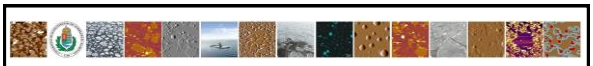

Structure of matter, matter waves, atomic and molecular interactions

As an example: atomic force microscopy

Tamás Bozó

Nanobiotechnology and Molecular Biophysics Workgroup
Department of Biophysics and Radiation Biology

09 October 2017

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Overview

Topics:

- atomic structure
- atomic modells
- dual nature of electron
- propagation of free and bound electron
- quantum states
- atomic and molecular interactions
- atomic force microscopy

Related exam questions:

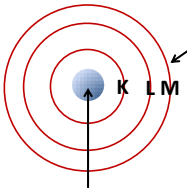
6. Proofs of particle-wave duality in case of electron. Matter waves in bound and free cases.

7. General description of atomic and molecular interactions.

Textbook chapters: ***I/1.1, I/1.2, I/1.3, I/1.4, I/2, X/2***

Related practices: *Light emission, Light absorption, Resonance*

Atomic structure



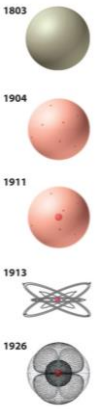
energy levels (shells) with
K: max. 2 e^-
L: max. 8 e^-
M: max. 18 e^-

nucleus, including nucleons:
protons (p^+)
neutrons (n^0)

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 10.)

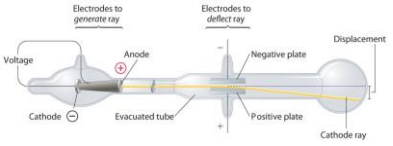
History of the atom



~ 400 B.C.	**Demokritus:** atoms are miniscule quantities of matter.
1803	**J. Dalton:** stoichiometric law, every elements consists of identical constituens, billiard ball model
1900	**M. Plack:** Radiation law, quantum physics
1897-1904	**J.J. Thomson:** cathode ray: discovery of electron, mass of electron „plum pudding" model
1910	**R.A. Millikan:** charge of electron
1909-11	**E. Rutherford:** discovery of nucleus, planetary model
1913	**N. Bohr:** discrete energy states, Bohr-model
1914	**J. Franck, G.L. Hertz:** evidence of energy quanta
1923	**L.V. de Broglie:** electron wave
1926	**E. Schrödinger:** wave function, quantummechanical atomic model
1927	**W. Heisenberg:** uncertainty relation
1927-28	**C.J. Davisson, L.H. Germer, G.P. Thomson:** evidence of electron waves
1932	**J. Chadwick:** discovery of neutron

Discovery of electron (1897)

Sir Joseph John Thomson
1856-1940



deflection of cathode ray (CR)

Observations	Conclusions
Ray deflects in electric and magnetic field toward positively charged electrode	CR consist of negatively charged particles („corpuscules") .
Very low *m/q* ratio.	These particles are either very light or highly charged.
The *m/q* ratio is independent of the nature of cathode (or filling gas).	These particles are fundamental components of all atoms.

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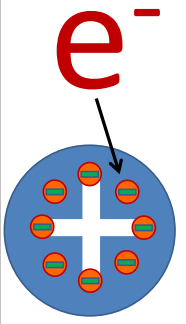
Thomson's plum-pudding model (1904)



- Particles of small mass and negative charge (electrons)
- distributed distributed symmetrically around the center
- of a homogeneous,
- positively charged,
- liquid-like substance that
- gives the vast majority of mass of the atom.

Problems with the model:

- e.g.: Could not explain the line spectrum of H_2 gas.

$$m_{electron} = 9{,}109 \cdot 10^{-31} kg$$
$$q_{electron} = -e = 1.602 \cdot 10^{-19} C$$

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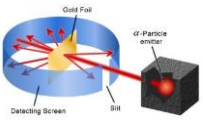
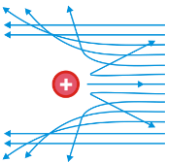
Discovery of atomic nucleus (1909)

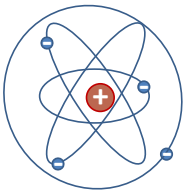
Sir Ernest Rutherford
1871-1937



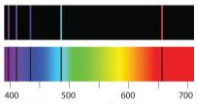


Observations	Conclusions
99.995% of all α particles suffered only slight deflection.	Density of the atom is inhomogeneous. bulk mass is concentrated in a small volume inside. This volume in 10^5 times smaller than that of the atom.
0.005% of all α particles bounced back through 180°.	This core has to be positively charged.

