



Atomic and molecular interactions

Atomic force microscopy



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Overview

Topics:

- (quantum states)
- atomic and molecular interactions
- atomic force microscopy

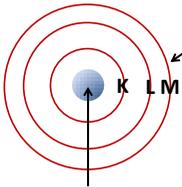
Textbook chapters: I/2, X/2

Related practice: Resonance

Related exam question:

7. General description of atomic and molecular interactions.

Atomic structure



energy levels (shells) with

K: max. 2 e⁻

L: max. 8 e⁻

M: max. 18 e⁻

N: max. 32 e⁻

O: max. 50 e⁻

P: max. 64 e⁻

Q: max. 98 e⁻

nucleus, including nucleons:
protons (p⁺)
neutrons (n⁰)

chemical properties!

Z: atomic number = number of protons (= number of electrons)
N: neutron number
A: mass number = Z+N
(Nuclear structure will be detailed in Lecture 11.)

Properties of quantized atomic electron states

Bound electrons – quantized energy levels. The state of the electron can be described by **quantum numbers**:

quantum number	possible values	characterizes	describes
principal	$n=1,2,3...7$	electron shell	energy level
azimuthal	$l=0,1,2,...(n-1)$ or: s, p, d, f	subshell	magnitude of orbital angular momentum
magnetic	$m_l=-l,...,0,...,+l$	specific orbital within subshell	direction of orbital angular momentum
spin	$m_s=\pm 1/2$	intrinsic angular momentum (spin*) of an electron	direction of the spin (magnitude is constant)

All the four quantum numbers are required to characterize a bound-state electron.

Atomic interactions

Noble gases: found in their atomic form in nature (*He, Ne, Ar, Kr, Xe, Rn*)

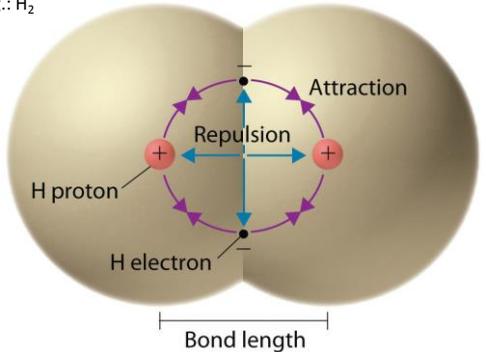
Other elements: form molecules held together by chemical bonds. (e.g. *H₂, HCl, H₂O, ...*) Each atom has a (more or less) fixed position in the molecule.

For elements with no stable isotopes, the mass number of the isotope with the longest half-life is in parentheses.

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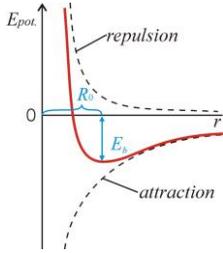
Atomic interactions

e.g.: H₂



Atomic interactions

Bringing two atoms (ions/molecules/...) close to each other attractive and repulsive forces emerge between them resulting in a net potential energy function with an energy minimum at a certain distance:



$$E_{pot} = E_{attraction} + E_{repulsion}$$

$$E_{pot} = -\frac{A}{r^n} + \frac{B}{r^m}$$

E_{pot} : potential energy of the system
 $E_{attraction}$: E contribution of attractive forces
 $E_{repulsion}$: E contribution of repulsive forces
 A and B : interaction-specific constants (atom dependent)
 $n < m$
 r : distance of atomic nuclei
 E_b : binding energy
 R_0 : binding distance

Bond Types

Classification systems:

- Intra/intermolecular bonds
- According to the strength of bonds:
 - Strong/weak
 - Primary (covalent, metallic, ionic)
 - Secondary (dispersion, dipole-dipole, hydrogen)
- Other Bond types...



