Structure of matter, matter wave, atomic and molecular interactions. Atomic force microscopy.

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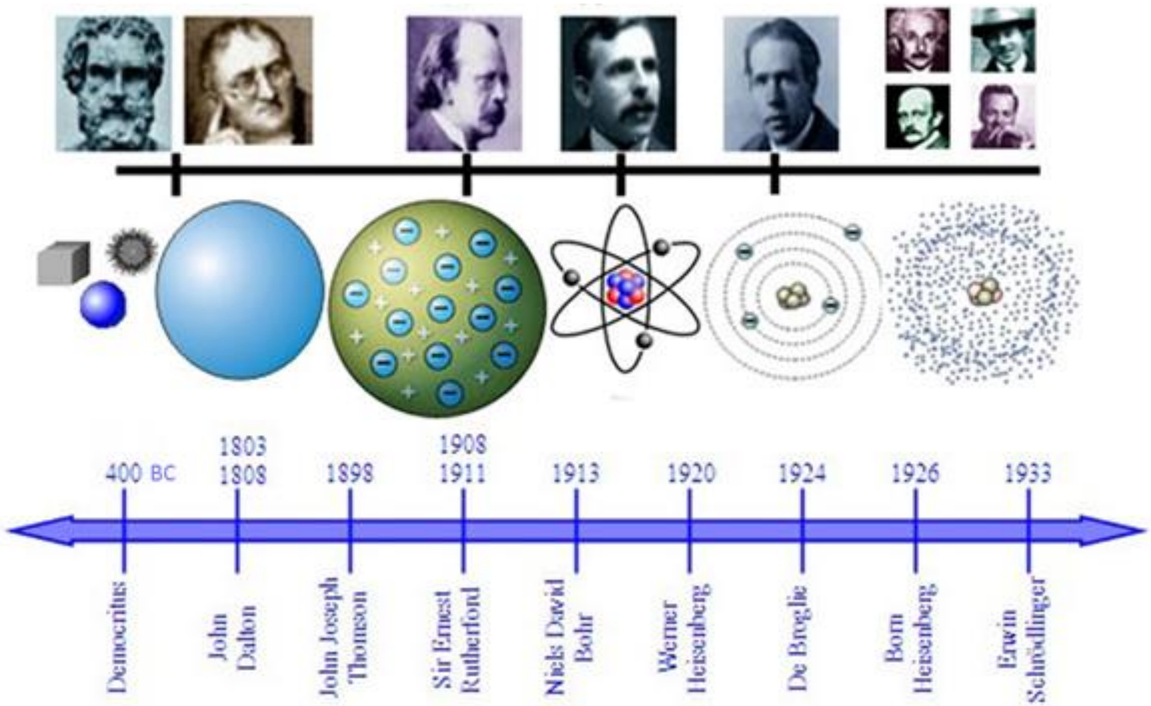
Textbook: pages 23-37

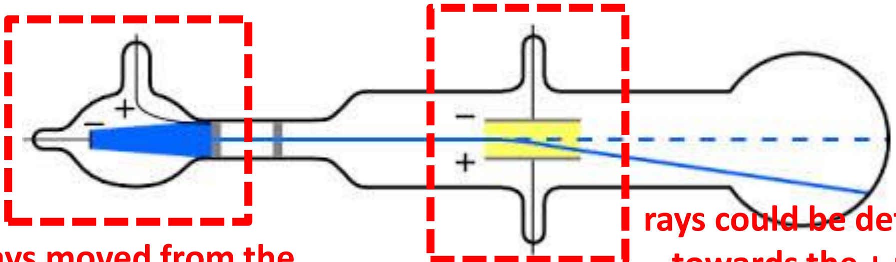
Atomic models - History



- **Democritus (~400 BC):** proposition of atomic structure („atomos”: indivisible)
- **Dalton (1803):** stoichiometric law: elements consist of identical constituents
- **Thomson (1897):** discovery of electron (cathode rays)
- **Rutherford (1909-1911):** nucleus (nucleons: p^+ and n_0) and electrons
- **Bohr (1913):** discrete energy states

Thomson and Rutherford

Thomson: discovery of cathode rays

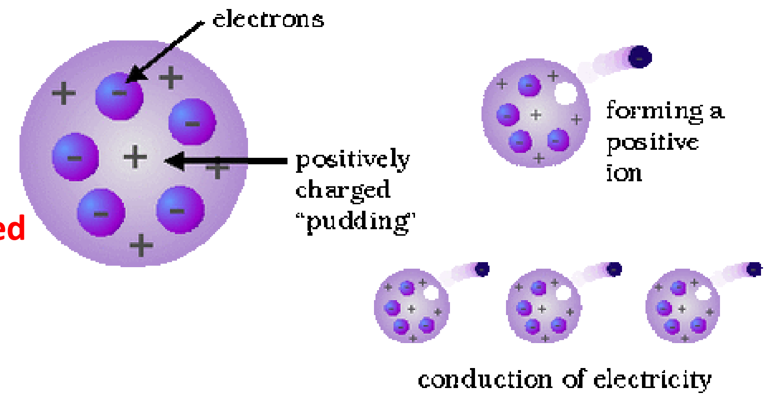


rays moved from the negative electrode to the positive electrode

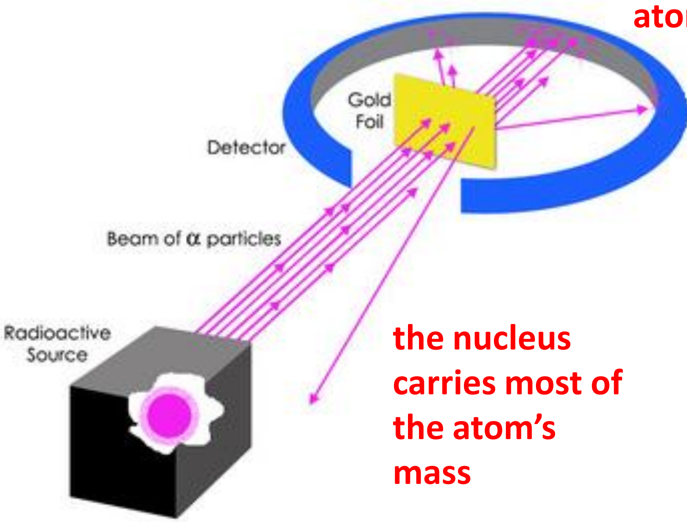
rays could be deflected towards the + plate

gas discharge tube

„plum pudding atom" or „blueberry muffin atom"



Rutherford: experiments with α-particles

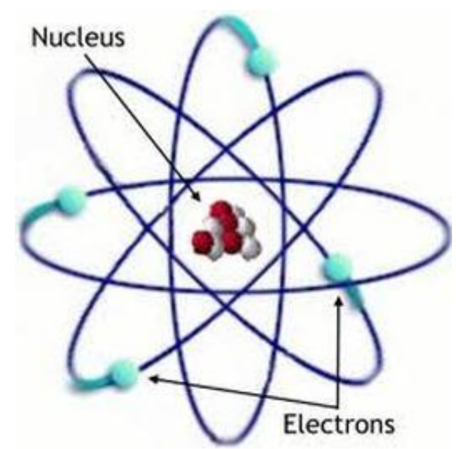


atoms are mostly empty space

atoms are made of a small positive nucleus

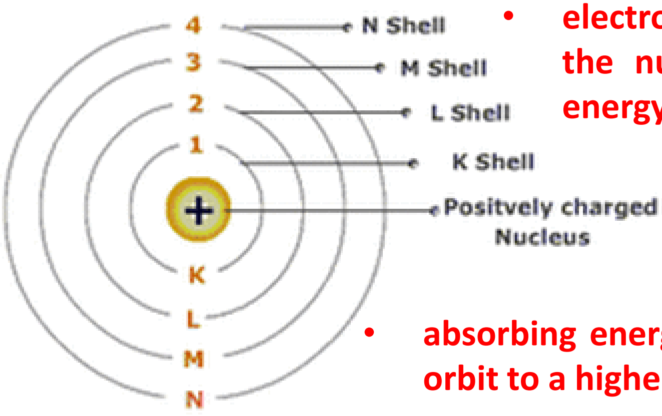
the nucleus carries most of the atom's mass

„planetary model"



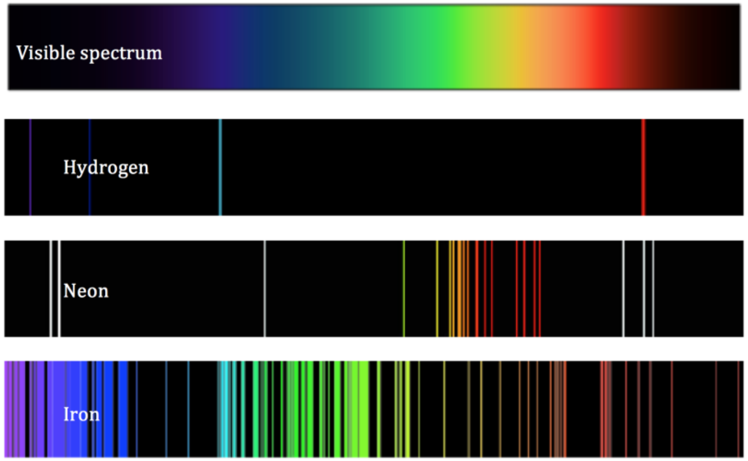
Bohr and Schrödinger

Bohr: describing the electron shells



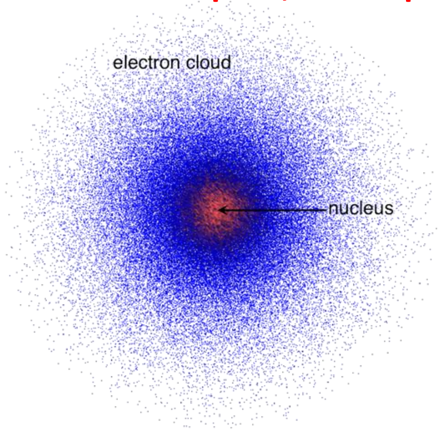
- **electrons furthest from the nucleus have higher energy**
- **absorbing energy: jump from a lower orbit to a higher**
- **losing energy: emission of photons**

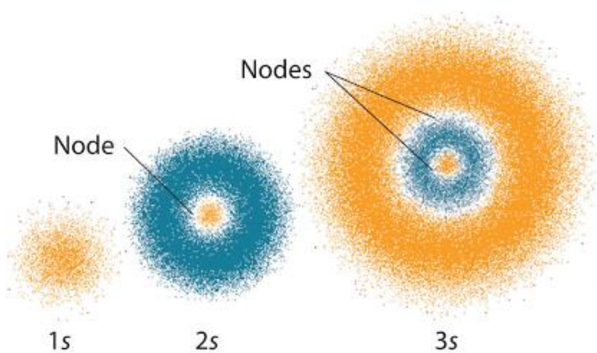
Emission spectra of certain elements



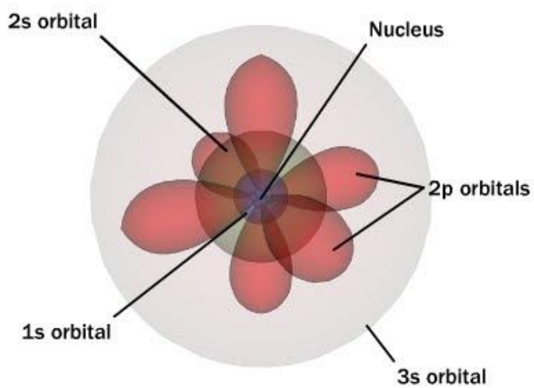
Schrödinger: quantum mechanical model of the electrons

- **no exact path, rather predicts the odds of the location of the electron**

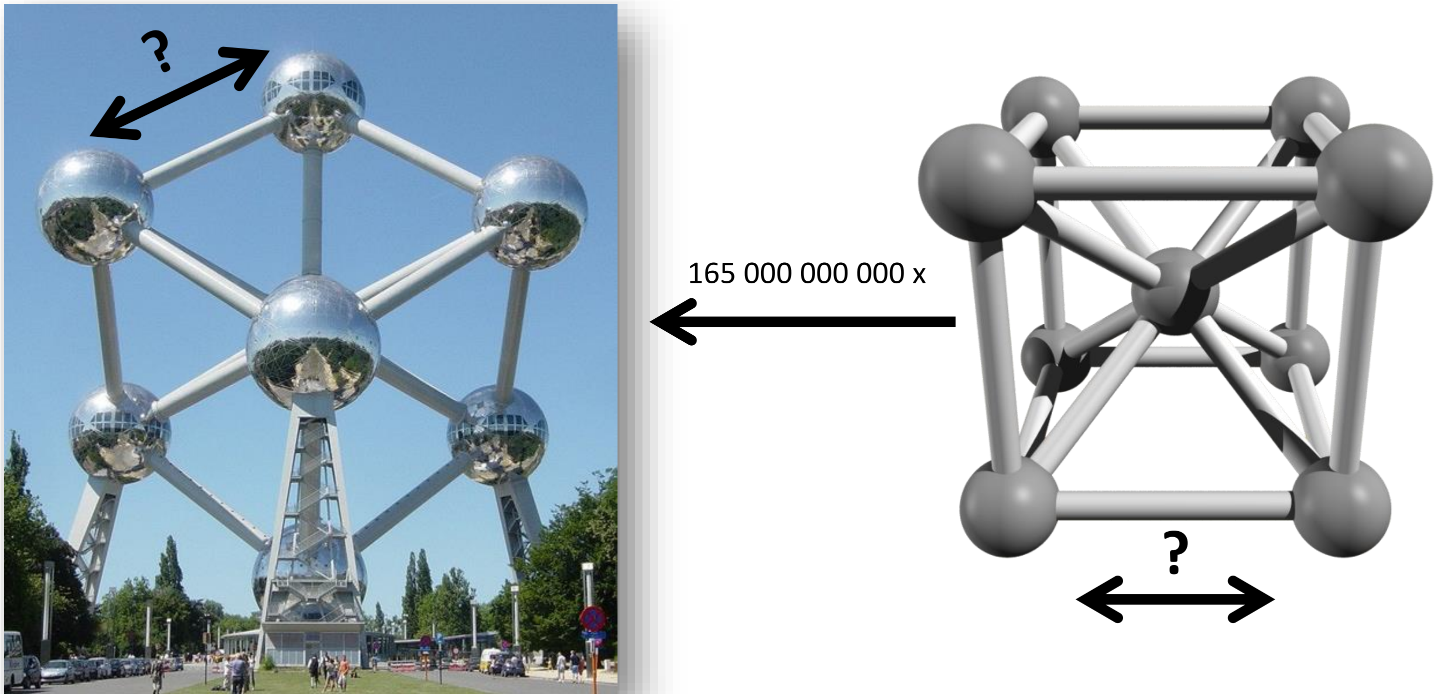




Complex shapes of orbitals: electron clouds



How are stable structures created/formed?