Rutherford's modell



- „Tiny solar system"
- Electrons (light, negatively charged particles) orbiting around the nucleus (heavy, positively charged particle).
- Coulomb interactions keep electrons orbiting.



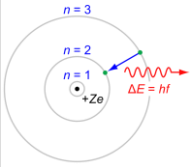
(b) H_2 emission spectrum (top), H_2 absorption spectrum (bottom)

Problems with the model:

- Such an atom cannot be stable (orbiting electrons accelerates→ accelerated charges radiate → they lose energy and fall into nucleus)
- Could not explain the line spectrum of H_2 gas.

Niels Bohr's atomic model (1913)

Niels Henrik David Bohr
1885-1962

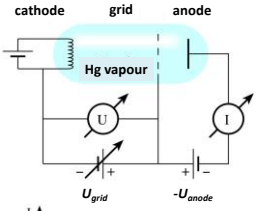


- Electrons can occupy only certain distinct orbits (numbered as 1, 2, 3, ...).
- Being on these orbits they do not radiate, but have constant energy (E_1, E_2, E_3,...).
- Emission (radiation) take splace when an electron jumps to a lower energy orbit.
- Upon absorption of energy electron can jump to a higher energy orbit.

$$\Delta E = E_m - E_i = h \cdot f$$

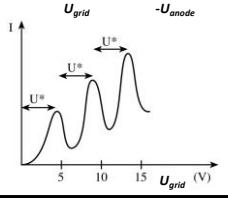
- Explained well the line spectrum of H_2.
- BUT failed to explain the spectra of larger atoms, relative intensities of spectral lines, and a few further phenomena.

Franck-Hertz experiment (1914)



James Franck
1882-1964

Gustav Ludwig Hertz
1887-1975



Conclusion
Energy cannot change continously but only by certain discrete values: quanta. *(Direct evidence of energy quanta!)*

The wave nature of the electron

Einstein: mass-energy equivalence	**Planck:** radiation law	**Maxwell:** speed of light
$E = mc^2$	$E = h \cdot f$	$c = \lambda \cdot f$

de Broglie: If light is a particle, can electron be a wave? (1923):

Louis Victor de Broglie
1892-1978

$$m \cdot c^2 = h \cdot \frac{c}{\lambda}$$

$$p = m \cdot v$$

$$\lambda = \frac{h}{p} = \frac{h}{m \cdot v} = \frac{h}{p}$$

$$p = \frac{h}{\lambda}$$

Wave-particle duality: Electron is at once a subatomic particle, with well defined mass and charge AND a wave.

Generalization: Matter waves (particles of matter have wave-like properties.)

Interference experiments (1927-28)

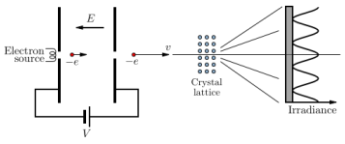
J.Davisson and L.H.Germer

G. P. Thomson

Experimental proof of wave nature: Interference of electron beams on crystals and metal foils.

Davisson, *Germer* and *Thomson* used electron beams to induce diffraction on a thin metal foils or crystals.

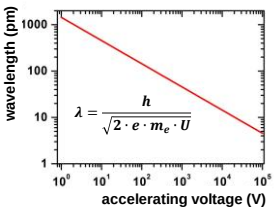
Interference pattern appeared, which is a clear evidence of wave-like properties.



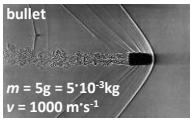
Wavelength of electron (e.g.: in a cathode ray tube)

$$\lambda = \frac{h}{p}, \quad p = m_e \cdot v \quad \Rightarrow \quad \lambda = \frac{h}{m_e \cdot v}$$

$$E_{pot} = e \cdot U, \quad E_{kin} = \frac{1}{2} \cdot m_e \cdot v^2, \quad E_{kin} = E_{pot} \quad \Rightarrow \quad v = \sqrt{\frac{2 \cdot e \cdot U}{m_e}}$$



Why don't we observe the wave properties of macroscopic objects?