I. Covalent bond



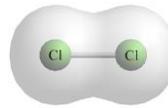
- Atoms are held together by electrons of common orbitals, called molecular orbitals.
- Valence electrons interact the most.
- Single, double or triple bond depending on the number of shared electrons.
- Some electrostatic component may be present (see later), but not predominant.
- Strong interaction: $E_b > 1$ eV
- $(1 \text{ eV} = 1,6 \cdot 10^{-19} \text{ J}) = 96 \text{ kJ/mol} \sim 100 \text{ kJ/mol}$

	R_0	E_b
H₃C-CH₃ ethane	154 pm	-331 KJ·mol ⁻¹
H₂C=CH₂ ethylene	139,9 pm	-590 KJ·mol ⁻¹
HC≡CH acetylene	120,3 pm	-812 KJ·mol ⁻¹

I. Covalent bond

Apolar (nonpolar or homeopolar) bond

Centers of (+) és (-) charges of the molecule coincide
 Binding electron(s) shared equally
 „purely covalent”
 E.g. H₂, Cl₂, O₂, ...



Polar (heteropolar) bond

Centers of (+) and (-) charges do not coincide
 Electrostatic contribution appears
 Electron cloud is polarized
 Electric dipole is formed
 E.g.: HCl, HF, H₂O, ...

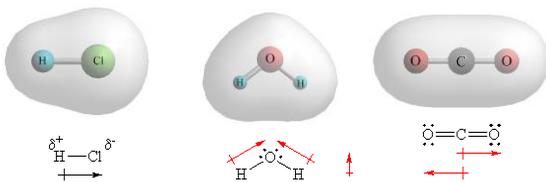


I. Covalent bond

Electric dipole moment: measure of the separation of positive and negative electric charges.

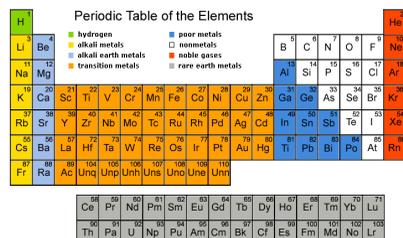
$$p = q \cdot d$$

p : electric dipole moment
 q : charge
 d : distance of separation
 [D, debye] ($1\text{D} = 3,34 \cdot 10^{-30} \text{ Cm}$)



I./b Metallic bond

- Atoms are held together by common electrons (delocalized orbital)
- Valence electrons form continuous electron band
- Strong interaction: $E_b > 1$ eV
- Multi atomic systems



I./b Metallic bond

Metallic lattice: positively charged metal ions in a crystall lattice surrounded by a cloud of delocalized electrons.

I./b Metallic bond

Physical properties:
Metals are:

- Non transparent
- Ductile (shapeable)
- Good electric conductors
- etc.

II. Bond types involving electrostatic interactions

Electronegativity

- is a chemical property that describes the tendency of an atom or a functional group to attract electrons towards itself.
- Calculated with different methods (*Pauling, Mulliken, Sanderson...*)

$$EN = |E_{ionization}| + |E_{elektronaffinity}|$$

II. Bond types involving electrostatic interactions

Electronegativity according to L. Pauling (dimensionless units)

Lanthanides: 1.0 – 1.2
Actinides: 1.0 – 1.2

II. Bond types involving electrostatic interactions

Classic bonds classified according to electronegativity:

I. ΔEN : < 0.6 (apolar covalent) 0.6 – 2.1 (polar covalent) 2.1 < (ionic)

II. Bond triangles (van Arkel-Ketelaar triangles)

II. Bond types involving electrostatic interactions

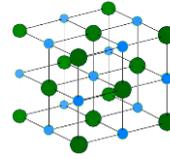
Classic bonds classified according to electronegativity: an example

(This model uses Norman (and not Pauling) EN values.)