macroscopic scale: Atomium

nanoworld: face-centered cubic lattice of Fe

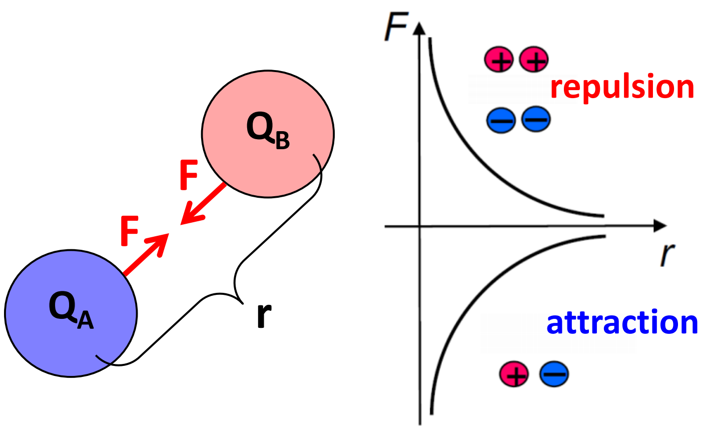
<u>Governing principle:</u>

consequence: DISORDER — **repulsive interaction** ⟷ **attractive interaction** — consequence: ORDER

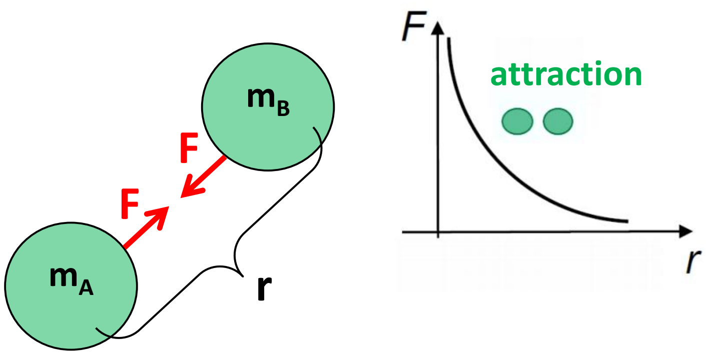
Fundamental interactions in physics

Interaction type	Binding particle	Range (m)	Relative strength
gravitation	every particle	infinite (~1/r^2)	10^{-40}
electrostatic (Coulomb)	charged particles	infinite (~1/r^2)	10^{-2}
strong nuclear	nucleons	10^{-15}	1
weak nuclear	every particle	10^{-18}	10^{-13}

Coulomb-interaction ⟷ **Gravitation**

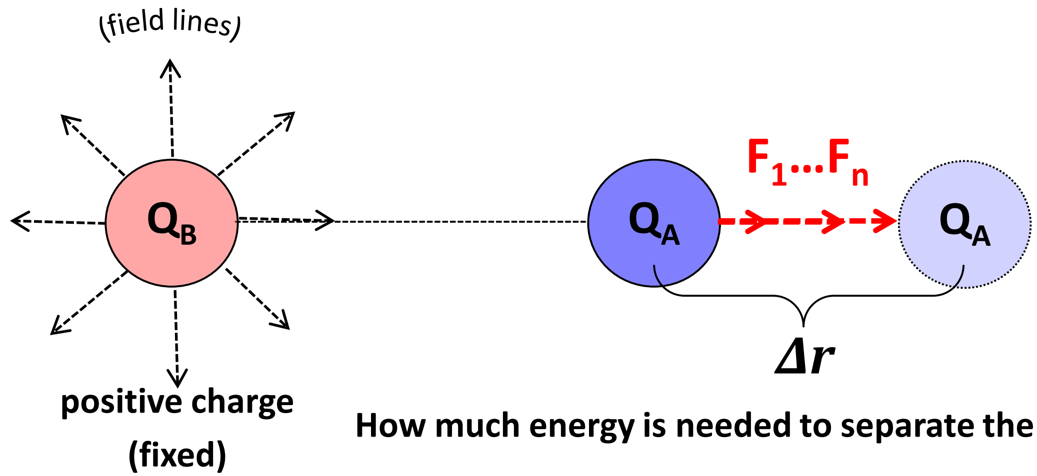


$$F_C = k \cdot \frac{Q_A \cdot Q_B}{r^2}$$



$$F_g = G \cdot \frac{m_A \cdot m_B}{r^2}$$

Electric potential energy (E_{pot})

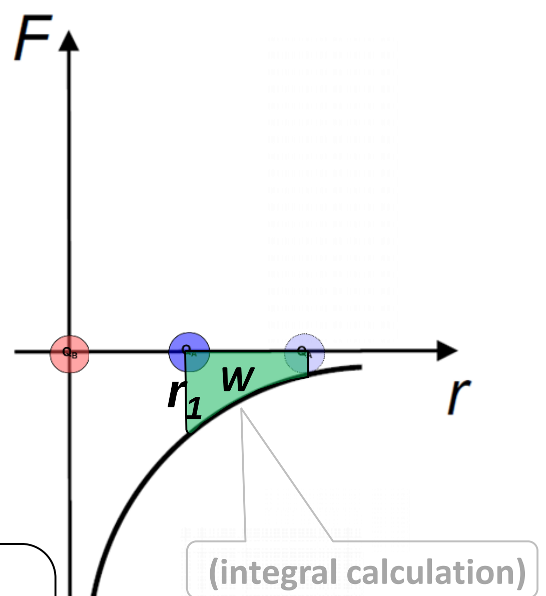


$$W = F \cdot s = F \cdot \Delta r$$

$$F = ?$$

changes continuously!

How much energy is needed to separate the negative charge?



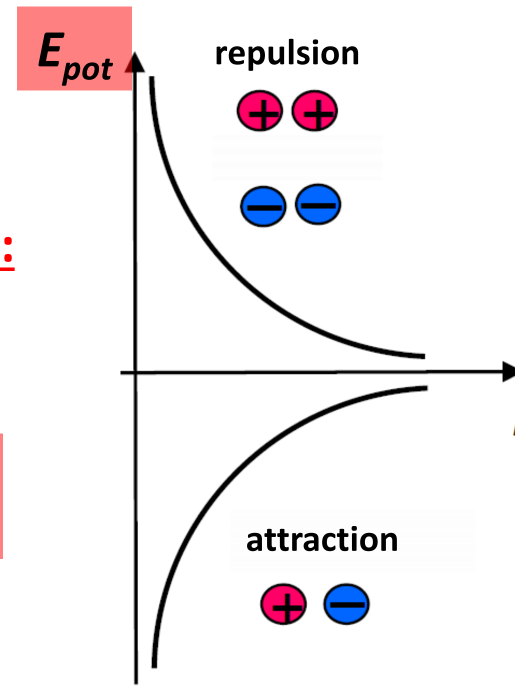
the negative charge is transported into infinite

$$W_{r \to \infty} = -k \cdot \frac{Q_A \cdot Q_B}{r}$$

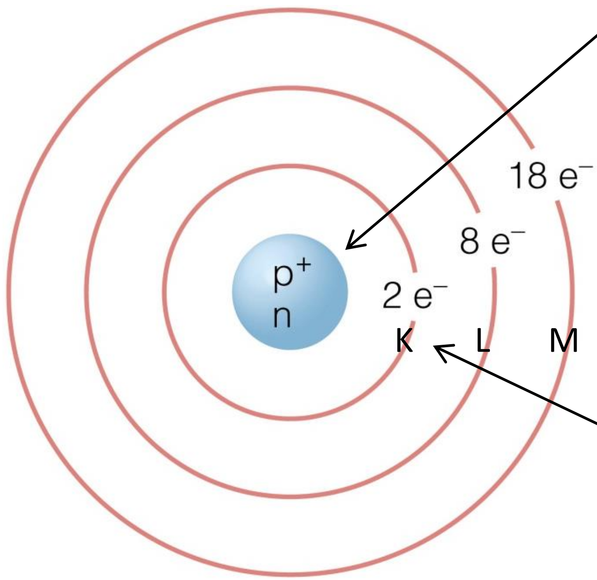
Electric potential energy:

$$E_{pot} = W_{\infty \to r}$$

$$E_{pot} = k \cdot \frac{Q_A \cdot Q_B}{r}$$



Structure of the Atom



nucleus, including:

- **protons (p^+)**
- **neutrons (n_0)**

} **nucleons**

$$Q_{total,nucl} = Z \cdot e$$

← **shells**

electrons

$$Q_{total,e^-} = -Z \cdot e$$

Z: atomic number

(number of protons)

N: neutron number

A: mass number

(=Z+N)

d_{atom}~0.1 nm

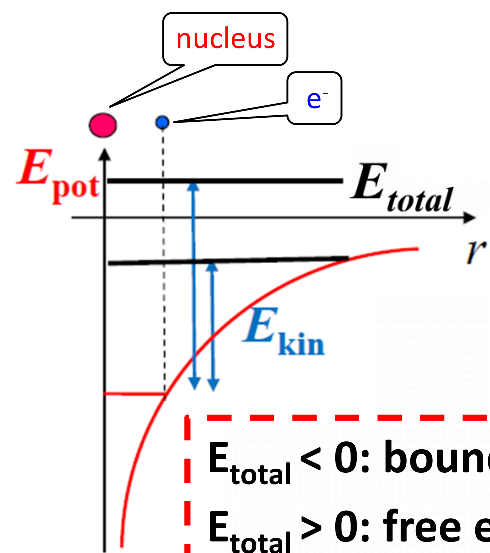
E_{kin} $\frac{1}{2}mv^2$

kinetic energy

E_{pot} $k \cdot \frac{Q_A \cdot Q_B}{r}$

potential energy

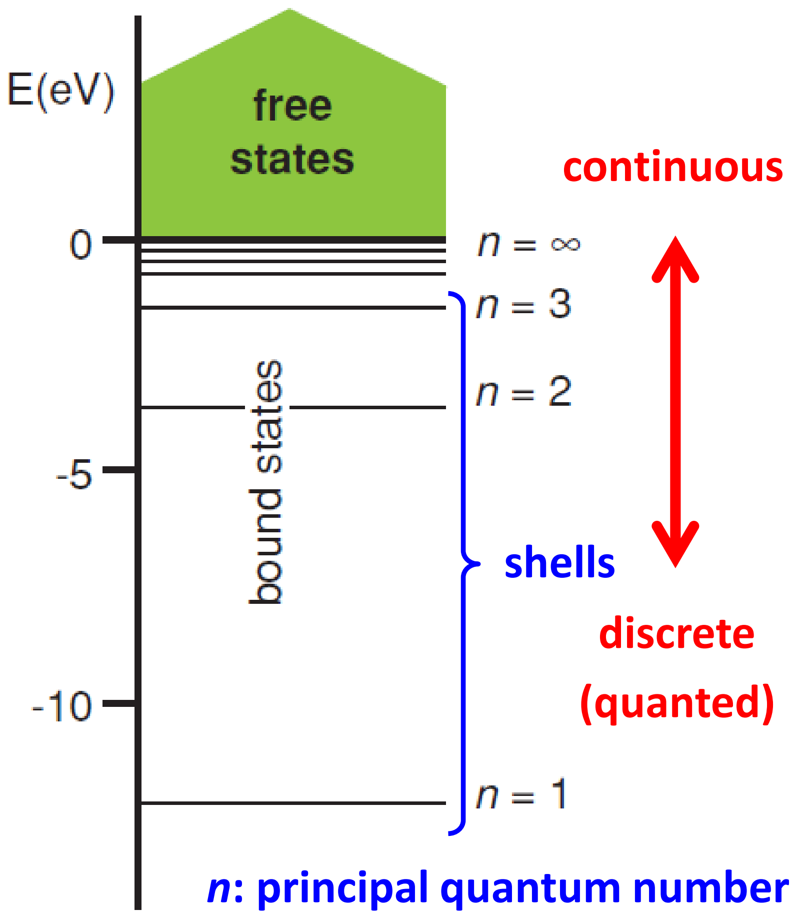
$$E_{total} = E_{pot} + E_{kin}$$



E_{total} < 0: bound electron

E_{total} > 0: free electron

The energy states of the electron

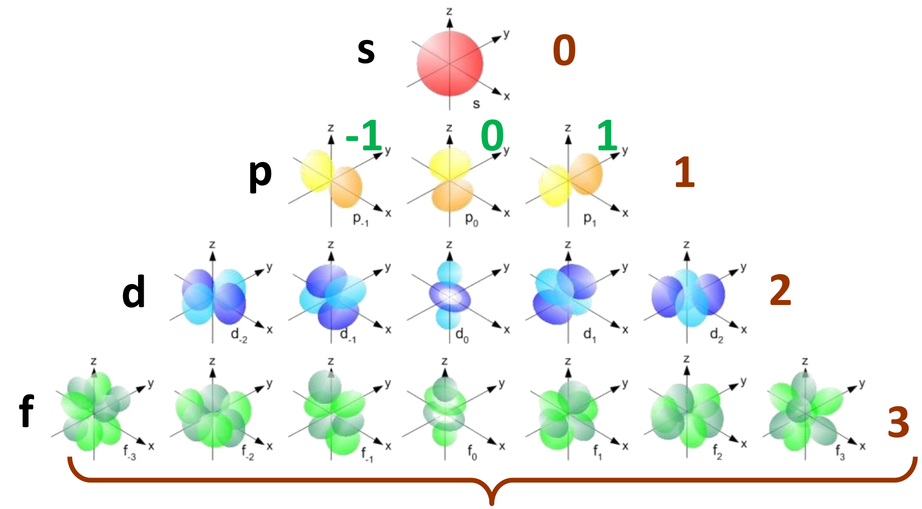


***n*: principal quantum number**

an electron's possible energy levels in the hydrogen atom

***l*: azimuthal quantum number**

***m*: magnetic quantum number**



s: sharp;
p: principal;
d: diffuse;
f: fundamental.

