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Molecular shapes

Pere Alemany
Universitat de Barcelona

Sorting objects by shape

Sorting a set of objects by their shape, color or size is one of the first intellectual abilities acquired by humans

We have all the ability to distinguish between different shapes, but defining precisely the concept of shape is not a trivial task

Shape (Merriam-Webster):
Spatial form or contour

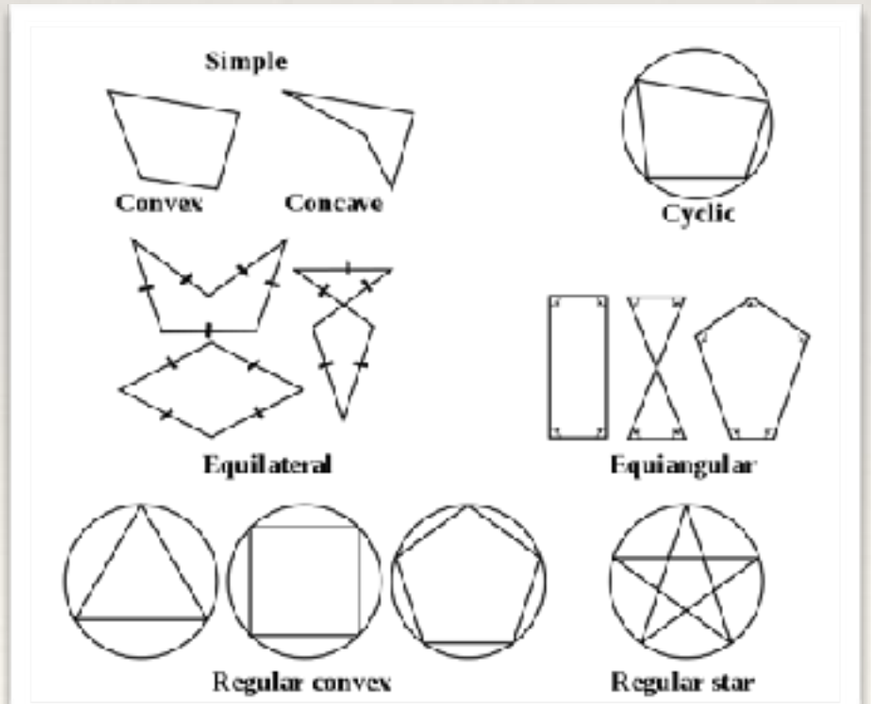
Form (Merriam-Webster):
The shape and structure of something as distinguished from its material

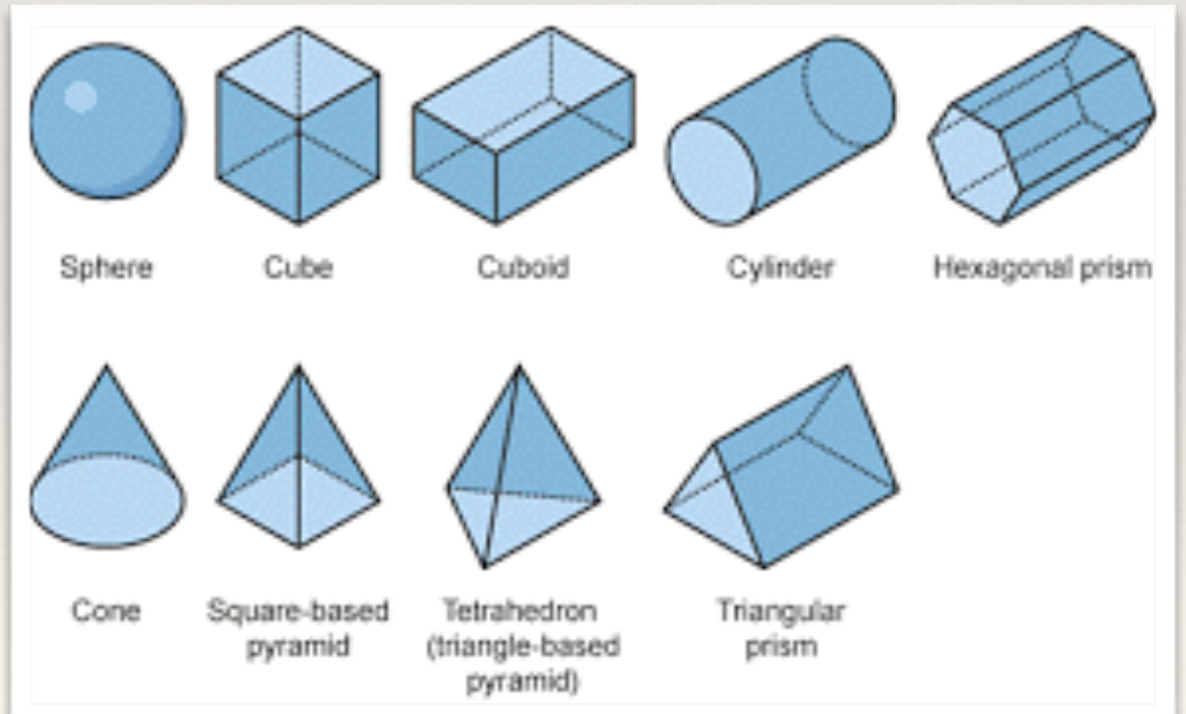
Forma (RAE):
Configuración externa de algo

Geometrical shapes

A shape or figure is a **graphical representation of an object** or its external boundary, as opposed to other properties such as color, texture, or material type.

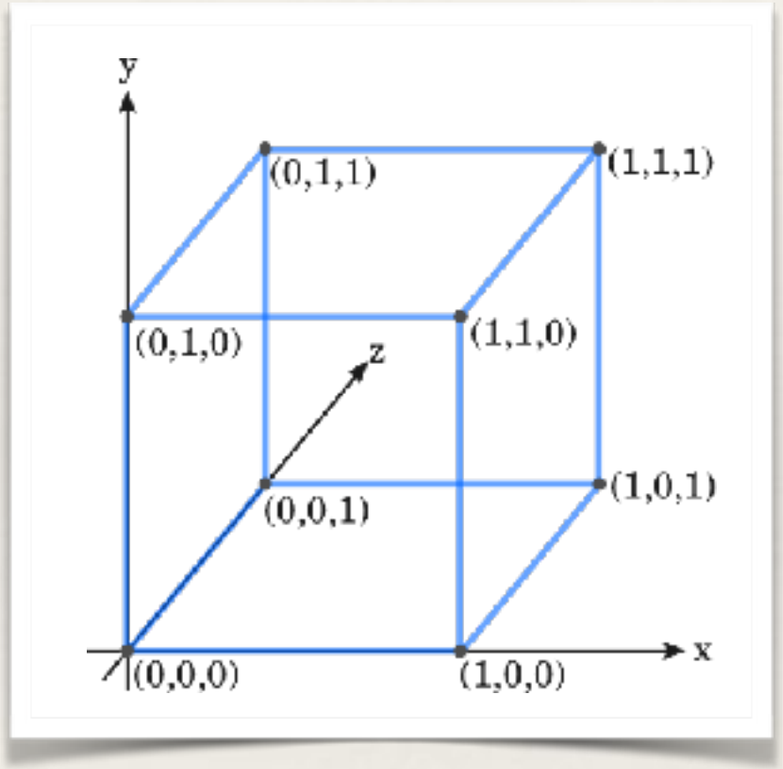
A plane figure is constrained to lie on a plane, in contrast to solid 3D shapes. Figures are classified according to the types and number of faces (edges), with special names for regular shapes (equal faces, angles, lengths, …)



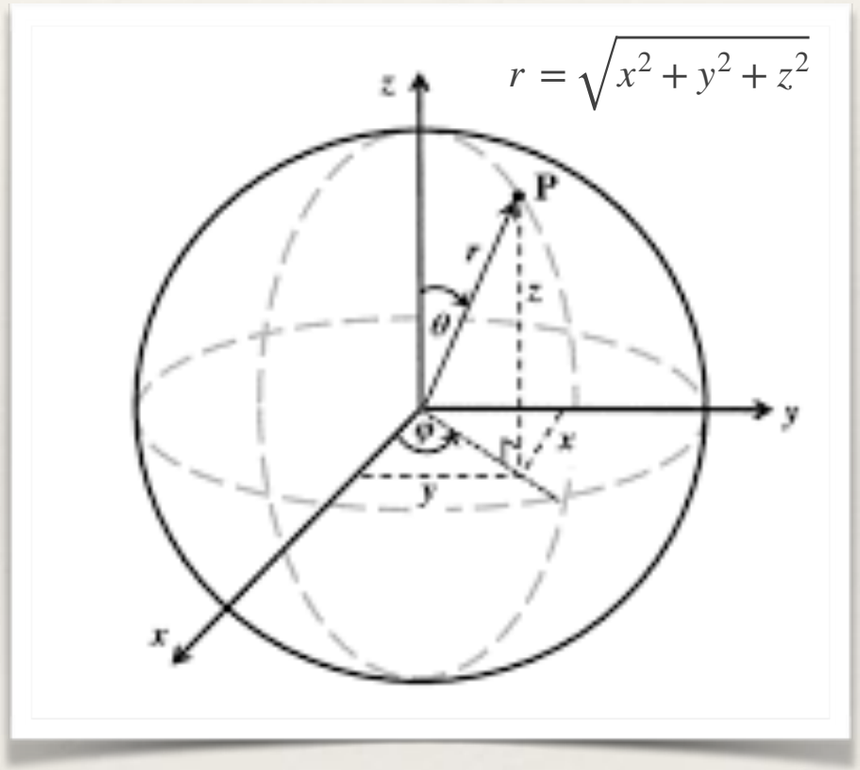


Defining a geometrical figure

A simple geometrical figure may be described by a set of points (vertices) in space