II./a Ionic bond

- Model: atoms are held together by Coulombic forces between (+) and (-) point charges
- „Limiting case of heteropolar bonds“
- Formed between atoms of significantly different electronegativity (e.g.: NaCl, $\Delta EN = 3 - 0.9 = 2.1$)
- Can form between two atoms, but ions are usually multi-atom systems.
- Long range interaction - attraction is inversely proportional to the distance (decreases slowly with it).
- Electrostatic interaction can be largely affected by other charged components (eg. *dissociation in water!*)
- Strong interaction ($E_b > 1$ eV)

II./a Ionic bond



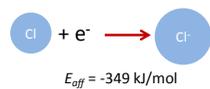
Ionic crystals: stoichiometric ratio of positive and negative ions are structured into a periodic crystalline structure. (e.g.: NaCl)



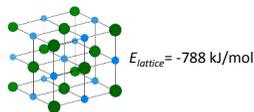
II./a Ionic bond



Ionization energy: is the energy required to remove electrons from gaseous atoms or ions.



Electron affinity: amount of energy released when an electron is added to a neutral atom or molecule to form a negative ion (measured in the gaseous state).



Lattice energy: measure of the strength of bonds in an ionic compound. Energy required to completely separate one mole of a solid ionic compound into gaseous ionic constituents.

II./b Dipole-dipole interaction

- Constant charge distribution is present in a (given part of a) molecule
- Partially (+) and (-) segments are held together by electrostatic interactions (Coulombic forces)
- Intra/intermolecular interaction.
- Weak interaction ($E_b = 0,003-0,02$ eV)

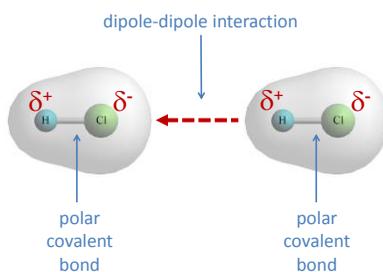
Energy of attracting interaction between dipoles:

$$E_{\text{attraction}} = p E$$

p : dipole momentum
 E : electric field strength generated by the surrounding partners

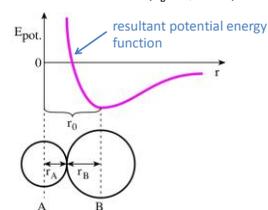
($E_{\text{repulsion}}$: stems from the repulsion of the participant's electron cloud)

II./b Dipole-dipole interaction



III. Van der Waals-interactions

- Sum of attractive and repulsive interactions between two apolar atoms, molecules or apolar molecular parts.
- The attractive contribution (also called *London-*, or *dispersion force*) is a result of temporarily created dipoles that can induce the polarization of other apolar molecule or molecular part.
- Intermolecular or intramolecular interaction.
- Important biological role: formation of organic structures.
- Weak connection ($E_b \sim 0,02$ eV)

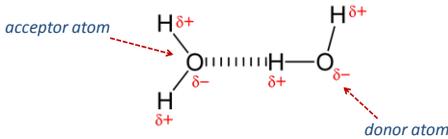


r_0 : equilibrium (binding) distance

r_A and r_B : Van der Waals radii of atom A and B

IV. Hydrogen bond

- Two atoms of high electronegativity are held together with a Hydrogen-bridge.
- Primarily between **F, N, O** atoms (pillar atoms).
- Intermolecular/intramolecular interaction
- Typical bond distance: 0,23 – 0,35 nm
- Well defined geometry.
- Important role in structural biology and biochemical reactions.
- Medium strong interaction (typical $E_b = 0,2$ eV)



V. Hydrophobic interaction



- Appears in aqueous systems (like biological environments!)
- Apolar, hydrophobic molecules tend to aggregate (form bonds with each other) in aqueous environment in order to exclude the polar water molecules and minimize their surface area exposed to water.
- Intra/intermolecular interaction
- It has mostly entropic origin (see later at Thermodynamics) through reduction of highly structured water cage around the apolar surfaces. (see Organisation of Water later)
- Important role in structural biology and biochemical reactions.
- Weak interaction.

Scanning Probe Microscopy (SPM)

Family of instruments used for studying surface properties of various materials.
How do they work?

