

Chemical bonding

A-Level Chemistry

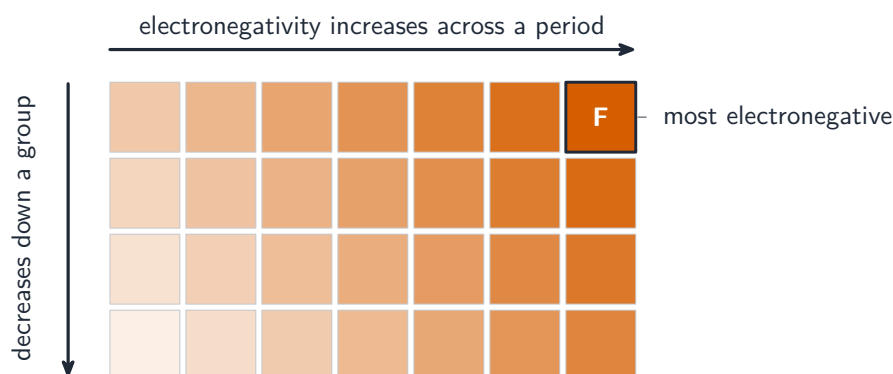
Electronegativity

Electronegativity 电负性 is the power of an atom to attract the **electrons** 电子 in a bond towards itself.

Three factors decide how electronegative an atom is:

- **nuclear charge** 核电荷: more protons pull the bonding electrons more strongly.
- **atomic radius** 原子半径: the closer the bond is to the nucleus, the stronger the pull.
- **shielding** 屏蔽 by inner shells and sub-shells: more inner electrons weaken the pull on the bonding electrons.

So electronegativity **rises** across a period (more nuclear charge, smaller radius) and **falls** down a group (larger radius, more shielding). Fluorine is the most electronegative element.



Electronegativity rises across a period and falls down a group, so fluorine is the most electronegative element

You can use the difference in **Pauling electronegativity** 鲍林电负性 values to predict the bond type. A large difference gives an **ionic** bond; a small difference gives a **covalent** bond.

Ionic bonding

Ionic bonding 离子键 is the **electrostatic attraction** 静电引力 between oppositely charged **ions** 离子—positive **cations** 阳离子 and negative **anions** 阴离子.

It forms when a metal gives electrons to a non-metal. Good examples are sodium chloride (NaCl), magnesium oxide (MgO) and calcium fluoride (CaF₂). The ions pack into a regular giant **lattice** 晶格, held together by the attraction in every direction.



sodium gives its outer electron ($\times$) to chlorine

Ionic bonding in NaCl: sodium transfers its single outer electron to chlorine, giving Na^+ and a full-octet Cl^-



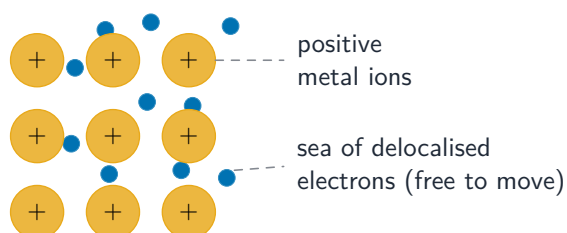
A real crystal of rock salt (halite, NaCl); the cubic shapes mirror the giant ionic lattice inside

Image: Didier Descouens, CC BY-SA 4.0 (commons.wikimedia.org)

Metallic bonding

Metallic bonding 金属键 is the electrostatic attraction between positive metal ions and a "sea" of **delocalised electrons** 离域电子.

The outer electrons are free to move through the whole metal. This explains why metals conduct electricity and are strong.



Metallic bonding: positive metal ions sit in a sea of delocalised electrons that are free to move

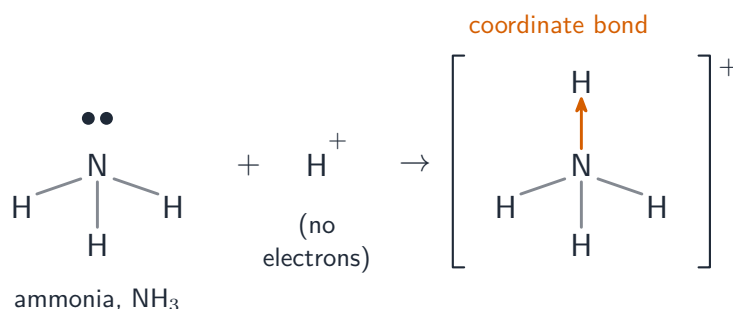
Covalent and coordinate bonding

Covalent bonding 共价键 is the electrostatic attraction between the nuclei of two atoms and a shared pair of electrons.

