

Fundamental Interactions: 6 Forces

Prof. Dr. Ulrich Jonas
Macromolecular Chemistry
Department Chemistry - Biology
University of Siegen

In nuclear and high-energy physics 6 fundamental forces are recognized, which describe the structure of matter.

- the **strong interaction**
- the **weak interaction**

⇒ act inside the nucleus, range $< 10^{-5}$ nm
~ 1/10000 of the diameter of an atom

- the **electromagnetic interaction**

⇒ source of all intermolecular forces !
(Hellman-Feynman)

- **gravitation**

⇒ very long-range between macroscopic objects,
negligible between molecules

- the **super-strong interaction**
- the **super-weak interaction**

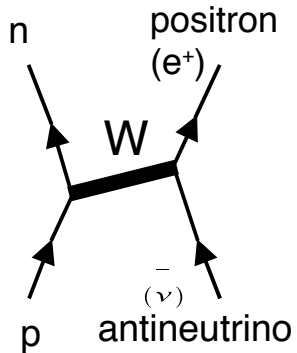
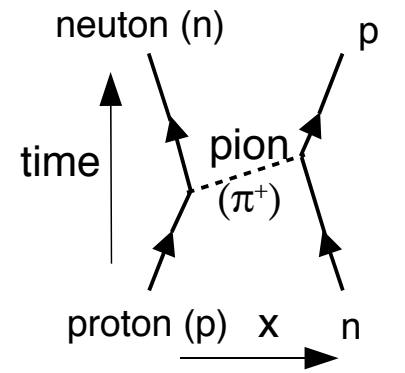
⇒ very particular forces only used in nuclear
physics (don't bother...)

Hellman-Feynman theorem: "Once the spatial distribution of the electron clouds has been determined by solving the Schrödinger equation, the intermolecular forces may be calculated on the basis of straightforward classical electrostatics."

Fundamental Interactions: Details

- the **strong interaction**: nuclear interaction (holds protons & neutrons in the nucleus together by exchange of pions), very fast (about the time a photon c travels through a proton $\sim 10^{-23}$ s), acts between "hadron" (nucleons, mesons, hyperons), **not** between "leptons" (electrons, myons, neutrinos) at a distance of $< 10^{-15}$ m

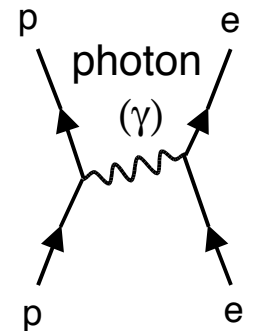
Feynman diagrams



- the **weak interaction**: nuclear interaction (responsible for nuclear β -decay / electron emission & and slow decay of elementary particles), time scale varies considerably (10^{-10} - 10^3 s), interaction involves "leptons", depends on the parity (symmetry of translation & spin) of the particles, acts over distances $\ll 10^{-15}$ m (below strong interaction)

(W: hypothetical particle mediating weak force)

- the **electromagnetic interaction**: binds electrons to nucleus, binds atoms to molecules, responsible for all chemistry and biology, acts in electron-positron annihilation, time scale lies between strong and weak interaction, interaction is mediated by the photon, acts primarily between charged particles over infinite distance (in principle), is neutralized by opposite charge



- **gravitation**: longest known & least understood, negligible in molecular dimensions, but important for mesoscopic to macroscopic objects (like in buoyancy or droplet deformation), acts attractive between all matter, very long range (between galaxies, e.g.) $w(r) = -G m_1 m_2 / r$ $G = 6.67 \times 10^{-11} \text{ N m}^2 \text{ kg}^{-2}$

⇒ **relative interaction strength**: strong (15) : el.mag. (1/137) : weak (10^{-12}) : gravitation (10^{-35})

Pair Potentials

- **van der Waals:** deviation of behavior of real gases from ideal gas law ($pV = nRT$):

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

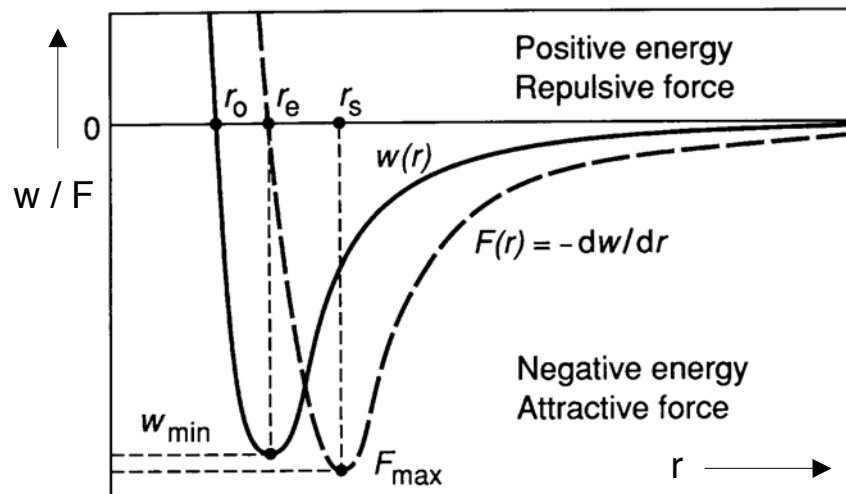
$\underbrace{\left(p + \frac{a}{V^2}\right)}_{\downarrow}$ attractive intermolecular forces (\rightarrow van der Waals forces)
 $\underbrace{(V - b)}_{\rightarrow}$ excluded volume of atoms / molecules

attractive intermolecular forces (\rightarrow van der Waals forces)

- **Mie:** general interaction "pair potential" to describe complex intermolecular interactions:

$$w(r) = -\underbrace{\frac{A}{r^n}}_{\downarrow \text{attractive term}} + \underbrace{\frac{B}{r^m}}_{\rightarrow \text{repulsive term}}$$