Etimology and function:

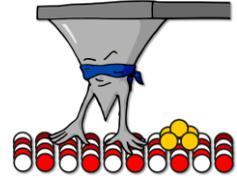
Microscopy: a method being able to form image of small objects.
How small? Size of resolvable objects spans from few pm-s to several μ m-s.

They are not „scope“-s in the classic sense of the word: They do not „see“ the object, they „touch“ it.

Scanning Probe Microscopy (SPM)

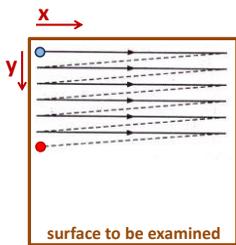
Probe:

- A tiny, specifically designed component particularly sensitive to *atomic interactions*.
- The probe is brought very closed to the sample surface.
- The sensed interactions can be correlated with the distance between the probe and the sample.
- Various interactions can be observed depending on the design of the probe.
- SPM methods are named after the type of atomic interaction sensed by a certain probe.



Scanning Probe Microscopy (SPM)

Scan pattern:

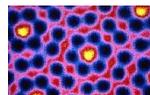


- starting point
- actual position of the probe

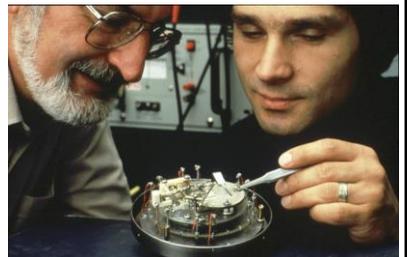
Scanning:

- A scanner controls the precise position (X; Y) of the probe and its distance (Z) from the surface to be imaged.
- The probe can be moved with pm sensitivity in X; Y; Z directions.
- The surface of region of interest (ROI) is scanned point by point during a measurement.
- (The material that enables such precise positioning is *piezoelectric ceramic*. If voltage is applied on it, the ceramic changes its geometry. See details in Ultrasound lecture, 2nd semester)

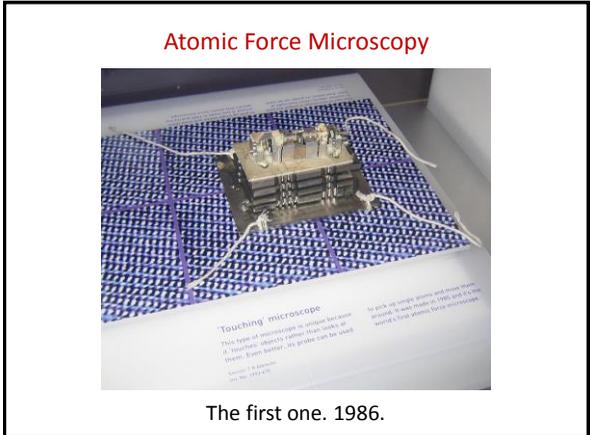
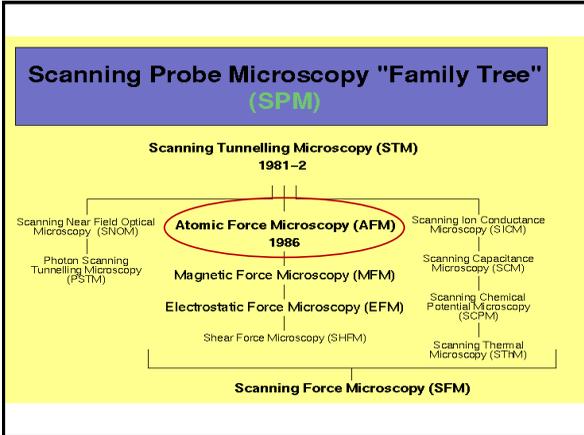
Scanning Tunneling Microscope (STM) 1981



