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

Balázs Kiss

kissb3@gmail.com

Myofilament Mechanobiophysics Research Group,

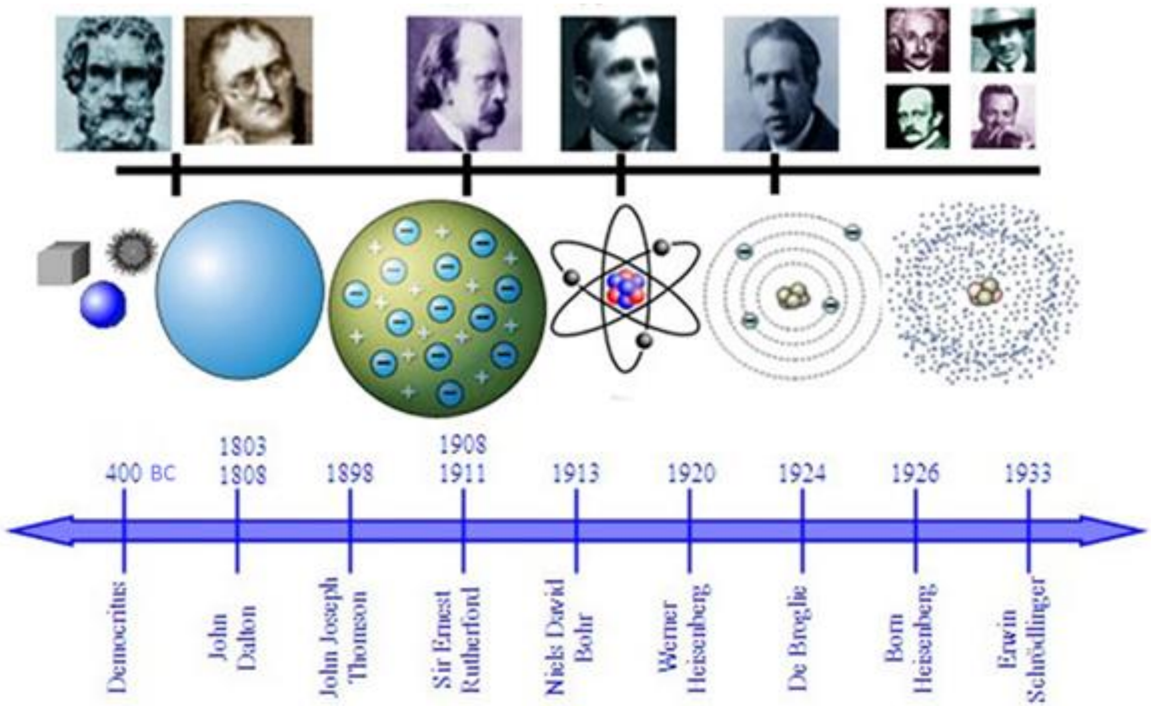
Department of Biophysics and Radiation Biology,

Semmelweis University

05. October 2022.

Textbook: pages 23-37

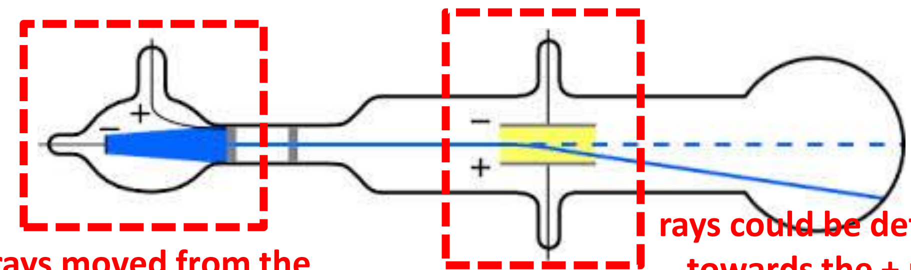
Atomic models - History



- **Democritus (~400 BC):** proposition of atomic structure (ἄτομος, átomos: 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

