Intra-atomic and Intermolecular Interactions

II.1. Introduction

Intra-atomic and intermolecular interactions are fundamental concepts in chemistry and physics that describe the forces acting between atoms and between molecules. These interactions are essential for understanding the structure and behavior of atoms and molecules. They play a fundamental role in chemistry, biology, and physics, influencing the structure of molecules, their physical properties, and chemical reactions.

II.2. Key Definitions

2.1. The Molecule

A molecule is the smallest portion of a substance that retains its chemical and physical properties. Each molecule is a system composed of a set of atoms organized and linked together by chemical bonds of various types. These atoms may belong to the same element or to different elements, in which case they are called compounds.

Examples: the water molecule (H_2O), the dioxygen molecule (O_2), etc.

2.2. Electronegativity

Electronegativity, denoted by χ, is a physical quantity that reflects the ability or tendency of an atom to attract electrons toward itself. In a covalent bond, the more electronegative atom draws the bonding electrons closer to itself, giving it a negative pole, while the less electronegative atom acquires a positive pole. This creates a polar molecule in which the sharing of electrons is unequal.

Examples:

Element (Atom)	Electronegativity χ (according to Mendeleev's periodic table)
Oxygen (O)	3.44
Carbon (C)	2.5
Nitrogen (N)	3.0
Fluorine (F)	4.0
Hydrogen (H)	2.2
Sodium (Na)	0.9

Table 1. Electronegativity χ of some chemical elements.

2.3. Polarity – Dipole

Polarity is the result of the unequal distribution of partial charges (smaller than the elementary charge of an electron) between two different atoms with slightly different (neighboring) electronegativities in a molecule forming a covalent bond, provided that $\mathbf{0.5 < \Delta\chi < 1.7}$. The dipole is therefore the resulting polar molecule arising from this unequal distribution, possessing two poles: one positive, symbolized by $\mathbf{(\delta^+)}$, and the other negative, symbolized by $\mathbf{(\delta^-)}$.

Example: the HCl molecule (χ_H = 2.2 and χ_{Cl} = 3.0).



> **Remark**
>
> The electronegative pole (δ^-) of a polar molecule is the more electronegative atom of the covalent bond, whereas the electropositive pole (δ^+) is the less electronegative atom of that bond.

2.4. Polar Molecule

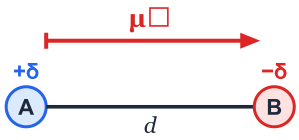
A polar molecule is a molecule that does not share electric charge uniformly across a covalent bond and exhibits a dipole on the atoms forming the bond.

2.5. Dipole Moment

In electricity, two electric charges of equal magnitude but opposite signs, +q and (−q), separated by a distance *r*, form a dipole. It is characterized by a vector whose magnitude is equal to the product $\mathbf{q \times r}$, oriented by convention from the negative charge to the positive charge (from − to +).

In a polar diatomic molecule, each atom carries a partial charge δ^+ or δ^-, where $\mathbf{0 < \delta < |e|}$, with *e* being the elementary charge of the electron ($e = -1.6 \times 10^{-19}$ C).

The dipole moment is represented by an arrow pointing from the positive pole (partial positive charge δ^+) toward the negative pole (partial negative charge δ^-). The dipole moment is thus a vector directed toward the more electronegative atom. It characterizes the strength and direction of the dipole, reflecting the imbalance of electric charges within a dipole. It is represented by a vector named "mu" and denoted $\mu\square$, expressed in Debye (D) or C·m.



Let q be the positive charge ($q = \delta^+$). If d is the distance separating the two barycenters (centers of charge), the electric dipole moment is a vector whose magnitude is, by definition:

$$\boldsymbol{\mu = q \times d = \delta \times d}$$

Where:

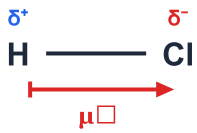
- **q:** is the charge carried by the atom (unit: Coulomb, C).
- **d:** is the bond length in meters (m) (1 Å = 10^{-10} m).
- **δ:** is the partial charge ($0 < \delta < |e|$).