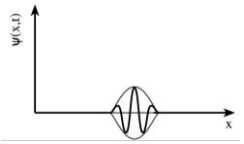


$$\lambda = \frac{h}{m \cdot v} = \frac{6.626 \cdot 10^{-34}\ m^2 \cdot kg \cdot s^{-1}}{5 \cdot 10^{-3}\ kg \cdot 1000\ m \cdot s^{-1}} = 1.325 \cdot 10^{-34} m$$

The wave nature of the electron

Ervin Schrödinger
1887-1961

A wave function(or state function) ***Ψ(x,t)*** is used to describe the amplitude of the electron wave as a function of position ***(x)*** and time ***(t)***.
Electron is pictured as a continous charged cloud of finite size with a charge density proportional to Ψ^2 at any point in space.



visualization: wave package

location: where *Ψ(x,t)* ≠ 0
momentum (*p*): given by the shape

Propagation law of free electrons (1926) (e.g. vacuum tube electron)

1. Ψ(x,t) ≠ 0 holds for more than one point → position cannot be determined with a simple numeric value.

2. The function is nonperiodic → cannot be characterised by a single wavelength → Any λ between an approximate largest λ_1 and smallest λ_2 wavelength can characterize the wave package.

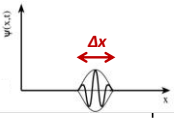
Since $p = \frac{h}{\lambda}$, $v = \frac{p}{m_e}$ and $s = v \cdot t$

Neither momentum (p), nor speed (v) nor displacement (s) can be described by a well determined single value → they can be characterised by any value between p_1 and p_2, v_1 and v_2, s_1 and s_2 → Ψ(x,t) will disperse while propagating and new wave cycles appear on the graph.

Heisenberg uncertainty relation (1927):

Werner Karl Heisenber
1901-1976

A wave function(or state function) ***Ψ(x,t)*** is completely determided, although some pieces of the information it carries (e.g. position, momentum, velocity of the electron) are uncertain.



$$\Delta x \cdot \Delta p \geq h$$

Δx: uncertainty of position
Δp: uncertainty of momentum
h: Planck's constant

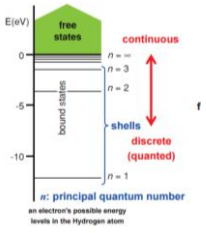
Conclusion: *The more determined the positon (x) of an electron, the less determined the momentum (p), and vice versa.*

It can be extended to other pairs of physical properties (complementary variables) of a particle, eg. energy and time:

$$\Delta E \cdot \Delta t \geq h$$

What about electrons bound in an atom?

1. External force field is present due to the positively charged nucleus.
2. The field will move (distort) the state function of the electron to its own direction.
3. Electrons do not have enough energy to leave the proximity of the nucleus, they are in bound state.
4. Electrons disperse due to the uncertainty of their momentum.



As a result:
A dynamic equilibrium evolves between the attractive effect of nucleus and the dispersing nature of the state function.
Stationary , symmetric state functions emerge to form discrete, strictly differentiated, well defined atomic electron states.

$\psi_{(x)}$

Properties of quantized atomic electron states

Bound electrons – quantized energy levels. Their 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=±1/2	intrinsic angular momentum (spin*) of an electron	direction of the spin (magnitude is constant)

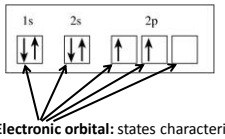
All the four quantum numbers are required to characterize a bound-state electron.

How will electrons occupy their quantum states?

Pauli exclusion principle: Within an atom there cannot be two electrons with all four quantum numbers being identical.

Principle of minimum energy: The total energy of the system should be minimized.

Hund principle: For a given electron configuration, the state with maximum total spin has the lowest energy.