see „Light emission" lab practical

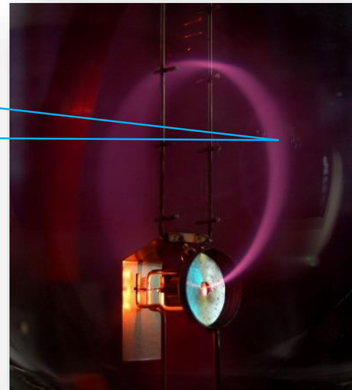
- **Principle of minimum energy**
- **Pauli exclusion principle**

Particle-wave duality of the electron

cf. particle-wave duality of the photon

e^- beam is bent due to the presence of magnetic field

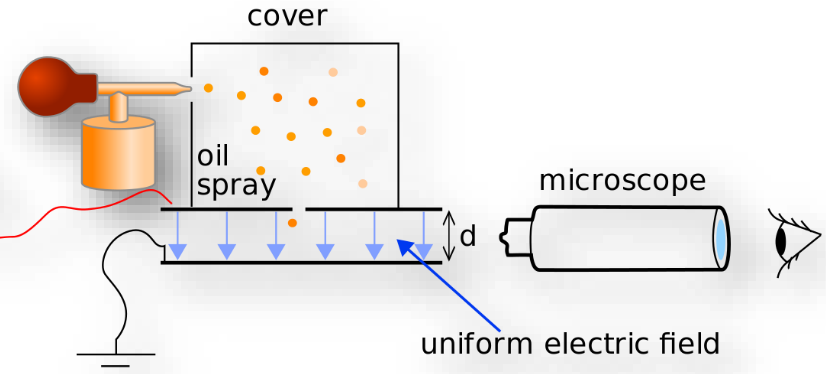
particle



mass

(Thomson, 1897; mass-to-charge ratio)

$m_e = 9.1 \cdot 10^{-31}$ kg

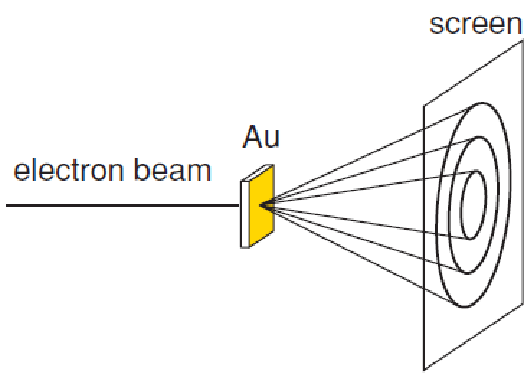


charge

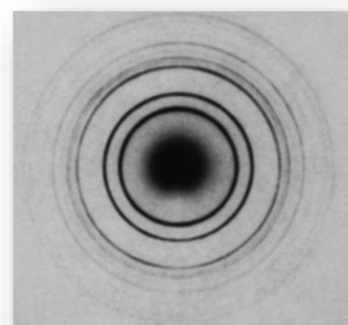
(Millikan, 1910)

$e = -1.6 \cdot 10^{-19}$ C

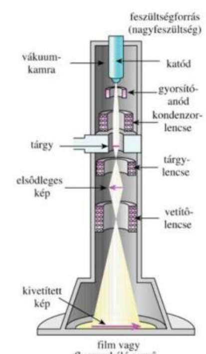
wave



Davisson and Germer, 1927



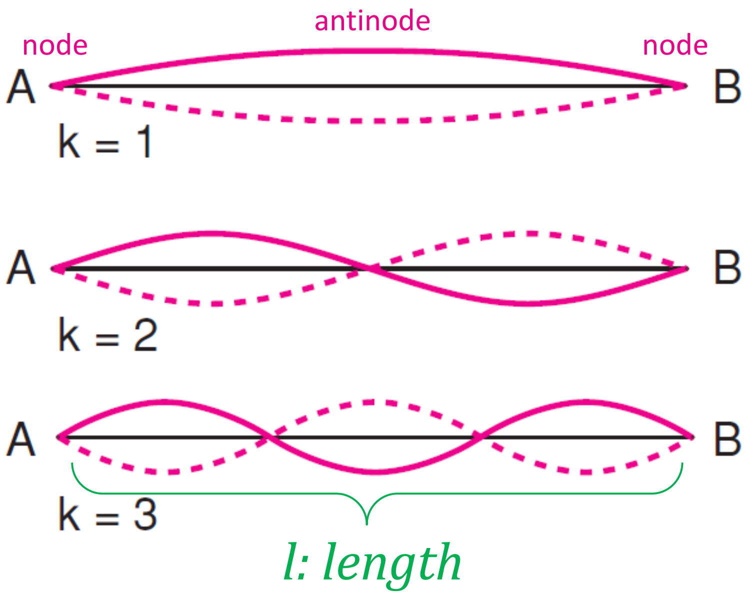
diffraction of fast electrons through a gold foil



electron microscope

The electron as a wave

Analogy: stationary waves of a stretched string



$$l = k\,\frac{\lambda_k}{2} \qquad k = 1,2,\ldots$$

only discrete values are allowed!

λ: wavelength of the matter wave

$$\lambda = \frac{h}{p} = \frac{h}{m_{e^-} \cdot v}$$

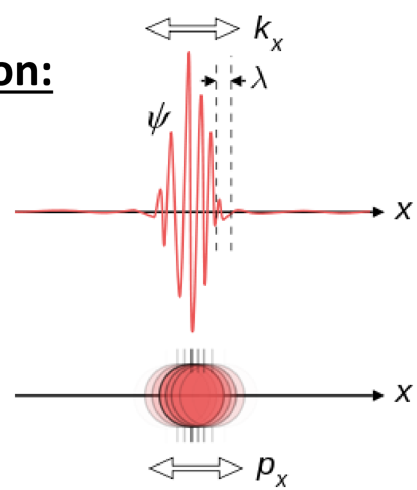
De Broglie, 1923

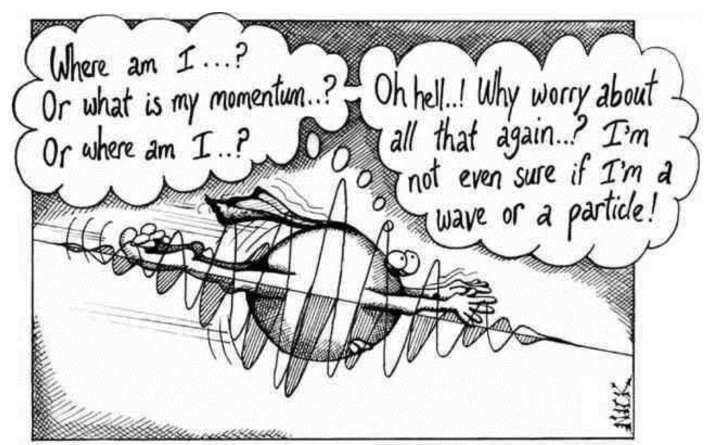
The state function of the electron:

ψ(x,t)

(Schrödinger)

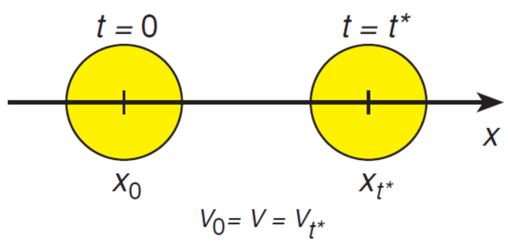
- **location (x): where ψ(x,t)=1**
- **momentum (p): ”shape” of ψ(x,t)**



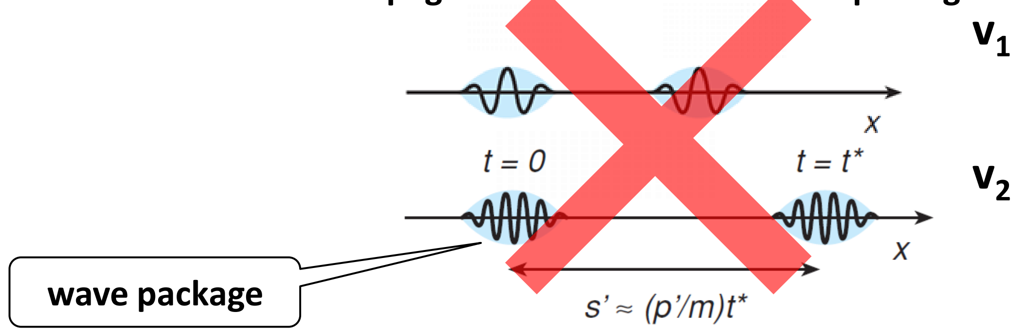


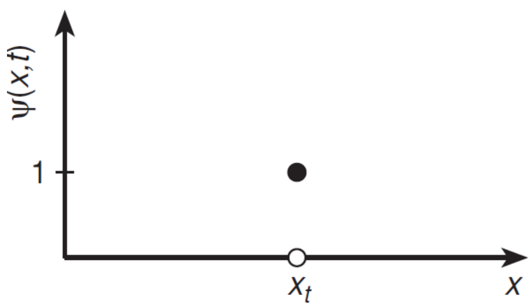
The propagation law of free electrons

Classical mechanics: state of motion

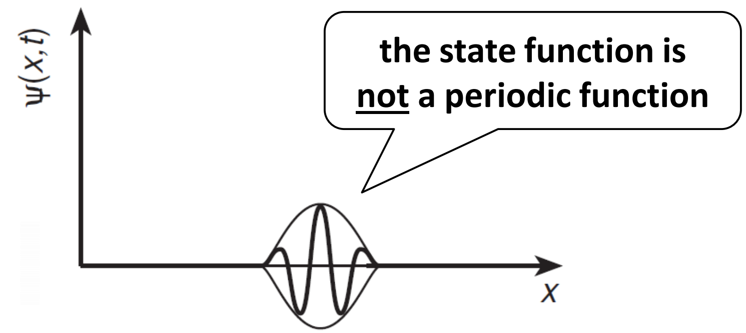


Propagation of electrons as wave package

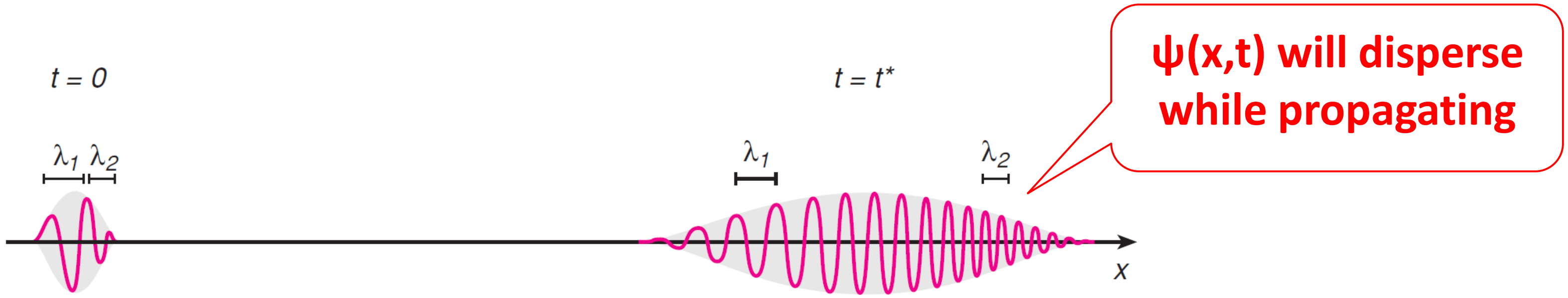




position of a classical object can be determined exactly

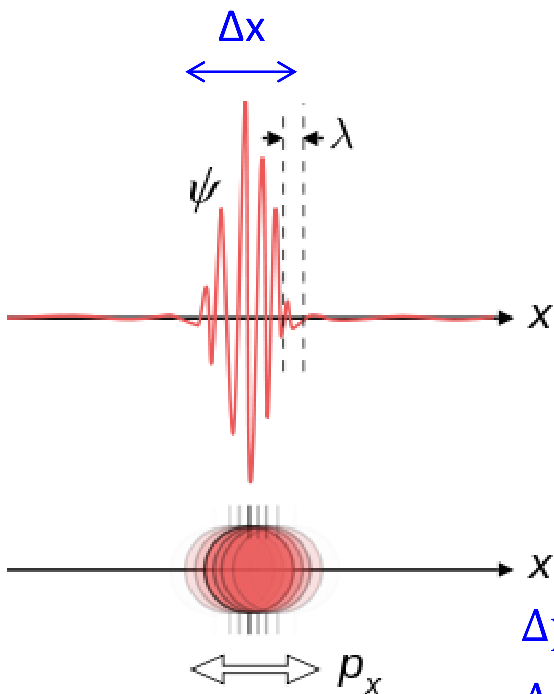


the state function of the electron



The electron bound in an atom

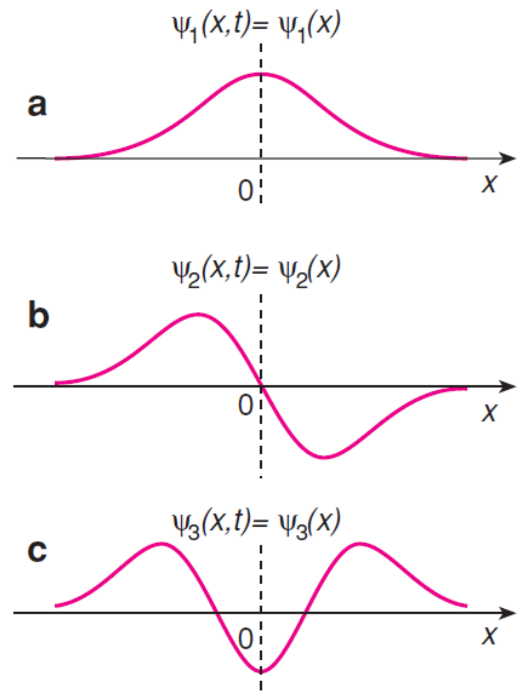
in the electric field of the atomic nucleus (or proton)



deformed state function

$\Delta p \sim \Delta(1/\lambda)$

$\Delta(1/\lambda) \geq 1/\Delta x$



"one-dimensional H-atom"