Simple molecules with covalent bonds include H_2 , O_2 , N_2 , Cl_2 , HCl , CO_2 , NH_3 , CH_4 , C_2H_6 and C_2H_4 . A double bond shares two pairs; a triple bond (as in N_2) shares three pairs.

Atoms in Period 3 and below can **expand the octet** 扩展八隅体—hold more than eight electrons in their outer shell. Examples are SO_2 , PCl_5 and SF_6 .

A **coordinate bond** 配位键 (also called a dative covalent bond) is a covalent bond where both shared electrons come from the same atom. For example, when ammonia and hydrogen chloride gases meet, the lone pair on the nitrogen forms a coordinate bond to H^+ , making the ammonium ion NH_4^+ . Coordinate bonds also join the two halves of the Al_2Cl_6 molecule.



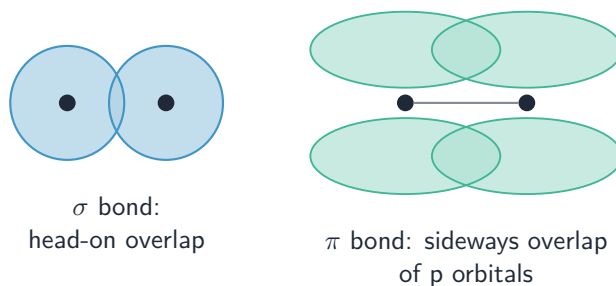
A coordinate (dative) bond: nitrogen's lone pair forms the fourth N–H bond, both electrons coming from N

Sigma and pi bonds

Covalent bonds form when **orbitals** 轨道 overlap:

- a **sigma bond** σ 键 forms by the direct, head-on **overlap** 重叠 of orbitals between the two atoms.
- a **pi bond** π 键 forms by the sideways overlap of two p orbitals, above and below the sigma bond.

A single bond is one sigma bond. A double bond (as in C_2H_4) is one sigma plus one pi bond. A triple bond (as in N_2 and HCN) is one sigma plus two pi bonds.



A σ bond forms by direct head-on overlap; a π bond forms by the sideways overlap of two p orbitals, above and below

Hybridisation

Hybridisation 杂化 mixes orbitals in the same shell to make new, equal orbitals for bonding:

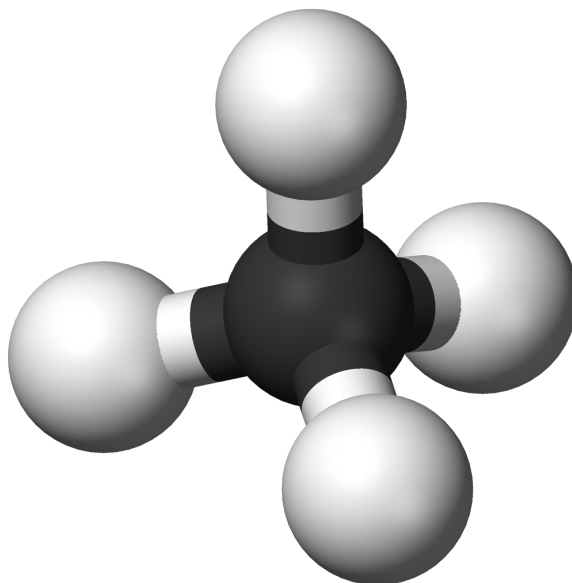
- sp : two equal orbitals, used in a linear molecule.
- sp^2 : three equal orbitals, used in a flat molecule like C_2H_4 .
- sp^3 : four equal orbitals, used in CH_4 .

Bond energy and bond length

- **bond energy** 键能 is the energy needed to break one mole of a particular covalent bond in the gas state.
- **bond length** 键长 is the distance between the centres of the two bonded atoms.

A shorter bond is usually stronger (higher bond energy). Triple bonds are shorter and stronger than double bonds, which are shorter and stronger than single bonds. Stronger bonds make a molecule harder to react.

Shapes of molecules



A molecular model shows the three-dimensional shape of a covalent molecule.