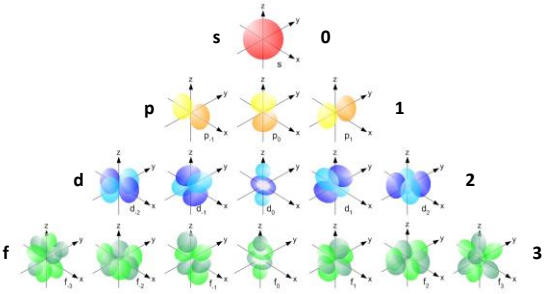


Carbon , Z=6

Electronic orbital: states characterized by n, l and m_l quantum numbers, which may be occupied by at most 2 electrons of oposite spins.

Configuration: Gives the (partially or fully) occupied subshells and the number of equivalent (same subshell)electrons.

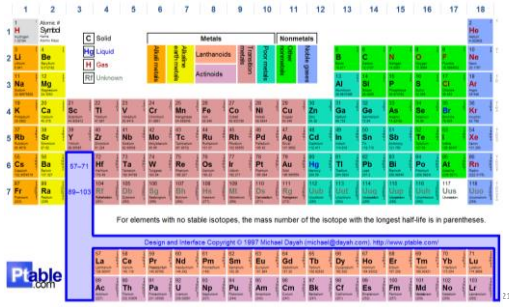
Visualization of subshell structure



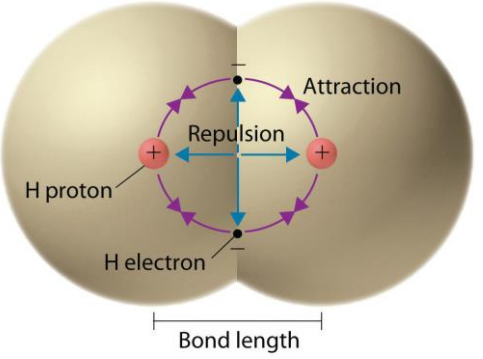
Atomic interactions

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. H_2, HCl, H_2O, …)* Each atom has a (more or less) fixed position in the molecule.

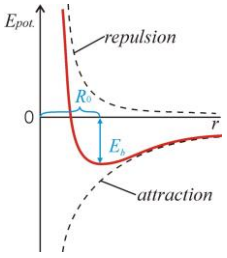


Atomic interactions



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:



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

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

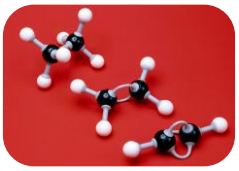
E_{pot}: potential energy of the system
$E_{attraction}$: E contribution of attractive forces
$E_{repulsion}$: E contribution of repulsive forces
A and B: interaction-specific constants (atom dependent)
$n<m$
r: distance of atoms
E_b: bindig energy
R_0: binding distance

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



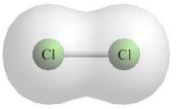
	R_0	E_b
$H_3C\text{-}CH_3$ ethane	154 pm	-331 KJ·mol^{-1}
$H_2C{=}CH_2$ ethylene	139,9 pm	-590 KJ·mol^{-1}
$HC{\equiv}CH$ acetylene	120,3 pm	-812 KJ·mol^{-1}

- 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 eV = 1,6*10^{-19}J = 96 kJ/mol ~ 100 kJ/mol)

I. Covalent bond

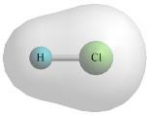
Apolar (nonpolar or homeopolar) bond

Center of (+) és (-) charges of the molecule coincides
Binding electron(s) shared equally
„purely covalent"
E.g. H_2, Cl_2, O_2, …