<u>Thomson:</u> discovery of cathode rays

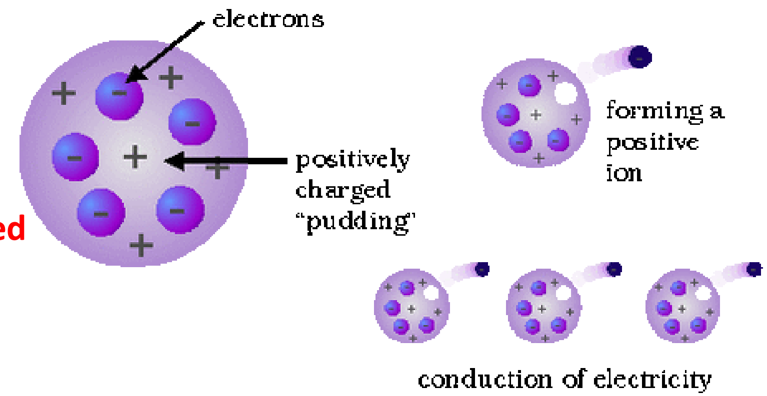


rays moved from the negative electrode to the positive electrode

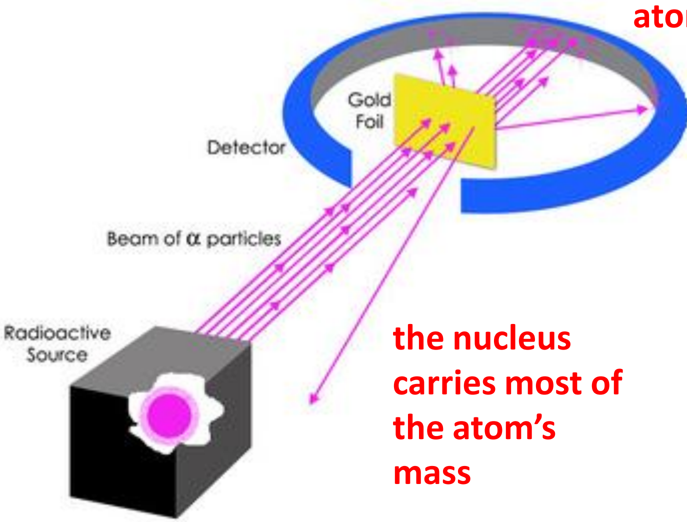
gas discharge tube

rays could be deflected towards the + plate

„plum pudding atom" or „blueberry muffin atom"



<u>Rutherford:</u> experiments with α-particles

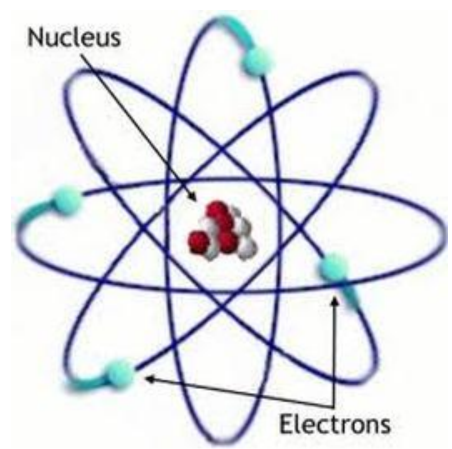


atoms are mostly empty space

atoms are made of a small positive nucleus

the nucleus carries most of the atom's mass

„planetary model"

