COMMONWEALTH OF AUSTRALIA

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Symmetry in Matter

Lecture 1

Unit Outline

Role of Models

Models and Mathematics

Classical vs Quantum

Lecture 2

Interparticle Interactions

Molecular Symmetry

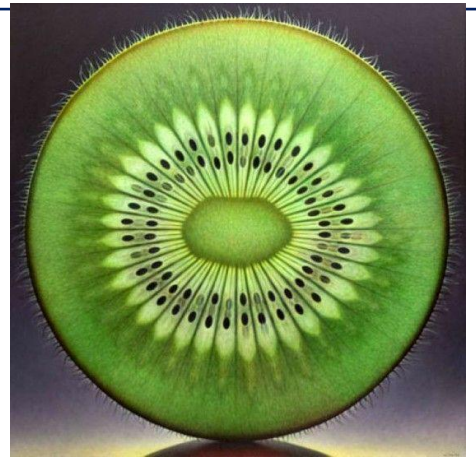
Lecture 3

Symmetry Elements

Point Groups

Symmetry in Nature













Symmetry in Art

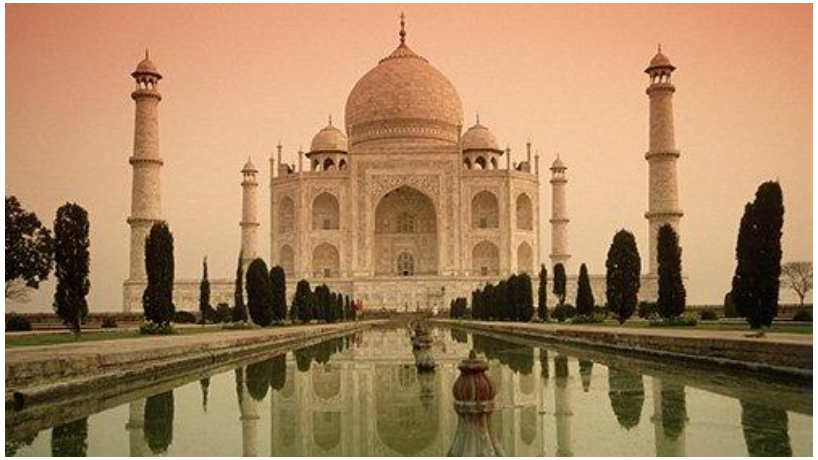






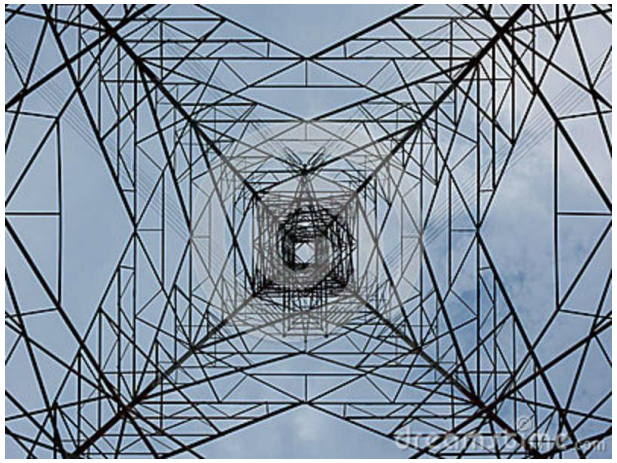


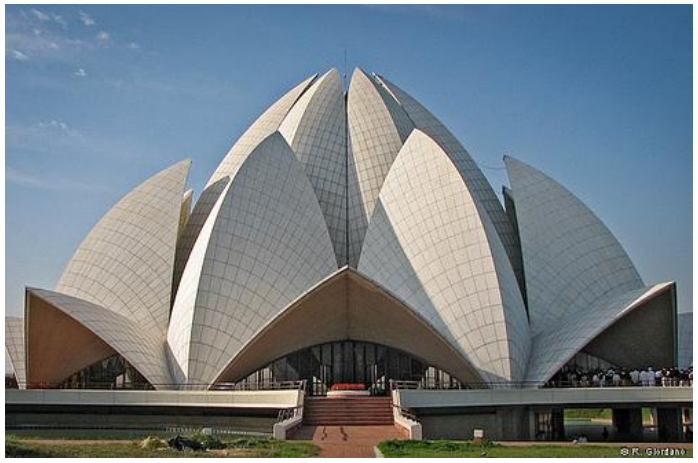
Symmetry in Architecture





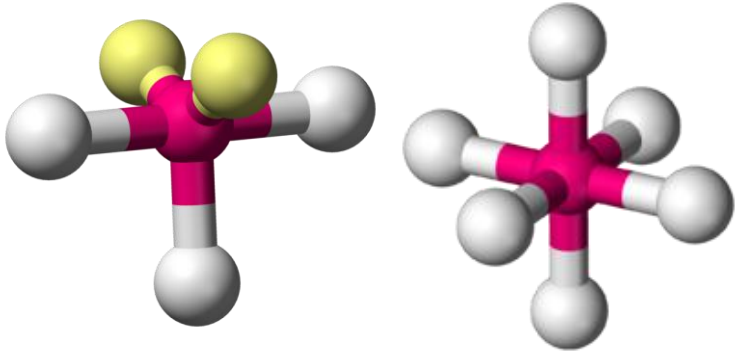


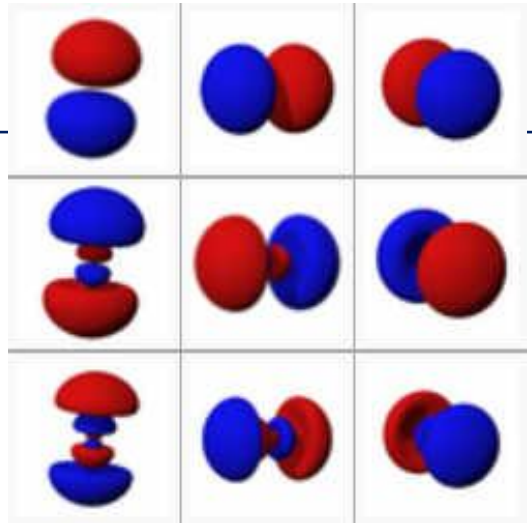


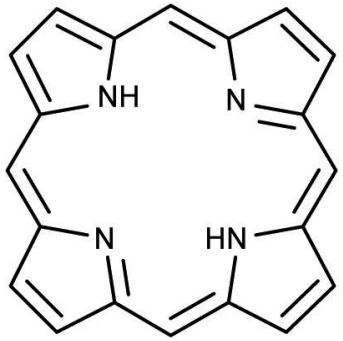


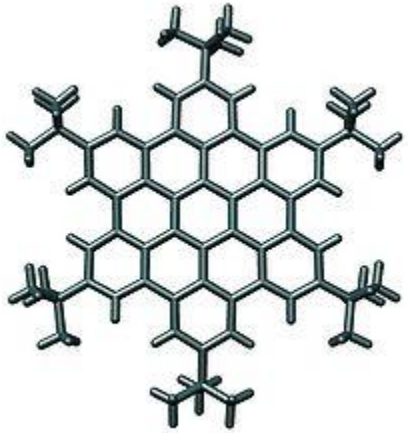


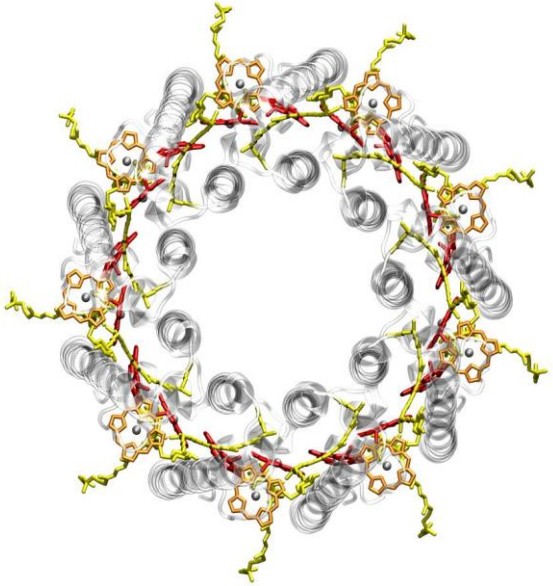
Symmetry in Chemistry







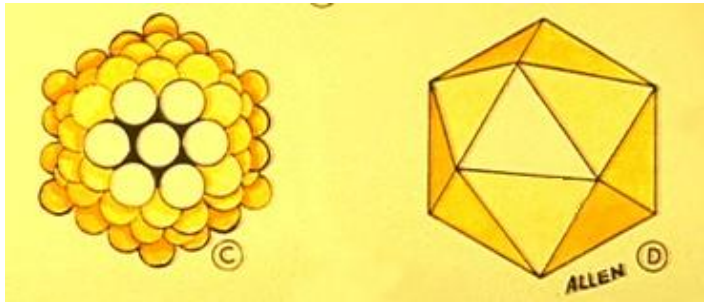


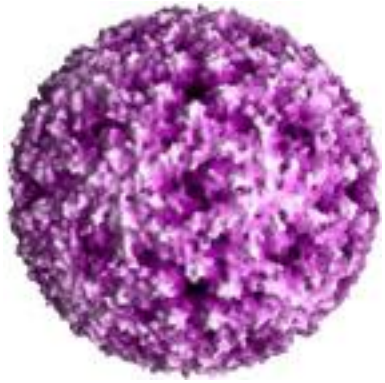


Molecular structure, electronic structure, supramolecular structure

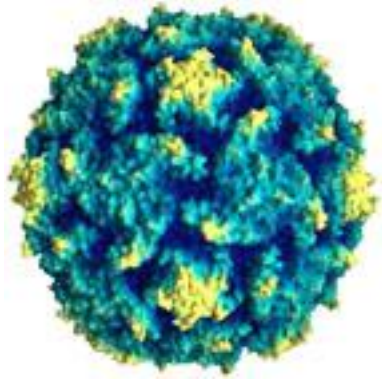
Symmetry in Biochemistry

Icosahedral viruses: 60+ units self-assemble into a supramolecular structure



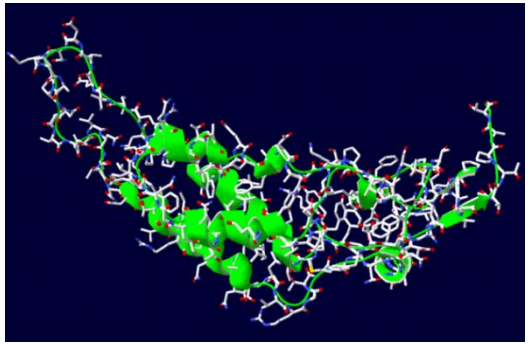


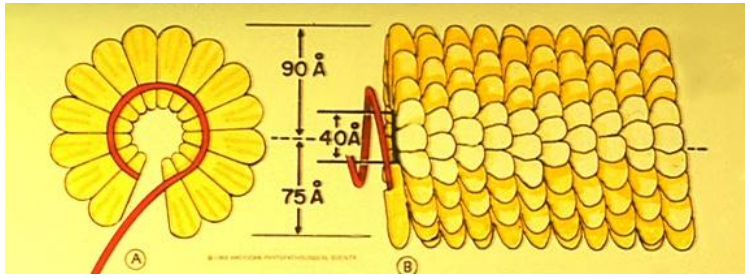
Foot and mouth

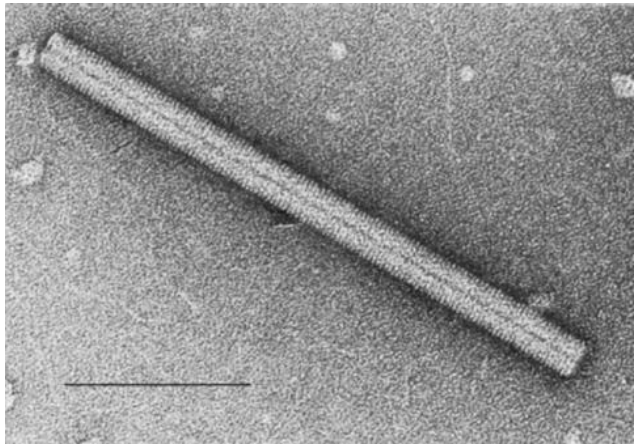


Polio

Tobacco mosaic virus: 2130 protein units self-assemble around a RNA strand via non-covalent interactions





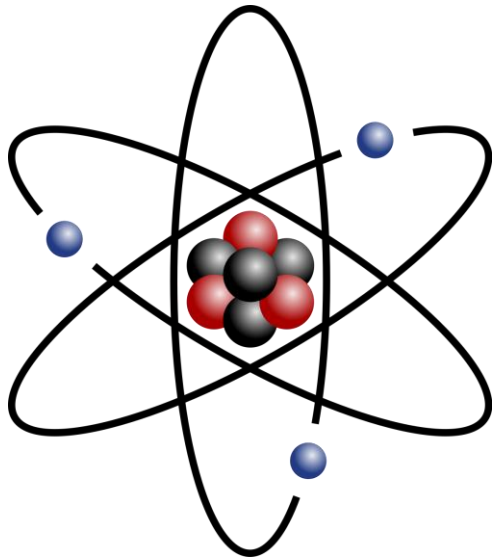


The Paradox of Matter

Matter is held together by Coulombic forces, whether in atoms or in the bulk.