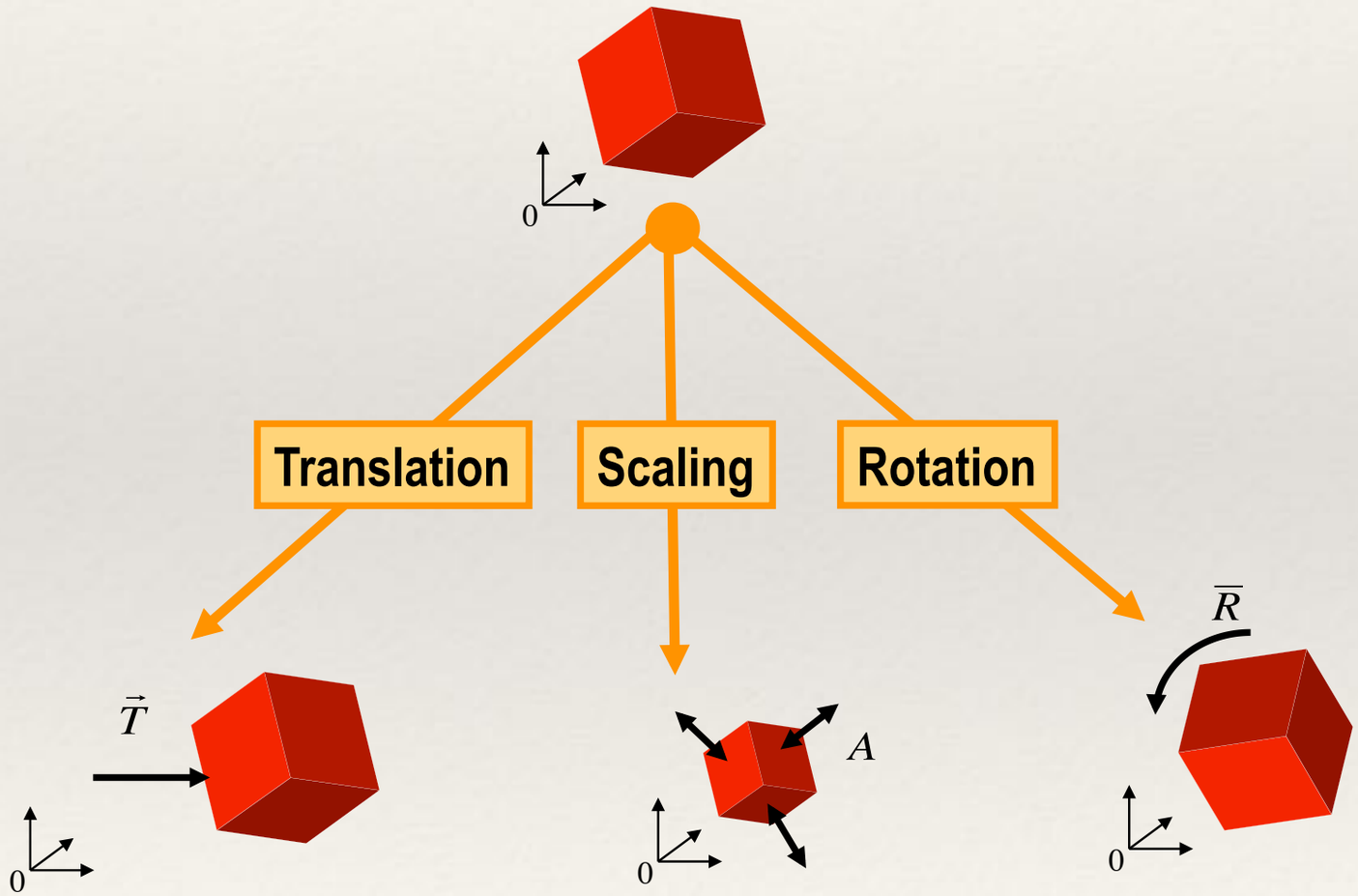
An other way to specify a geometrical figure is to give the equation that is satisfied by all points on the shape



Although we usually consider a shape formed by the points on its surface only, in some cases we may include also the points in the interior as part of the figure.

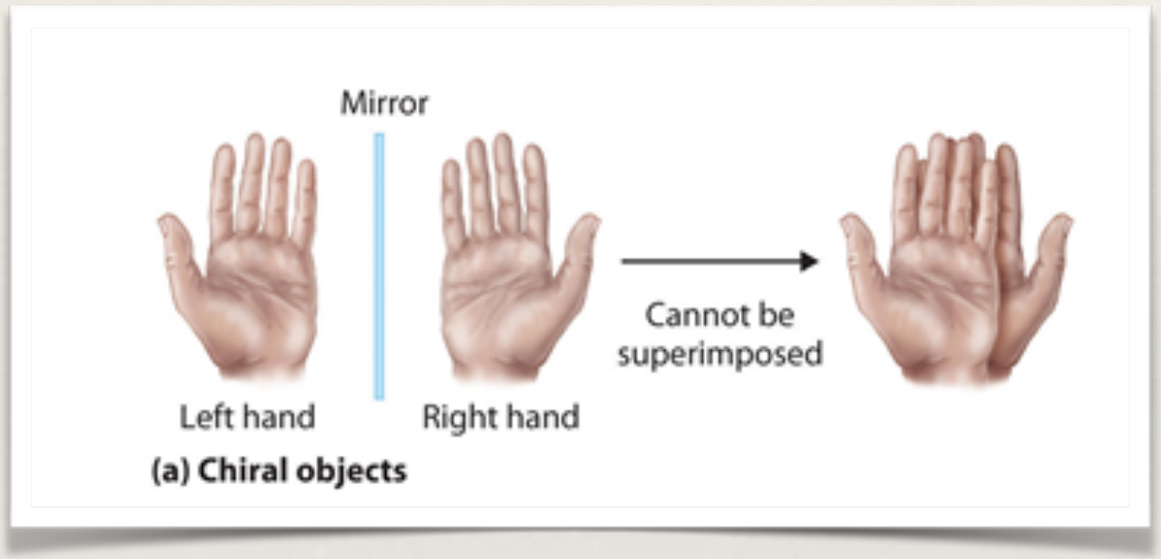
Mathematical properties of shape

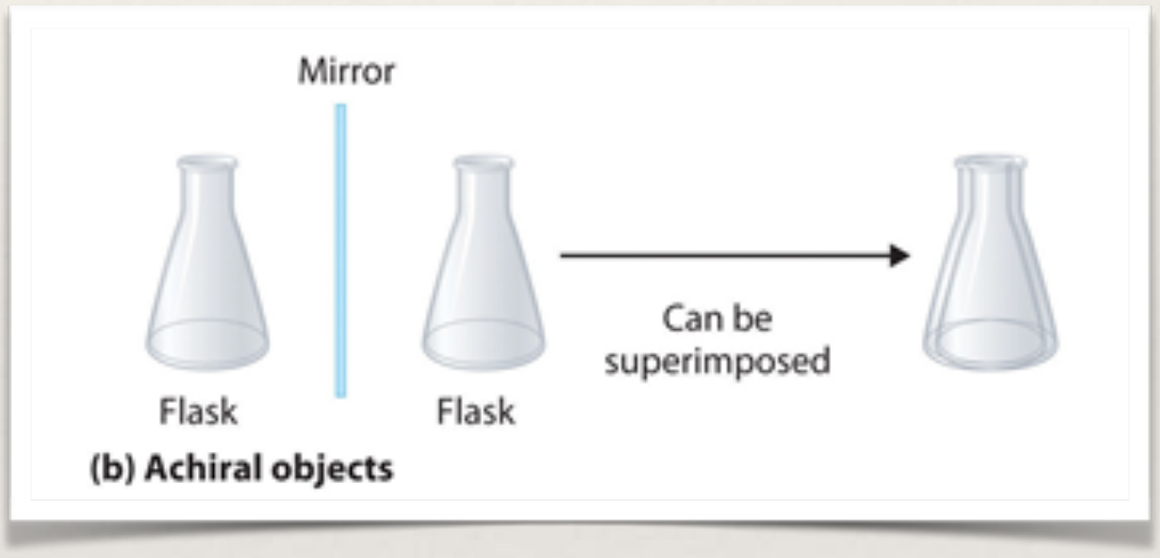
A geometric shape consists of the geometric information which remains **invariant** when **location**, **scale**, and **orientation** are removed from the description of a geometric object.



Chiral objects

Shape is also invariant with respect to **reflections**, but in some cases we can have two objects with the same shape that are, however, specular images which cannot be superimposed by translations and rotations alone.