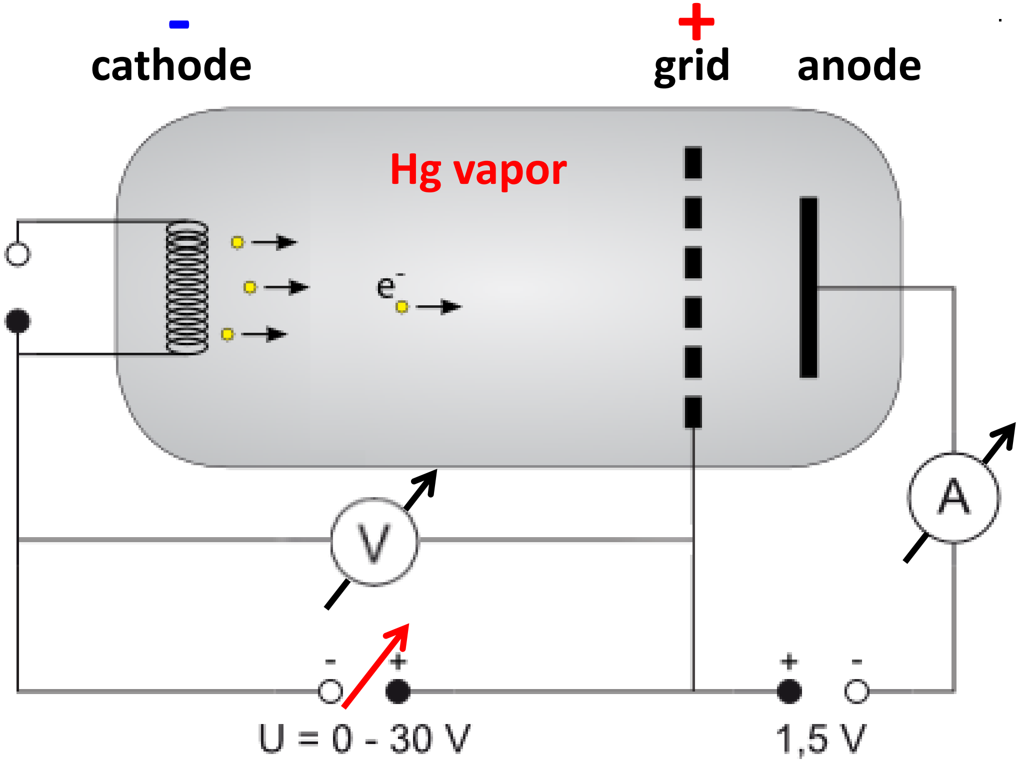


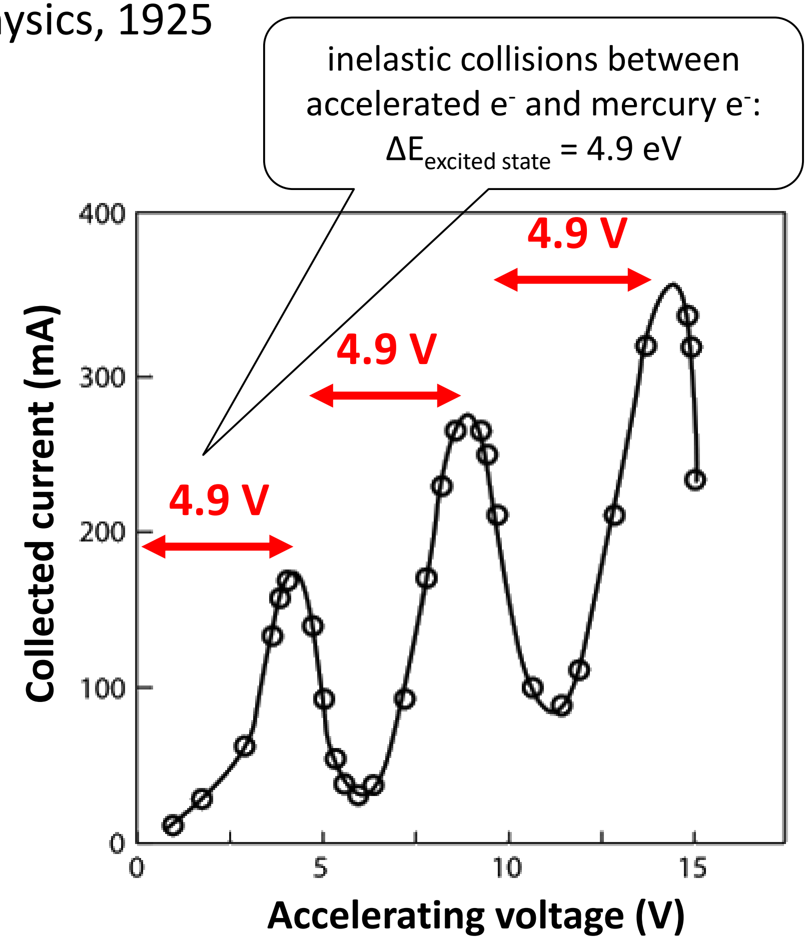
Franck-Hertz Experiment

James Franck

Gustav Hertz

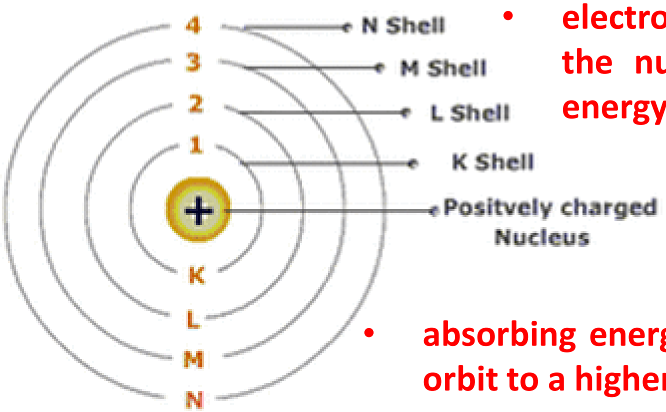
- in 1914: **electrons of excited mercury atoms occupy only discrete, quantized energy states**
- Nobel Prize in physics, 1925