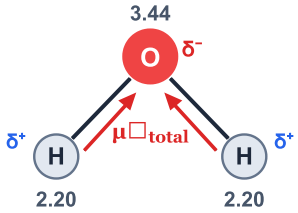
Examples:

1 Debye (D) = 10^{-18} esu·cm = 3.33×10^{-30} C·m. Precisely: $\mathbf{1\ D = 3.33564 \times 10^{-30}\ C{\cdot}m}$ (esu: electrostatic unit)

1. In the hydrogen chloride molecule (HCl), we saw that the negative charges are shifted toward the chlorine atom.

2. In the H_2O molecule ($\chi_H = 2.20$ and $\chi_O = 3.44$), the two arrows along the polar covalent bonds are the two components of the total electric dipole moment of the molecule.





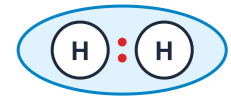
N.B.: Two contradictory conventions previously existed: the convention now established is the chemists' convention, in which the dipole moment is oriented from the partial positive charge $\boldsymbol{\delta^+}$ to the partial negative charge $\boldsymbol{\delta^-}$ (from the less electronegative atom toward the more electronegative atom). Both conventions can still be found in reference textbooks.

2.6. Nonpolar (Apolar) Molecule

A nonpolar molecule is a molecule that possesses no net electric charge or partial charges.

Nonpolar molecules are composed of atoms that have identical or very similar electronegativity values ($\boldsymbol{\Delta\chi = 0}$). When two atoms of similar electronegativity share electrons in a covalent bond, the electrons are attracted equally toward both atoms. Consequently, there is an equal distribution of charge, and the entire molecule is electrically neutral and therefore nonpolar.

Examples of nonpolar molecules: Dioxygen O=O (O_2) and hydrogen gas H–H (H_2).



Hydrogen molecule (H_2)

II.3. The Chemical Bond

A chemical bond is the physical phenomenon that binds atoms together by exchanging or sharing one or more electrons through electrostatic forces. The formation of a chemical bond between two atoms requires the pooling or transfer of electrons so as to minimize energy. The purpose of forming chemical bonds between atoms is to acquire the most stable electronic configuration, which is that of the nearest noble gas in the periodic table.

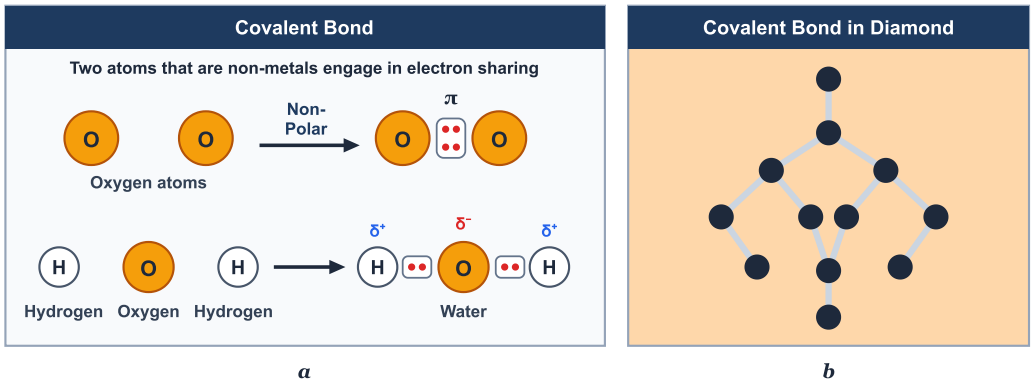
Depending on the bond energy and the mechanism of bond formation, chemical bonds can be classified into two categories: **strong intra-atomic bonds** and **weak intermolecular bonds**.

II.3.1. Intra-atomic Interactions (Bonds)

Intra-atomic interactions are due to forces acting between atoms. These are strong bonds that hold atoms together to form compounds. They exist in molecules, crystals, or metallic solids, organizing atoms into structured arrangements. There are three types of intra-atomic bonds: **covalent, ionic, and metallic**.

A. The Covalent Bond

A covalent bond is a very strong chemical bond that is difficult to break. It forms between two non-metal atoms of identical or similar electronegativities that share two or more electrons (one or more electrons from each atom, or a pair supplied by the same atom) belonging to their outermost valence shells in order to form one or more shared electron pairs linking the two atoms—as in hard solids such as diamond (condensed carbon atoms) where the carbon atoms are very difficult to separate (Figure 1b), in dioxygen (O_2), and in the water molecule (polar covalent bonds, Figure 1a).



a *b*

Figure 1. Covalent bond in: a – Dioxygen and the water molecule (or ice); b – Diamond.