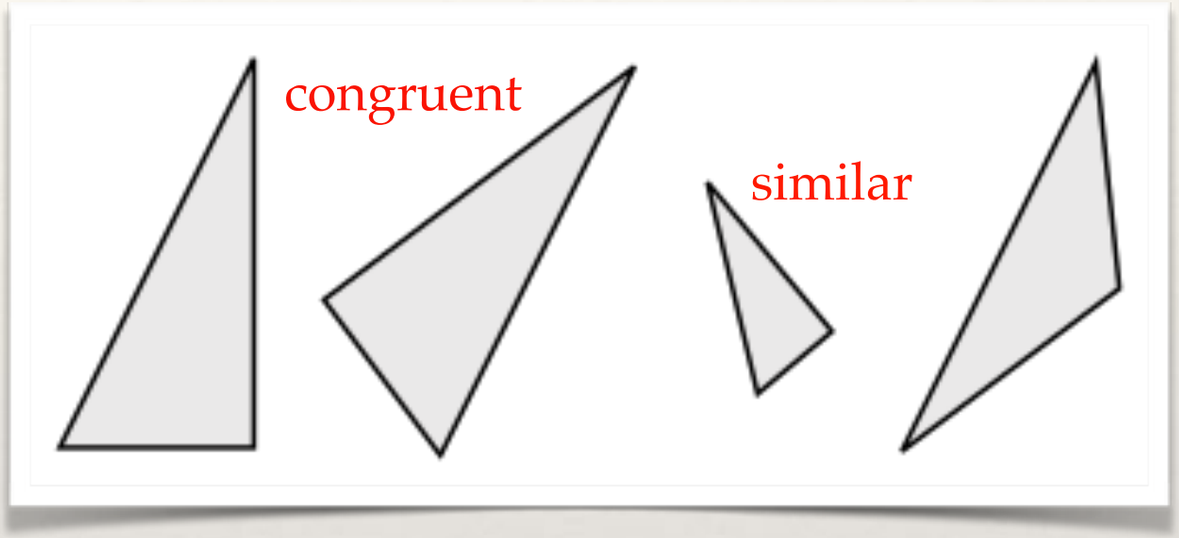


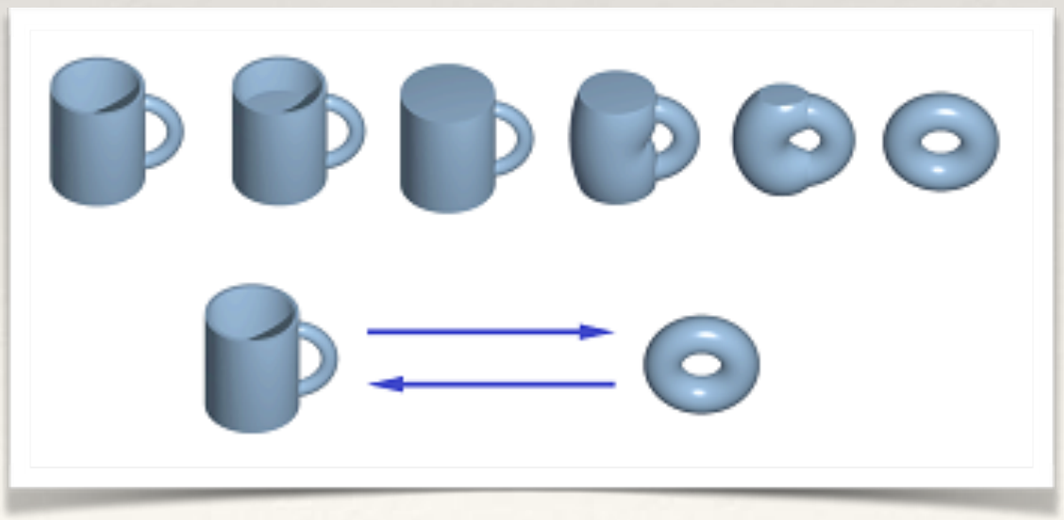
In geometry, a figure is **chiral** (and said to have chirality) if it cannot be mapped to its mirror image by rotations and translations alone. An object that is not chiral is said to be **achiral**. A chiral object and its mirror image are said to be **enantiomorphs**.

Congruence and similarity

Two objects are **congruent** if one can be transformed into the other by a sequence of rotations, translations, and/or reflections.

Two objects are **similar** if one can be transformed into the other by a uniform scaling, together with a sequence of rotations, translations, and/or reflections.



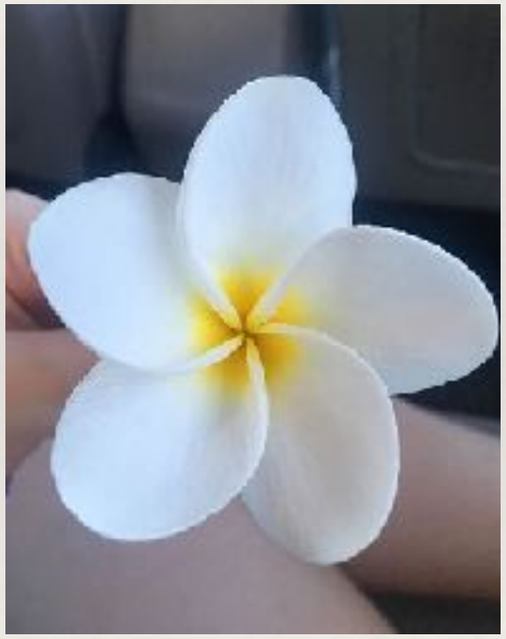


Two objects are **isotopic** if one can be transformed into the other by a sequence of deformations that do not tear the object or put holes in it.

Geometrical symmetry

Symmetry in everyday language refers to a sense of harmonious and beautiful proportion and balance. In mathematics, "symmetry" has a more precise definition, meaning that an object is **invariant under some transformations** including reflection, rotation or combinations of both.

reflection



5-fold rotation

5-fold rotation
reflection

Symmetry elements

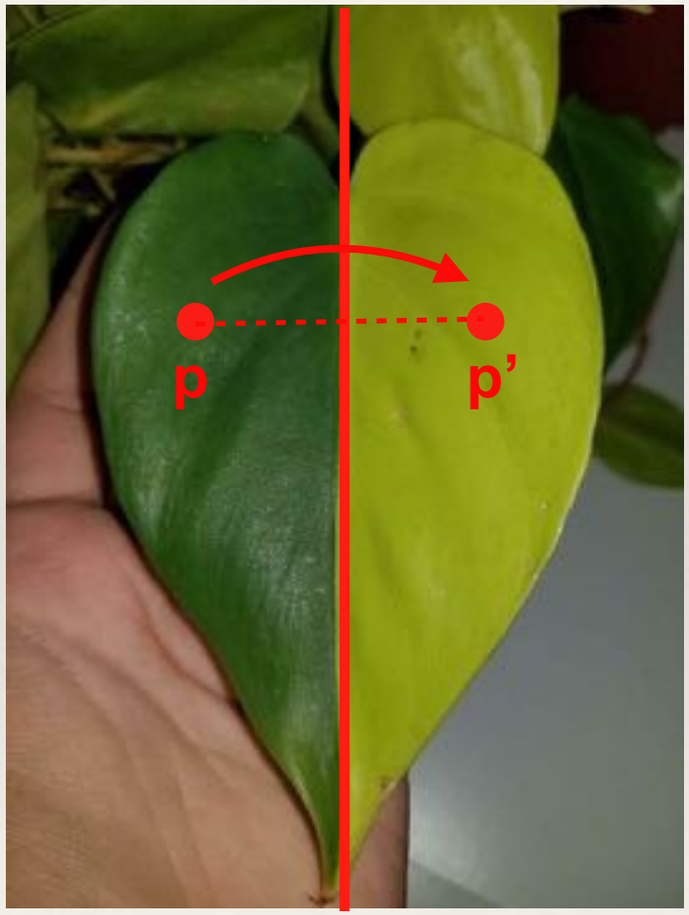
Symmetry elements refer to **geometric objects** (points, lines or planes) about which symmetry operations can take place.

reflection plane (line in 2D)

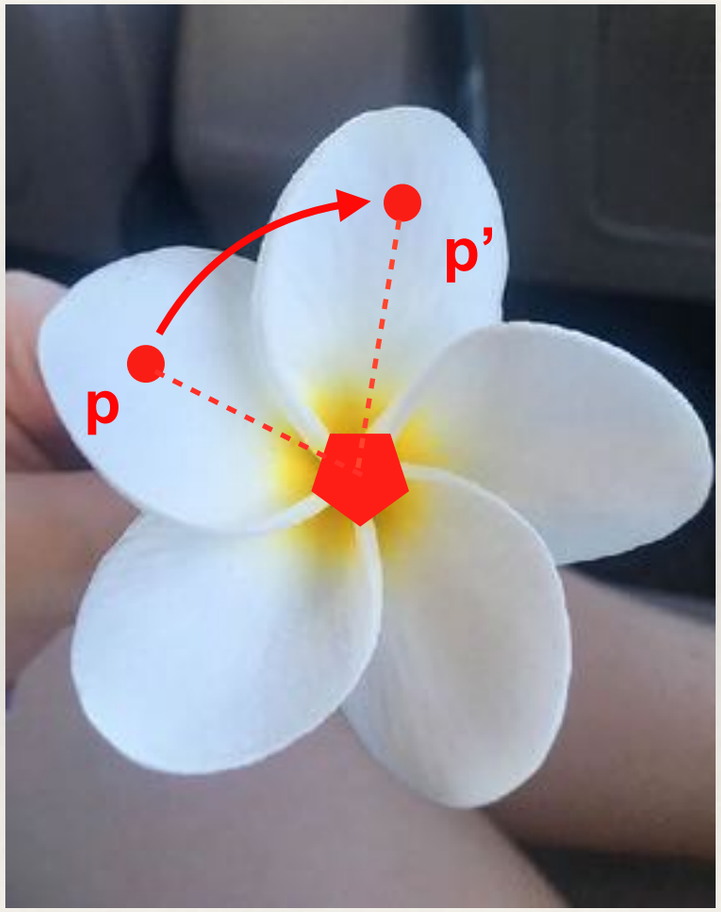
rotation axis (point in 2D)

Symmetry operations

Symmetry operations refer to **rigid transformations** employing the symmetry element that leave the object unchanged.



reflection plane (line in 2D)