Question: Why doesn't an atom collapse?

Answer: The balance of kinetic and potential energy in an atom is what keeps its electrons from collapsing into the nucleus.



https://en.wikipedia.org/wiki/Atomic_mass

For interest – some further reading:

https://chem.libretexts.org/Bookshelves/General_Chemistry/Chem1_(Lower)/05%3A_Atoms_and_the_Periodic_Table/5.08%3A_Why_Don't_Electrons_Fall_into_the_Nucleus

https://www.bu.edu/quantum/notes/GeneralChemistry/WhyAtomsDon'tCollapse.pdf

Stability of Atoms

Using the be Broglie relation $p = h/\lambda$ between the momentum $p = m\,u$ of a particle of mass m and speed u and the wavelength λ of the matter wave associated with it, we can express the kinetic energy of the electron as

$$\mathrm{KE} = \frac{1}{2}\,m\,u^2 = \frac{p^2}{2\,m} = \frac{h^2}{2\,m\,\lambda^2}.$$

Using Coulomb's law, we can write the potential energy of the electron of charge $-e$ a distance r from a nucleus of charge $+\,Z\,e$ ($Z = 1$ for hydrogen atom) as

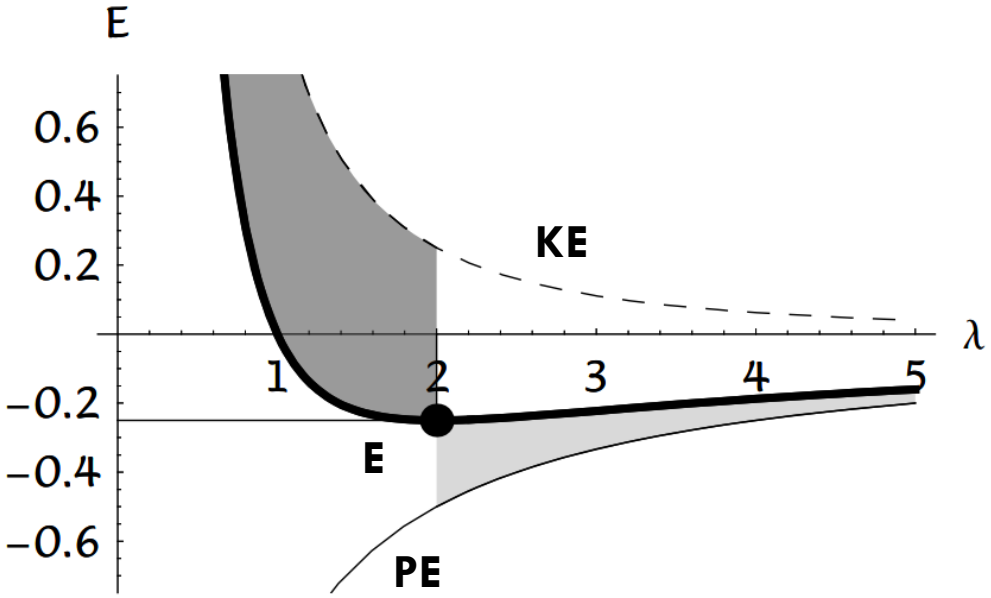
$$\mathrm{PE} = \frac{(Z\,e)\,(-e)}{4\,\pi\,\epsilon_0\,r} = -\frac{Z\,e^2}{4\,\pi\,\epsilon_0\,r} \approx -\frac{Z\,e^2}{4\,\pi\,\epsilon_0\,\lambda}$$

In the last expression we interpret the distance r as approximately equal to the matter wave wavelength λ. Combining the expressions for kinetic energy and potential energy, we see that the total energy depends on matter wave wavelength as