Remark

- **Molecular compounds** refer to covalently bonded species, generally of low molecular weight.
- **Macromolecular compounds** are high-molecular-weight compounds that are covalently bonded and linear, branched, or cross-linked.
- To break strong covalent bonds, dissociation energies on the order of **200 to 500 kJ per mole** of diatomic bond must be supplied (i.e., approximately **50 to 100 kcal/mol**, or about **2 to 5 eV** per bond).

Noble gases (Ar, Kr, Xe, and Ne) do not form molecules because they do not combine with any other atom, as there are no bonding forces between their atoms—their valence shells are saturated.

B. The Ionic Bond

An ionic bond is a type of chemical bond formed between two atoms—a metal and a non-metal—possessing a large difference in electronegativity (by convention, $\Delta\chi > 1.7$). The metal donates one or more valence electrons to form a positively charged ion called a **cation**. The non-metal captures these electrons to form a negatively charged ion called an **anion**. The bond thus results from the electrostatic attraction between the resulting cation and anion. This bond is very strong and can break under impact or deformation that brings ions of the same sign close together.

Examples:

- Table salt or sodium chloride, NaCl (halite);
- Magnesium oxide (MgO).

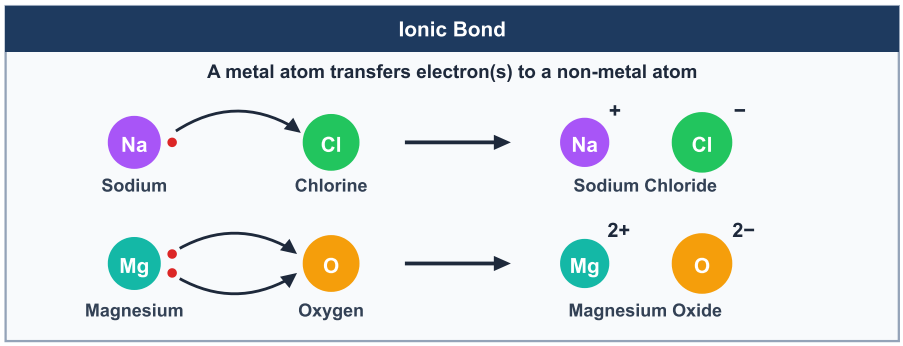
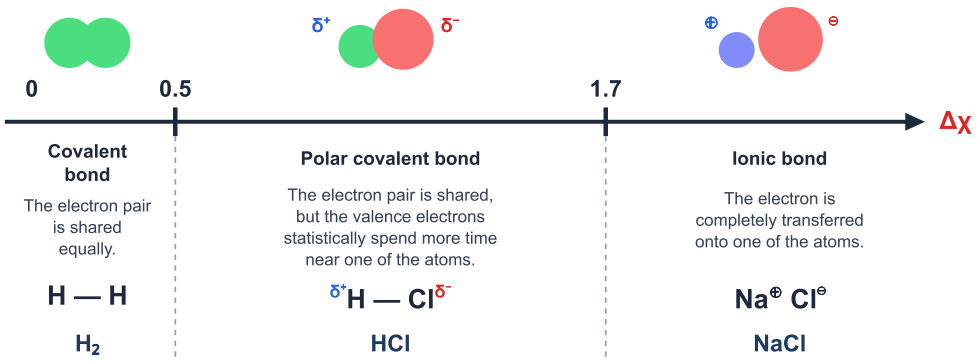


Figure 2. Examples of ionic bonding in sodium chloride (NaCl) and magnesium oxide (MgO) molecules.



Classification of chemical bonds between atoms according to the difference in their electronegativities Δχ.

> **Remark**
>
> - The bond is purely covalent or neutral covalent (nonpolar) if: $\delta = 0$;
> - The covalent bond is polarized if: $0 < \delta < e$;
> - The bond is ionic if: $\delta = e$.

C. The Metallic Bond

A metallic bond is a bond resulting from the electrostatic attraction between relatively immobile metallic cations (positively ionized atoms) and delocalized free electrons surrounding them (mobile negative charges released by the metal atoms due to thermal agitation at room temperature), as shown in Figure 3. The metallic bond keeps matter solid at room temperature (with the exception of mercury) and makes metallic solids very hard.