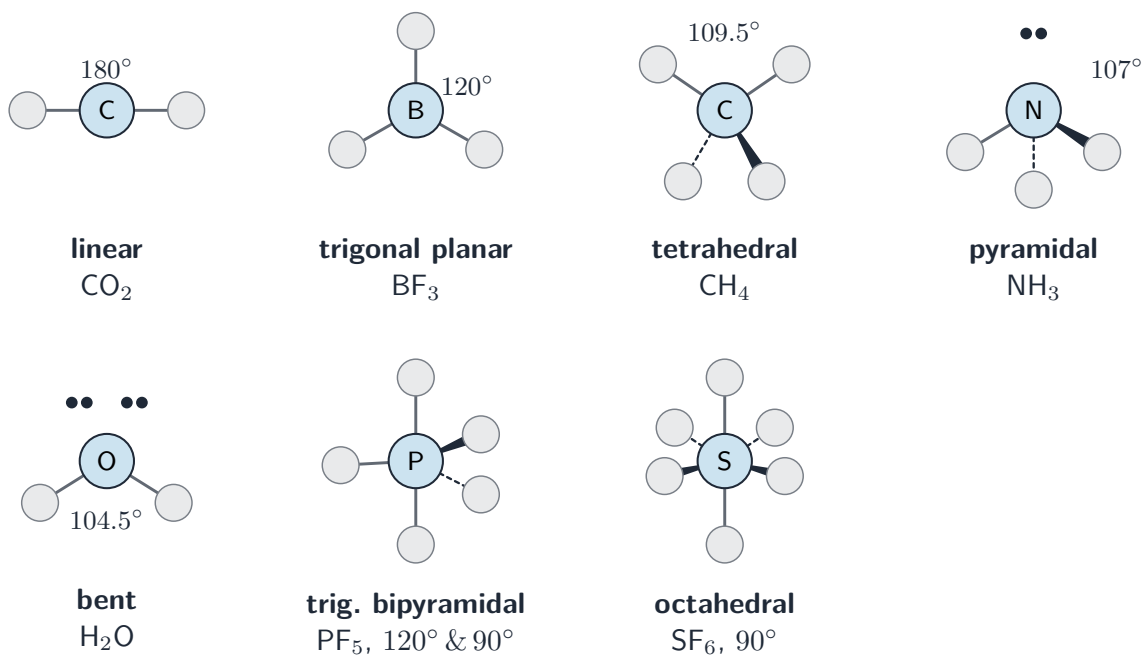
Image: Public domain (commons.wikimedia.org)

To work out a shape, use **VSEPR theory** 价层电子对互斥理论: the pairs of electrons around the central atom push apart as far as possible, because like charges repel.

A **lone pair** 孤对电子 (not in a bond) pushes more strongly than a **bonding pair** 成键电子对. Each lone pair squeezes the **bond angle** 键角 by about 2.5° .

Molecule	Shape	Bond angle
CO ₂	linear 直线形	180°
BF ₃	trigonal planar 平面三角形	120°
CH ₄	tetrahedral 四面体形	109.5°
NH ₃	pyramidal 三角锥形	107°
H ₂ O	bent 角形	104.5°
PF ₅	trigonal bipyramidal 三角双锥形	120° and 90°
SF ₆	octahedral 八面体形	90°

NH₃ has one lone pair and H₂O has two, which is why their angles drop below the 109.5° of CH₄. You can predict the shapes of similar molecules and ions in the same way.



The seven shapes from VSEPR theory; the lone pairs on NH_3 and H_2O push harder, squeezing the bond angle below 109.5°

Worked example. Predict the shape and bond angle of NH_3 and of H_2O . Nitrogen has 5 outer electrons and forms 3 bonds, leaving **3 bonding pairs and 1 lone pair** - four pairs in total, so they start from the tetrahedral 109.5° . The lone pair repels more strongly and squeezes the angle by about 2.5° , giving a **pyramidal** shape at about 107° . Oxygen forms 2 bonds and keeps **2 lone pairs**: still four pairs, but now two squeezes, so the shape is **bent** at about 104.5° . Count **all** the pairs to fix the basic geometry, subtract 2.5° for **each** lone pair, and name the shape from the **atoms** - NH_3 has four pairs but is pyramidal, not tetrahedral.

Intermolecular forces

Intermolecular forces 分子间作用力 are the forces *between* **molecules** 分子. They are much weaker than the ionic, covalent and metallic bonding *inside* substances.

Bond polarity and dipoles

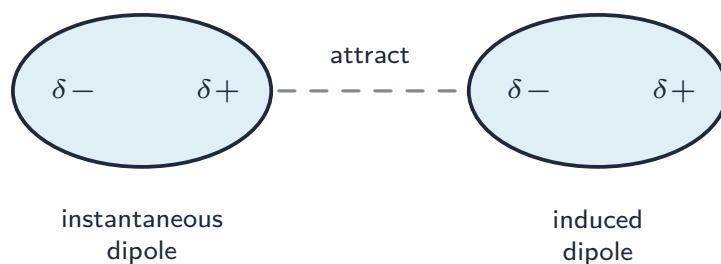
When two atoms with different electronegativity share a bond, the electrons sit closer to the more electronegative atom. The bond then has a **polarity** 极性: one end is slightly negative (δ^-) and the other slightly positive (δ^+). This separation of charge is a **dipole** 偶极.