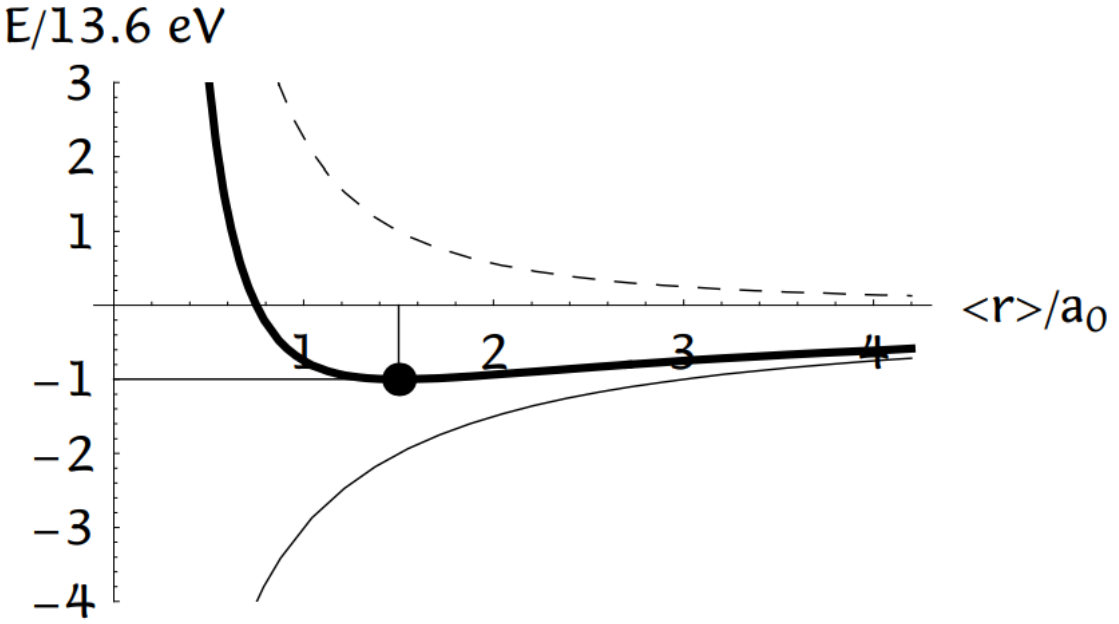
$$E = \mathrm{KE} + \mathrm{PE} \propto \frac{1}{\lambda^2} - \frac{1}{\lambda}.$$

Stability of Atoms

$$E = \text{KE} + \text{PE} \propto \frac{1}{\lambda^2} - \frac{1}{\lambda}$$



After accounting for the shape of the electron matter wave, we can plot E vs r (the distance from the nucleus).

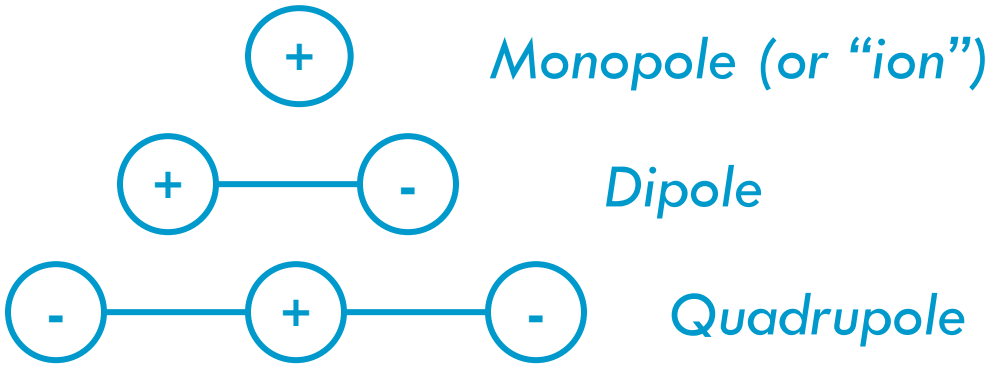


E_{min} at $\langle r \rangle = 1.5$

When $\langle r \rangle < 1.5$ the KE becomes very large, opposing the spherical wave becoming more compact, preventing the collapse into the nucleus.

Bonding: Electrostatic Potentials

The potential energy (V) of bonds is related to the electronic properties of atoms and molecules:



$$V \propto \frac{1}{r^{n+m-1}}$$

where r = separation between charges

n, m = 1 for monopole

= 2 for dipole

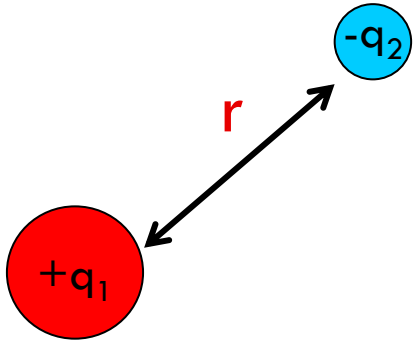
= 4 for quadrupole

V	$\propto$	$1/r$	for	ion-ion (i.e., ionic bond)
	$\propto$	$1/r^2$	for	ion-dipole
	$\propto$	$1/r^3$	for	dipole-dipole
	$\propto$	$1/r^7$	for	quadrupole-quadrupole

Bonding: Electrostatic Potentials

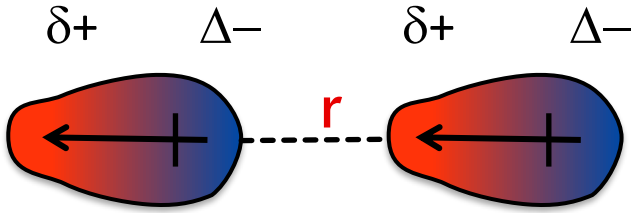
- Coulomb: q_1, q_2

$$V(r) = -\frac{q_1 q_2}{4\pi\varepsilon_0 r}$$



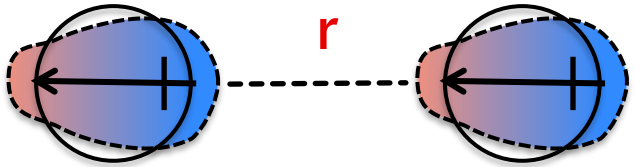
- Dipole-Dipole: μ_1, μ_2

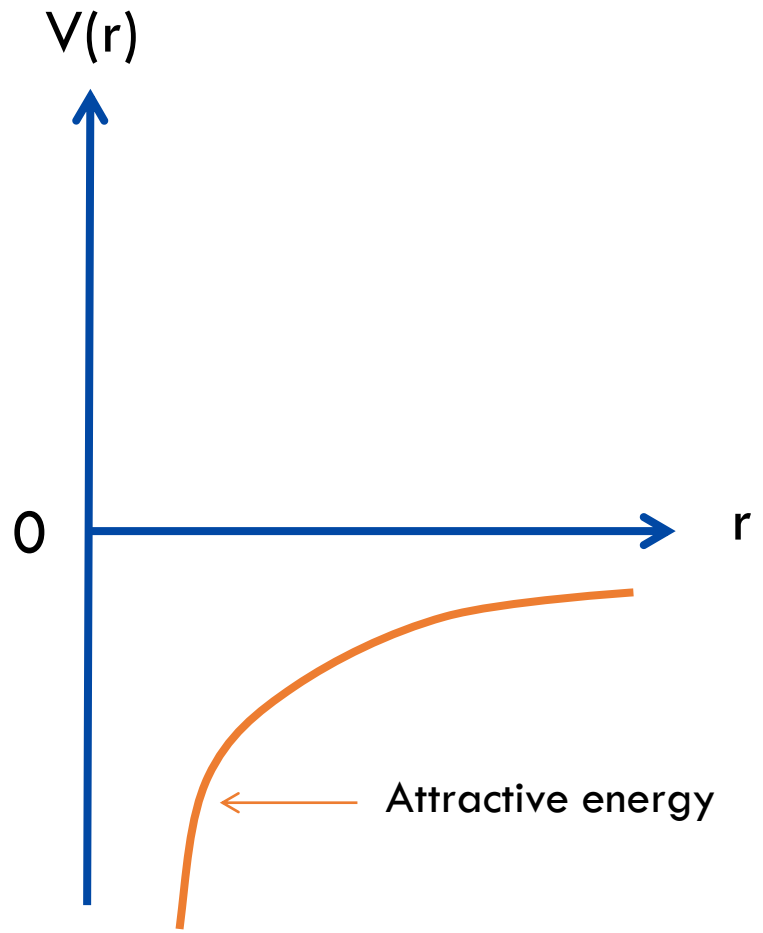
$$V(r) = -\frac{\mu_1 \mu_2}{2\pi\varepsilon_0 r^3}$$



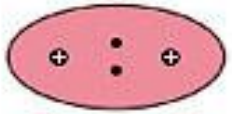
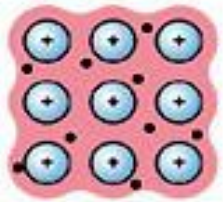
- Induced Dipole-Induced Dipole: μ_1, I_1, μ_2, I_2

$$V(r) = -\frac{C_6}{r^6} \approx -\frac{\frac{3}{2}\alpha_1\alpha_2}{r^6}\frac{I_1 I_2}{I_1 + I_2}$$