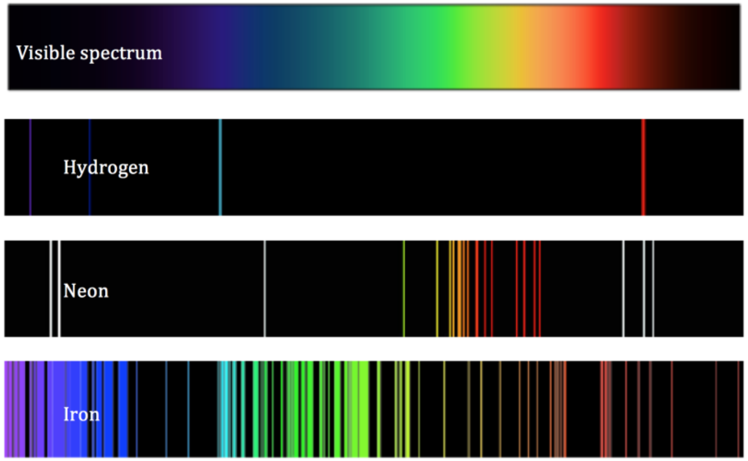
Bohr and Schrödinger

<u>Bohr:</u> describing the electron shells



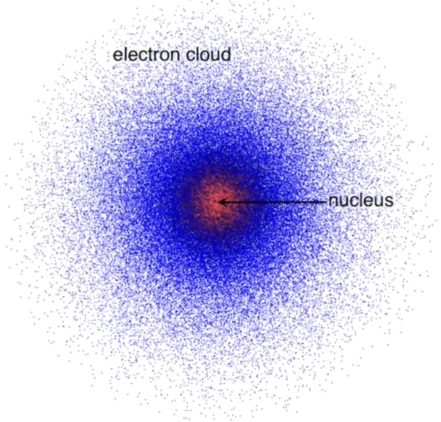
- electrons furthest from the nucleus have higher energy
- absorbing energy: jump from a lower orbit to a higher
- losing energy: emission of photons

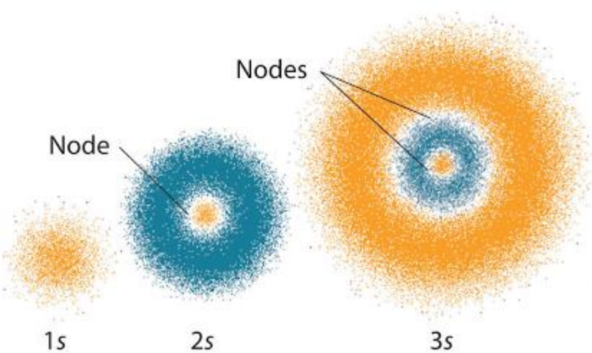
<u>Emission spectra of certain elements</u>



<u>Schrödinger:</u> quantum mechanical model of the electrons

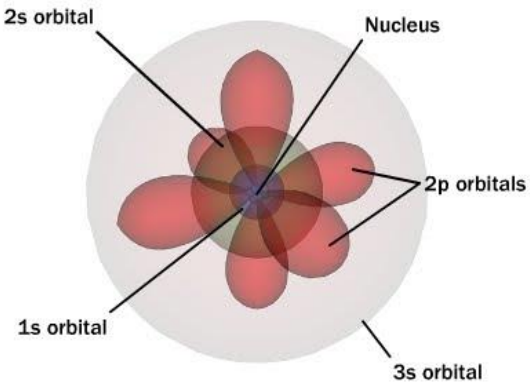
- no exact path, rather predicts the odds of the location of the electron





Complex shapes of orbitals:

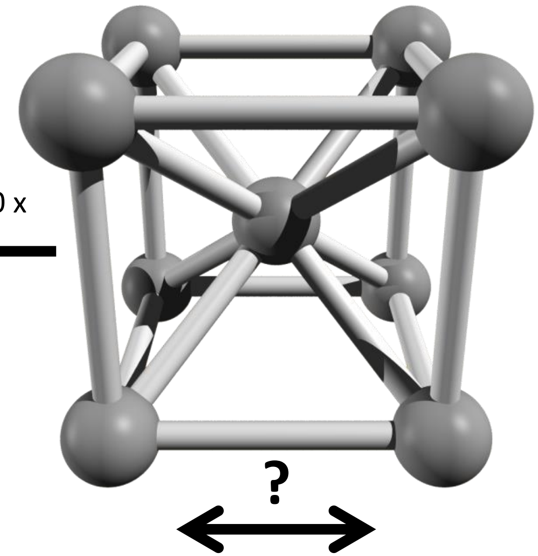
<u>electron clouds</u>



How are stable structures created/formed?

macroscopic scale: Atomium

165 000 000 000 x



nanoworld: face-centered cubic lattice of iron

Governing principle:

consecutive: DISORDER

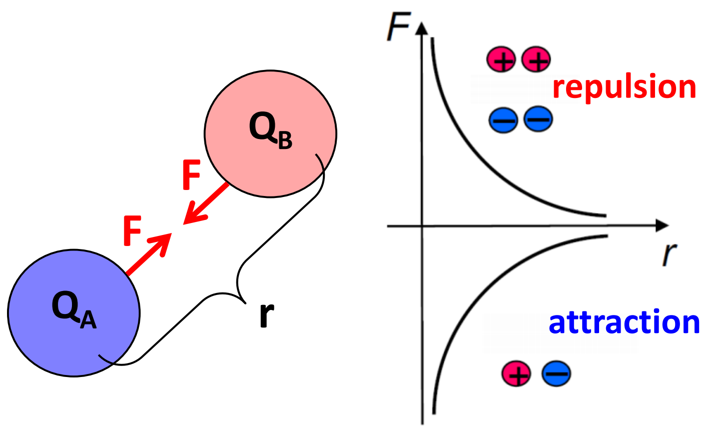
repulsive interaction ⟷ **attractive interaction**