- **Lennard-Jones:**

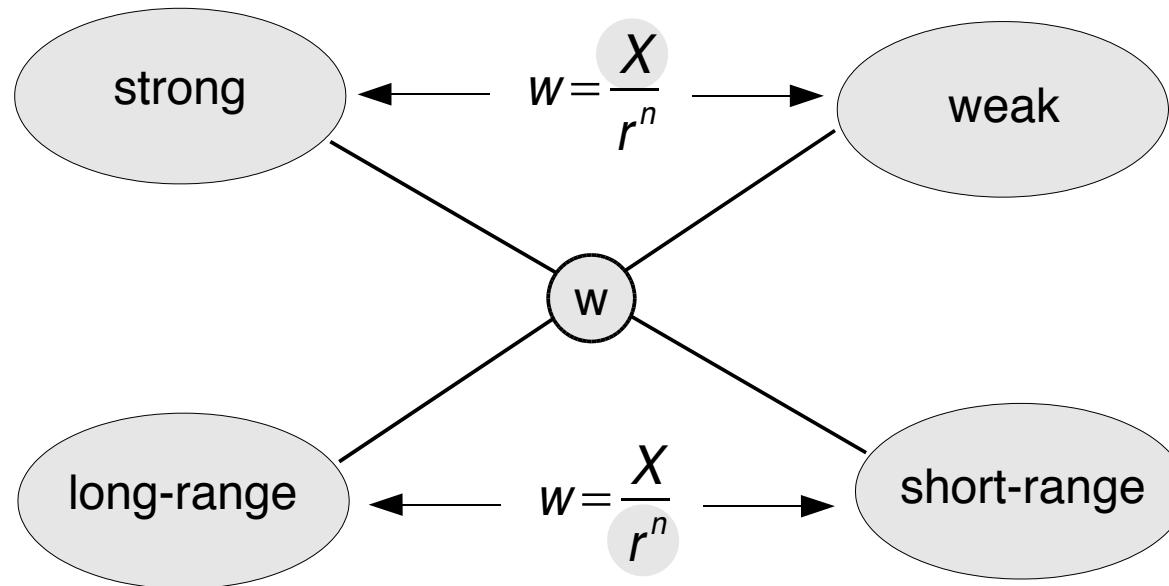


$$w(r) = -\underbrace{\frac{A}{r^6}}_{\downarrow \text{long-range attractive van der Waals interaction}} + \underbrace{\frac{B}{r^{12}}}_{\rightarrow \text{very short-range "hard sphere" repulsion}}$$

Long / Short-Range Forces and Strong / Weak Forces

The interaction parameter X determines the strength of the interaction.

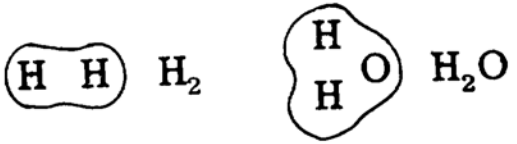
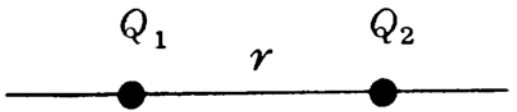
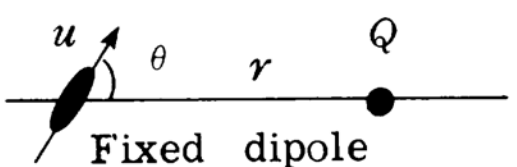
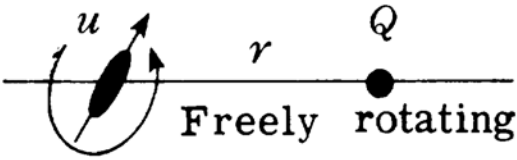
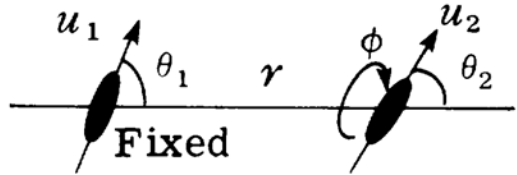
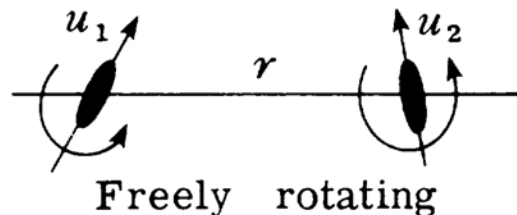
→ the larger X the stronger the interaction



The exponent in the distance variable r determines the range of the interaction.

→ the larger the exponent n the shorter the interaction range

Types of Interactions: Overview 1

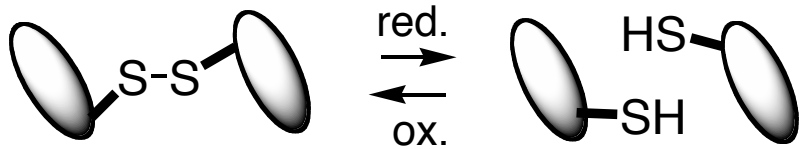
type of interaction		interaction energy $w(r)$
Covalent, metallic		Complicated, short range
Charge–charge		$Q_1 Q_2 / 4\pi\epsilon_0 r$ (Coulomb energy)
Charge–dipole	 <p>Fixed dipole</p>	$-Qu \cos \theta / 4\pi\epsilon_0 r^2$
	 <p>Freely rotating</p>	$-Q^2 u^2 / 6(4\pi\epsilon_0)^2 k T r^4$
Dipole–dipole	 <p>Fixed</p>	$-u_1 u_2 [2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos \phi] / 4\pi\epsilon_0 r^3$
	 <p>Freely rotating</p>	$-u_1^2 u_2^2 / 3(4\pi\epsilon_0)^2 k T r^6$ (Keesom energy)

Types of Interactions: Overview 2

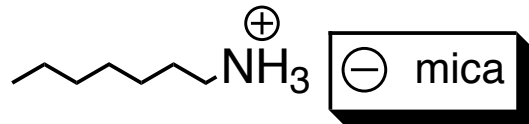
type of interaction		interaction energy $w(r)$
Charge–non-polar	<p>A horizontal line represents the interaction axis. On the left, a black dot is labeled Q. On the right, another black dot is labeled α. The distance between them is labeled r.</p>	$-Q^2\alpha/2(4\pi\epsilon_0)^2r^4$
Dipole–non-dipolar	<p>A horizontal line represents the interaction axis. On the left, a dipole is shown as an arrow labeled u pointing up and to the right, at an angle θ to the horizontal. Below it is the word "Fixed". On the right, a black dot is labeled α. The distance between the dipole and the dot is labeled r.</p>	$-u^2\alpha(1 + 3\cos^2\theta)/2(4\pi\epsilon_0)^2r^6$
	<p>A horizontal line represents the interaction axis. On the left, a dipole is shown as an arrow labeled u pointing up and to the right, with a circular arrow around it indicating rotation. Below it is the word "Rotating". On the right, a black dot is labeled α. The distance between the dipole and the dot is labeled r.</p>	$-u^2\alpha/(4\pi\epsilon_0)^2r^6$ (Debye energy)
Two non-polar molecules	<p>A horizontal line represents the interaction axis. On the left and right, two black dots are labeled α. The distance between them is labeled r.</p>	$-\frac{3}{4} \frac{h\nu\alpha^2}{(4\pi\epsilon_0)^2r^6}$ (London dispersion energy)
Hydrogen bond	<p>A network of water molecules is shown. Each molecule consists of one oxygen atom (O) and two hydrogen atoms (H). Solid lines represent covalent bonds. Dashed lines represent hydrogen bonds between the oxygen of one molecule and a hydrogen of another. A double-headed arrow labeled r indicates the distance between two oxygen atoms.</p>	Complicated, short range, energy roughly proportional to $-1/r^2$