Recall: Intra- and Inter-molecular Forces

Force	Model	Basis of Attraction	Energy (kJ/mol)	Example
Intramolecular				
Ionic		Cation–anion	400–4000	NaCl
Covalent		Nuclei–shared e^- pair	150–1100	H—H
Metallic		Cations–delocalized electrons	75–1000	Fe
Intermolecular				
Ion-dipole		Ion charge–dipole charge	40–600	$Na^+\cdots O\begin{matrix}H\\H\end{matrix}$
H bond		Polar bond to H–dipole charge (high EN of N, O, F)	10–40	$:\ddot{O}-H\cdots:\ddot{O}-H$ (H, H)
Dipole-dipole		Dipole charges	5–25	I—Cl····I—Cl
Ion-induced dipole		Ion charge–polarizable e^- cloud	3–15	$Fe^{2+}\cdots O_2$
Dipole-induced dipole		Dipole charge–polarizable e^- cloud	2–10	H—Cl····Cl—Cl
Dispersion (London)		Polarizable e^- clouds	0.05–40	F—F····F—F

https://phet.colorado.edu/sims/html/states-of-matter/latest/states-of-matter_en.html

Bonding: Potential Energy Curves

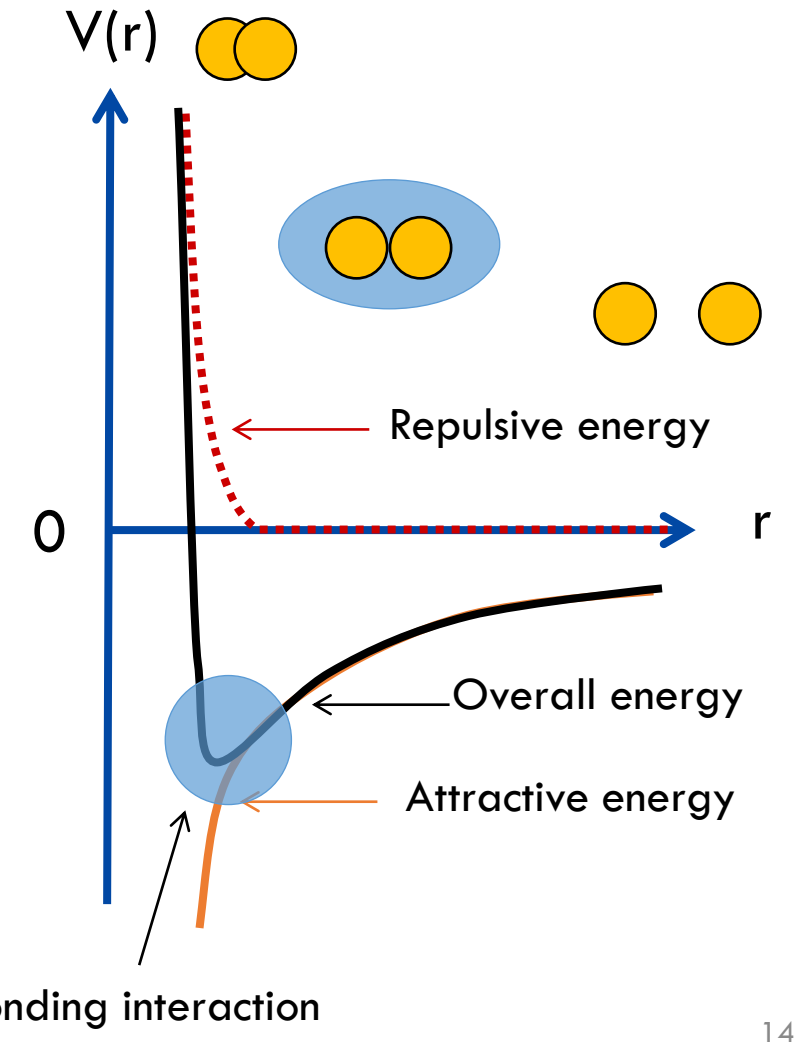
Consider a diatomic molecule

At large r there is no interaction between the atoms.

As the atoms approach each other, the attractive force between electron of each atom and the nucleus of the other atom lowers the potential energy.

(This outweighs the repulsive force between the electrons.)

At close distance, the repulsive force (very strong) between the + charged nuclei dominates.



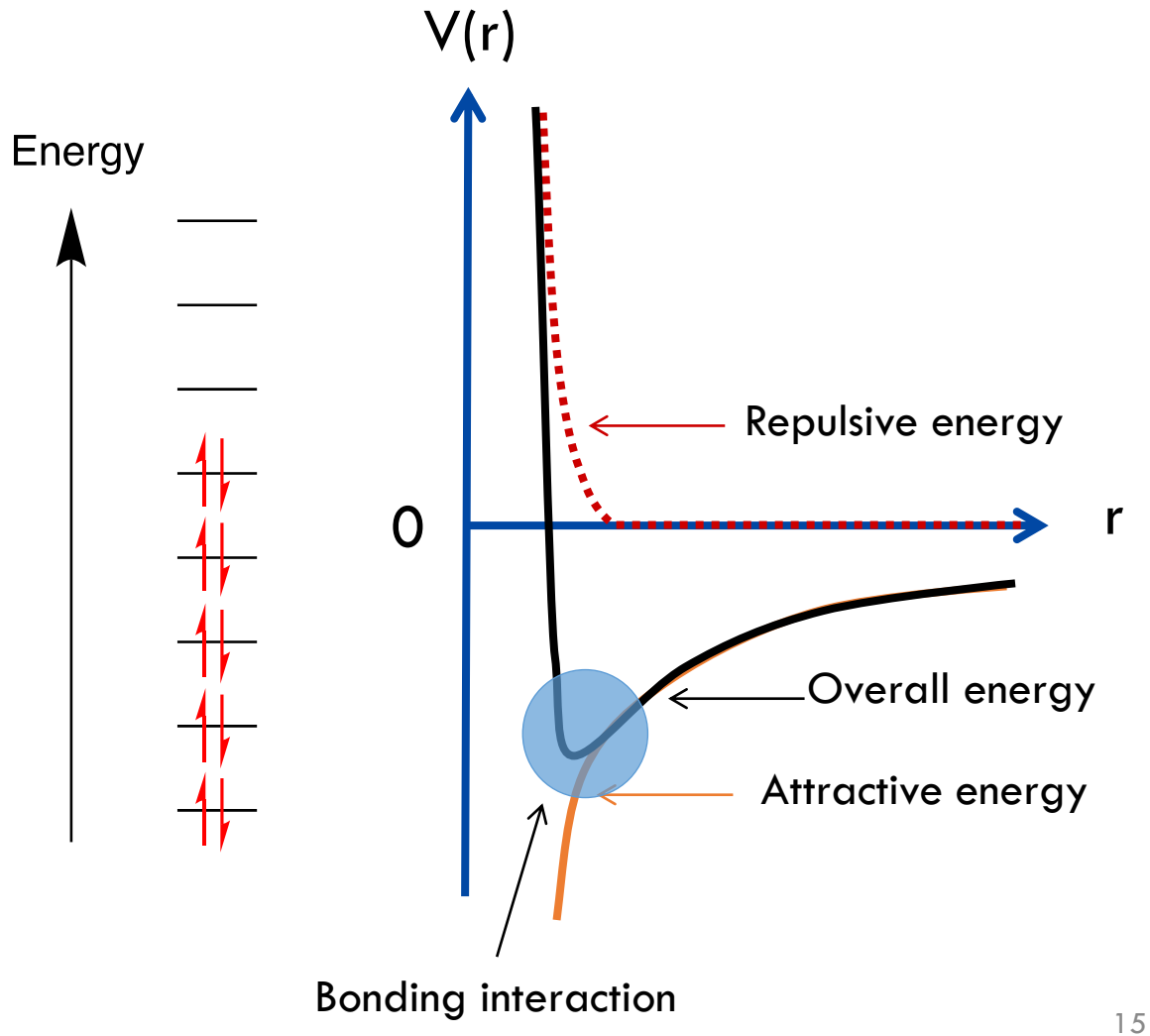
https://phet.colorado.edu/sims/html/states-of-matter/latest/states-of-matter_en.html

Bonding: Potential Energy Curves

Pauli Exclusion Principle

No two electrons in an atom may be in the same quantum state.

- No two electrons can have same four quantum numbers, *n*, *l*, *m*, and s.
- No orbital (specified by *n*, *l*, *m*) can be occupied by more than two electrons.