The Heisenberg uncertainty relation

the uncertainty of the momentum (Δp) in the case of a free electron:

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

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

Δt: uncertain, so E can be certain:

discrete energy levels

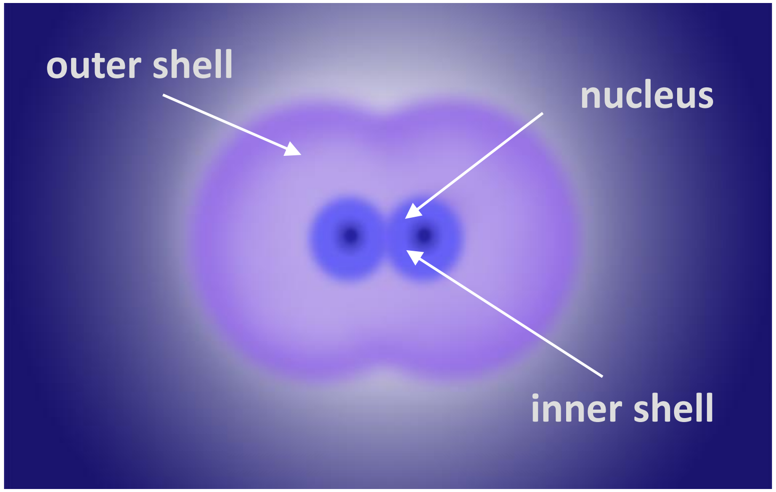
Atomic interactions

<u>short range</u>

interaction:

repulsion between nuclei

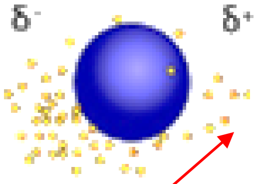
(electron cloud overlap)

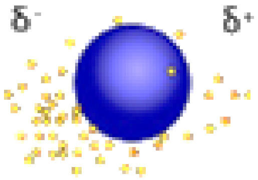


<u>long range</u>

interaction:

coulombic attraction

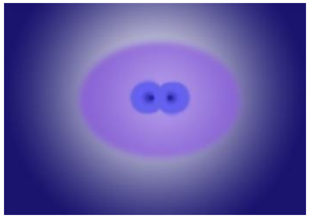


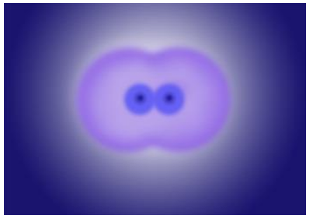


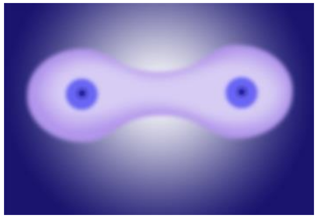
repulsion
(inner shells and nuclei)

equilibrium
attraction = repulsion

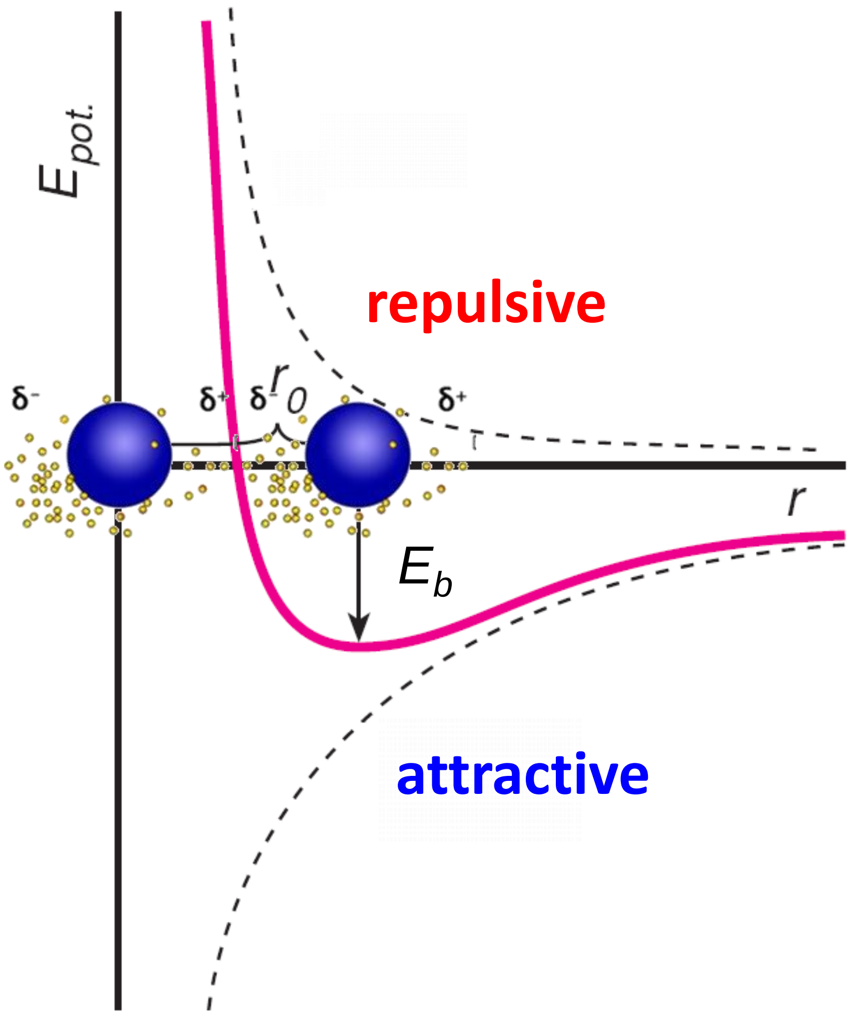
attraction
(outer shells)







Atomic interactions



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

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

A, B: interaction-specific constants

(atom-dependent)

n (attraction) < m (repulsion)

r_0: binding distance

E_b: binding energy

Primary bonds

intramolecular ⟷ **intermolecular**
strong ⟷ **weak**
primary ⟷ **secondary**

„tendency of an atom to attract electrons”

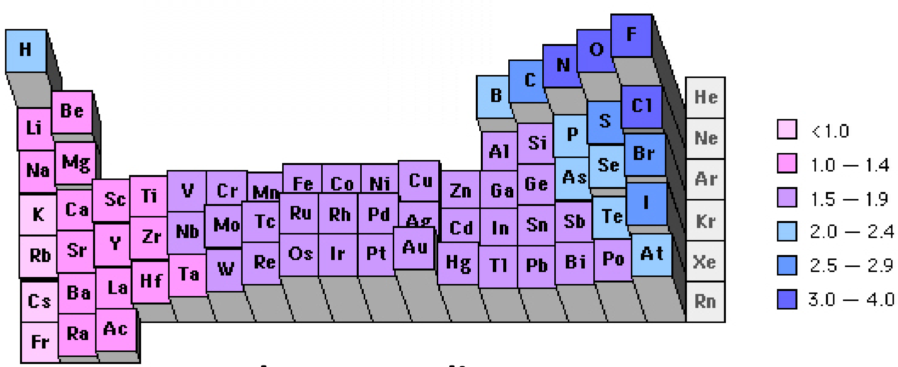
- **covalent:** common electron state around the participating nuclei, strong: $E_b > 1eV$
- **metallic bond:** multi-atomic system, $E_b > 1eV$
- **ionic bond:** Coulomb-forces between ions, $E_b > 1eV$

type depends from electronegativity (EN)

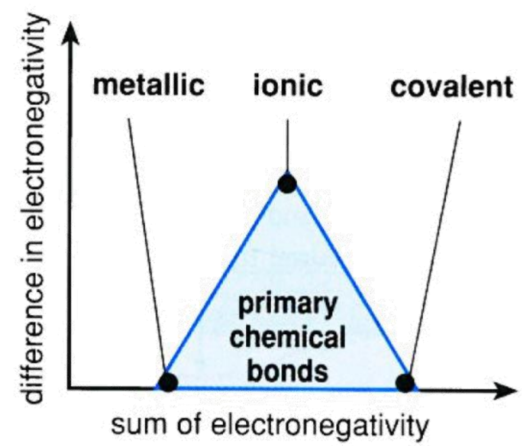
$$EN = |E_i| + |E_{ea}|$$

ionization energy (E_i)

electron-affinity (E_{ea})

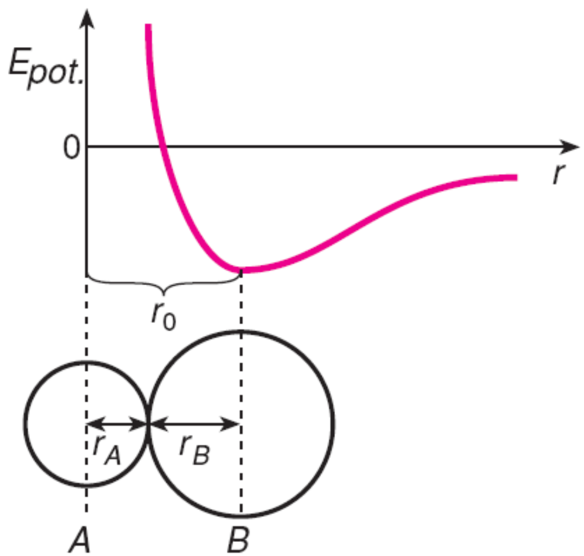


EN values according to Pauling

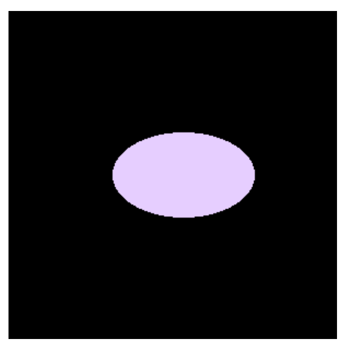


Secondary bonds 1

- **<u>Van der Waals:</u>** between two apolar atoms (without permanent dipole moment) where a temporarily created dipole interacts with an apolar molecule or atom thus converting it into a dipole **(induced dipole)**
  - **Van der Waals radius: $r_0=r_A+r_B$**
  - **Intermolecular or intramolecular**
  - **Important biological role: formation of organic structures**
  - **Weak: (E_b ~ 0,02 eV)**

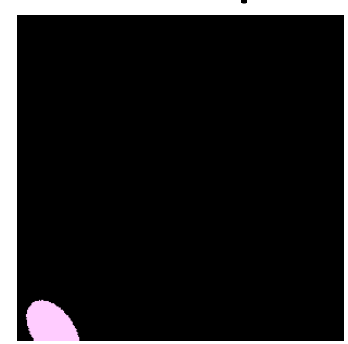


fluctuation



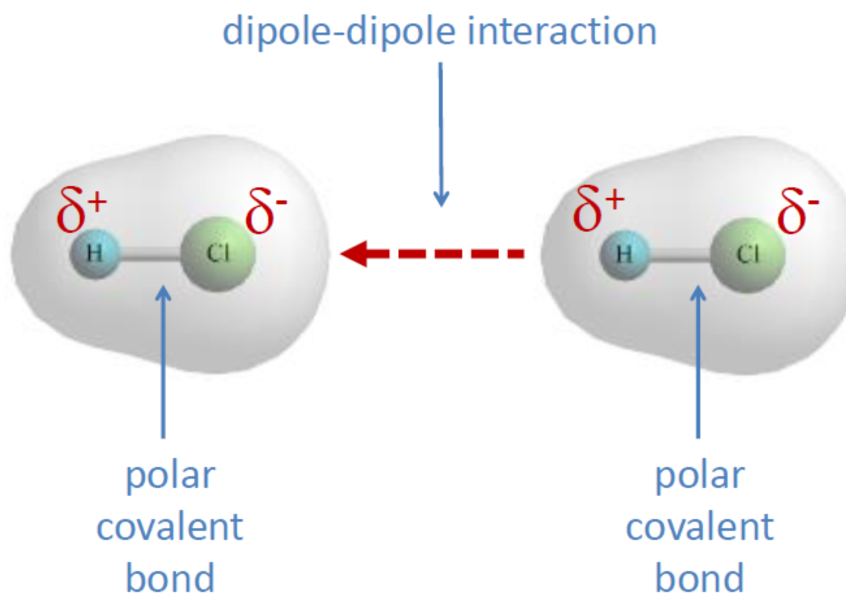
ion-dipole

induced dipole



Secondary bonds 2

- **Dipole-dipole interaction:**
  - constant charge distribution is present in a (given part of a) molecule
  - partially (+) and (-) segments are held together by electrostatic interactions (Coulomb-forces)
  - intra-/intermolecular
  - weak interaction (E_b = 0.003-0.02 eV)