Atoms in a silicon chip

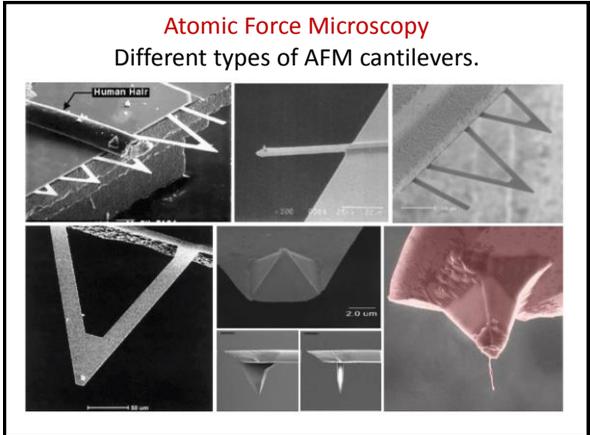


Heinrich ROHRER and Gerd BINNING
Nobel prize: 1986



Atomic Force Microscopy

- The probe is a tiny, sharp tip, usually few μm -s tall, and only few nm-s in diameter at the apex.
- The tip is located at the free end of a cantilever that is usually 50-500 μm long.
- Material: usually silicon or silicon nitride
- May be coated with a thin metal layer.
- Radius: 0.1 nm – 100 μm
- spring constant: ~ 0.1 -10 N/m
- f_0 : ~ 50 -500 kHz



Atomic Force Microscopy

- Bringing the tip very close (few nm-s) to the sample atomic interactions arise between the very last atoms of it and the atoms of the sample.

Depending on the tip-sample distance:

- Net attraction or repulsion may occur.
- Attraction at „longer“ distances.
- Repulsion at very short distances.

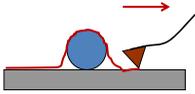
Atomic Force Microscopy

- Attractive and repulsive effects cause the cantilever to bend.
- Deflection of the cantilever is detected by an optical system.
- A laser beam is pointed at the very end of the cantilever, and reflected back to be sensed by a position-sensitive photodetector (PSD).
- Thus vertical deflection of the cantilever is amplified and can be detected with sub-Å sensitivity..

Atomic Force Microscopy

Contact mode:

- The tip is in perpetual contact with the sample surface.
- The deflection of the cantilever (i.e. the force exerted on the sample by the tip) is held constant.
- A z feedback system is utilized to maintain the deflection at a constant value (setpoint) by lifting or lowering the cantilever.
- Topography data (i.e.: height) in each x,y point is calculated from these z movements



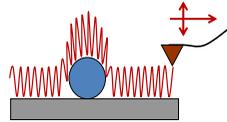
Disadvantage:

- Lateral forces exerted by the scanning tip may damage softer samples.

Atomic Force Microscopy

Oscillating mode: (Tapping mode, Non-contact mode)

- Cantilever is oscillated close to its resonant frequency (see resonance practice).
- The tip taps the surface gently
- The amplitude of cantilever oscillation changes with surface topography.
- A z feedback system is utilized to maintain the amplitude at a constant value (setpoint) by lifting or lowering the oscillating cantilever.
- Topography data (i.e.: height) in each x,y point is calculated from these z movements



Advantage:

- Virtually eliminated lateral forces.
- Allows more gentle imaging.
- Applicable for soft samples.

Atomic Force Microscopy (AFM)

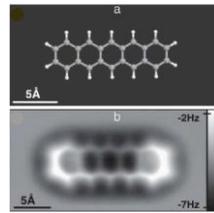
Main advantages:

- ✓ 3D surface profile.
- ✓ Images are collected with ~10 pm vertical and somewhat worse horizontal resolution.
- ✓ Any surfaces (conductors, insulators and semiconductors) can be imaged.
- ✓ Works in ambient air, special gas or in fluid environment as well.
- ✓ Usually does not require fixation or staining of the sample.
- ✓ Biological samples can be examined in their native state and physiological environment.