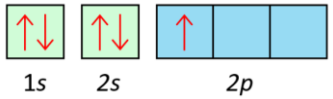
Bonding and the Implications on Structure

Number of valence electrons < number of valence atomic orbitals

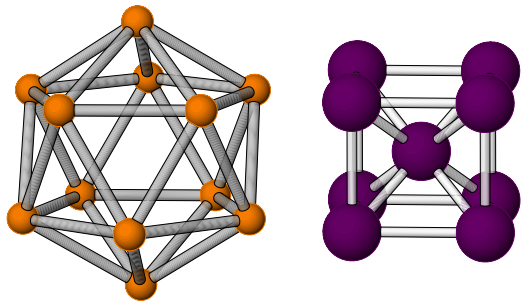
Number of valence electrons ≥ number of valence atomic orbitals

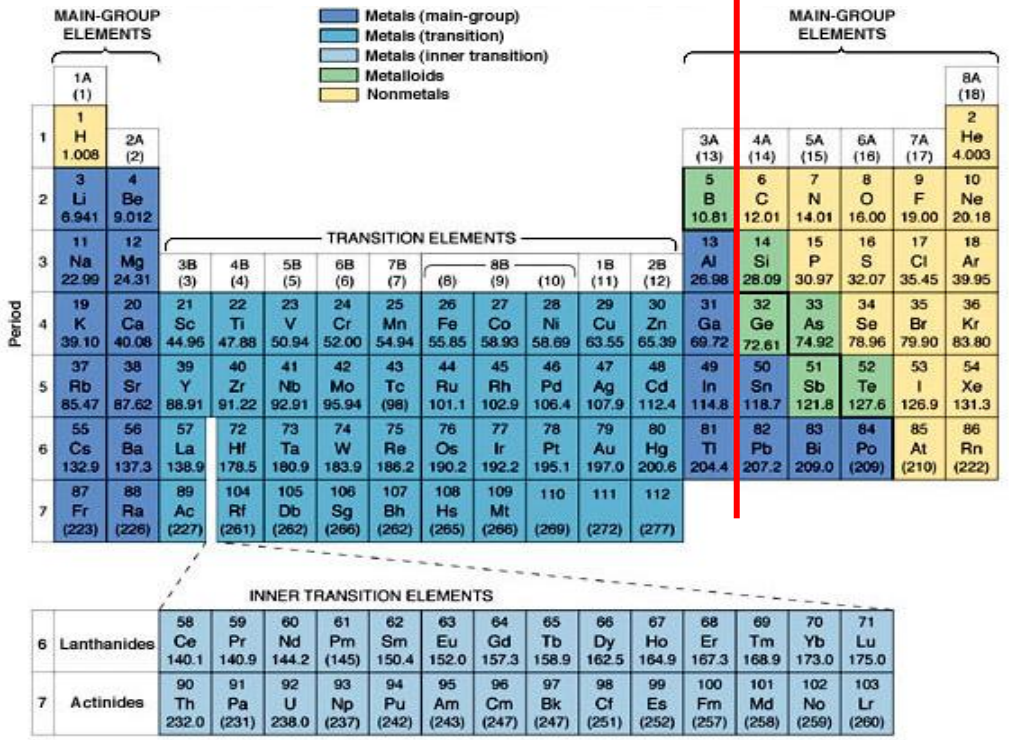
E.g., **boron**
No. of valence electrons = 3
No. of valence atomic orbitals = 4

$1s^2, 2s^2, 2p^1$



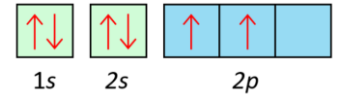
Can't achieve inert gas configuration through covalent bonding



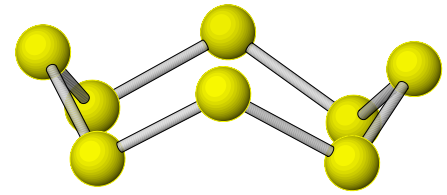


E.g., **carbon**
No. of valence electrons = 4
No. of valence atomic orbitals = 4

$1s^2, 2s^2, 2p^2$



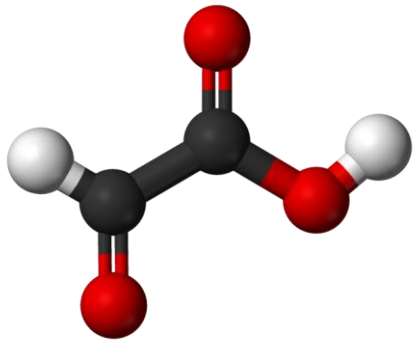
Inert gas configuration can be achieved through 2-centre, 2-electron covalent bonds (and lone pairs)



Bonding and the Implications on Structure

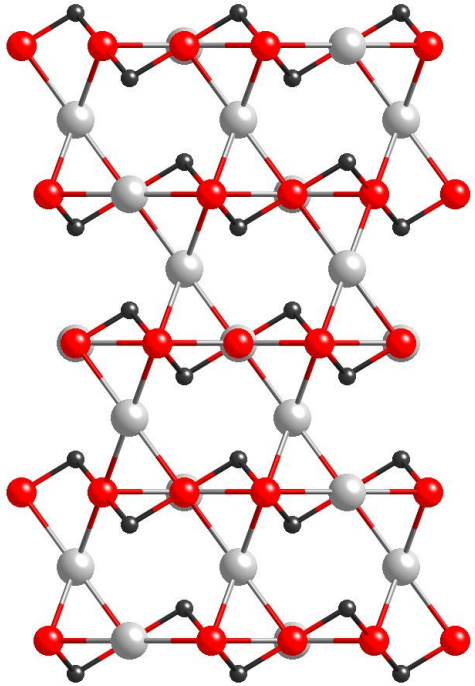
Elements in the same group near the “line” show different bonding

Consider these two compounds built of (valence) isoelectronic elements:



$C_2H_2O_3$
Glyoxylic acid

vs.



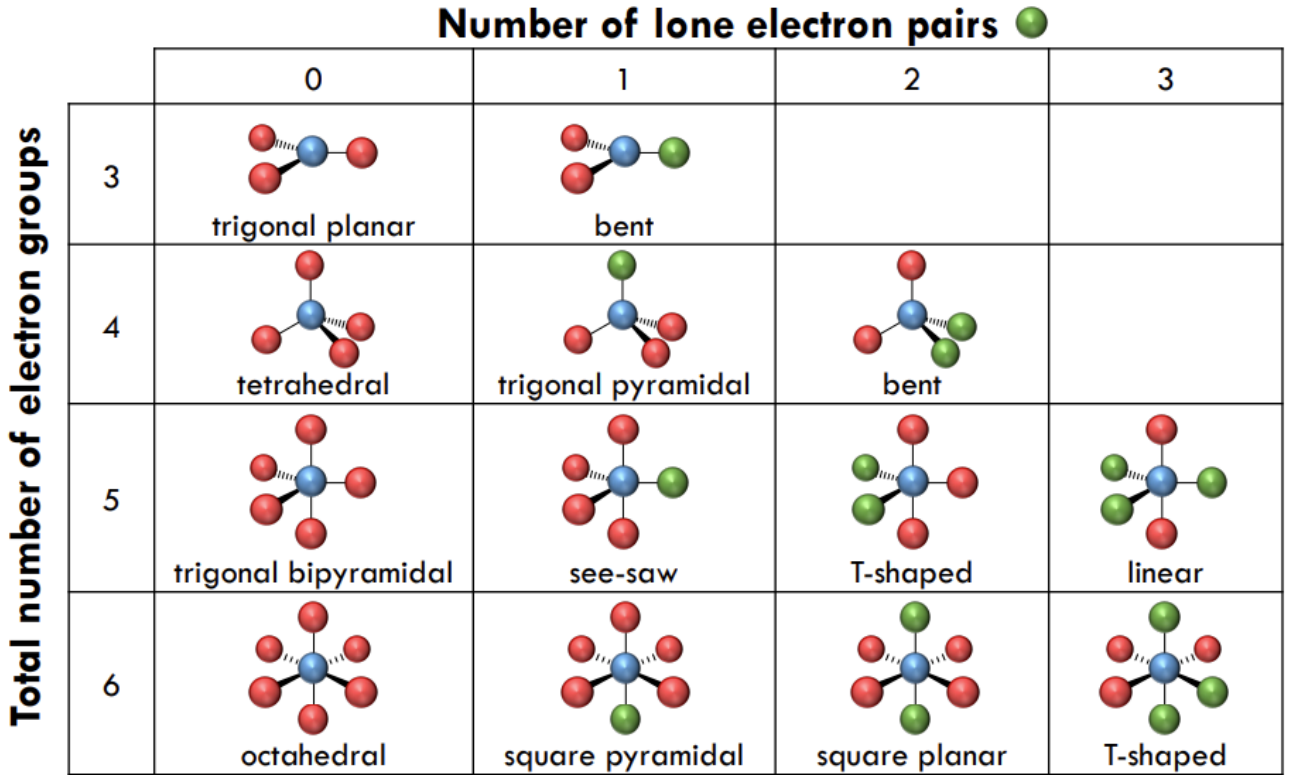
$Sn_2K_2O_3$

Isoelectronic elements have the same number of valence electrons. I.e., elements in the same group.

Electron and Molecular Geometry

To minimise the potential energy of these repulsive interactions, electron groups need to be arranged so they are as far away from each other as possible.