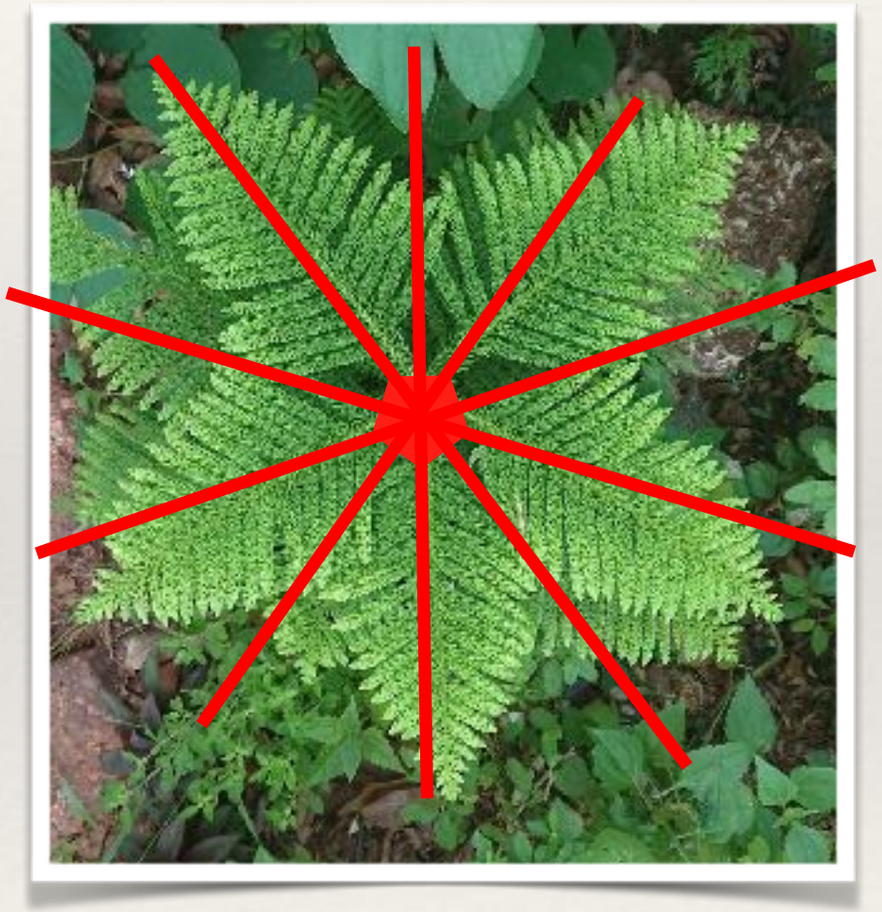


rotation axis (point in 2D)

Combined symmetries

The presence of a symmetry transformation implies often the necessary presence of other transformations.

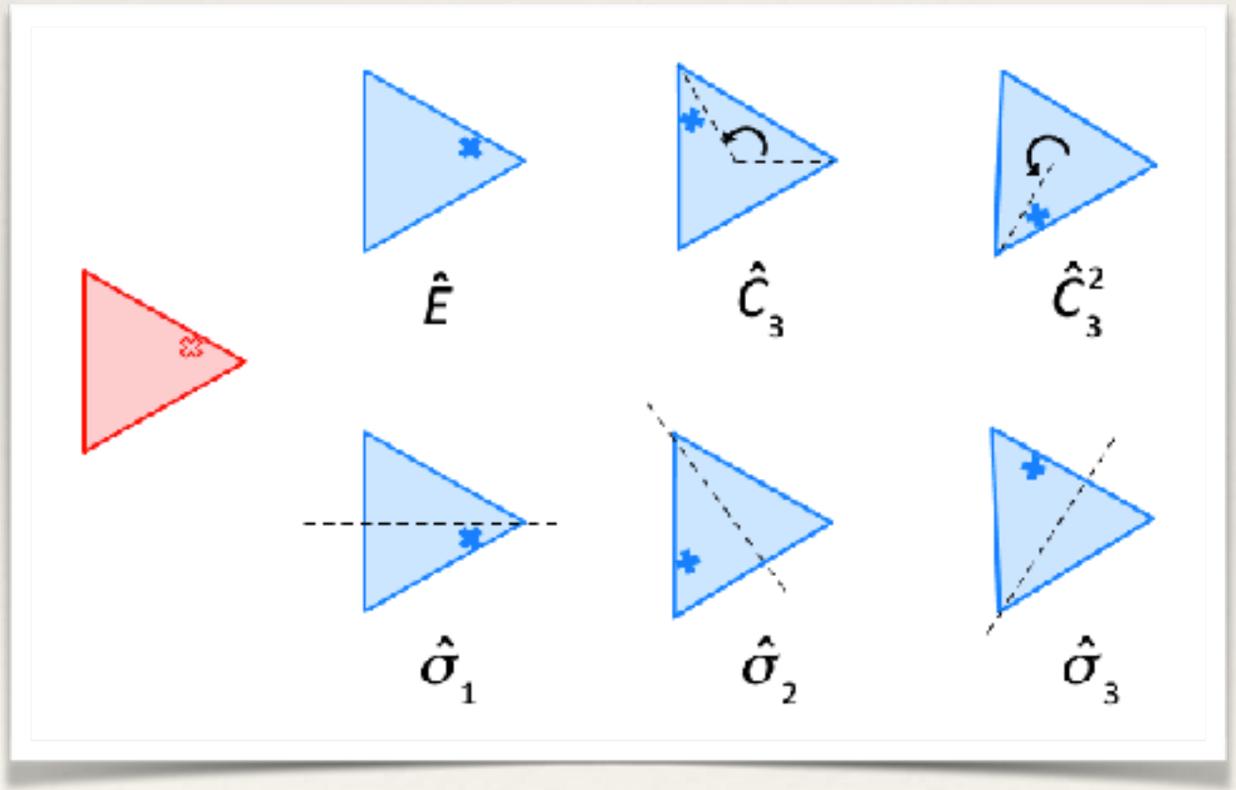
a 5-fold rotation axis contained in
a reflection plane implies
4 additional reflection planes



In natural systems, symmetry
is normally only approximate.

Symmetry groups

The set of all **symmetry operations for a given object** together with the sequential application of symmetry operations forms an algebraic structure called a **group**.



Symmetry group for the equilateral triangle

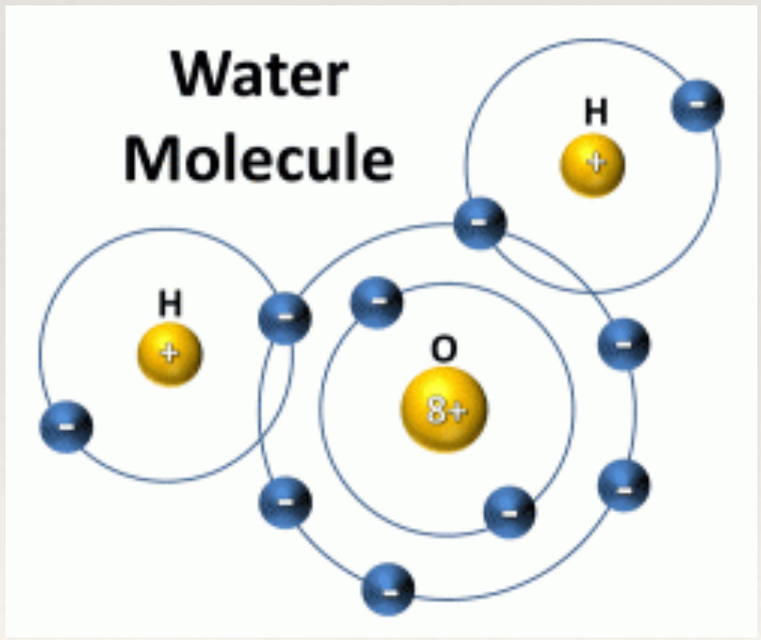
$$C_{3v} = \{\hat{E}, \hat{C}_3, \hat{C}_3^2, \hat{\sigma}_1, \hat{\sigma}_2, \hat{\sigma}_3\}$$

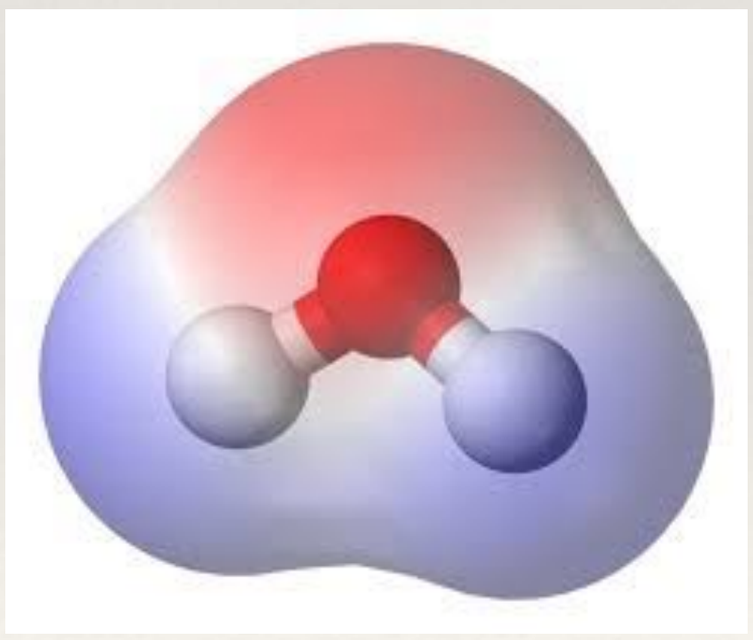
C_{3v} Schönflies notation
3m Hermann–Mauguin notation

What is the shape of a molecule?

Shape is a concept that is useful to describe more or less rigid macroscopic object, that does not change its external appearance in time.

A molecule is formed by a set of interacting particles (nuclei and electrons) in constant movement. A static version of this is given by the **average position of nuclei** plus the **probability density of finding one electron** in a given point of space.