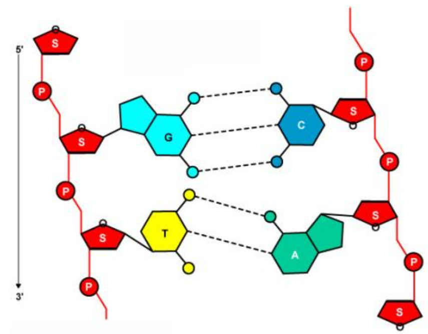
$$E_{attraction} = p * E$$

p: dipole momentum (p=Q*d)

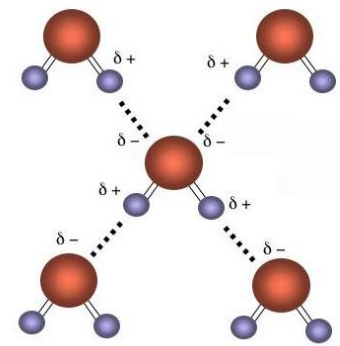
E: electric field strength generated by the surrounding partners

Secondary bonds 3

- **H-bond**: the H-atom interbridges two other atoms (F, O, N) of high electronegativity
  - **r ~ 0.23 - 0.35 nm**
  - **E ~ 0.2 eV**

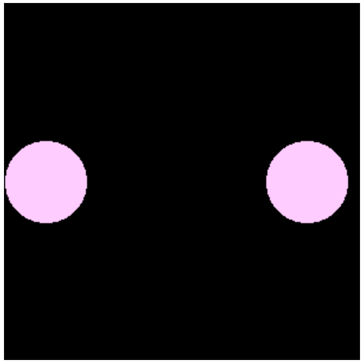


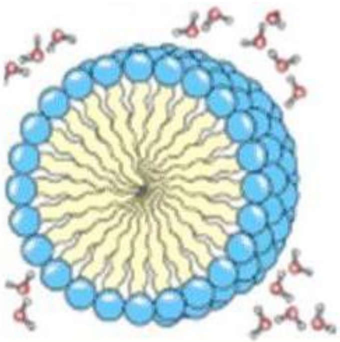
DNA



water

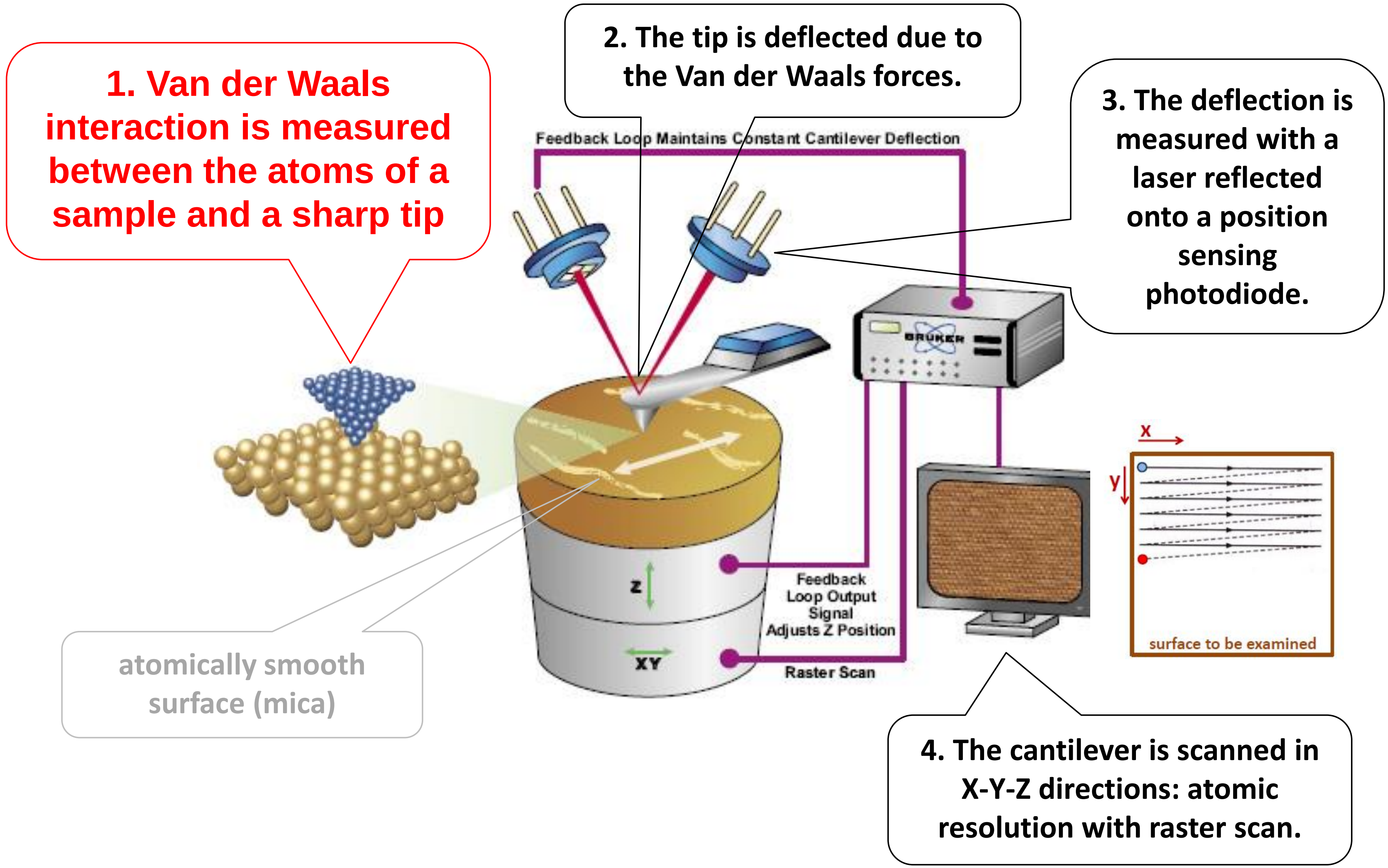
- **Hydrophobic interaction:** weak Van der Waals interaction (E_b = 0.003 - 0.02 eV), thermal motion (*kT* ~ 0.025 eV) could disrupt the system
  - ordered water molecules exclude the apolar structures (contact surface can be minimized)



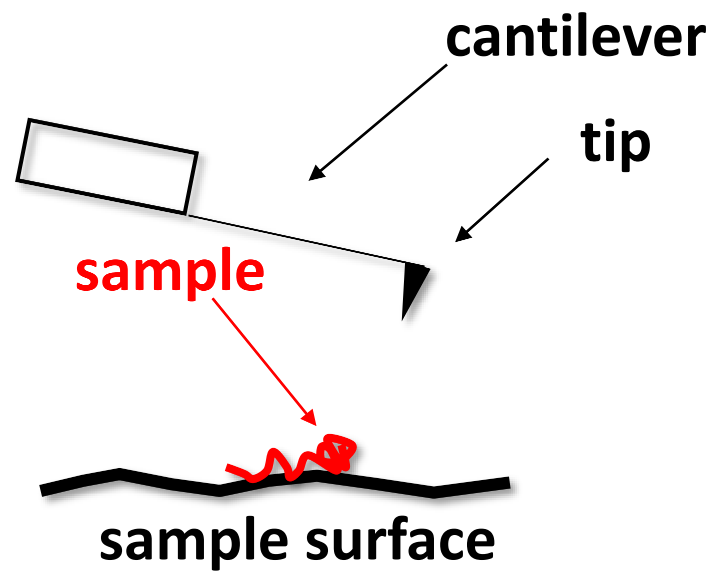


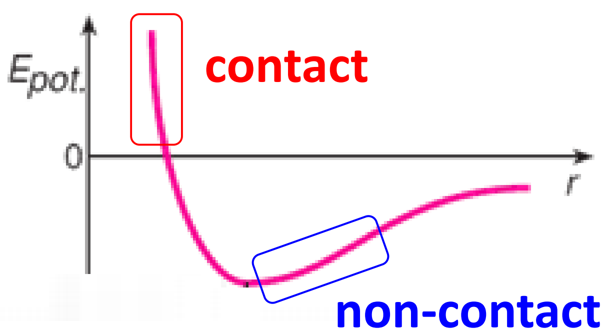
lipids in water

Atomic force microscope (AFM)



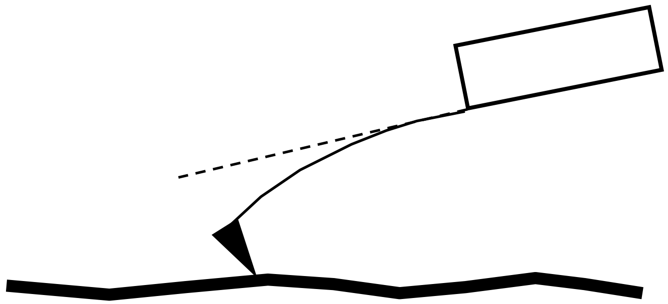
AFM operating modes

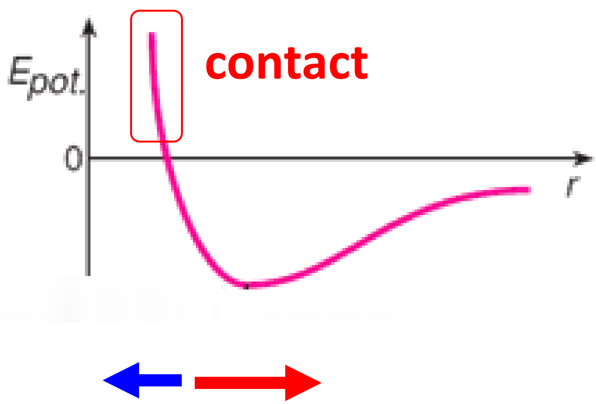


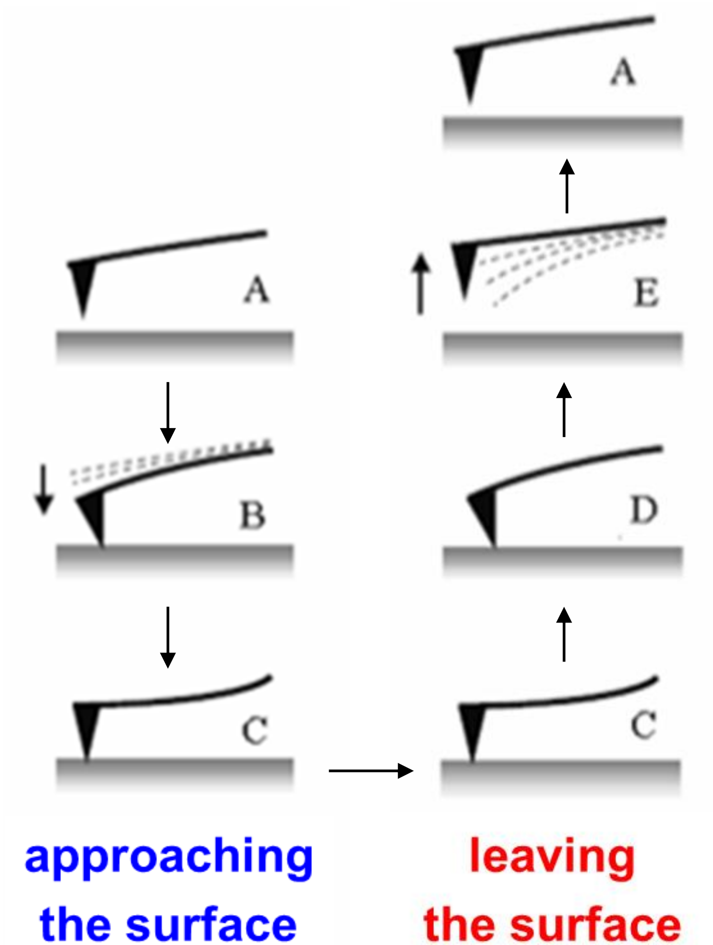


- **Contact:** the tip touches the surface, the **deflection of the cantilever** (i.e. the force exerted on the sample by the tip) is held **constant**.
  - **Z-feedback** system: deflection is maintained at a constant value (setpoint) by lifting or lowering the cantilever.
  - **topography data** (i.e.: height) in each x;y point is calculated from these Z movements
- **Non-contact:** the **cantilever is oscillated without contact** with the surface: resonant frequency (f_0) and the amplitude of the oscillation changes with surface topography.
  - **Z-feedback:** maintains the amplitude by lifting or lowering the oscillating cantilever.