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, H_2O, …

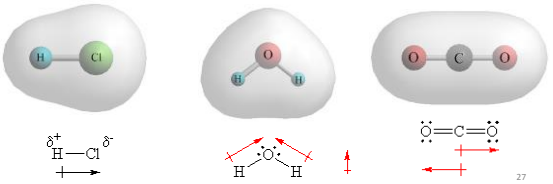


I. Covalent bond

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

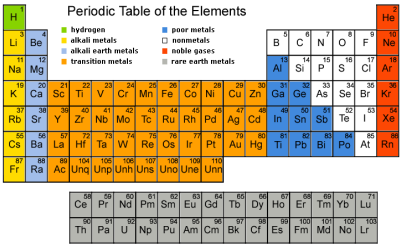
$$p = q \cdot d$$

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

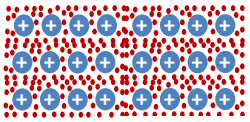


I./b Metallic bond

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

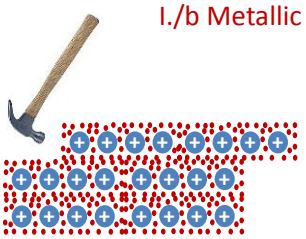


I./b Metallic bond



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

I./b Metallic bond



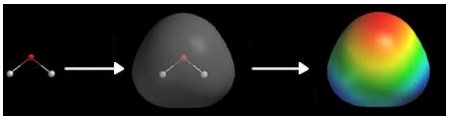
Physical properties:
Metals are:
- Non transparent
- Ductile (shapeable)
- Good electric conductors
- etc.

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…)*

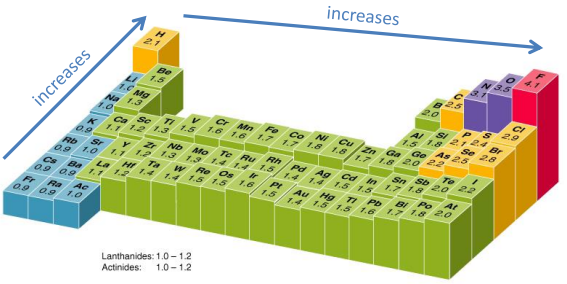
$$EN = |E_{ionization}| + |E_{elektronaffinity}|$$



31

II. Bond types involving electrostatic interactions

Electronegativity according to L. **Pauling** (dimensionless units)

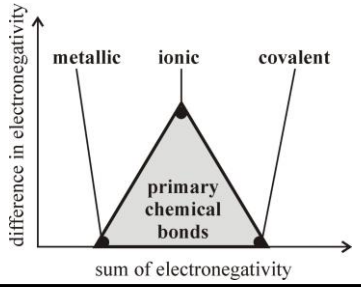


32

II. Bond types involving electrostatic interactions

Classic bonds classified according to electronegativity:

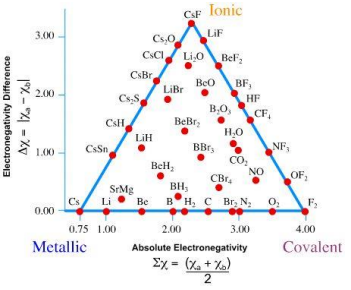
ΔEN **: < 0.6** (apolar covalent) **0.6 – 2.1** (polar covalent) **2.1 <** (ionic)



33

II. Bond types involving electrostatic interactions

Classic bonds classified according to electronegativity: an example



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

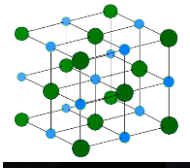
34

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, ΔEN = 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)

35

II./a Ionic bond

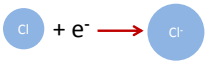


Ionic crystals: stochiometric ratio of positive and negative ions are structured into a periodic crystalline structure. *(e.g.:NaCl)*

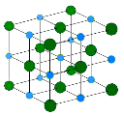
36

II./a Ionic bond

E_i = 496 kJ/mol



E_{aff} = -349 kJ/mol



$E_{lattice}$= -788 kJ/mol

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.

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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/intermolekular interaction.
- Weak interaction (E_b = 0,003-0,02 eV)

- Energy of attracting interaction between dipoles:

$E_{attraction} = p\,E$

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

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

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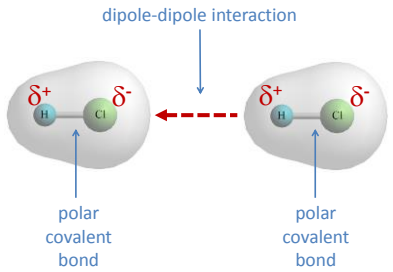
II./b Dipole-dipole interaction



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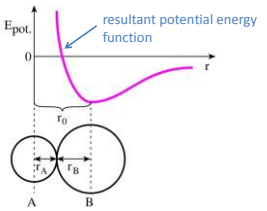
III. Van der Waals-interactions

- 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.
- Week connection (E_b ~ 0,02 eV)



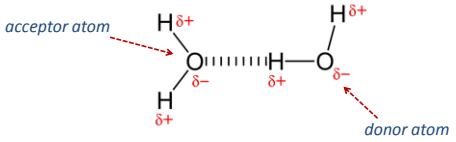
r_0 **:** equilibrium (binding) distance

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

40
40

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)



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V. Hidrophobic interaction

- Appears in aqeous systems (like biological environments!)
- Apolar, hydrophobic molecules tend to aggregate (form bonds with each other) in aqeous 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.