consequence: ORDER

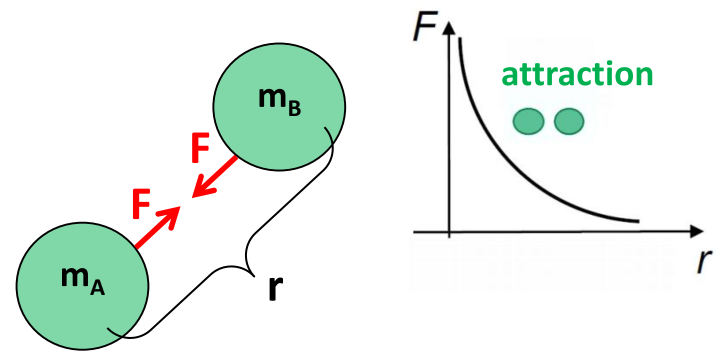
Fundamental interactions in physics

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**

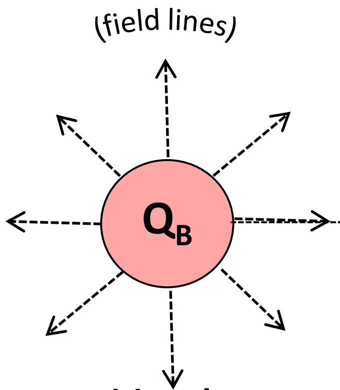


$$F_C = k \cdot \frac{Q_A \cdot Q_B}{r^2}$$

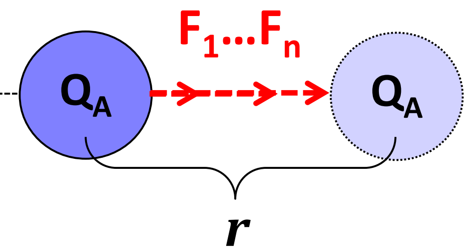


$$F_g = G \cdot \frac{m_A \cdot m_B}{r^2}$$

Electric potential energy (E_{pot})



positive charge (fixed)

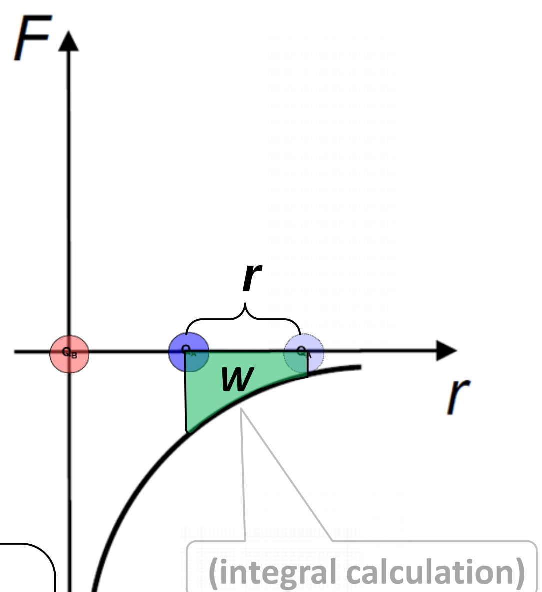


$$W = F \cdot r$$

$$F = ?$$

changes continuously!

How much energy is needed to separate the negative charge?



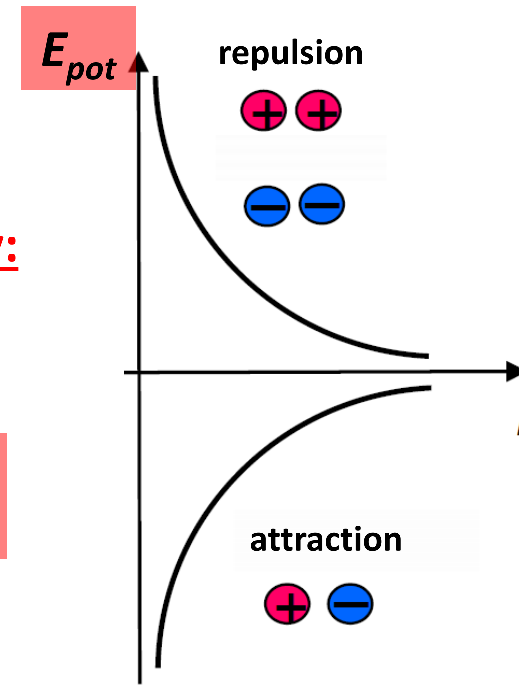
the negative charge is transported into infinite

