beta_k\,, \quad \beta_k = \langle\, b_k \,|\, v \,\rangle\,. \tag{97}$$

Substitution of this expression for β_k gives an expression for the identity (or unit) operator $\widehat{1}$ which is known as 'resolution of the identity':

$$|\,v\,\rangle = \sum_{k=1}^{n} |\,b_k\,\rangle\langle\, b_k \,|\, v \,\rangle = \left(\sum_{k=1}^{n} |\,b_k\,\rangle\langle\, b_k \,| \right) |\,v\,\rangle = \widehat{1}\,|\,v\,\rangle \tag{98}$$

$$\Rightarrow \qquad \widehat{1} = \sum_{k=1}^{n} |\,b_k\,\rangle\langle\, b_k \,|\,. \tag{99}$$

The **distance** d between two vectors $|\,u\,\rangle$, $|\,v\,\rangle$ can be obtained from

$$d = \|u - v\| = \|v - u\|\,, \tag{100}$$

and — with restriction to cases where $\langle\, u \,|\, v \,\rangle \in \mathbb{R}$ — the **angle** $\phi = \measuredangle(|\,u\,\rangle, |\,v\,\rangle)$ between them can be defined as

$$\cos(\phi) = \frac{\langle\, u \,|\, v \,\rangle}{\|u\|\,\|v\|} \qquad (0 \le \phi \le \pi) \tag{101}$$

Hilbert space:
A complete unitary linear vector space (a rigorous definition is not attempted here).

Some examples for linear spaces:

- $|\,v\,\rangle \to \boldsymbol{v}$ (associate 'ket' vectors with 'ordinary' vectors):
  This yields the n-dimensional Euclidean space $\mathbb{R}^n$ with a basis set $\{\boldsymbol{b}_k\}$ ($k = 1, \ldots, n$), so that the expansions

$$\boldsymbol{c} = \sum_{k=1}^{n} \boldsymbol{b}_k\,\gamma_k = (\boldsymbol{b}_1, \ldots, \boldsymbol{b}_n) \begin{pmatrix} \gamma_1 \\ \vdots \\ \gamma_n \end{pmatrix}, \qquad \boldsymbol{d} = \sum_{k=1}^{n} \boldsymbol{b}_k\,\delta_k$$

  exist and a scalar product can be defined as

$$\boldsymbol{c}\cdot\boldsymbol{d} = \mathbf{c}^{\mathsf{T}}\mathsf{M}\mathbf{d}\,, \quad \text{with} \quad \mathbf{c}^{\mathsf{T}} = (\gamma_1,\ldots,\gamma_n) \quad \text{and} \quad \mathbf{d} = \begin{pmatrix}\delta_1\\ \vdots \\ \delta_n\end{pmatrix},$$

and the metric matrix $\mathsf{M} = (m_{ij})$ where $m_{ij} = \boldsymbol{b}_i \cdot \boldsymbol{b}_j = m_{ji}$. When the basis is chosen to be orthonormal ($\boldsymbol{b}_i \cdot \boldsymbol{b}_j = \delta_{ij}$), the metric matrix reduces to the $n \times n$ unit matrix, and the scalar product collapses to the simple familiar form where only the coefficients (coordinates) γ_k and δ_k are involved:

$$\boldsymbol{b}_i \cdot \boldsymbol{b}_j = \delta_{ij} \quad \Rightarrow \quad \boldsymbol{c}\cdot\boldsymbol{d} = \mathbf{c}^{\mathsf{T}}\mathbf{d} = (\gamma_1,\ldots,\gamma_n)\begin{pmatrix}\delta_1\\ \vdots \\ \delta_n\end{pmatrix} = \sum_{k=1}^{n}\gamma_k\,\delta_k$$