Contact mode AFM

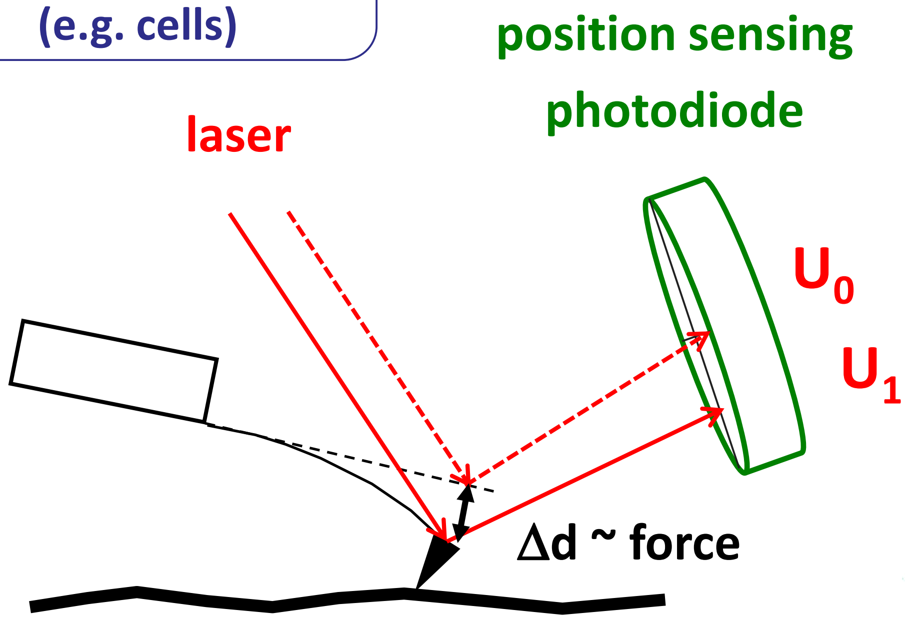






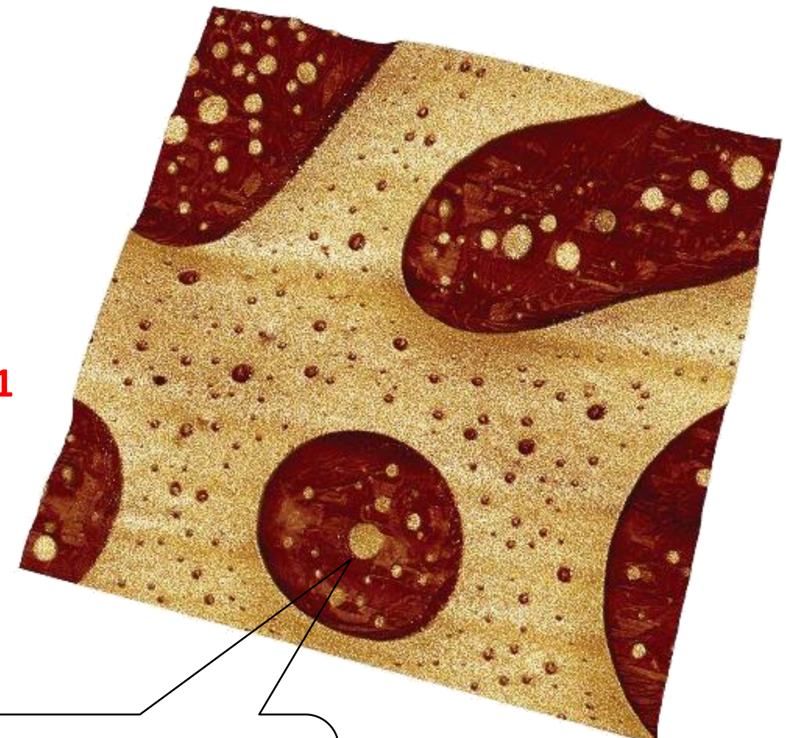
Contact mode AFM

suitable for soft biological samples (e.g. cells)



$F = D \cdot \Delta d$

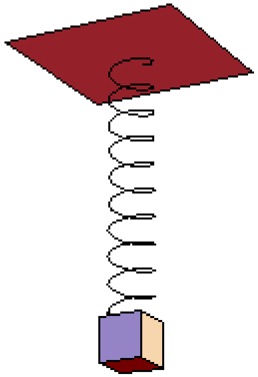
Δd: deflection
D: spring constant



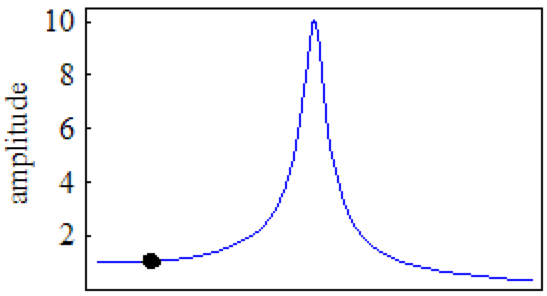
force / elasticity measurement on biological samples

Resonance

Resonance: a driven oscillation occurring when the oscillatory system is exposed to a driving force with a frequency close to its eigenfrequency (f_0). Amplitudes may become extremely large.

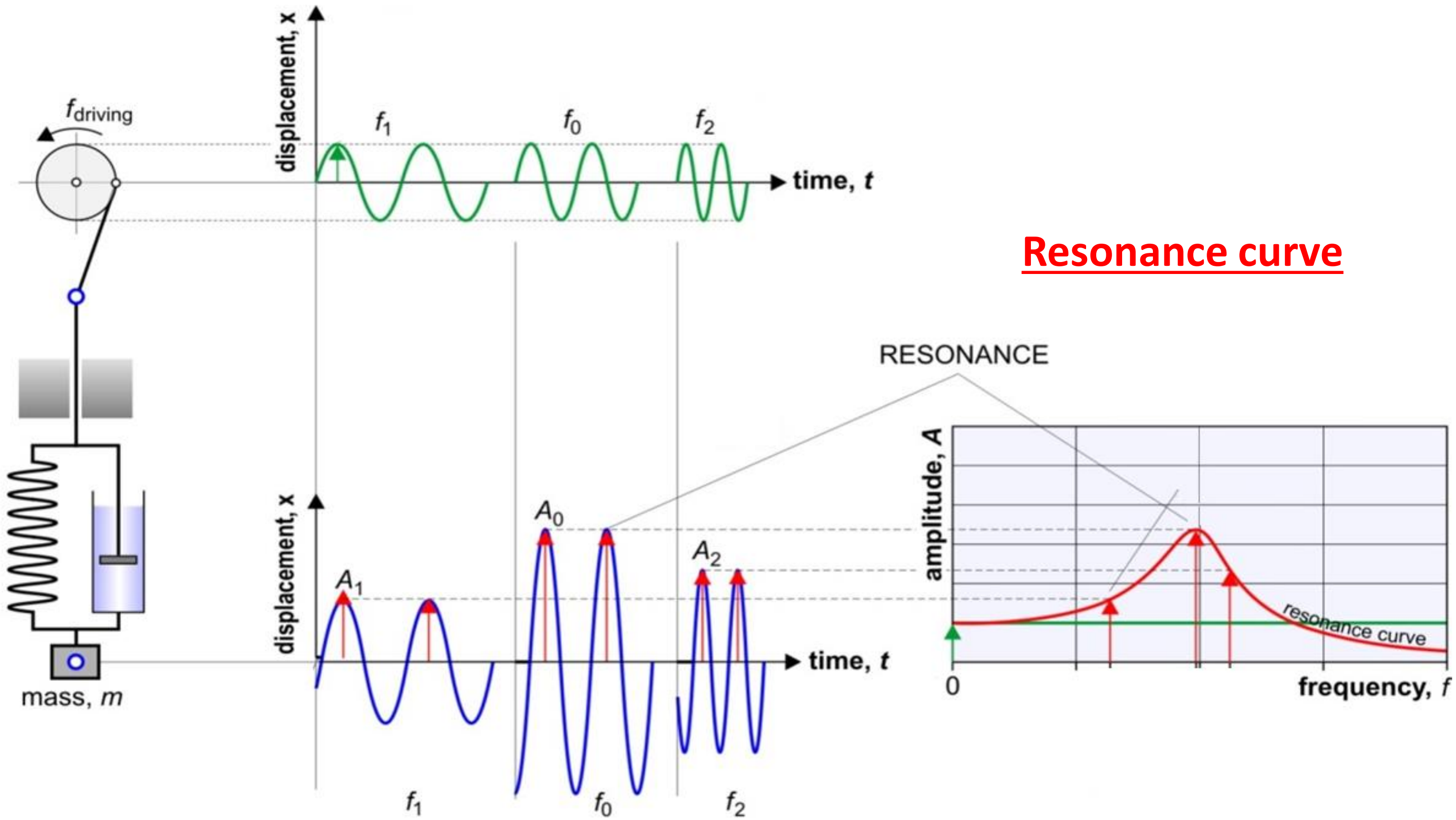


Driven oscillation

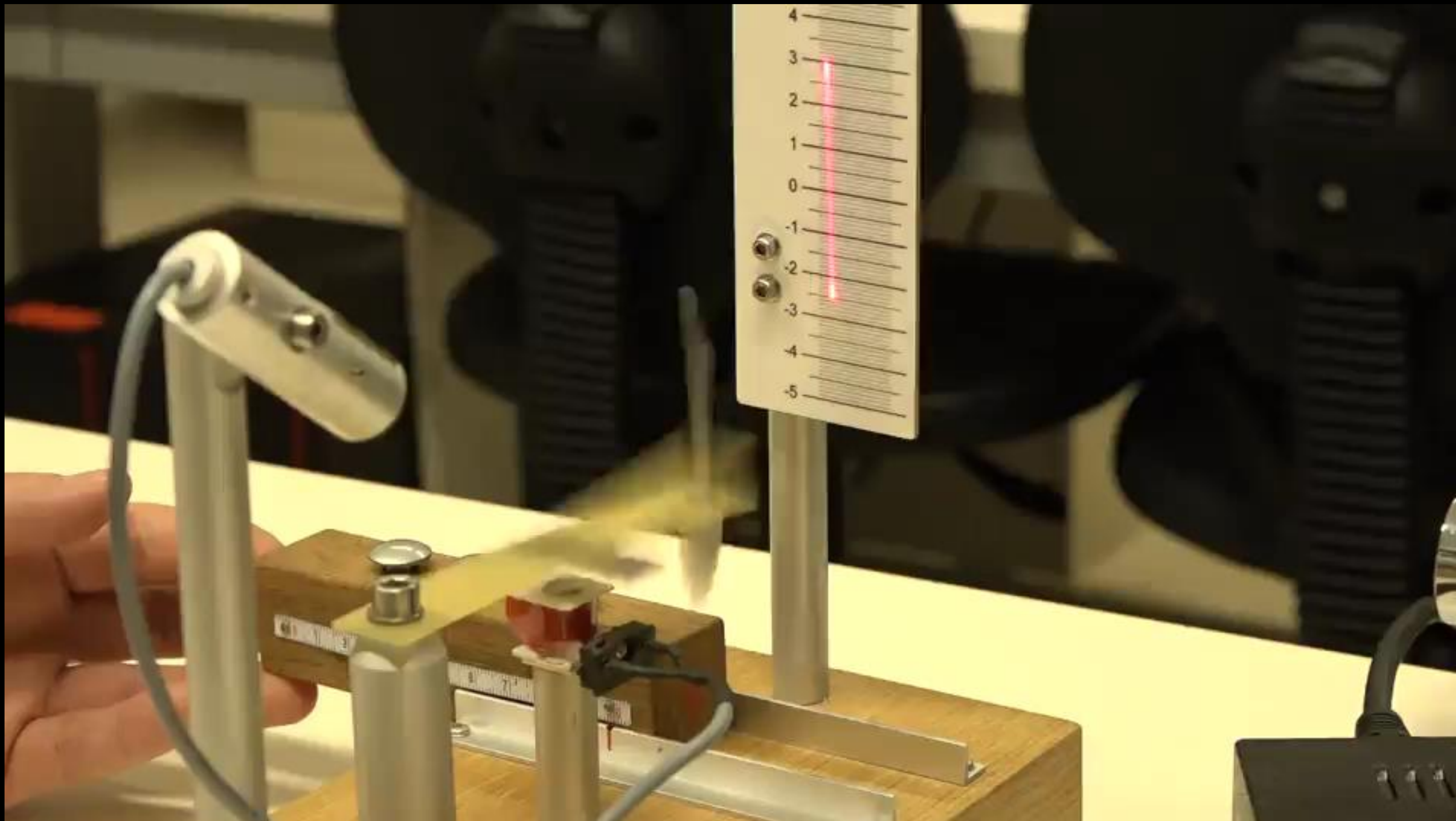


Non-contact/oscillating mode AFM

Resonance: a driven oscillation occurring when the oscillatory system is exposed to a driving force with a frequency close to its eigenfrequency (f_0). Amplitudes may become extremely large.