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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 μm-s.

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

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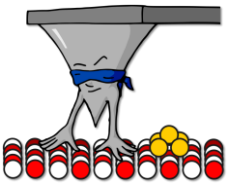
Scanning Probe Microscopy (SPM)

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.

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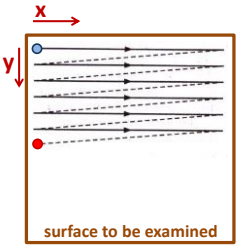
Scanning Probe Microscopy (SPM)

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*)

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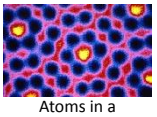
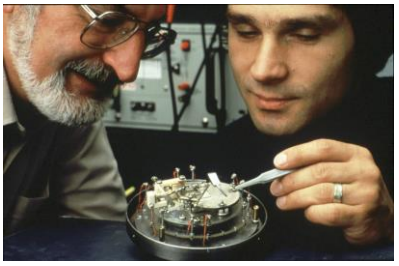
Scanning Tuneling Microscope (STM) 1981



Atoms in a silicon chip



Heinrich ROHRER and Gerd BINNING
Nobel prize: 1986

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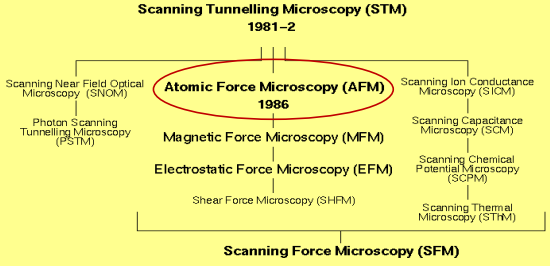
Scanning Probe Microscopy "Family Tree" (SPM)



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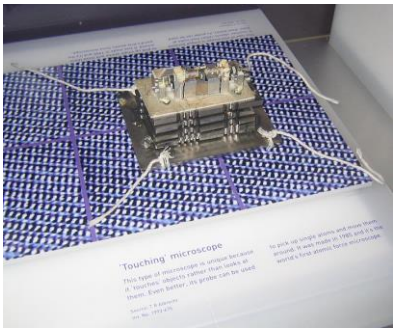
Atomic Force Microscopy



The first one. 1986.

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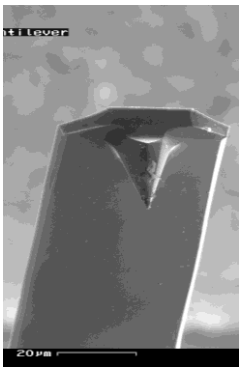
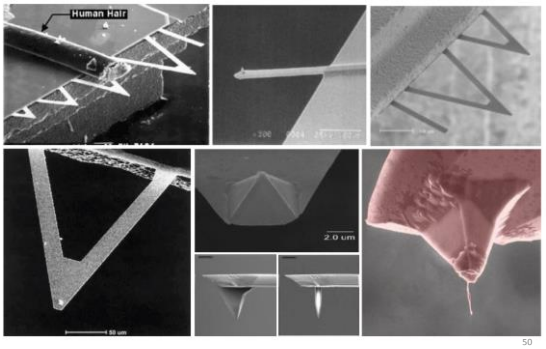
Atomic Force Microscopy



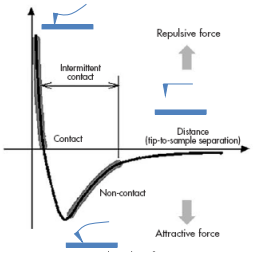
- The probe is a tiny, sharp tip, usually few µm-s tall, and only few nm-s in diameter at the apex.
- The tip is located at the free end of a cantilever that is usually 100-500 µm long.
- Material: usually silicon nitride
- May be coated with a thin metal layer.
- Radius: 0.1 nm – 100 µm
- spring constant: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

Atomic Force Microscopy
Different types of AFM cantilevers.