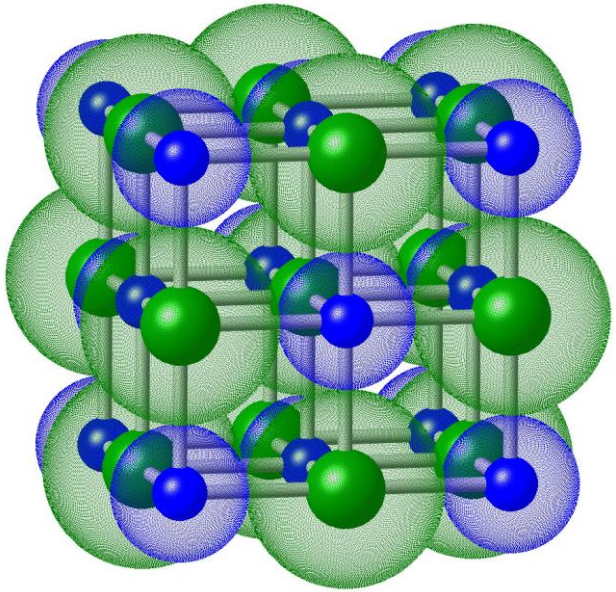
VSEPR tells us the geometry corresponding to the minimum potential energy (i.e., the 3D arrangement in which electron groups are farthest away from each other).



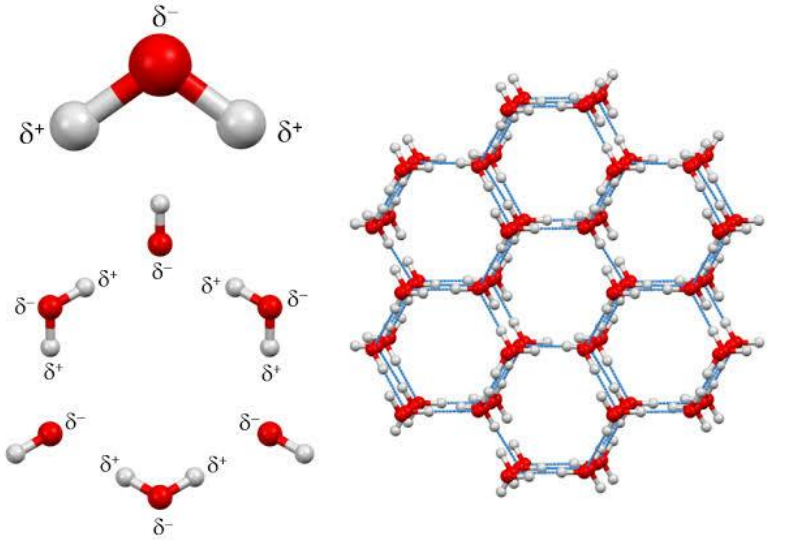
Bonding in Molecules and Crystals

Forces are acting in different (and sometimes opposite) directions in molecules and crystals.

NaCl

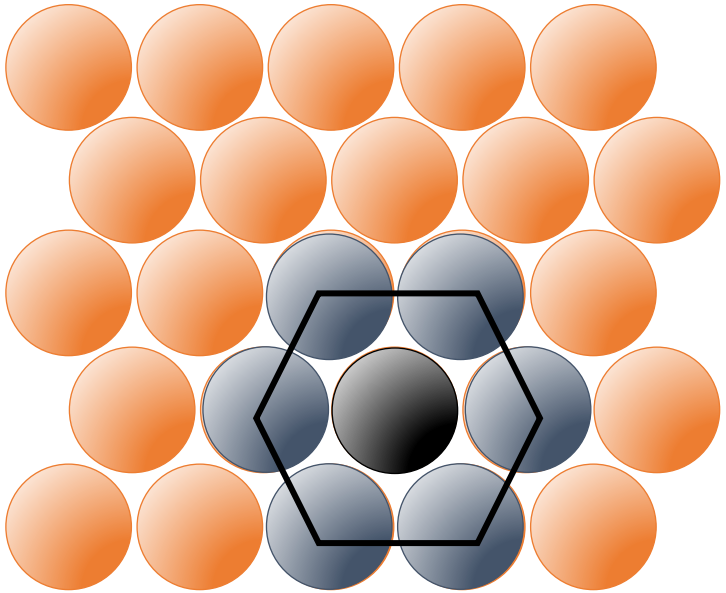


Ice



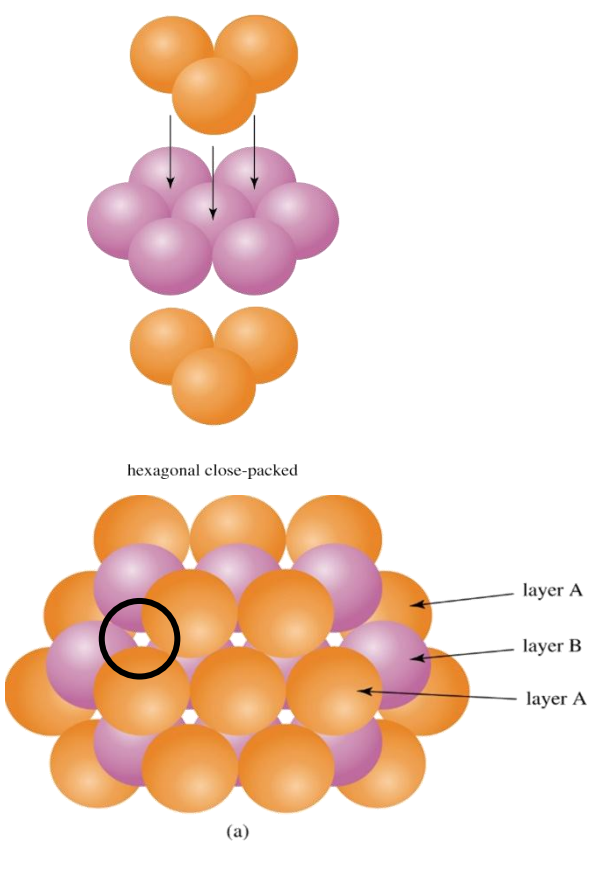
https://crystalsymmetry.wordpress.com/category/ice/