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

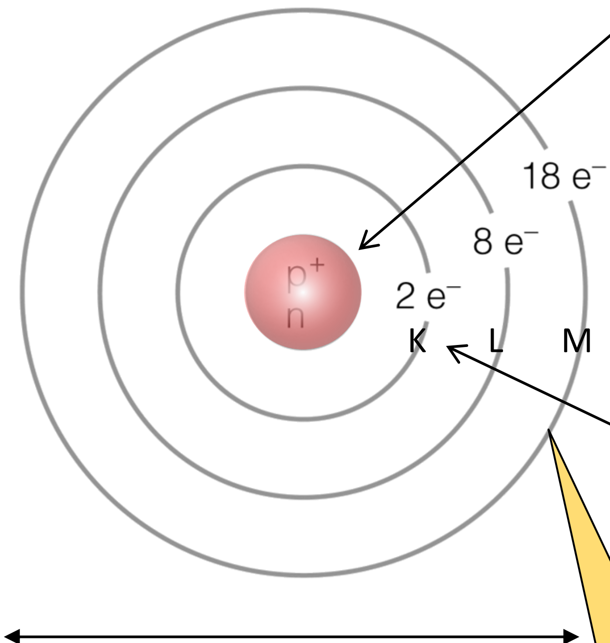
Electric potential energy:

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

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



Structure of the Atom



d ~ 0.1 nm

nucleus, including:

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

} nucleons

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

shells

electrons

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

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

potential energy

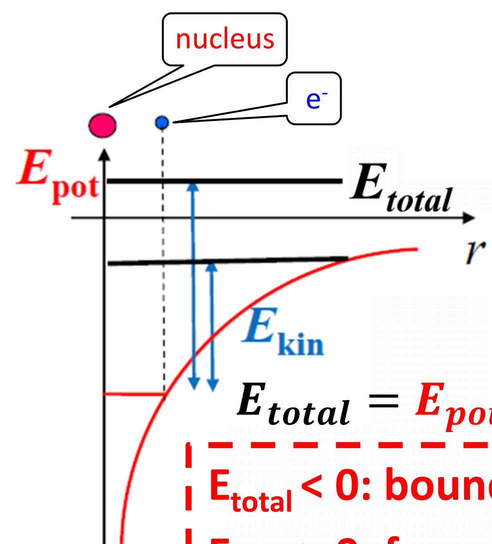
<u>Z: atomic number</u>

(number of protons)

<u>N: neutron number</u>

<u>A: mass number</u>

(=Z+N)