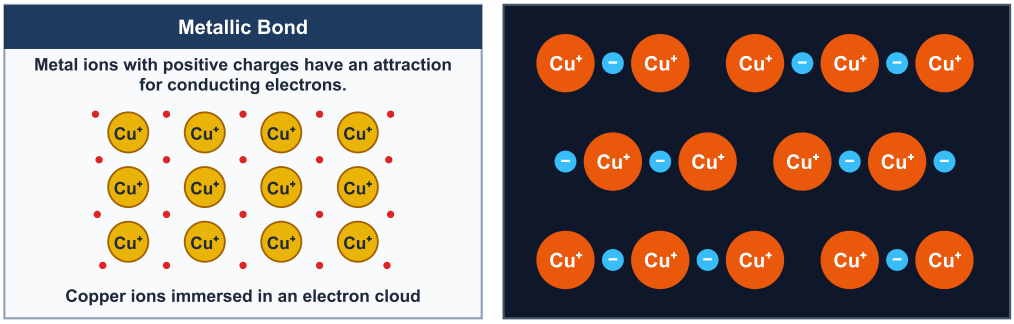


Figure 3. Example of metallic bonding in copper metal.

Examples: Metallic bonding exists in pure metals (iron, copper, aluminum, etc.) and metallic alloys such as cast iron Fe_3C (iron with 2% carbon by mass), steel (iron with 0.02% carbon by mass), bronze (copper and tin), NiZr, etc.

II.3.2. Intermolecular Interactions

Intermolecular interactions are due to cohesive forces acting between molecules whose strong intramolecular bonding capacities are already saturated. These bonds are very weak, easy to break, and require very little energy to rupture. A dissociation energy ranging from approximately **1 to 40 kJ·mol^{-1}** (less than 50 kJ·mol^{-1}) is sufficient to break them. Such intermolecular forces enable the solidification of gases. These interactions include:

A. The Hydrogen Bond

A hydrogen bond is the electrostatic attraction between a hydrogen atom covalently bonded to a highly electronegative atom (such as an O atom) in one molecule and another molecule containing at least one fluorine, oxygen, or nitrogen atom. This bond is very weak and keeps matter in the solid state at very low temperatures.

Example: The case of ice, where multiple water molecules are linked by hydrogen bonds, as shown in Figure 4.

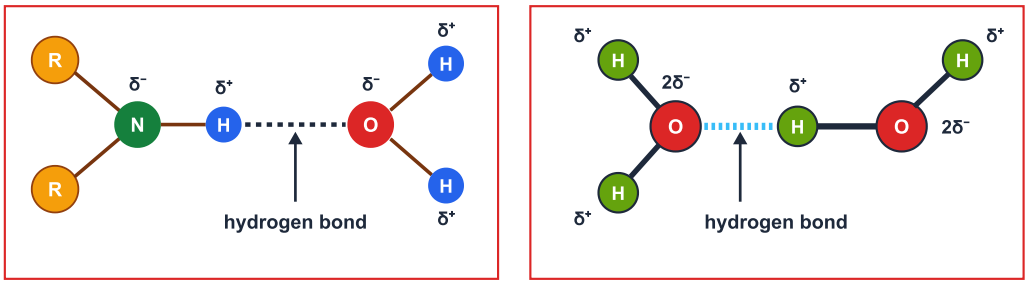


Figure 4. Hydrogen bonding in ice (solid water).

Hydrogen bonds regulate the structure of some of the most important biological macromolecules, including transmembrane proteins and deoxyribonucleic acid (DNA). Hydrogen bonds are represented by thin dotted lines (Figure 5). There are **two hydrogen bonds** between the complementary base pairs **thymine (T) and adenine (A)**, and **three hydrogen bonds** between the complementary base pairs **cytosine (C) and guanine (G)**.

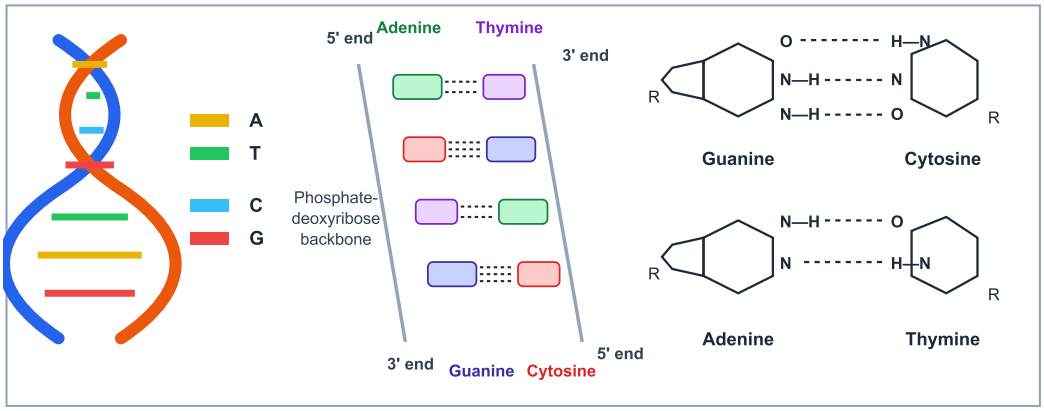
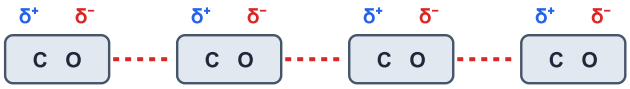