Cubic and Hexagonal Close-Packing

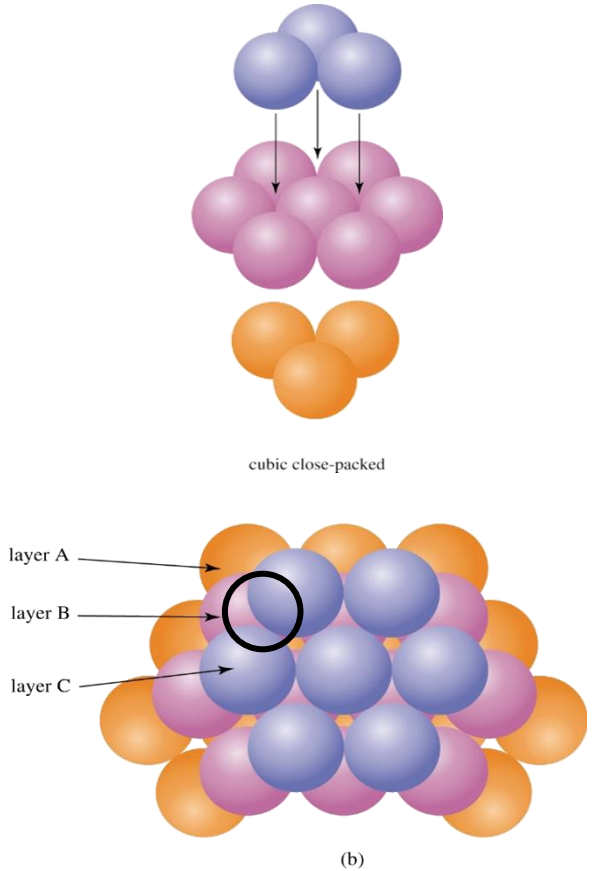


2 choices for the third layer

12 nearest neighbours



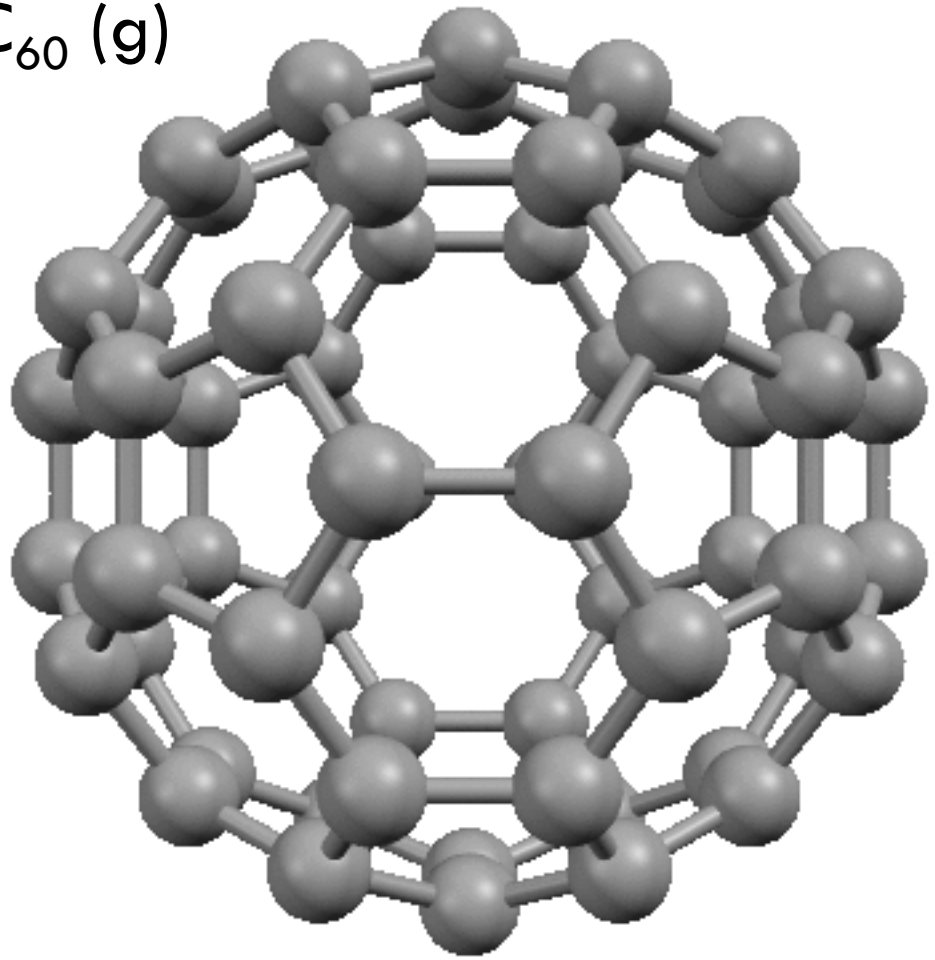
ABAB pattern
Hexagonal close-packed (hcp)



ABCABC pattern
Cubic close-packed (ccp) or
Face-centred cubic (fcc)

Why is symmetry useful?

C_{60} (g)

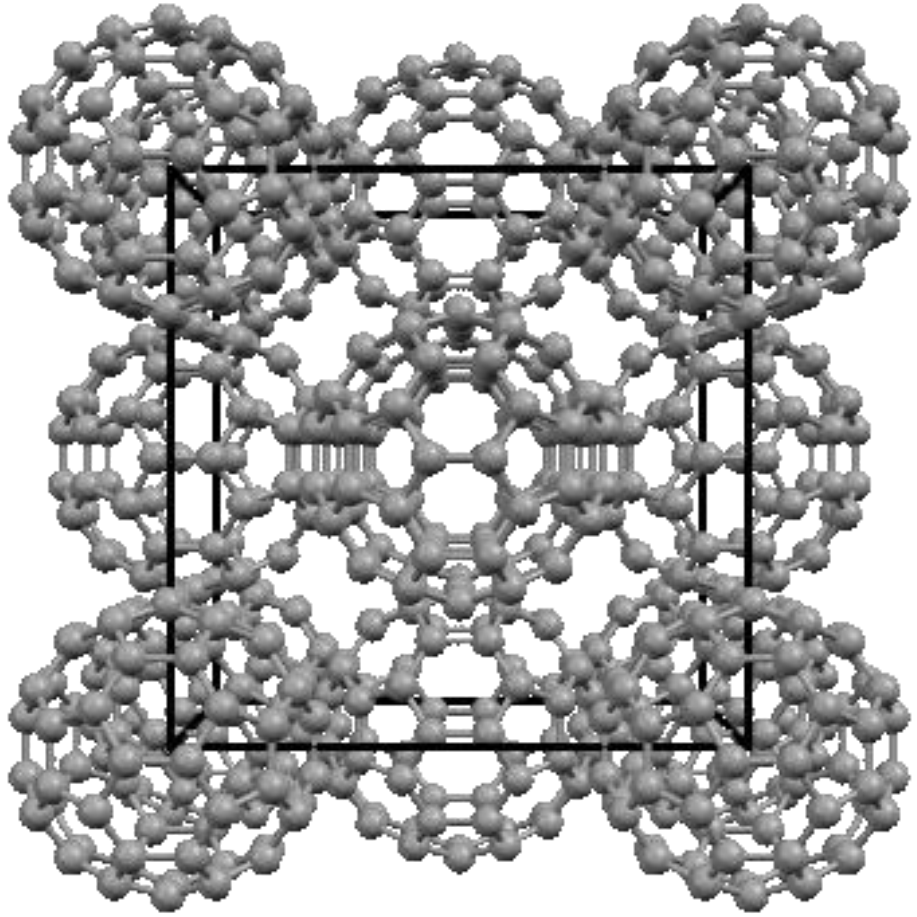


Computer modelling a C_{60} gas molecule:

x, y, z coordinates for each C atom = 3 x 60
= 180 numbers

Why is symmetry useful?

C_{60} (s)



Computer modelling a C_{60} solid:

12 g = Avogadro's number of atoms
x, y, z coordinates for each C atom = 3 x 6.022×10^{22}
= 2×10^{24} numbers

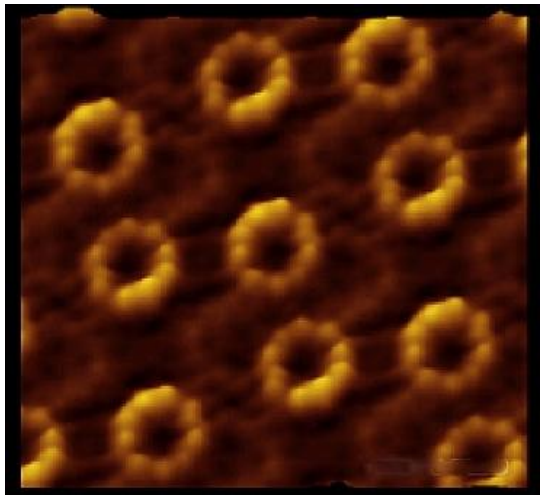
The amount of computer storage in the world is ~10^{21}

Symmetry Elements

- Rotational symmetry
- Reflection (mirror) symmetry
- Inversion symmetry
- Translational symmetry
- Symmetry combinations











Symmetry Definitions

Symmetry Operation:

- A transformation that maps a given molecular geometry onto itself, i.e. it moves atoms onto equivalent atoms/interchanges equivalent atoms.

Symmetry Element:

- Geometric elements (axes, planes, points) with respect to which symmetry operations are carried out.

Four symmetry operation for molecules:

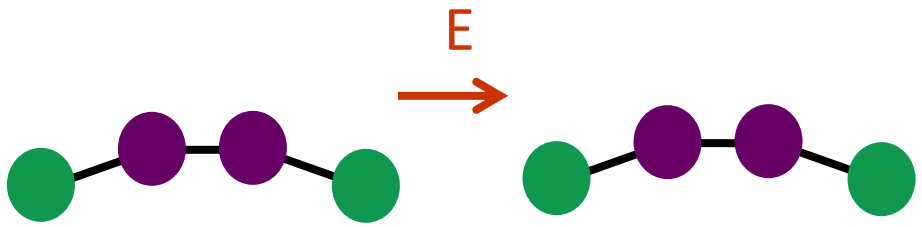
- Rotation
- Reflection
- Inversion
- Improper rotation

Three types of symmetry element:

- Axis of rotation
- Plane of reflections
- Inversion point
- (Improper rotation involves an axis of rotation and a plane of reflection)

The Identity Operator (E)

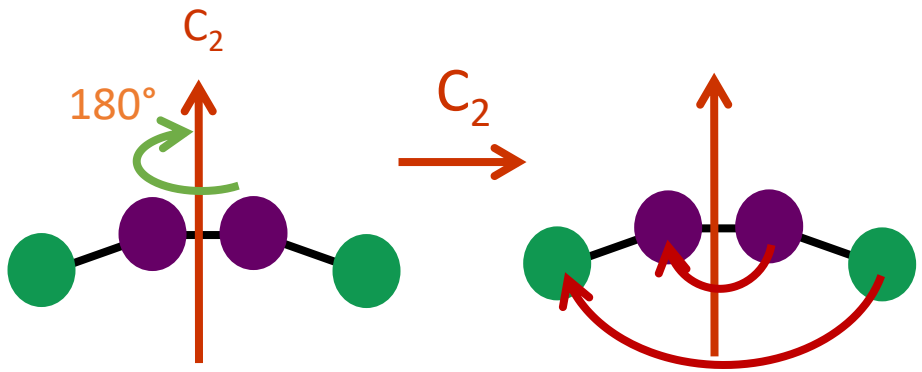
E is the identity operation, where we ‘do nothing’