Atomic Force Microscopy

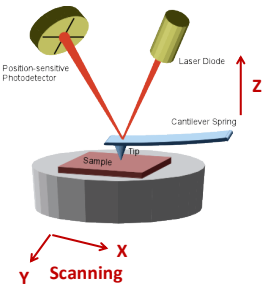
- Bringing the tip very close (few nm-s) to the sample atomic interactions arise between the very last atoms of it and the atoms of the sample.



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..

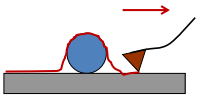
Atomic Force Microscopy (AFM)

- Topographic image is collected with ~10 pm vertical and somewhat worse horizontal resolution.
- Any surfaces (conductors, insulators and semiconductors) can be imaged.
- Works in air and 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.

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



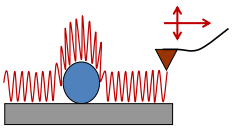
Disadvantage:

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

Atomic Force Microscopy

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

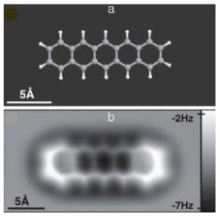
- Cantilever is oscillated close to its resonant frequency (see resonance practice).
- The tip taps the surface gently
- The amplitude of cantilever oscillation changes with surface topography.
- A z feedback system is utilized to maintain the amplitude at a constant value (setpoint) by lifting or lowering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



Advantage:

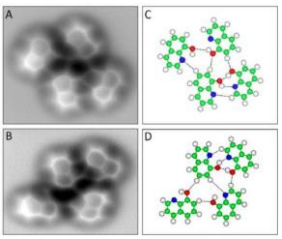
- Virtually eliminated lateral forces.
- Allows more gentle imaging.
- Applicable for soft samples.

Atomic Force Microscopy



Pentacene molecule imaged with AFM

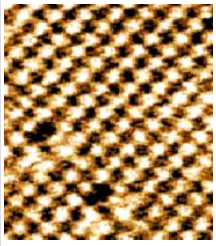
*Nature Chemistry **1**, 597 - 598 (2009)*



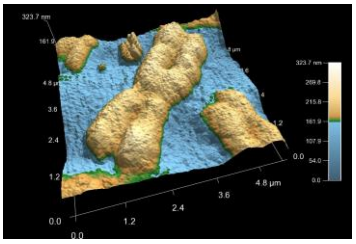
Hydrogen bonds between 8-hydroxiquinoline molecules scanned with AFM

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

Atomic Force Microscopy
Images

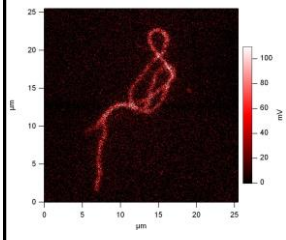


NaCl crystal surface

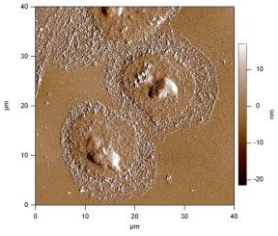


Human metaphase chromosomes

Atomic Force Microscopy
Images



„The thinker"
a single actin polimer



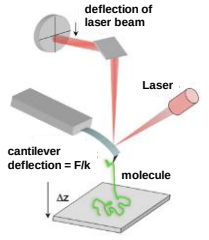
HeLa cells on glass

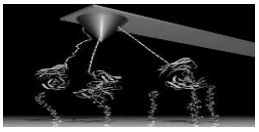
Atomic Force Microscopy

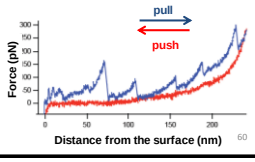
http://www.youtube.com/watch?v=BrsoS5e39H8

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

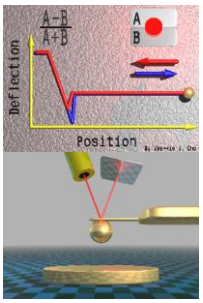






Atomic Force Microscopy

Force spectroscopy:



Deflection of the cantilever (Δx) is proportiaonal 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.

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Thank you for your attention!

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