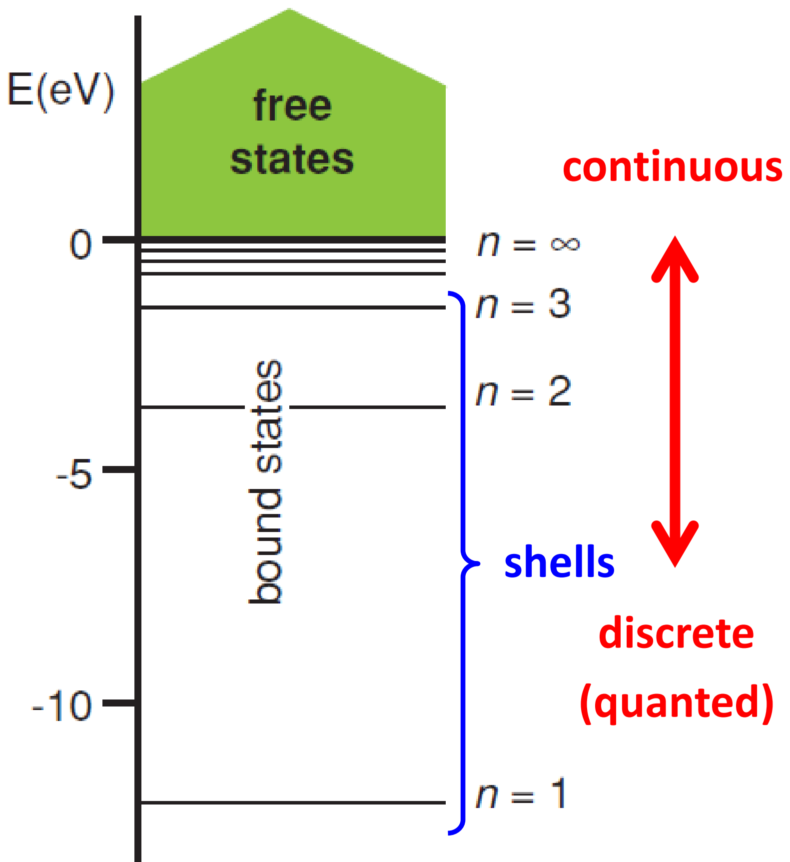


$$E_{total} = E_{pot} + E_{kin}$$

E_{total} < 0: bound electron

E_{total} > 0: free electron

The energy states of the electron

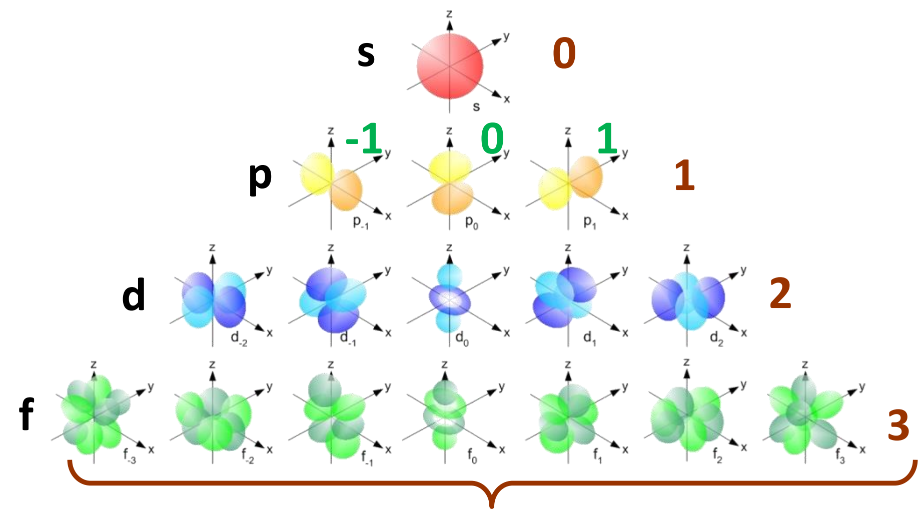


***n*: principal quantum number**

an electron's possible energy levels in the hydrogen atom

***l*: azimuthal quantum number** (n-1)

***m*: magnetic quantum number** (-l → +l)



subshells

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

see „Light emission" lab practical

m_s: spin quantum number (±1/2)

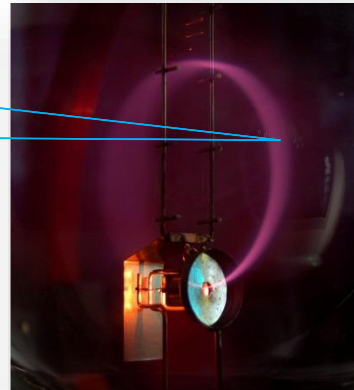
- **Principle of minimum energy**
- **Pauli exclusion principle**

Particle-wave duality of the electron

cf. particle-wave duality of the photon

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

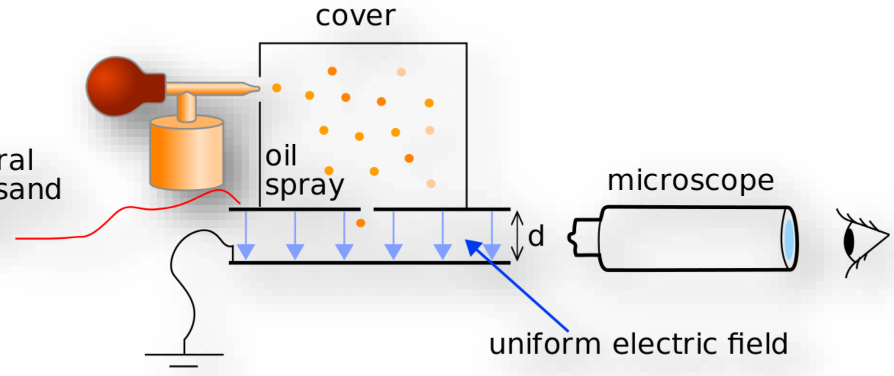
particle



mass

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

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

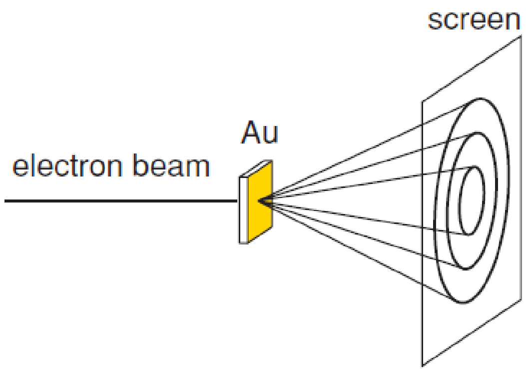


charge

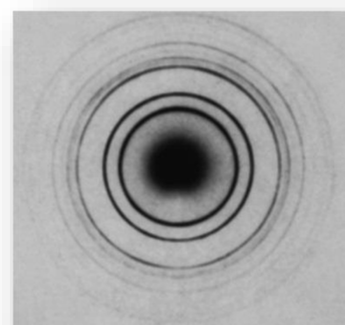
(Millikan, 1910)