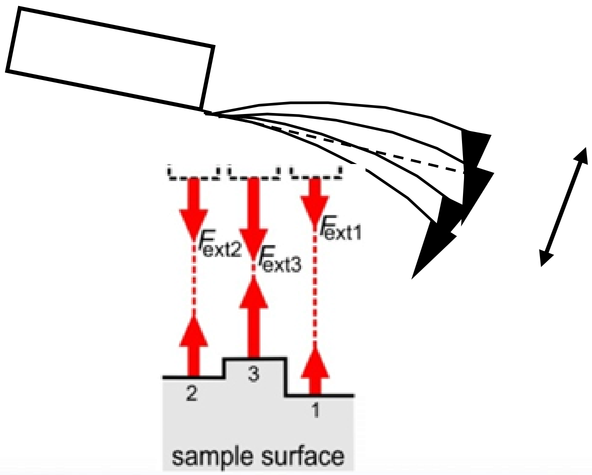


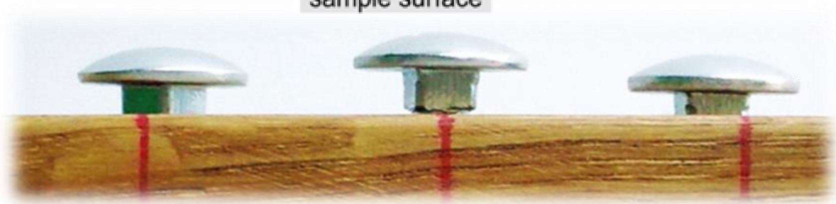
Non-contact/oscillating mode AFM model

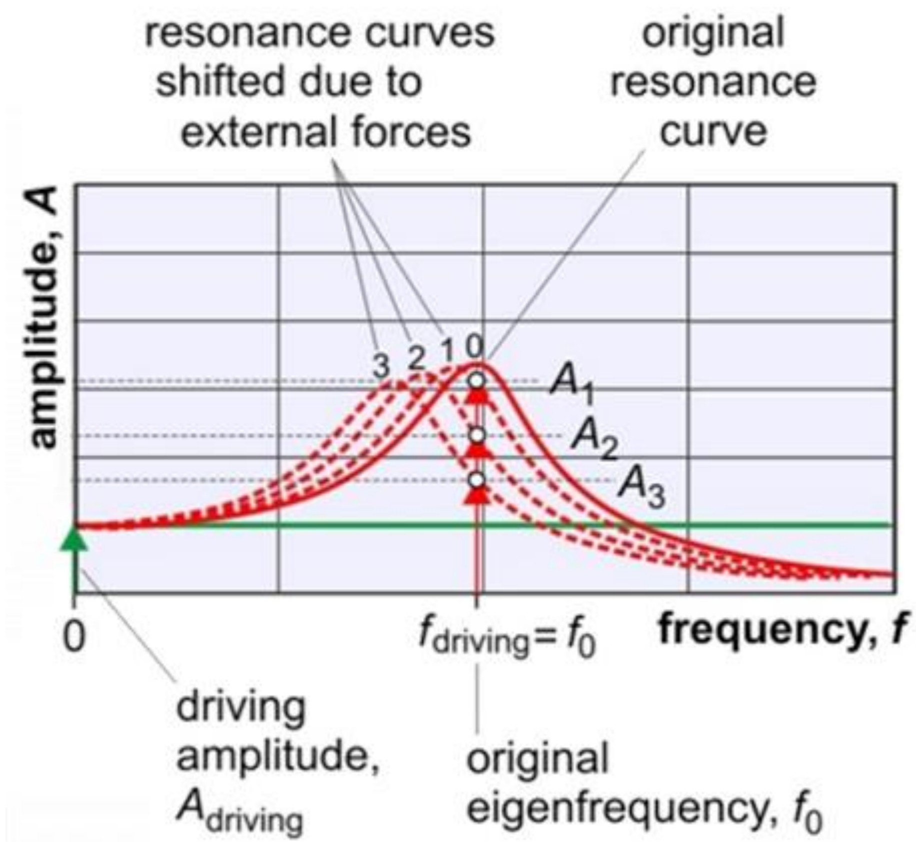


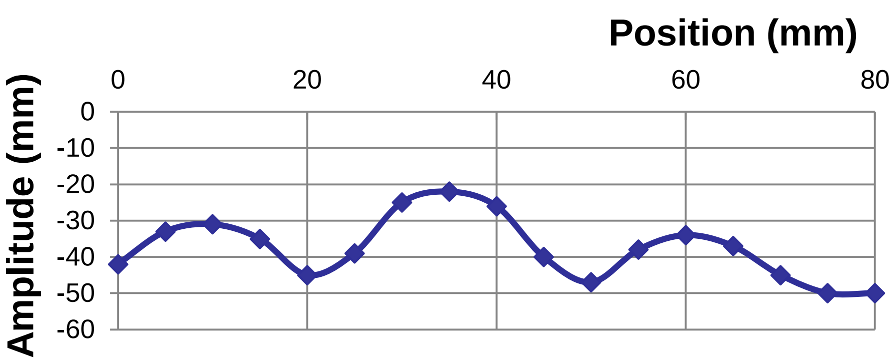
N.B.: magnetic interaction models the Van der Waals forces

Non-contact/oscillating mode AFM





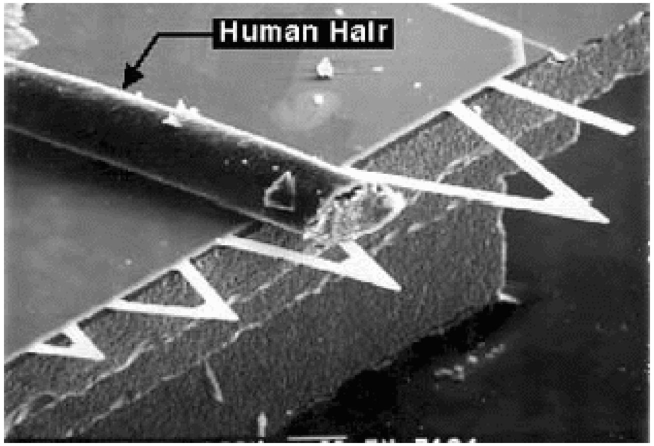


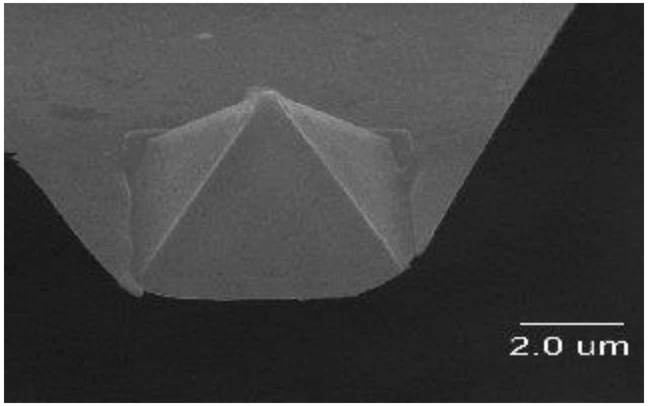


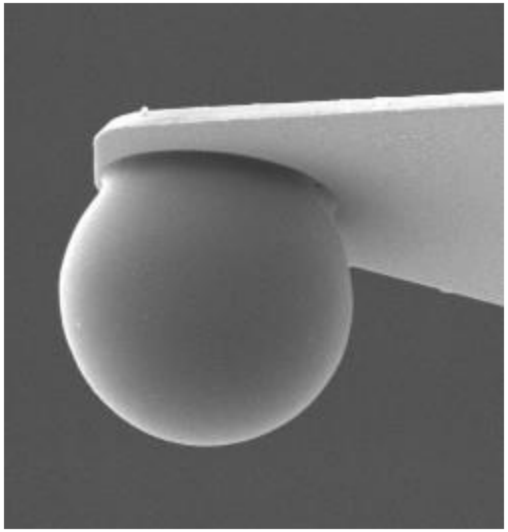
$$f_0 = \frac{1}{2\pi}\sqrt{\frac{D}{m}}$$

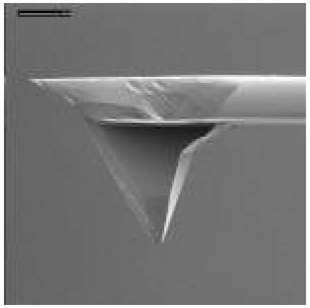
Cantilevers

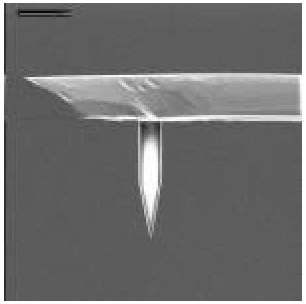
- Material: mainly silicon nitride
- Tip radius: 0.1 nm - 100 µm
- Spring constant ~ 0.1 - 10 N/m
- f_o ~ 50-500 kHz



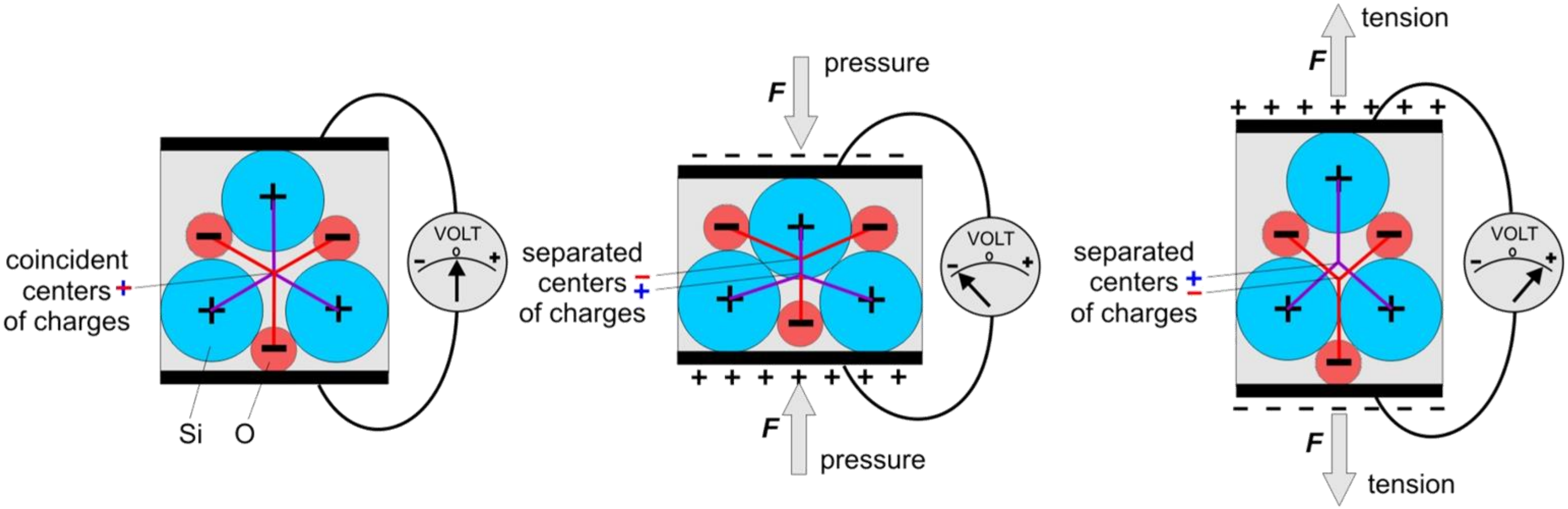








Principle of X-Y-Z raster scanning: piezoelectricity



- **direct piezoelectric effect: deformation → voltage**
- **inverse piezoelectric effect: voltage → deformation**
- **X, Y, Z axis piezo: e.g. 150 V → 40 µm**

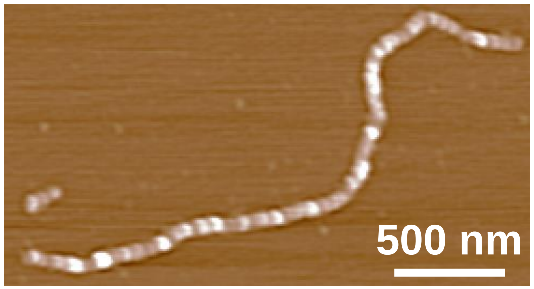
0.1-nm-accuracy possible

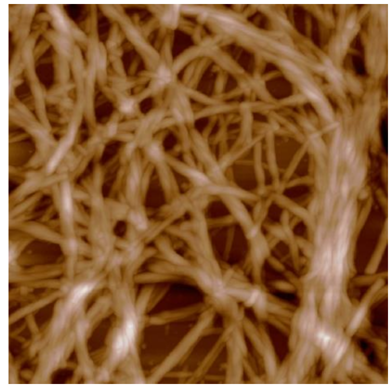
AFM - properties

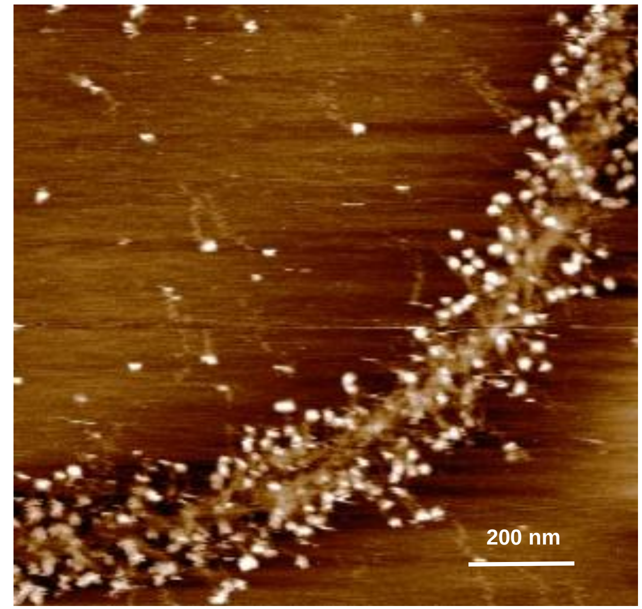
- **Main advantages:**
  - 3D surface profile.
  - Images are collected with ~10 pm vertical and somewhat worse horizontal resolution.
  - Any surfaces (conductors, insulators and semiconductors) can be imaged.
  - Works in ambient air, special gas or in fluid environment as well.
  - Usually does not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

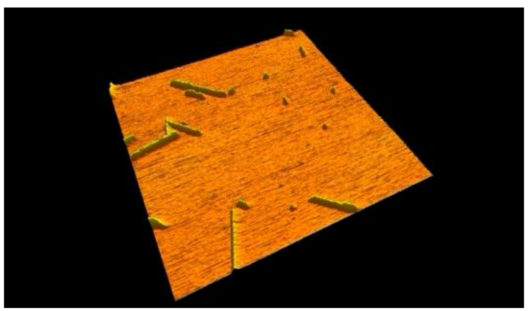
- **Main disadvantages:**
  - Samples must adhere to a substrate. Surface adhesion may lead to distortion.
  - Slow scan speed.
  - Scan height limited to few microns („the flatter the better”).
  - Scan size limited to few tens of microns.
  - High cost.