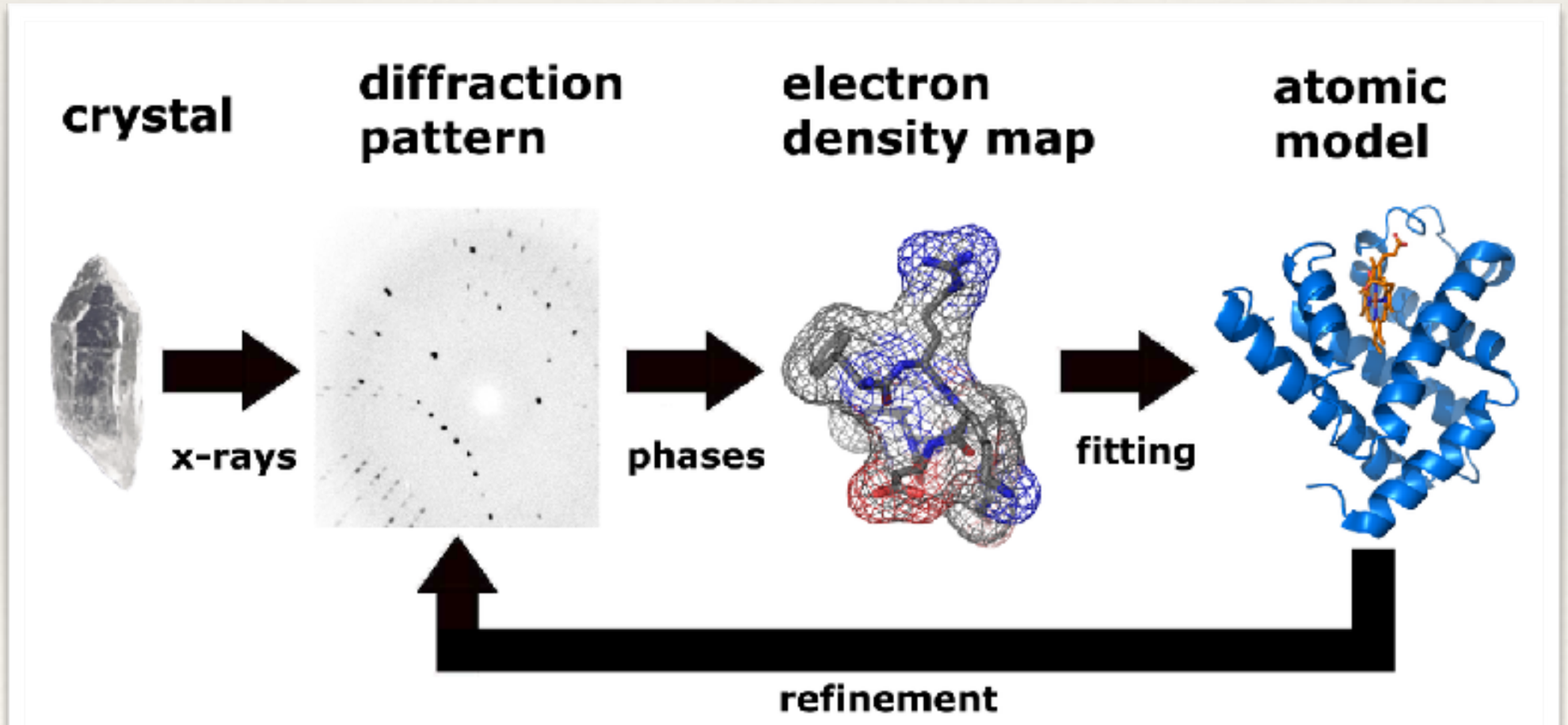




Surface enclosing a 99% probability for electron locations

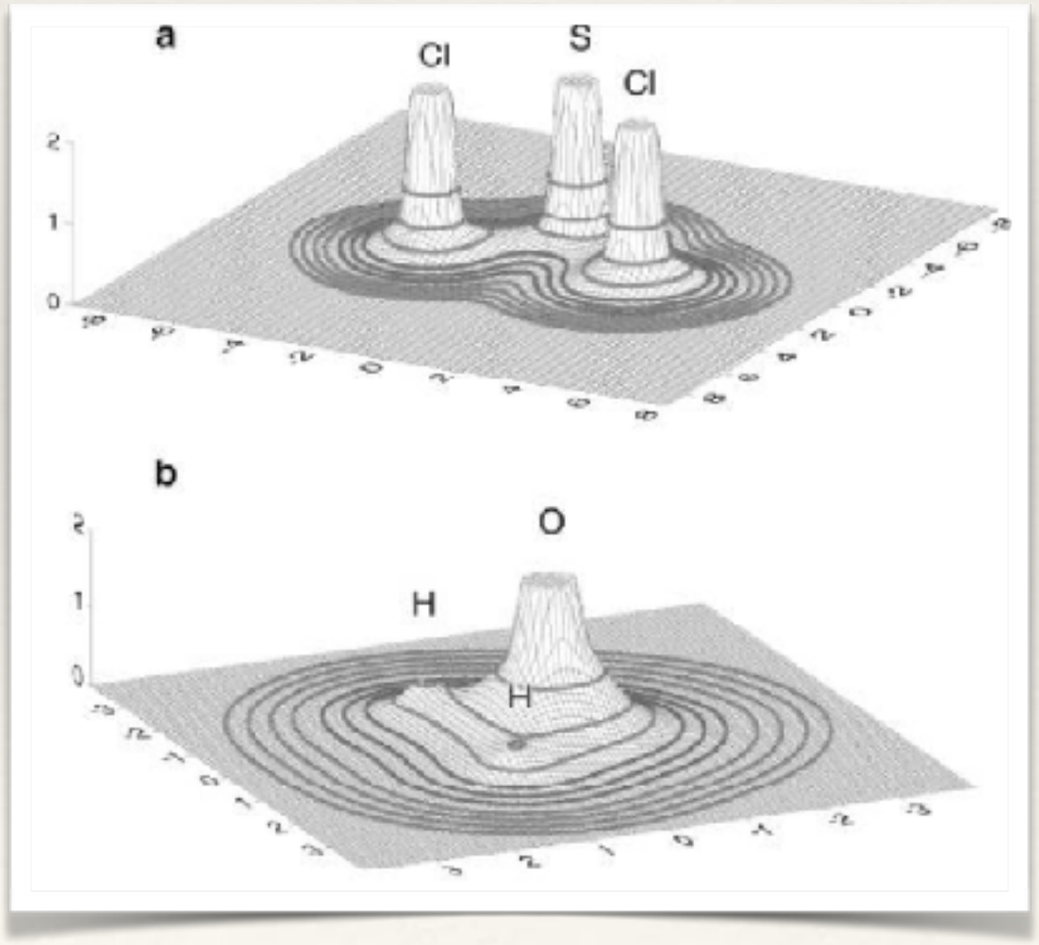
Determination of molecular structures

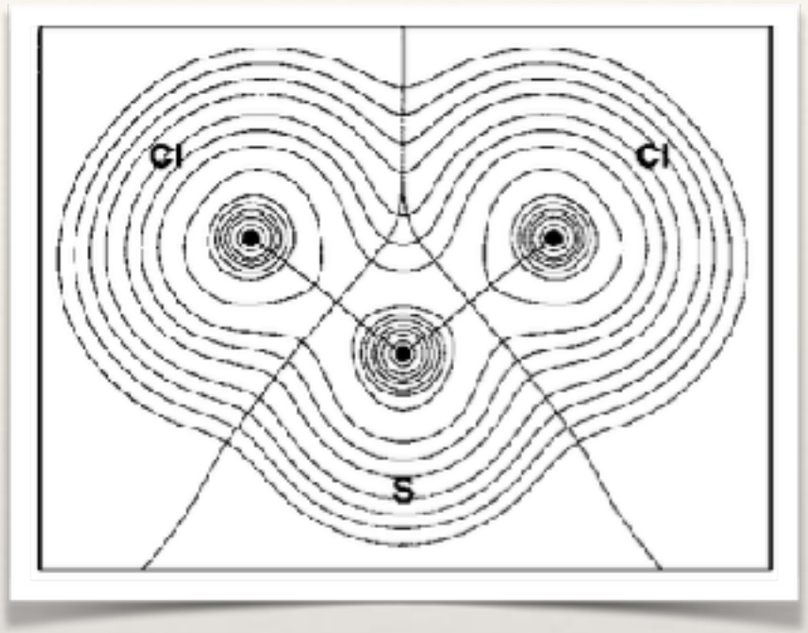
The principal source of molecular structures is X-ray diffraction in crystals, allowing us to determine the electron density from which a molecular structure (average position of atoms) may be guessed.