- $|\,f\,\rangle \rightarrow f$ (associate 'ket' vectors with 'ordinary' functions): This leads, e.g., to the infinite-dimensional spaces $L^2(G)$ of complex-valued functions of n variables, $f(\boldsymbol{r}) = f(x_1, x_2, \ldots, x_n) \in \mathbb{C}$ ($\boldsymbol{r} \in \mathbb{R}^n$), that are square-integrable over a range (or region) $G \subseteq \mathbb{R}^n$ in the sense of the scalar product

$$\langle\, f \,|\, g \,\rangle = \int_G f^*(\boldsymbol{r})\, g(\boldsymbol{r})\, \mathrm{d}\boldsymbol{r}$$

based on the Lebesgue** integral definition. This leads to normalization integrals

$$\|f\| = \left(\int_G f^*(\boldsymbol{r})\, f(\boldsymbol{r})\, \mathrm{d}\boldsymbol{r}\right)^{1/2} = \left(\int_G |f(\boldsymbol{r})|^2\, \mathrm{d}\boldsymbol{r}\right)^{1/2}$$

Special cases included herein are

- $L^2([-p/2, p/2])$ used in the harmonic analysis of periodic functions $f(x) = f(x+p) \in \mathbb{C}$; for period $p = 2\pi$:
  Orthonormal basis (dimension $d = \infty$, denumerably infinite):

$$\left\{\frac{1}{\sqrt{2\pi}}\,\mathrm{e}^{\mathrm{i}kx}\right\} \quad (k \in \mathbb{Z})\,, \qquad \frac{1}{2\pi}\int_{-\pi}^{\pi}\mathrm{e}^{-\mathrm{i}(k-l)x}\,\mathrm{d}x = \delta_{kl}$$

  Fourier†† series expansion:

$$f(x) = \sum_{k=-\infty}^{\infty}\frac{c_k}{\sqrt{2\pi}}\,\mathrm{e}^{\mathrm{i}kx}\,, \qquad c_k = \frac{1}{\sqrt{2\pi}}\int_{-\pi}^{\pi}\mathrm{e}^{-\mathrm{i}kx}\,f(x)\,\mathrm{d}x$$

** H. Lebesgue (1875-1941)

†† J. Fourier (1768-1830)

- $L^2(\mathbb{R})$ and Fourier transformation:
  Orthonormal basis (dimension $d = \infty$, continuum):

$$\left\{ \frac{1}{\sqrt{2\pi}} \mathrm{e}^{\mathrm{i}kx} \right\} \quad (k \in \mathbb{R}) , \qquad \frac{1}{2\pi} \int_{-\infty}^{\infty} \mathrm{e}^{-\mathrm{i}(k-k')x} \, \mathrm{d}x = \delta(k - k')$$

  Fourier transform pairs (symmetric form):

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \overline{f}(k) \, \mathrm{e}^{\mathrm{i}kx} \, \mathrm{d}k , \quad \overline{f}(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) \, \mathrm{e}^{-\mathrm{i}kx} \, \mathrm{d}x$$

- $L^2(\mathbb{R}^3)$ and the construction of molecular orbitals $\psi_k(\boldsymbol{r})$ by linear combination of basis functions $\chi_i(\boldsymbol{r})$ (for historical reasons, this is called 'molecular orbitals by linear combination of atomic orbitals', or '**MO-LCAO approach**'):

$$\psi_k(\boldsymbol{r}) = \sum_{i=1}^{m} \chi_i(\boldsymbol{r}) \, c_{ik}$$

  or equivalently

$$(\psi_1, \psi_2, \ldots, \psi_m) = (\chi_1, \chi_2, \ldots, \chi_m) \, \mathsf{C}$$

  when the MO coefficients c_{ik} are collected into MO (column) vectors $\mathbf{c}_k$, which form the matrix C. Completeness of the basis set is a delicate issue, which is usually left untouched in practical work.
- $L^2((\mathbb{R}^3 \times S)^n)$ [where S denotes a 'spin space'] and the construction of (spin-adapted) n-electron state functions Ψ_k by linear combination of Slater determinants Φ_i (called configuration interaction or '**CI expansion**', since every Slater determinant can be associated with an 'electron configuration'):

$$\Psi_k(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_n) = \sum_{i=1}^{m} \Phi_i(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_n) \, C_{ik}$$

  or equivalently

$$(\Psi_1, \Psi_2, \ldots, \Psi_m) = (\Phi_1, \Phi_2, \ldots, \Phi_m) \, \mathsf{C}$$

  when the CI coefficients C_{ik} are collected into CI (column) vectors $\mathbf{C}_k$, which form the matrix C. In the limit $m \to \infty$, the CI expansion is exact, if the spin orbitals — from which the Slater determinants are formed — constitute a complete basis (of single-particle functions).