Every molecule has the E operation

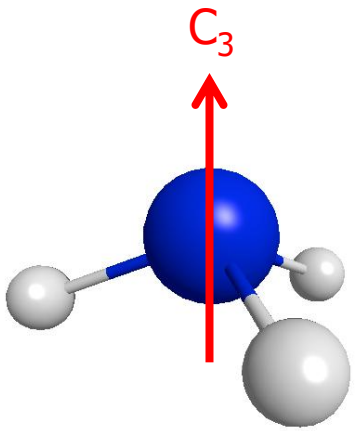
Rotation (C_n)

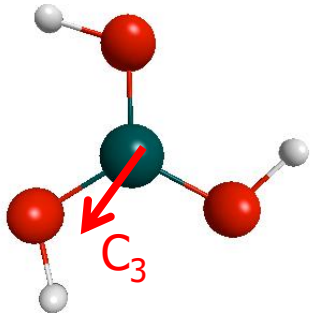
C_n is a rotation through $2\pi/n$ (or $360°/n$) about a fixed axis, i.e., the molecule has an n-fold rotation

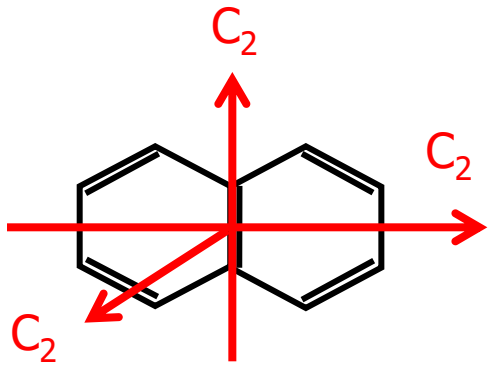


Rotation (C_n)

An axis about which an n-fold rotation by 360°/n gives an identical configuration.



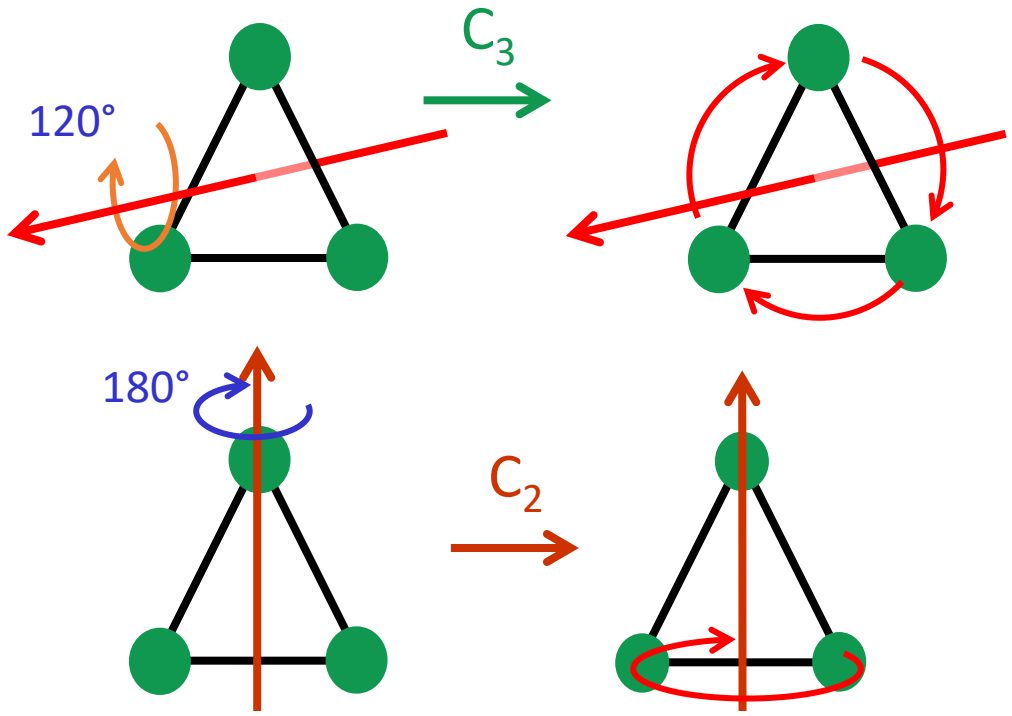




Rotation (C_n)

Some molecules have more than one axis of rotation.

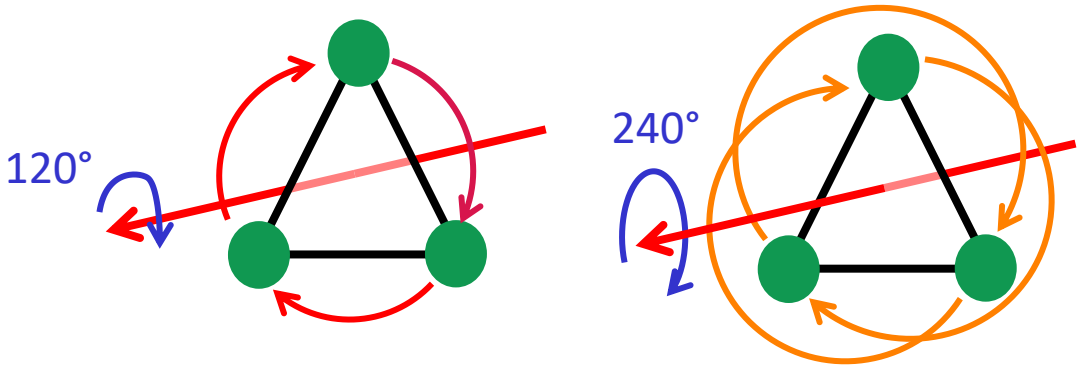
The **Principal Axis** is the axis with the highest n (here, C_3). By convention it is assigned as the z-axis.



Rotation (C_n)

Each C_n generates more than one operation.

There are (n-1) possible rotations about an n-fold (C_n) axis



120° = C_3

+240°= C_3^2

There are <u>two</u> C_3 rotations:

C_3 & C_3^2

Also e.g.,

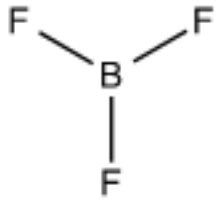
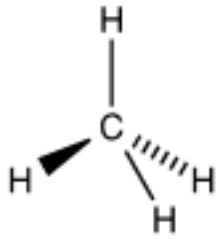
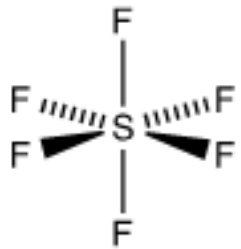
$C_4^2 \equiv C_2$

$C_n^n \equiv E$

Worksheet: What is Symmetry?

Critical thinking questions

1. Consider the following molecules. Which of these molecules do you think has the most symmetry?

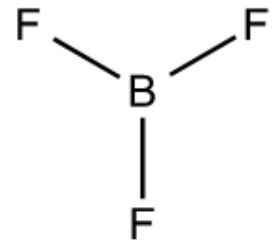
(a) 	(b) 	(c) 
(d)  $C_3H_3^+$	(e)  $C_5H_5^-$	(f)  C_6H_6

2. On what basis did you make your decision?

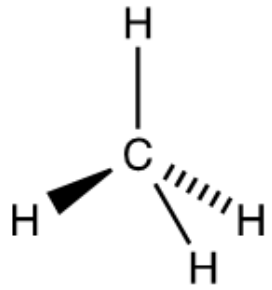
Worksheet Models 1-3: Rotational Symmetry

1. Identify the principal rotation axis in each of the molecules below. Draw the axis and write the label for the symmetry element.

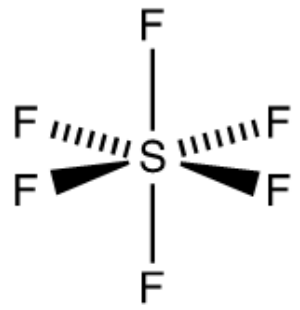
(a)



(b)



(c)



(d)



$C_3H_3^+$

(e)



$C_5H_5^-$

(f)



C_6H_6

Learning Outcomes

After this lecture you should be able to

- Understand the stability of matter.
- Understand what is meant by symmetry.
- Identify and name different types of rotational symmetries within objects and molecules.
- Complete the lecture worksheet and identify rotational symmetries in the molecules, pictures and objects given in Q1–4 of Tutorial Sheet 1 (in Week 2).

Further reading: Weller, Overton, Rourke & Armstrong, Inorganic Chemistry 6th Ed. OUP, 2014, Chapter 3.1–3.5; Blackman, Bottle, Schmid, Mocerino & Wille, Chemistry, 3rd Ed. Wiley & Sons, 2016, Chapter 7.