Figure 5. Hydrogen bonds in DNA.

B. Van der Waals Forces (Bonds)

Van der Waals bonds are the result of attractive electrostatic forces acting over short distances (0.1 nm) between molecules due to temporary dipoles caused by the random motion of electrons, as in ice. These bonds loosely hold molecules together, influencing the rigidity and strength of materials. These bonds are very weak and keep matter solid only at very low temperatures, as in ice and carbon monoxide (CO).



Van der Waals forces are divided into two main types:

1. Dispersion forces (or London forces): London dispersion forces are the weakest of all intermolecular forces; they exist between all types of molecules, whether ionic, polar covalent, or nonpolar covalent. The more electrons a molecule possesses, the stronger the London dispersion forces.

2. Permanent dipole–dipole forces (Keesom forces): Permanent dipole–dipole forces are a type of intermolecular force found between two molecules possessing permanent dipoles. Molecules whose individual bond dipole moments do not cancel one another out exhibit what is called a permanent dipole. One part of the molecule carries a partial negative charge, while another part carries a partial positive charge. Oppositely charged poles in neighboring molecules attract each other, whereas similarly charged poles repel each other.

> **Remark**
>
> 1. Hydrogen bonds are much stronger than permanent dipole–dipole forces and dispersion forces; they require more energy to be overcome.
> 2. Van der Waals forces increase with the size of the molecule. This is explained by the fact that larger molecules have more electrons, which creates stronger temporary dipoles.

Course Summary

- **Intramolecular forces** are forces within molecules, whereas **intermolecular forces** are forces between molecules. Intramolecular forces are much stronger than intermolecular forces.
- **Polarity** determines the type of intermolecular forces acting between molecules.
- **Polar molecules** occur when there is a difference in electronegativity between the bonded atoms.
- **Nonpolar molecules** occur when electrons are shared equally between the atoms.
- **The direction of the dipole moment** of a polar covalent bond is oriented from the positive pole (partial positive charge δ^+) toward the negative pole (partial negative charge δ^-).

- There are **3 types of intramolecular bonds**: covalent, ionic, and metallic.
- **Van der Waals forces**, also called London forces or dispersion forces, exist between all molecules and are caused by temporary dipoles. These temporary dipoles arise from the random motion of electrons and create induced dipoles in neighboring molecules.
- **Hydrogen bonds** are the strongest type of intermolecular force. They occur between molecules containing a fluorine, oxygen, or nitrogen atom bonded to a hydrogen atom.

H 2.2																	He
Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
Na 0.93	Mg 1.31											Al 1.61	Si 1.9	P 2.19	S 2.58	Cl 3.16	Ar
K 0.82	Ca 1	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.9	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 3
Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 1.9	Ru 2.2	Rh 2.28	Pd 2.2	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe 2.6
Cs 0.79	Ba 0.89	* Lu 1.27	Hf 1.3	Ta 1.5	W 2.36	Re 1.9	Os 2.2	Ir 2.2	Pt 2.28	Au 2.54	Hg 2	Tl 1.62	Pb 1.87	Bi 2.02	Po 2	At 2.2	Rn 2.2
Fr 0.7	Ra 0.9	** Lr 1.3	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og

*	La 1.1	Ce 1.12	Pr 1.13	Nd 1.14	Pm 1.13	Sm 1.17	Eu 1.2	Gd 1.2	Tb 1.2	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb 1.1
**	Ac 1.1	Th 1.3	Pa 1.5	U 1.38	Np 1.36	Pu 1.28	Am 1.13	Cm 1.28	Bk 1.3	Cf 1.3	Es 1.3	Fm 1.3	Md 1.3	No 1.3

Atomic radius decreases → Ionization energy increases → Electronegativity increases