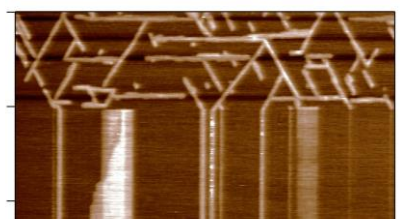
Images recorded in our lab at the Department

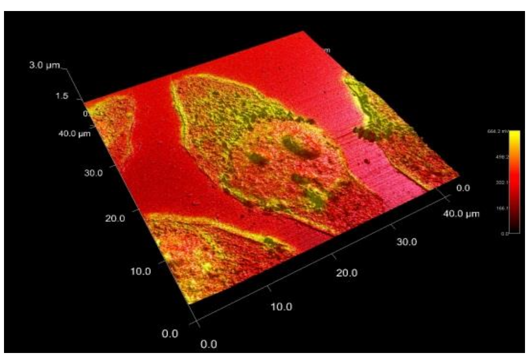


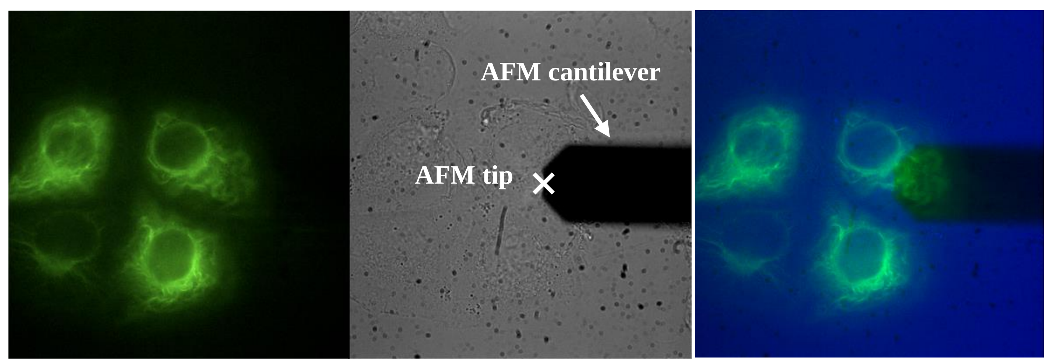










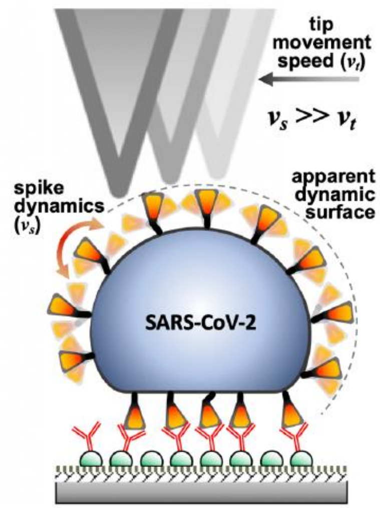


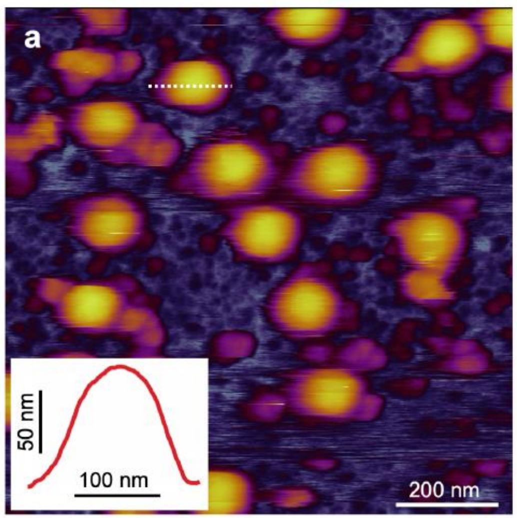
Native SARS-CoV-2 imaged in our lab

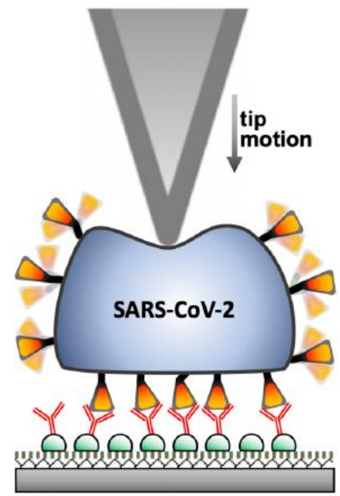
Topography, spike dynamics and nanomechanics of individual native SARS-CoV-2 virions

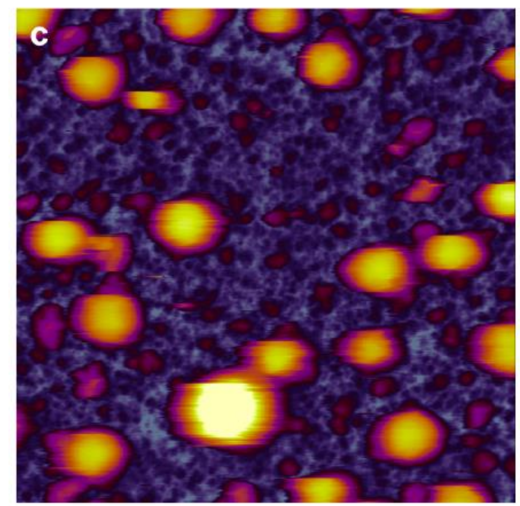
Bálint Kiss[1#], Zoltán Kis[2,3#], Bernadett Pályi[2], Miklós S.Z. Kellermayer[1*]

bioRxiv preprint doi: https://doi.org/10.1101/2020.09.17.302380

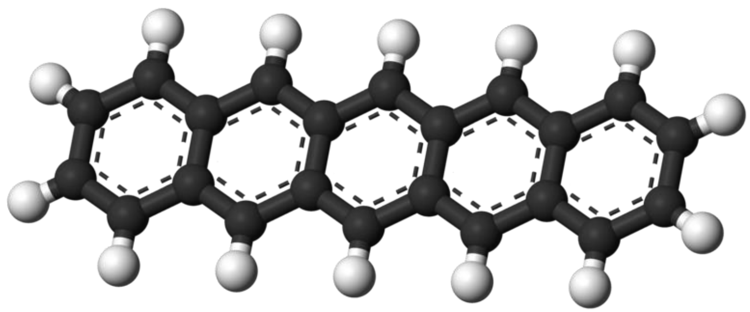




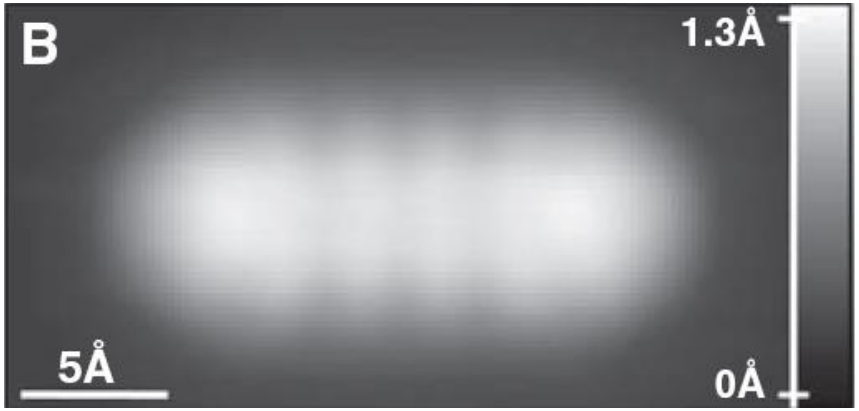




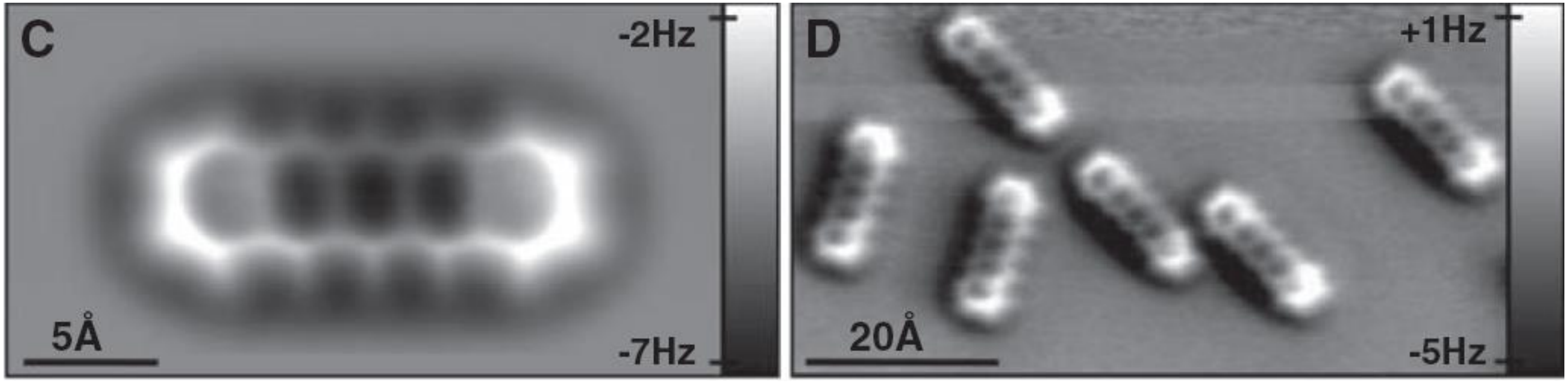
Pentacene molecule



electron current through the tip (STM)

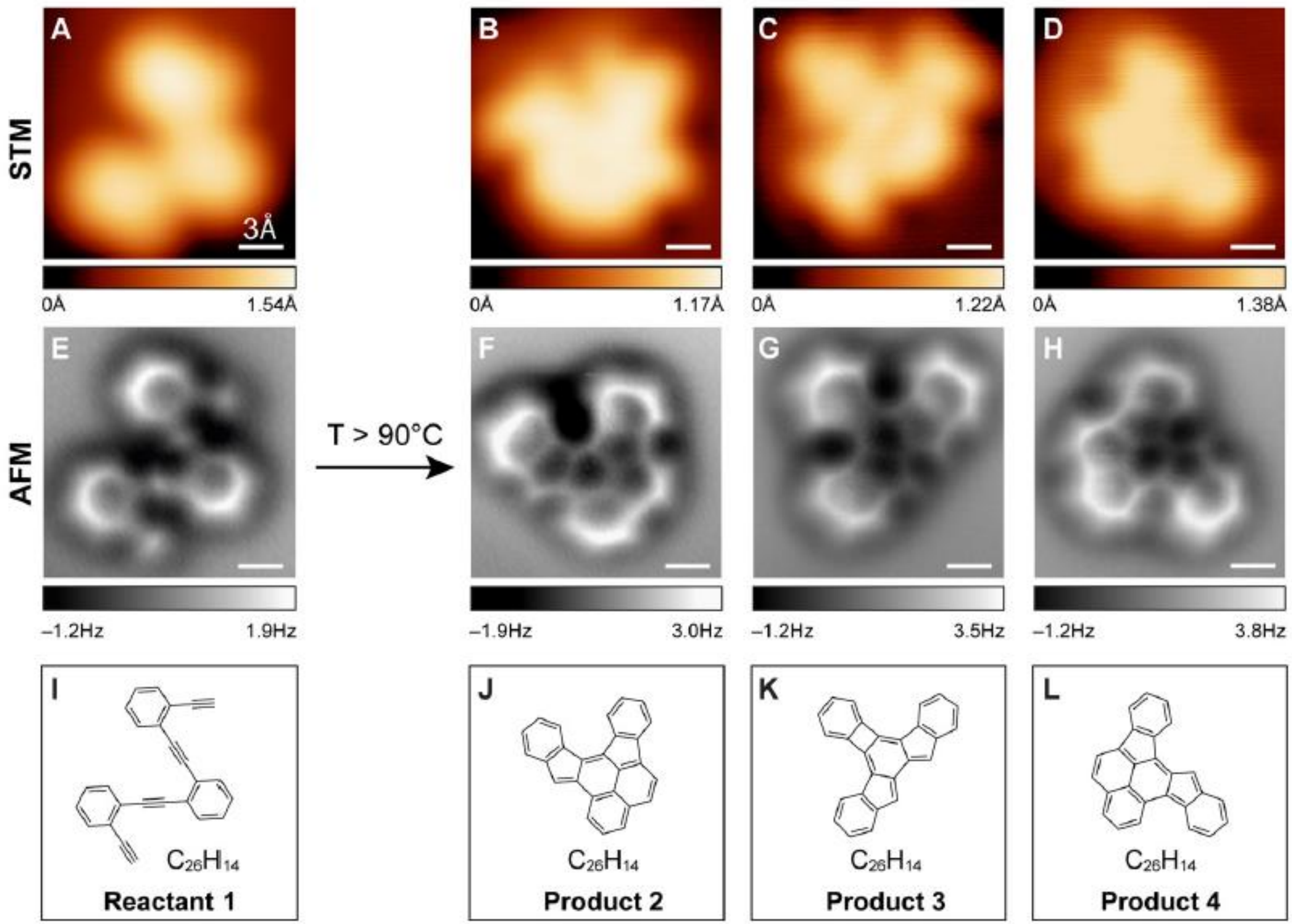


AFM images (tip covered with CO)



Nature Chemistry 1, 597 - 598 (2009)

Visualizing chemical reactions



Thank

you

for your attention!