Intermolecular Interactions:

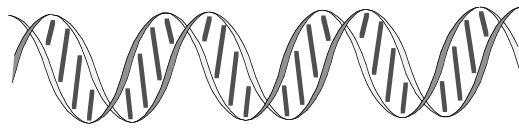
- **covalent:**
e.g. disulfide bonds



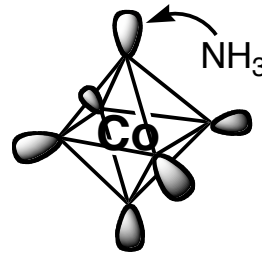
- **ionic:**
e.g. ammonium salts on mica



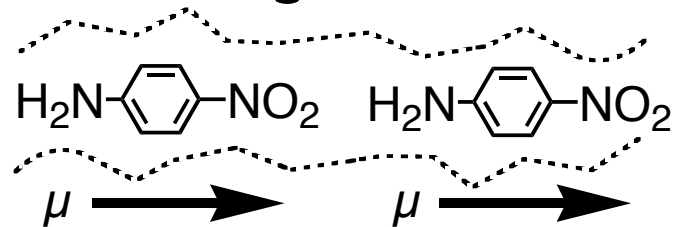
- **H-bonding:**
e.g. DNA double helix



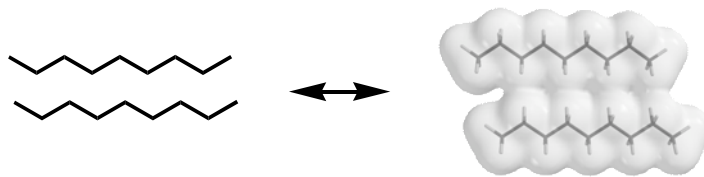
- **coordinative:**
e.g. transition metal complexes



- **dipole-dipole:**
e.g. nitroaniline in zeolite



- **dispersion:**
e.g. alkyl chains



- **charge transfer (CT):** e.g. intercalation of trinitrofluorenone into triphenylene columns

- **topological link:**
 - catenanes / rotaxanes
 - endohedral fullerene complexes

- **form anisotropy:**
 - liquid crystals
 - ordered colloidal dispersions

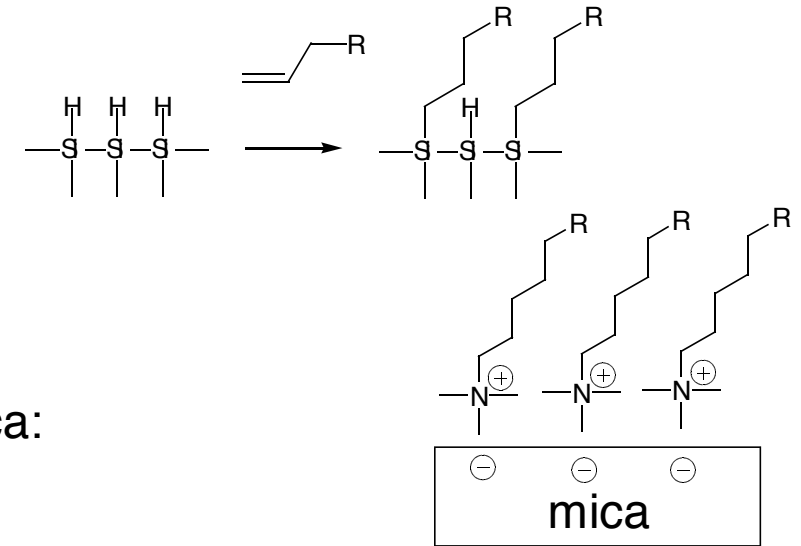
Chemical Bonds: Covalent, Ionic, Metallic, Coordinative

Chemical bonds: strong bonds between atoms to form molecules and extended solids.

→ relates to cohesion within a covalent bonded material

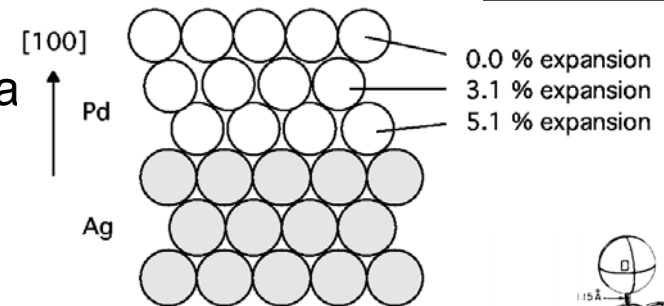
Examples in surface sciences:

-covalent surface bonds: hydrosilylation of hydrogen terminated silicon surface (radical, thermal, photochem., catalytic):

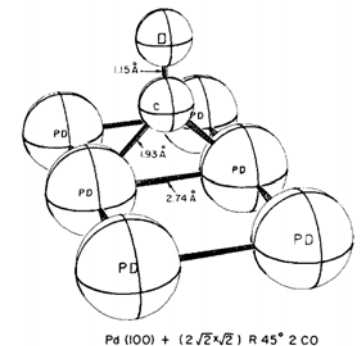


-ionic surface bonds: quaternary ammonium salts on mica:

-metallic surface bonds: interface between two metal la

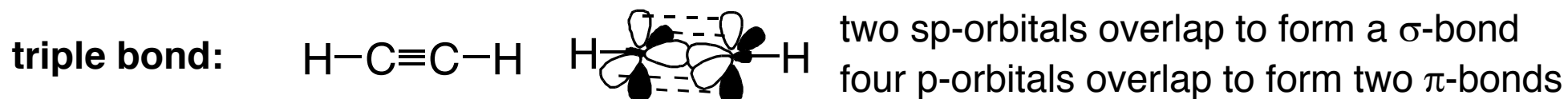
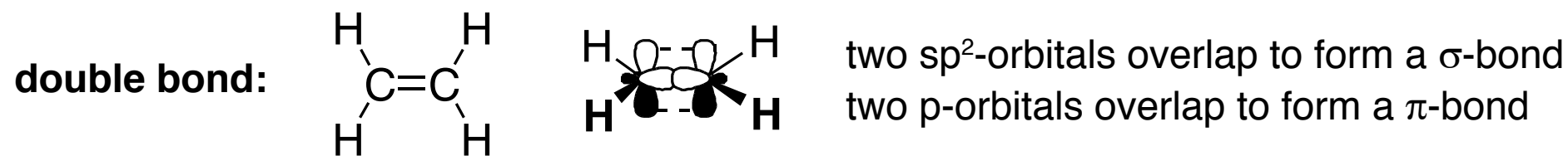
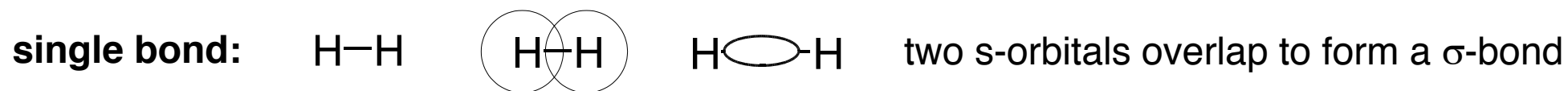


-coordinative surface bonds: CO adsorbates on d-transition metal surfaces (somewhere between covalent and coordinative):



Covalent Bond

Sharing of valence electrons (in pairs) between two atoms (usually non-metals) leads to a covalent bond between these atoms → molecules



<i>bond type</i>	<i>length (pm)</i>	<i>energy (kJ mol⁻¹)</i>
C-C	154	347-356
C=C	134	611-632
C≡C	120	833-837

→ equal distribution of bonding electrons between atoms leads to non-polar bond (H-H)

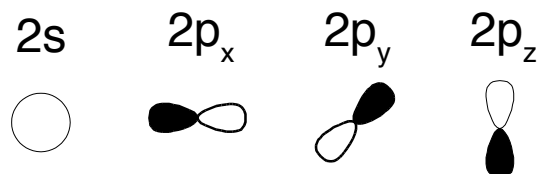
→ localization of bonding electron pair towards one atom (more electronegative) leads to polar bond ($\text{H}^{\delta+}-\text{Cl}^{\delta-}$) → extreme case: ionic bond

Covalent Bond: VB and MO theory

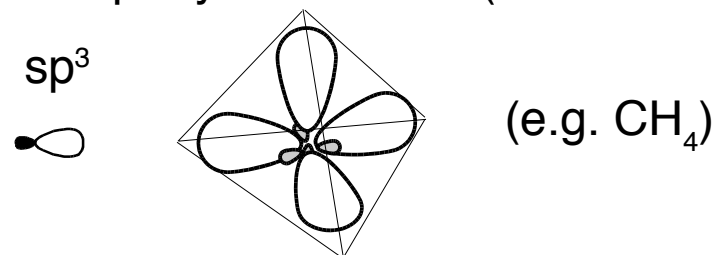
VB theory: In the valence bond (VB) theory resonance energy is gained by exchange of electrons between two atoms (orbital overlap). Bonding electrons are **localized** between two bonding atoms and are not distinguishable.

→ description of bonding **geometries** by **hybrid orbitals**:

four C valence electron orbitals:



four C sp³ hybrid orbitals (tetrahedral):

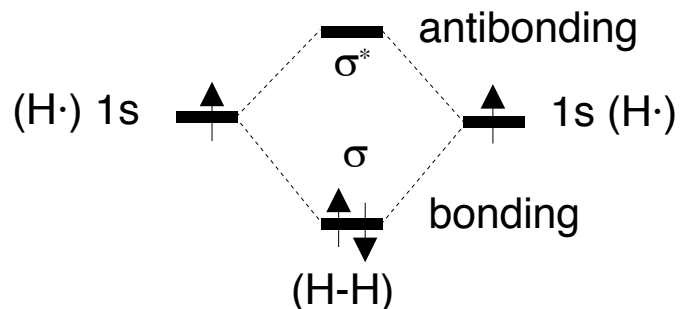


MO theory: In the molecular orbital (MO) theory bonding electrons are not localized between two atoms of a bond, but distributed in a group of molecular orbitals over the entire molecule.

→ quantum mechanical description by the Schrödinger equation: $H \psi_{MO} = E \psi_{MO}$

→ MO are generated by a linear combination of atomic orbitals (LCAO):

$$\psi_{MO} = c_1 \phi_1 + c_2 \phi_2 + c_3 \phi_3 + \dots + c_n \phi_n \rightarrow \text{wave function of MO: } \psi_{MO}; \text{ atomic orbital (AO): } \phi_n$$



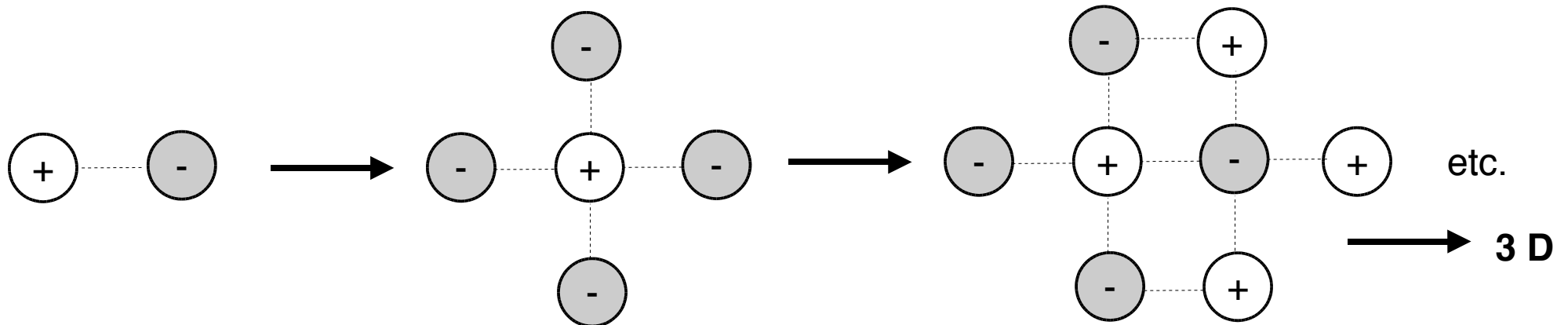
→ MO theory is basis for computational treatment of molecular structure (semi-empirical, *ab-initio*)