If the dipoles in a molecule do not cancel, the whole molecule has a **dipole moment** 偶极矩 and is polar. If they cancel by symmetry (as in CO_2), the molecule is non-polar.

Van der Waals' forces

Van der Waals' forces 范德华力 is the general name for all intermolecular forces. There are two main types.

The first type is the instantaneous dipole–induced dipole force, also called the **London dispersion force** 伦敦色散力. Moving electrons make a brief **instantaneous dipole** 瞬时偶极, which then creates a matching **induced dipole** 诱导偶极 in a nearby molecule. These forces act between all molecules and get stronger when there are more electrons.

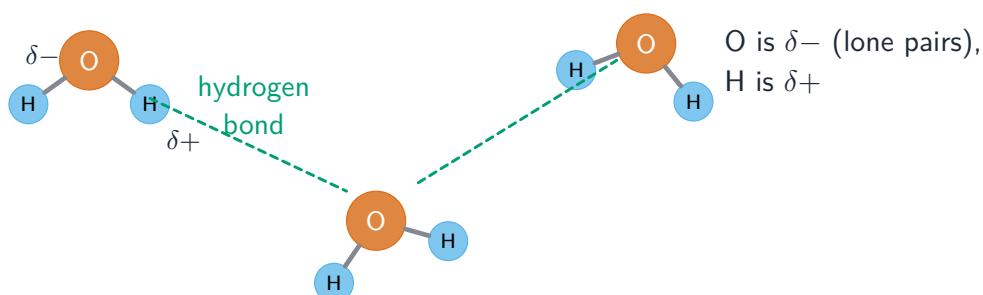


A London force: a momentary dipole in one molecule induces a dipole in its neighbour, so they attract —this acts between all molecules

The second type is the permanent dipole–permanent dipole force. It acts between molecules that are always polar, because each one has a **permanent dipole** 永久偶极.

Hydrogen bonding

Hydrogen bonding 氢键 is a strong, special case of permanent dipole forces. It forms when hydrogen is bonded to a very electronegative atom —nitrogen, oxygen or fluorine—and is attracted to a lone pair on an N, O or F atom in a neighbour. Look for N–H and O–H groups, as in ammonia and water.



Hydrogen bonding in water: a $\delta +$ hydrogen is attracted to a lone pair on the $\delta -$ oxygen of a neighbouring molecule

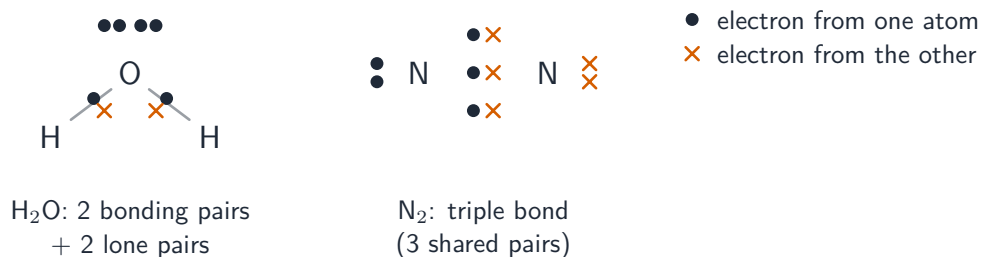
Hydrogen bonding explains the strange behaviour of water:

- its high melting and **boiling point** 沸点, because many hydrogen bonds must be broken.

- its high **surface tension** 表面张力.
- ice is **less dense** than liquid water, because hydrogen bonds hold the molecules in an open, spread-out structure, so ice floats.

Dot-and-cross diagrams

A **dot-and-cross diagram** 点叉图 shows the outer electrons of each atom, using dots for one atom and crosses for the other. This makes it clear where each bonding electron came from. You can draw them for ionic, covalent and coordinate bonding, including molecules with an expanded octet or an odd number of electrons.



Covalent dot-and-cross: each shared pair is one electron from each atom. Water has two bonding pairs and two lone pairs; nitrogen shares three pairs (a triple bond)

Exam tips

- For **shapes**, count bonding pairs and lone pairs, name the shape, then give the exact bond angle (e.g. NH_3 : pyramidal, 107°) —each lone pair lowers the angle by about 2.5° .
- A **dative (coordinate) bond** has both electrons from one atom (e.g. NH_4^+ , H_3O^+); draw the arrow from the lone pair.
- Name the intermolecular force precisely: **hydrogen bonding** needs H bonded to N, O or F; otherwise it is permanent-dipole or induced-dipole (van der Waals). Never call van der Waals forces "bonds".
- Explain a physical property by stating **which forces are broken**, not just "strong bonds".