Molecular models in X-ray diffraction

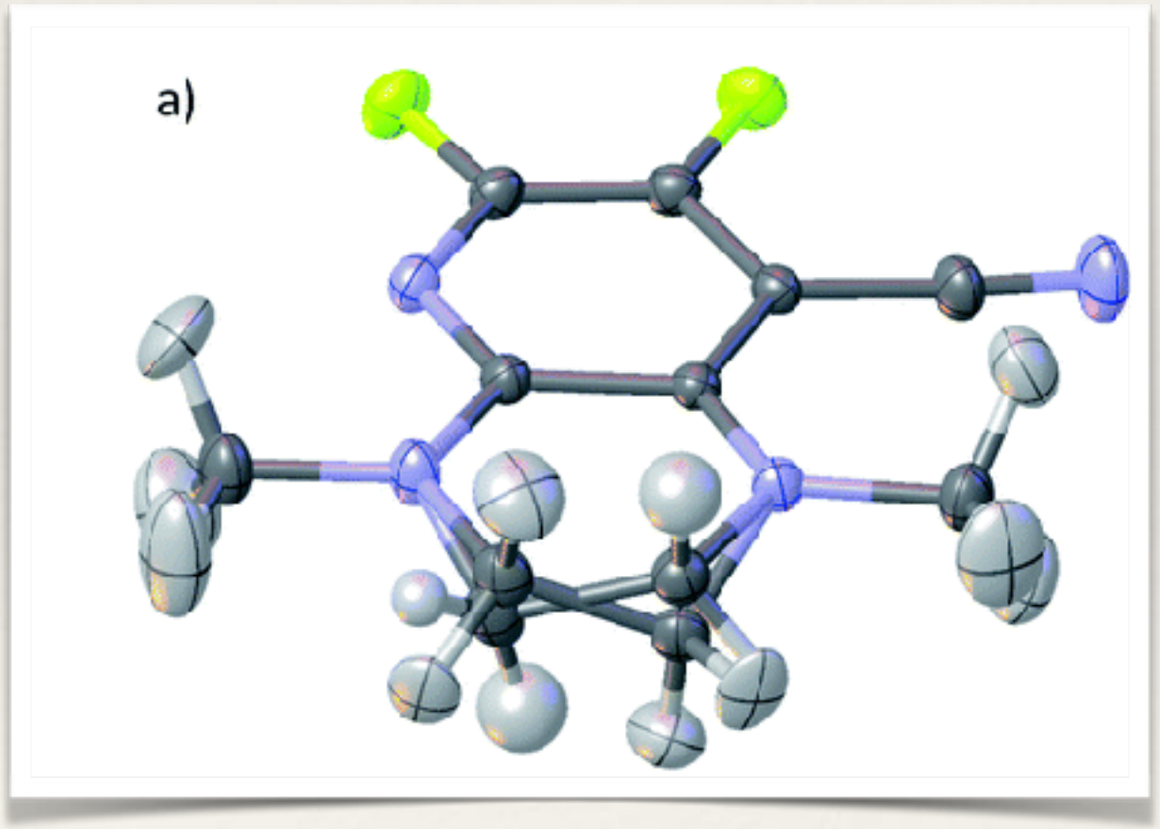
Guessing the position of light H atoms (1e$^-$) close to heavier atoms just from the electron density is not easy





Disordered structures

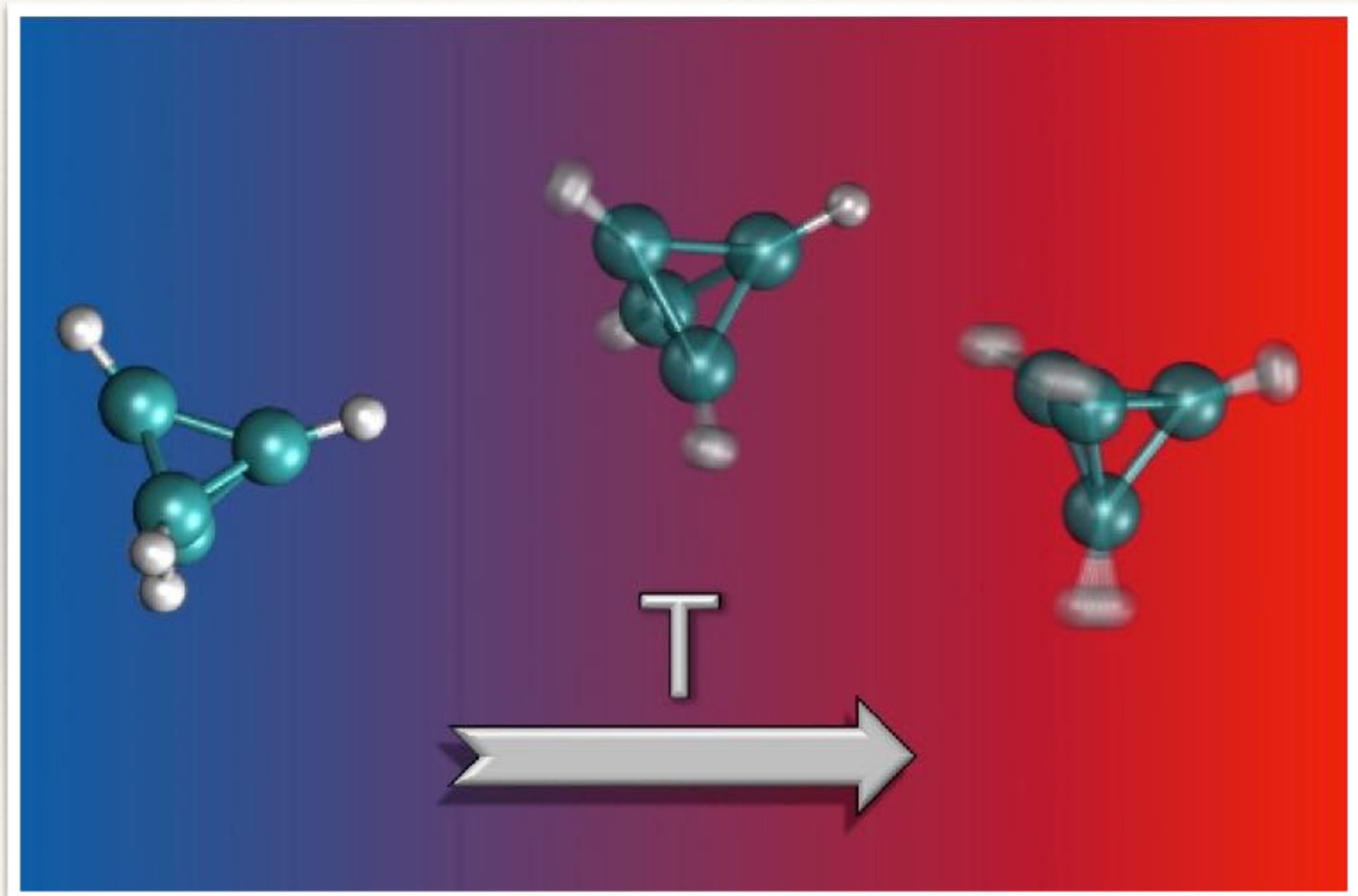
In some cases a simple molecular model is not enough to fit an electron density and a model with **disorder** (atomic positions with fractional occupations) is needed



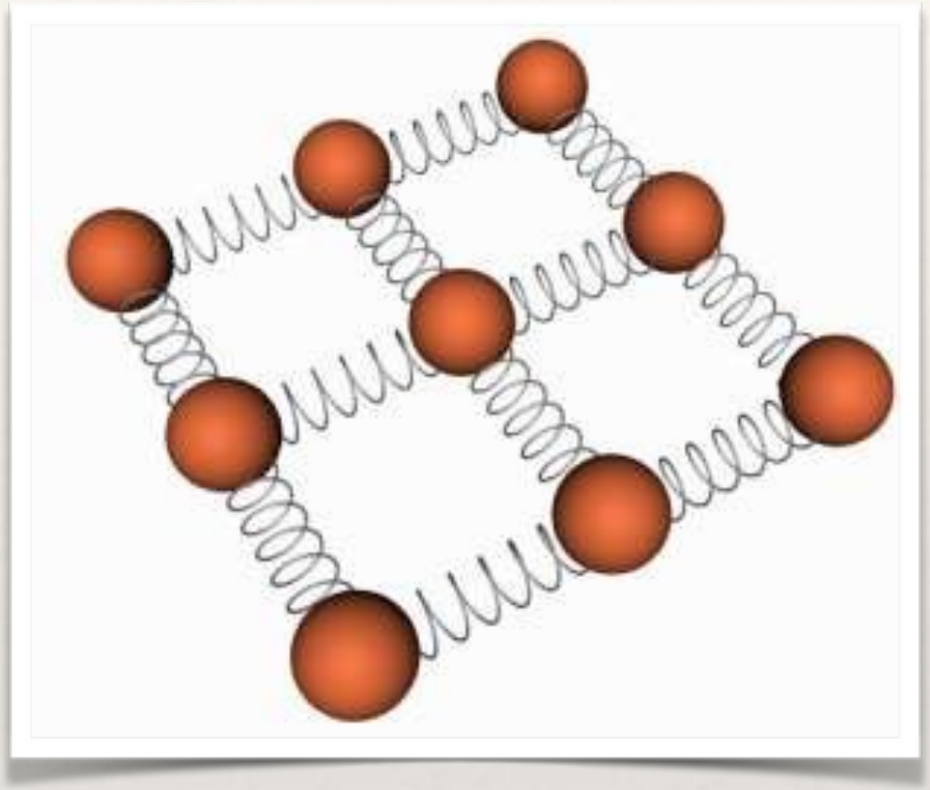
Main sources of disorder:

- Dynamic disorder
- Static disorder

Effect of temperature on molecular shape & symmetry



Effects of temperature on molecular geometry



Energy associated with
a displacement u of mass m

$$m\omega^2 \left\langle u^2 \right\rangle$$

Equating this mean
displacement energy with $k_B T$

$$\left\langle u^2 \right\rangle = \frac{k_B T}{m\omega^2}$$

$m \approx 0.05 / N_A \; kg$

$\omega / 2\pi \approx 5 \; THz$

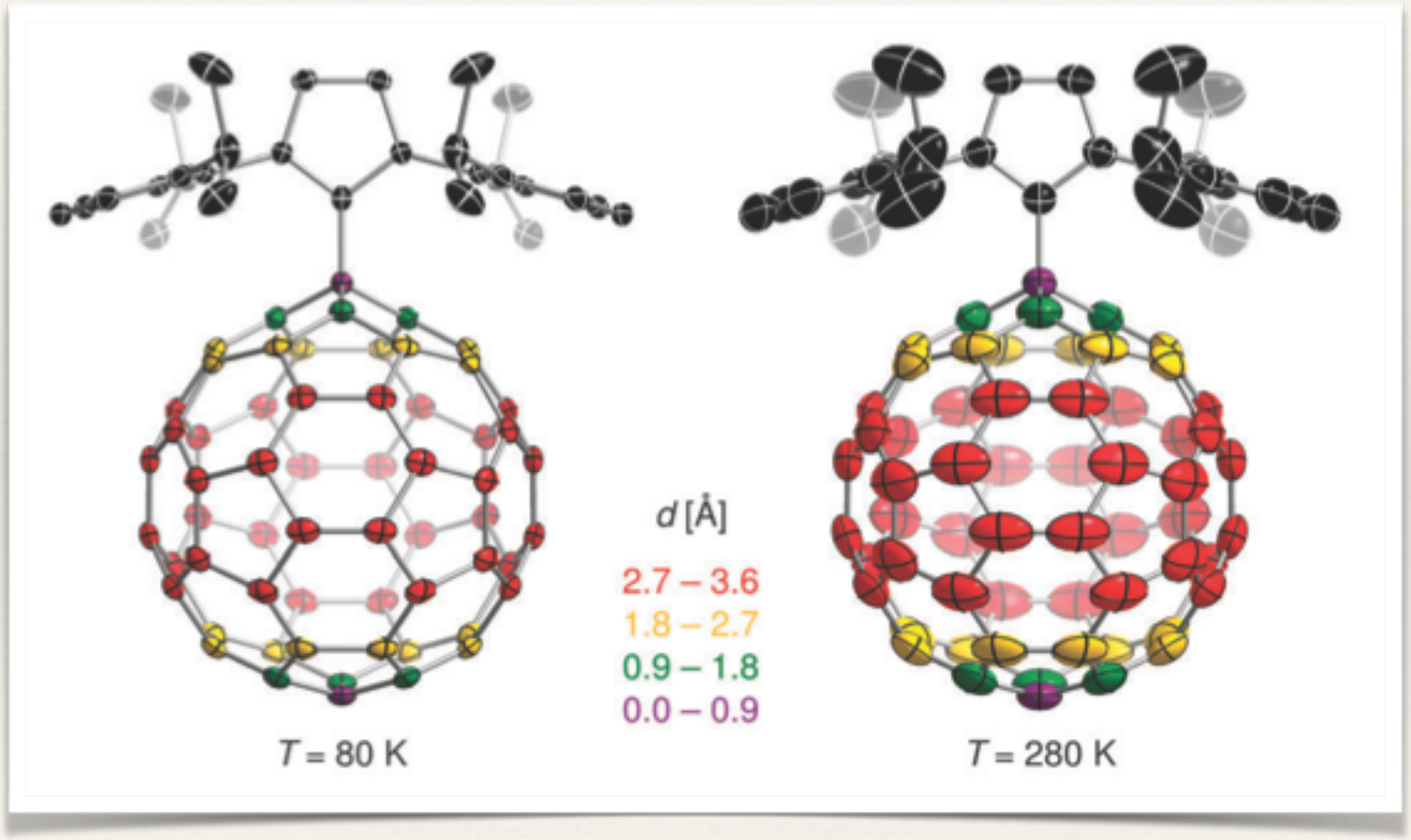
$d \approx 1.50 \text{Å}$

$T = 300 K$

$$\sqrt{\left\langle u^2 \right\rangle} \approx 0.07 \text{Å} \approx 5\% \; d$$

Thermal effects in crystal structures

Anisotropic displacement parameters (thermal ellipsoids) are used to describe the probability of finding a nucleus at a given position in space



Displacement ellipsoids
at 60% probability level

Molecular models for shape & symmetry analysis

To study the shape and symmetry of molecules we will consider simplified models equivalent to macroscopic objects with well defined geometrical features.

Ball and stick model

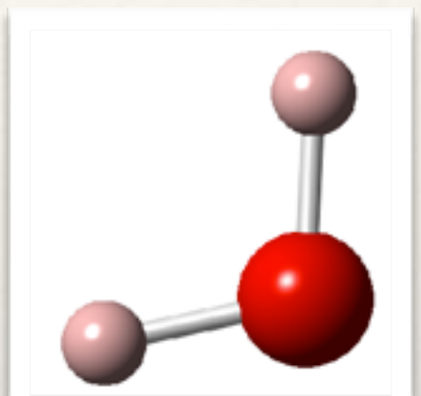
Space filling model

Computer rendering of molecular models

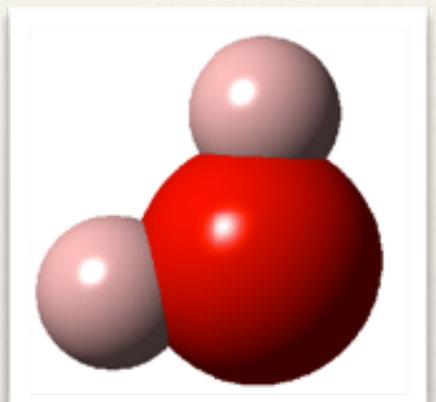
Physical models have been replaced nowadays by computer renderings

- Average position of atoms
- List of atomic radii (by default in plotting program)

```
3
Water
O 0.000   0.000    0.000
H 0.000   0.957    0.000
H 0.000  -0.240   -0.927
```

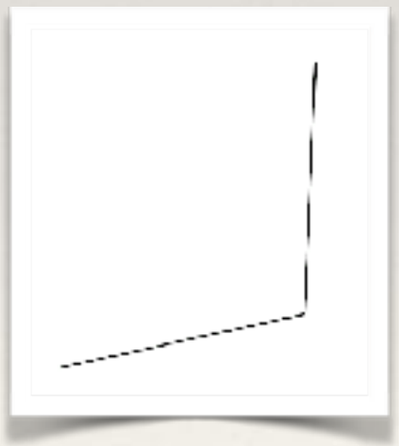


ball & stick



space filling

stick



wireframe

File in .xyz format:

```
number of atoms
title
Sy1   x1    y1    z1
Sy2   x2    y2    z2
…
```

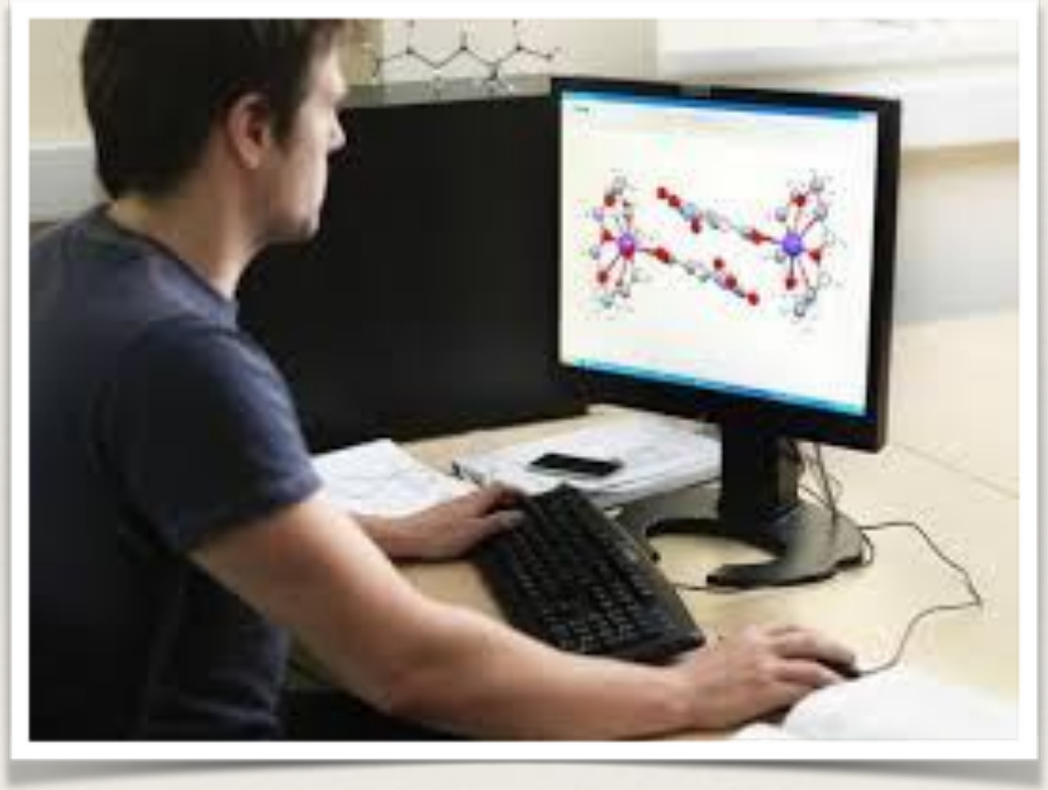
normally in Å,
but not mandatory

Other sources of molecular geometries

Theoretical and computational tools are nowadays another reliable source for molecular structures. Structures are obtained by **minimizing the energy** as a function of the relative position of nuclei.