→ frontier orbitals HOMO / LUMO

Ionic Bond

ionic bonds are formed by strong **Coulomb interactions** between two **oppositely charged** species (e.g. Na^+Cl^-)

- the potential energy varies with the distance r between the two ions by $1/r$ (the force varies with $1/r^2$)
- description by formal electron transfer from newly formed cation (usually metals) to newly formed anion (usually non-metals)
- "simplest bond" / extreme case of polar bond
- ionic bond is not localized / directed, but acts isotropically / radial-symmetrically around ions → leads to extended aggregation and ionic crystals with one cation being surrounded by many anions and *vice versa*

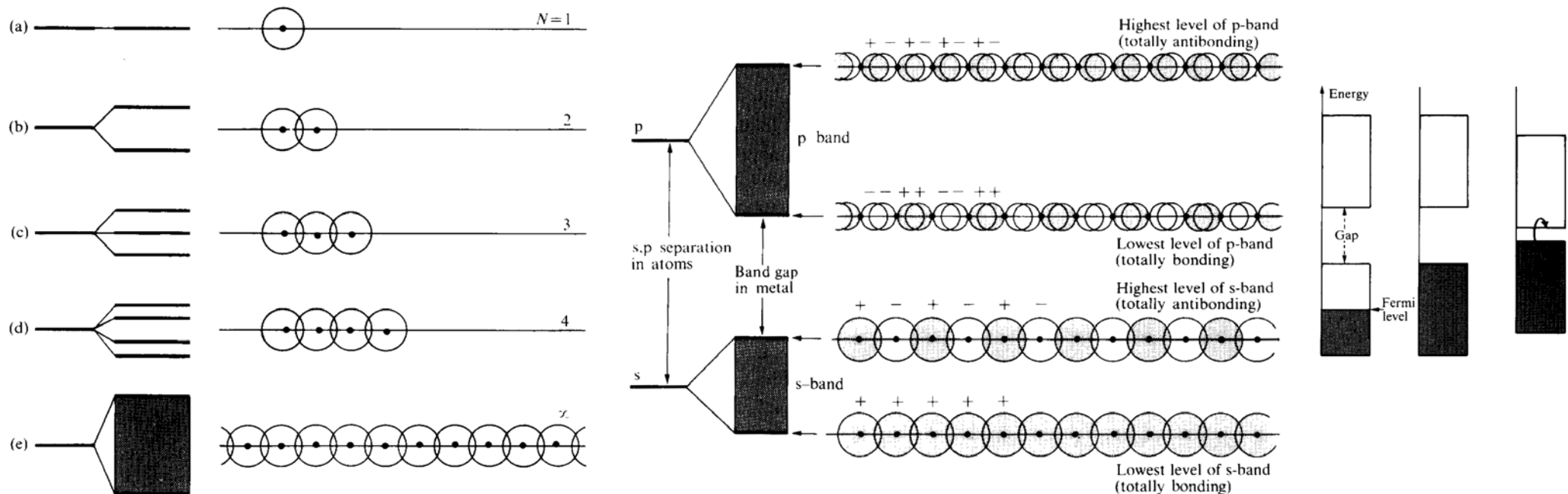


Metallic Bond

metallic bond: attractive interactions / bonds in metals are mediated by free moving valence electrons (electron sea) between positively charged atoms over entire sample

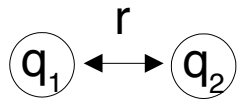
- **electron sea:** high electron mobility → good thermal and electrical conductivity
- metallic bond is **weak** (compared to covalent bond) → ductile metals

→ theoretical description of metallic bond by **band theory:**



Electrostatic Interactions

The force F (Coulomb force) acting between two charges q_1 and q_2 separated by a distance r in vacuum (ϵ_0) depends on the separation by $1/r^2$.

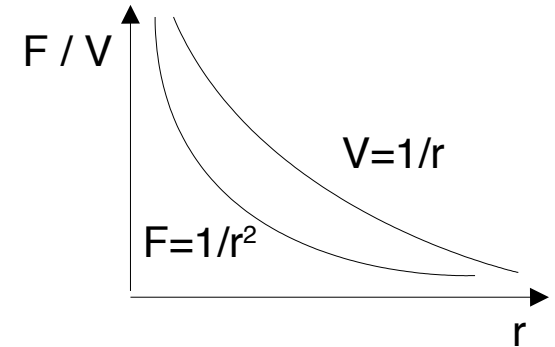


$$F = \frac{q_1 q_2}{4 \pi \epsilon_0 r^2}$$

→
in medium
with ϵ_r

$$F = \frac{q_1 q_2}{4 \pi \epsilon_0 \epsilon_r r^2}$$

(relative permittivity, dielectric constant)



→ the electrostatic forces are additive: in a system of many charges the force on a single charge is obtained by summing all the interactions with the other charges

- electrical work w_e :
potential energy V :

$$w_e \text{ or } V = - \int_{\infty}^r F dr = \frac{q_1 q_2}{4 \pi \epsilon_0 \epsilon_r r}$$

- electric potential:

$$\phi = \frac{q_2}{4 \pi \epsilon_0 \epsilon_r r} \quad \longrightarrow \quad w_e \text{ or } V = q_1 \phi$$

- electric field strength:

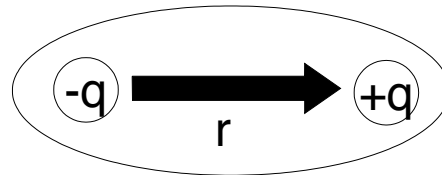
$$E = \frac{q_2}{4 \pi \epsilon_0 \epsilon_r r^2} \quad \longrightarrow \quad F = q_1 E$$

van der Waals Interactions

Collection of attractive interactions between molecules based on dipole / dipole, dipole / induced-dipole, and induced-dipole / induced-dipole interaction (Keesom, Debye, London dispersion energies)

dipole moment μ : equal charge q separated at a fixed distance r

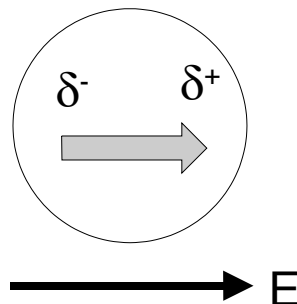
$$\mu = q r$$



unit: debye (D) = $3.336 \cdot 10^{-30}$ C m

induced dipole μ_i : dipole induced in a polarizable molecule by electric field

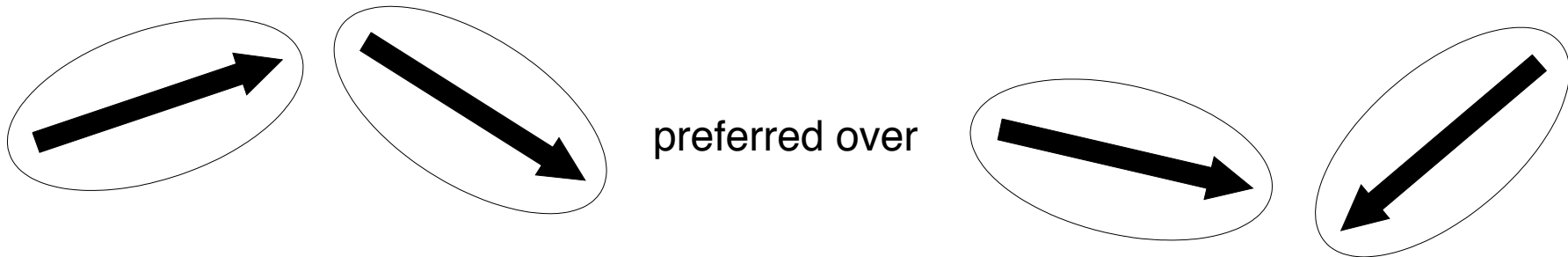
$$\mu_i = \alpha E$$



α : polarizability
 E : electric field

Dipole / Dipole Interactions

Interaction of freely rotating dipoles (liquid) depends on the thermal energy (kT) and is referred to as Keesom energy (Boltzmann distribution of orientations).



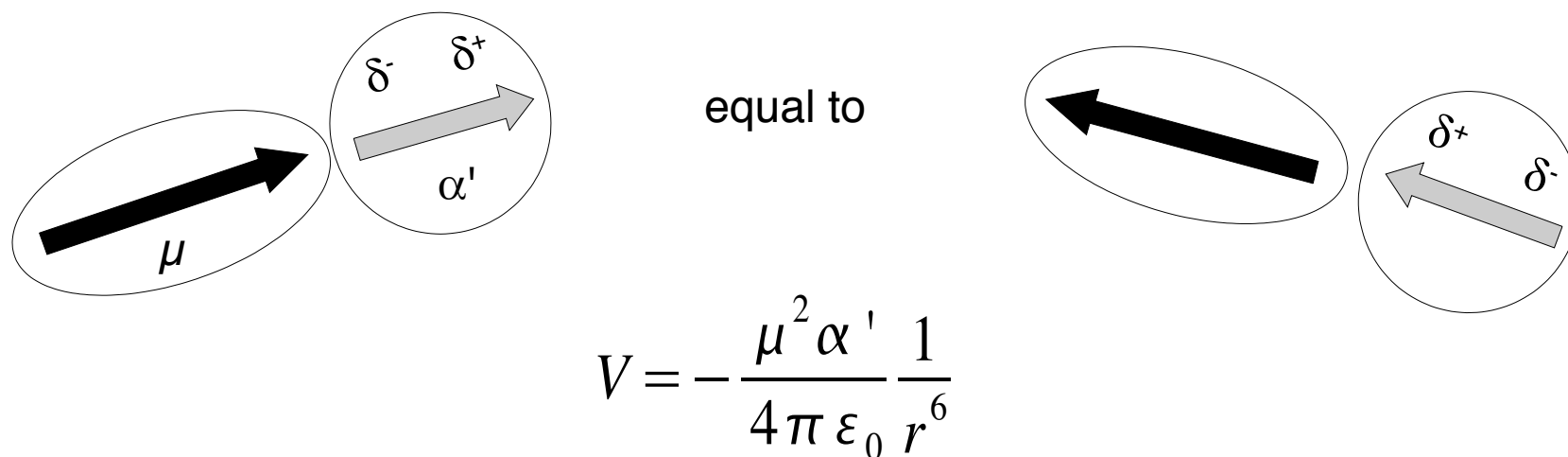
$$V = -\frac{2}{3kT} \left(\frac{\mu_1 \mu_2}{4\pi \epsilon_0} \right)^2 \frac{1}{r^6}$$

At 25°C the average interaction energy for pairs of molecules with $\mu = 1$ D is about -1.4 kJ mol^{-1} when the separation is 0.3 nm.

The average molar kinetic energy at 25°C is $3/2 RT = 3.7 \text{ kJ mol}^{-1}$.

Dipole / Induced-Dipole Interactions

A dipole near a polarizable molecule induces a dipole (charge dislocation) in the neutral molecule leading to an attractive interaction, the corresponding potential energy is referred to as Debye energy.



α' is the polarizability volume given by $\alpha' = \alpha / 4\pi \epsilon_0$ (unit: cm^3)

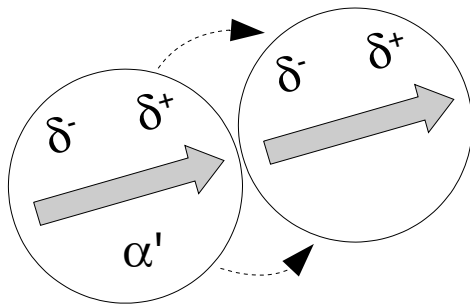
The interaction energy is independent of the temperature because the induced dipole follows immediately the motion of the permanent dipole and is thus not affected by thermal motion, and it depends on $1/r^6$ (like the dipole / dipole interaction).

For a molecule with $\mu = 1$ D (e.g. HCl) near a molecule with polarizability volume $\alpha' = 10^{-23}$ cm^3 (e.g. benzene) the average interaction energy is about -0.8 kJ mol^{-1} at a separation of 0.3 nm.