Main disadvantages:

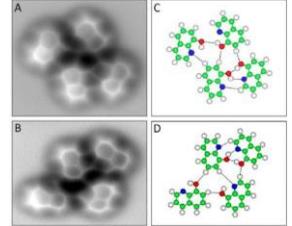
- x Samples must adhere to a substrate. Surface adhesion may lead to distortion.
- x Slow scan speed.
- x Scan height limited to few microns („the flatter the better”).
- x Scan size limited to few tens of microns.
- x High cost

Atomic Force Microscopy



Pentacene molecule imaged with AFM

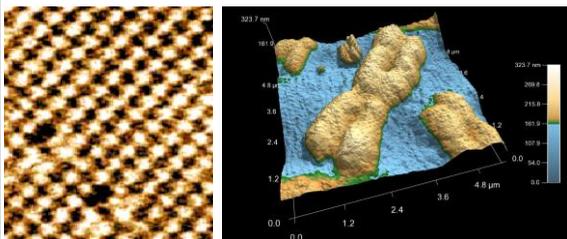
Nature Chemistry 1, 597 - 598 (2009)



Hydrogen bonds between 8-hydroxyquinoline molecules scanned with AFM

Science, 2013; 342 (6158), 611-614

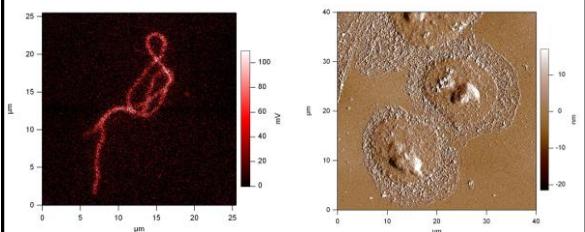
Atomic Force Microscopy Images



NaCl crystal surface

Human metaphase chromosomes

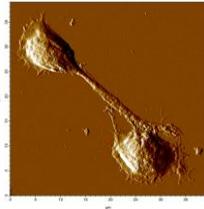
Atomic Force Microscopy Images



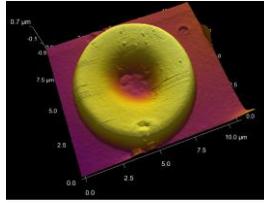
„The thinker”
a single actin polymer

HeLa cells on glass

Atomic Force Microscopy Images



B-lymphocytes interconnected by a membrane nanotube



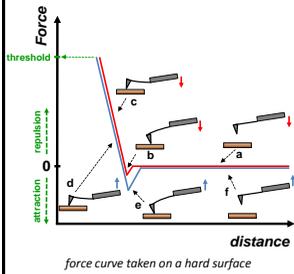
Human red blood cell with „VER“ nanolithographed on its surface

Atomic Force Microscopy

<http://www.youtube.com/watch?v=BrsoS5e39H8>

Atomic Force Microscopy

Force spectroscopy: Force-distance traces registered upon push-pull cycles of the AFM tip (movement only in Z direction)
~10 pN sensitivity



Deflection of the cantilever (Δx) is proportional to the force (F) (Hooke's law):

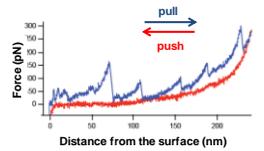
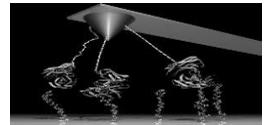
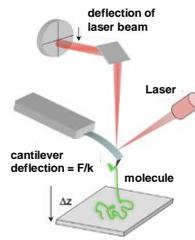
$$F = k \cdot \Delta x$$

k : spring constant of the cantilever

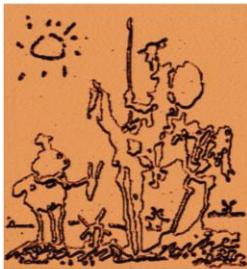
Binding forces, viscous and elastic properties can be measured perturbing the sample with the tip and registering the force response.

Atomic Force Microscopy

Force spectroscopy: Force-distance traces registered upon push-pull cycles of the AFM tip (movement only in Z direction)
~10 pN sensitivity



Thank you for your attention!



Pablo Picasso: "Don Quixote"
polikarbonát felszínbe rajzolja

1 μ m