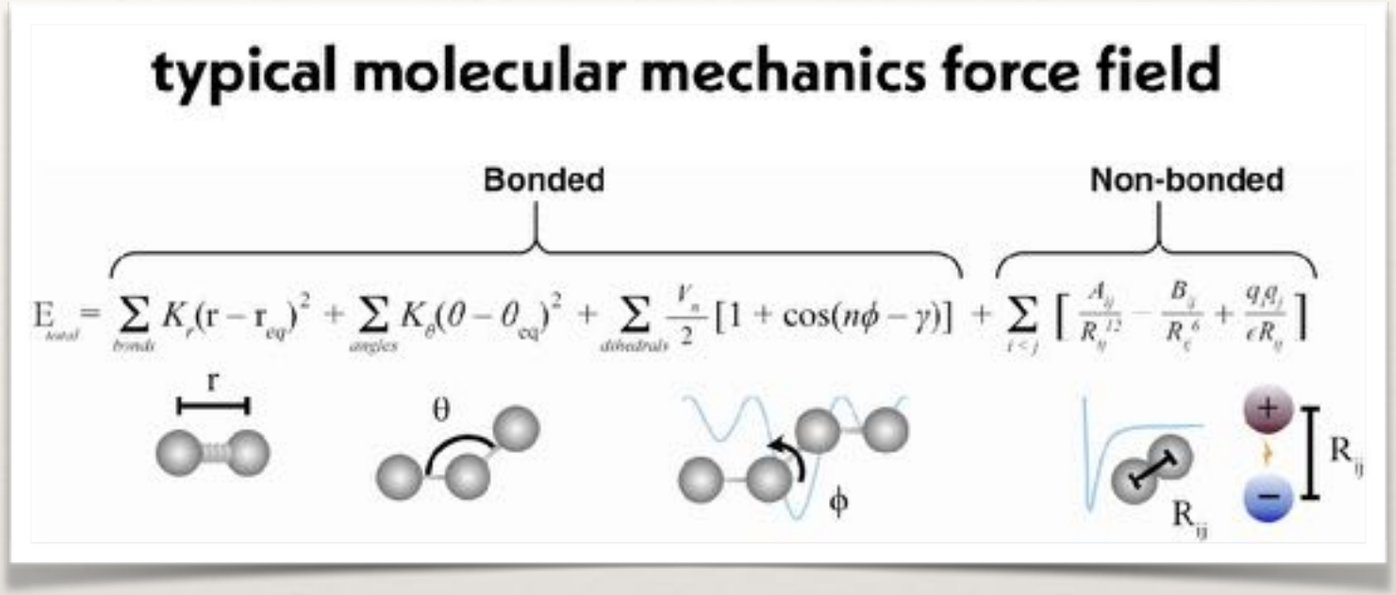
Two large families of computational models are readily available in standard programs:

- **Molecular mechanics** (atoms interacting through classical potentials)
- **Quantum chemistry** (explicit consideration of electrons)



Molecular mechanics

Molecular mechanics uses c**lassical mechanics** to model molecular systems. The potential energy for a set of interacting atoms is calculated as a function of the nuclear coordinates: $E(q_1, q_2, \ldots, q_N)$.



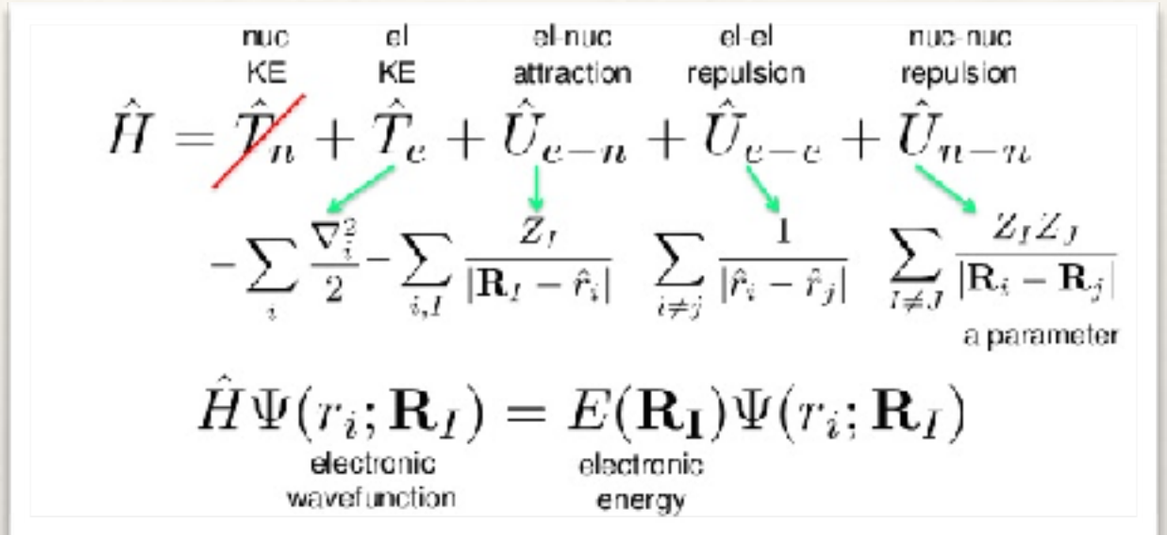
The **potential energy** in a given conformation is a **sum of individual energy terms using interatomic potentials**

- Simple mathematical expressions allow calculations for thousands of atoms
- Results depend on parametrization (force field)
- Reliable for organic molecules, application to coordination compounds is more difficult
- Provides only **molecular geometries**

Quantum chemistry

The total energy is determined by solving the **time-independent Schrödinger equation** within the **Born–Oppenheimer approximation**, which allows for the separation of electronic and nuclear motion.

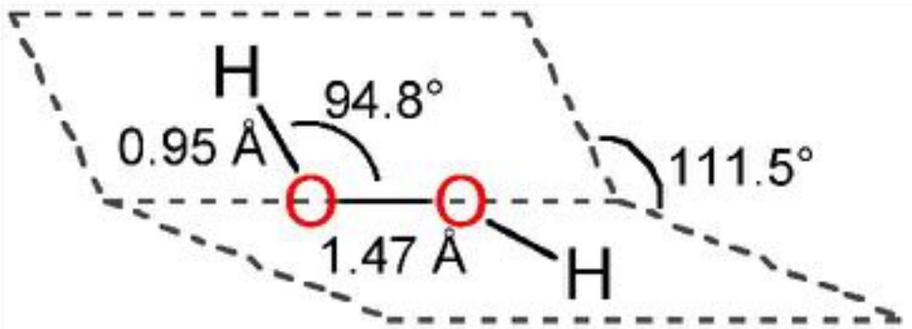
The total energy is a sum of the electronic energy at fixed nuclei positions and the nuclear repulsion energy.



- Computationally demanding, used for systems with hundreds of atoms
- Different approximations (*ab initio*, semiempirical, DFT, …)
- Using adequate approximations, reliable for all sorts molecules and geometries
- Provides **molecular geometry** and information on the **electron distribution**

Potential energy surfaces

The potential energy for a system with N atoms is a multidimensional function, which depends on 3N coordinates (positions of nuclei in space). Since E is invariant to translations and rotations, only 3N-6 (3N-5 for linear systems) coordinates are needed.



Molecular geometry is given either by a set of 3N cartesian coordinates (.xyz file) or by internal coordinates, a set of 3N-6 independent atomic distances, angles, and dihedral angles (Z-matrix).

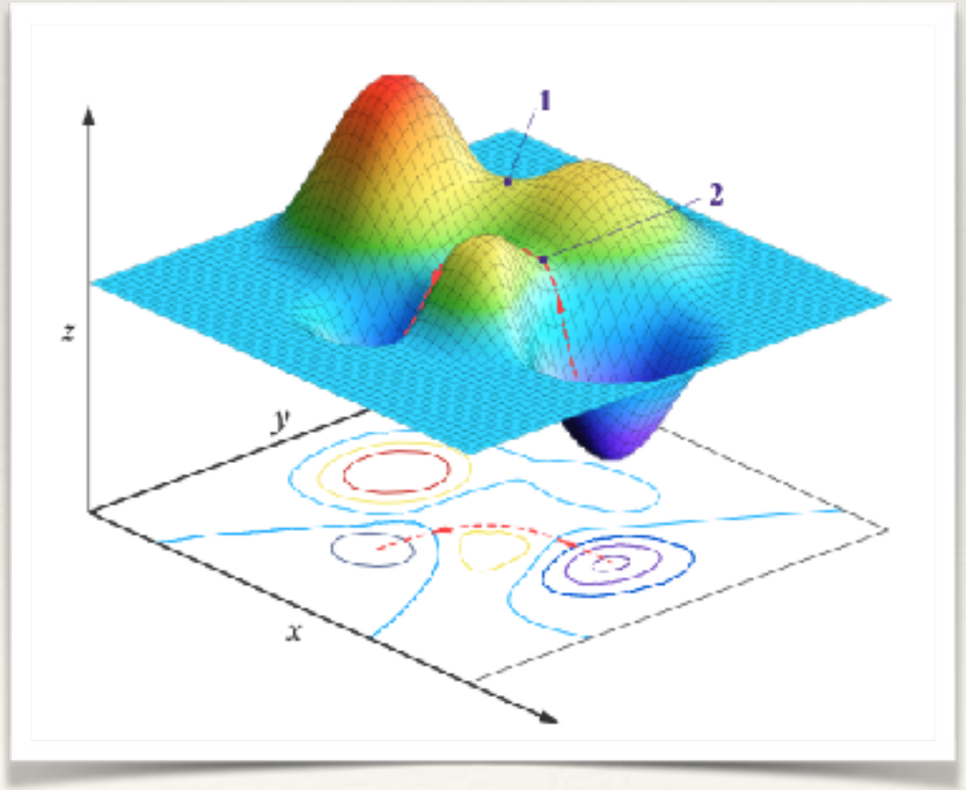
```
O
O    1    1.47
H    2    0.95   1    94.8
H    1    0.95   2    94.8   3   111.5
```

```
 O      0.000     0.000    0.000
 O      0.000     0.000    1.470
 H      0.947     0.000    1.549
 H     -0.347    -0.881   -0.079
```

Stationary points and paths

Any point on the E(q_1, q_2, …, q_{3N-6}) potential energy surface corresponds to a different molecular structure. Stationary points are points where the gradient of the PES vanishes:

$$\nabla E = \left(\frac{\partial E}{\partial q_1}, \frac{\partial E}{\partial q_2}, \ldots, \frac{\partial E}{\partial q_{3N-6}}\right) = 0$$



Relevant stationary points on E are:

- **minima** corresponding to stable **equilibrium geometries**
- **saddle points** corresponding to **transition states**

Other relevant geometries correspond to points in minimal energy paths joining two minima through a transition state (reaction paths).

Isomers, conformers & enantiomers