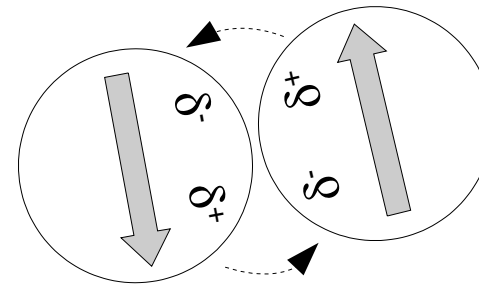
Induced-Dipole / Induced-Dipole Interactions

Random fluctuations in a polarizable molecule lead to a temporary dipole which induces a corresponding dipole in a nearby molecule, leading to attractive dispersion interactions. The involved potential energy is called the London dispersion energy.

parallel orientation



anti-parallel orientation



$$V = -\frac{3}{2} \frac{\alpha_1 \alpha_2}{(4\pi \epsilon_0)^2} \frac{1}{r^6} \frac{I_1 I_2}{I_1 + I_2} = -\frac{3}{2} \frac{\alpha_1' \alpha_2'}{r^6} \frac{I_1 I_2}{I_1 + I_2}$$

I_n is the ionization energy, with $I = h\nu$, ν is the electronic absorption frequency

In the case of two methane molecules with $\alpha' = 2.6 \cdot 10^{-24} \text{ cm}^3$ and $I = 7 \text{ eV}$ the dispersion energy becomes -5 kJ mol^{-1} for a separation of 0.3 nm (comparable to the enthalpy of vaporization of methane $\Delta H_{\text{vapor}} = 8.2 \text{ kJ mol}^{-1}$).

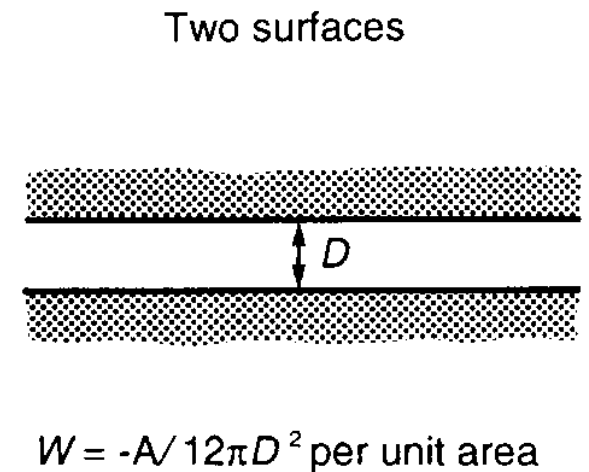
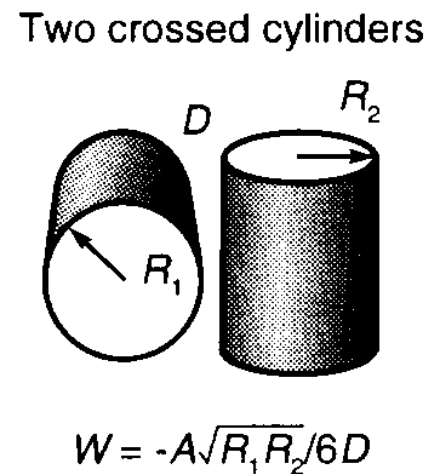
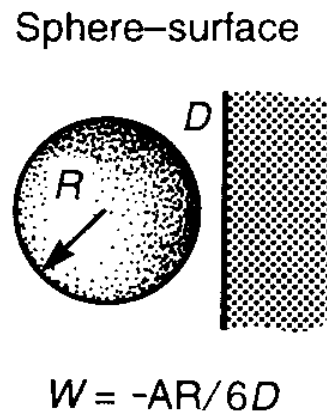
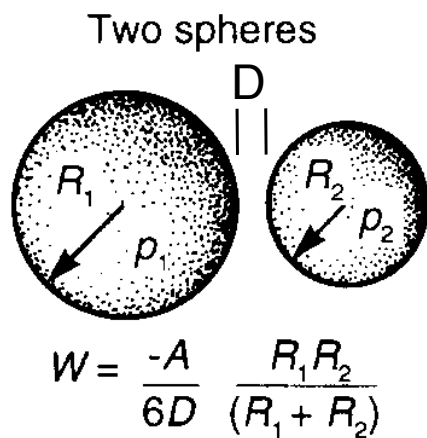
van der Waals Forces Between Macroscopic Objects

The van der Waals forces between two macroscopic bodies can be calculated (as approximation) by integrating over the molecular / atom-atom vdW pair potential ($w(r) = -C / r^6$) of all molecules / atoms in one body with all molecules / atoms in the other body.

→ interaction free energies are expressed in terms of the Hamaker constant:

$$A = \pi^2 C \rho_1 \rho_2 \sim 10^{-19} \text{ J (in vacuum)}$$

with $\rho_{1/2}$ being the atom density of body 1 / 2, C is the coefficient in the molecular / atom-atom pair potential



Hydrogen Bonding

highly polarized bond of hydrogen with heteroatom (e.g. $-X^{\delta-}-H^{\delta+}$, $X = O, N, F$) provides strong protonic character to hydrogen (proton donor) \rightarrow **H can interact with electron donating** group / atom / electron lone pair (proton acceptor) \Rightarrow H-mediated "bond"

\rightarrow elongation of bond in H-donor

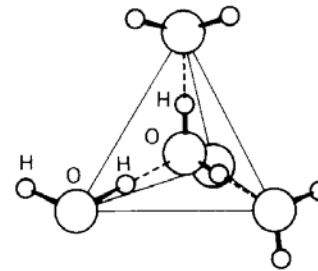
\rightarrow very short distance of H and electron donor (H-acceptor)

\Rightarrow for H_2O : $O-H = 0.10$ nm, $O\dots H = 0.176$ nm, theoretical vdW radius $O/H = 0.26$ nm

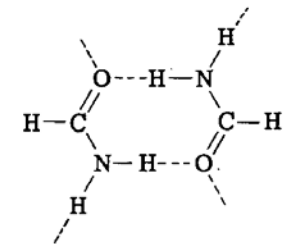
H-bonding in H_2O :

\rightarrow particular structure of ice

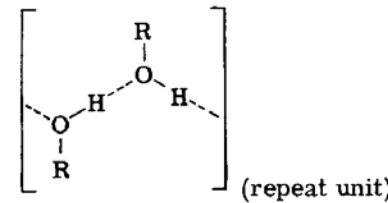
\rightarrow hydrophobic effect (restructuring of H-bonding network around hydrophobic solute is entropically unfavorable)



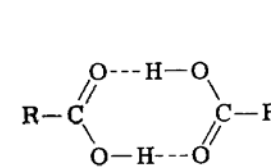
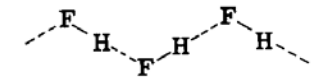
(a)



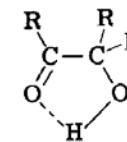
(b)



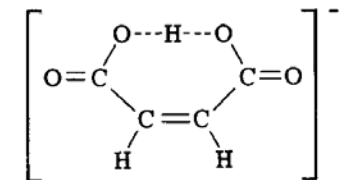
(c)



(d)



(e)



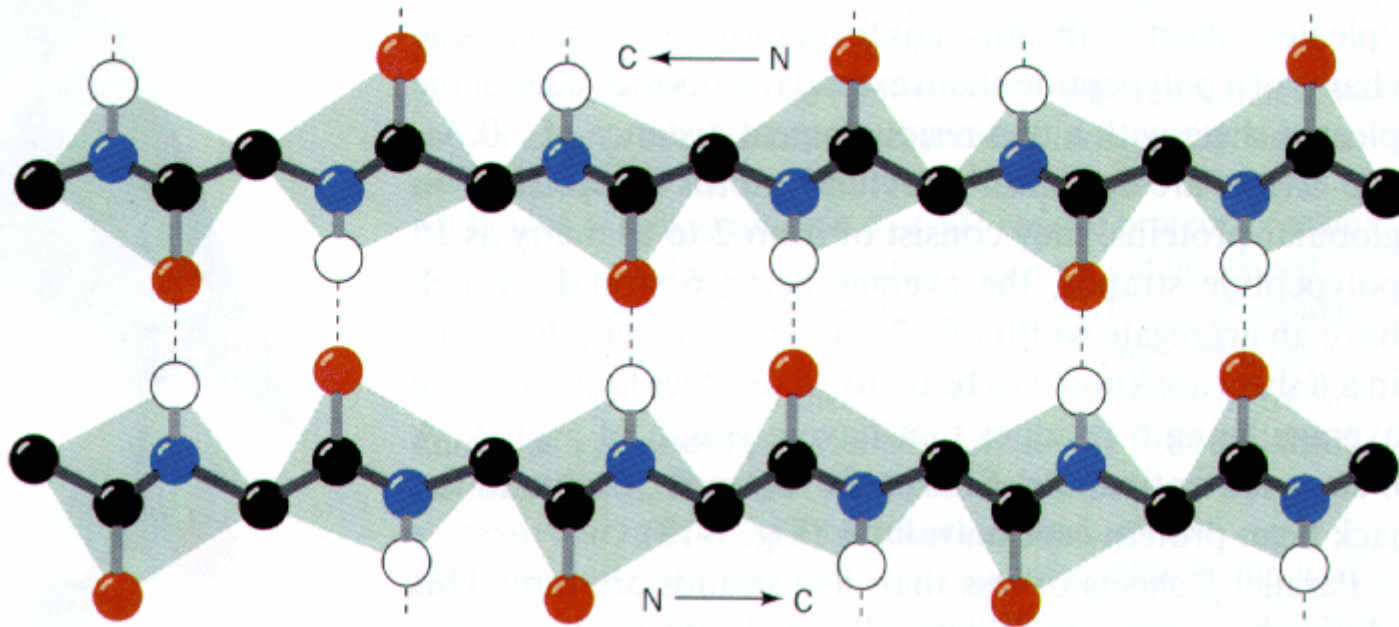
(f)

Hydrogen Bonding: Proteins

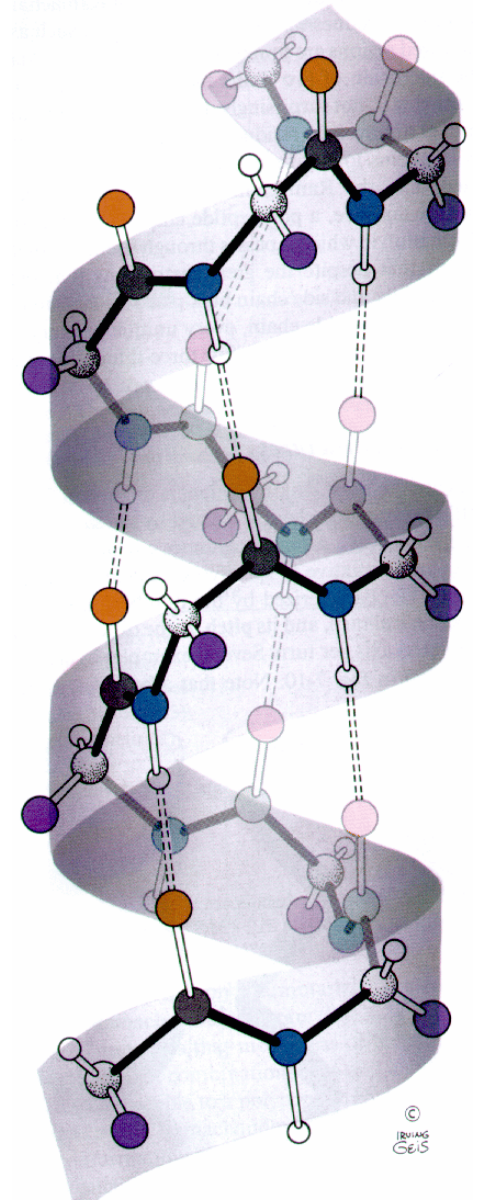
Hydrogen bonding of the amide groups via $N-H \dots O=C$ leads to **secondary and tertiary structures** of proteins:

- α -helix (chiral, tubular structure)
- β -pleated sheet (extended flat structure)

(a) Antiparallel



β -pleated sheet



α -helix

Hydrogen Bonding: DNA

The **base pairing** in the **DNA** double helix is mediated by **hydrogen bonding** between the **nucleic acid moieties**:

- **2 H-bonds** between **adenine** and **thymine**
- **3 H-bonds** between **guanine** and **cytosine**