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

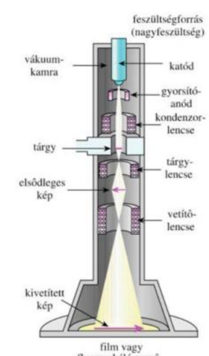
wave



Davisson and Germer, 1927



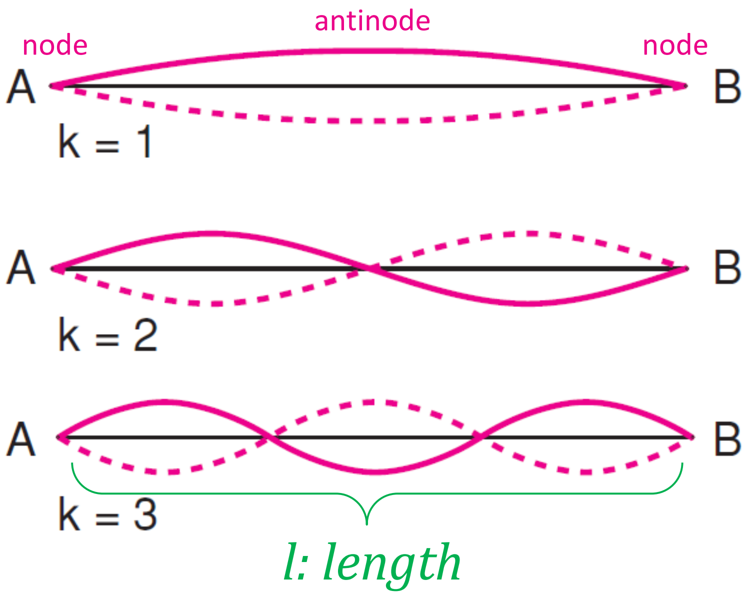
diffraction of fast electrons through a gold foil



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

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

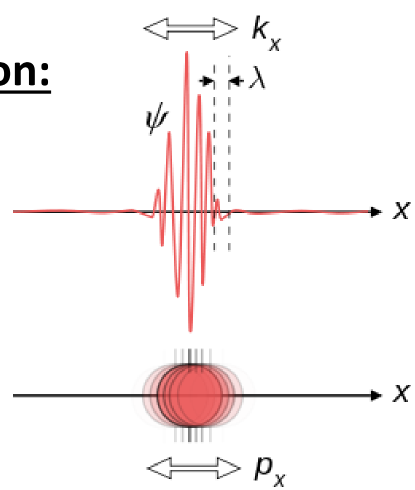
De Broglie, 1923

The state function of the electron:

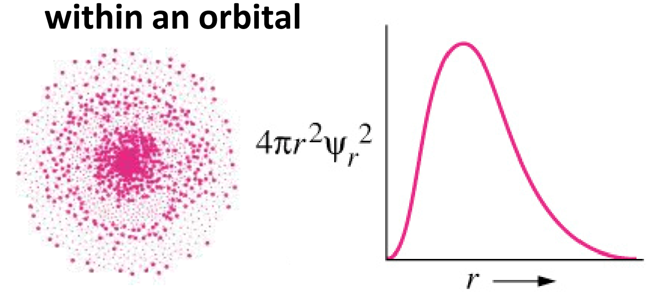
ψ(x,t)

(Schrödinger)

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

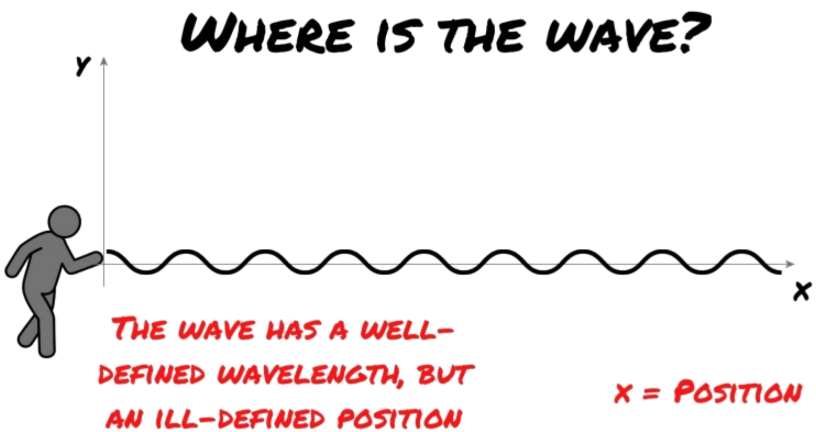


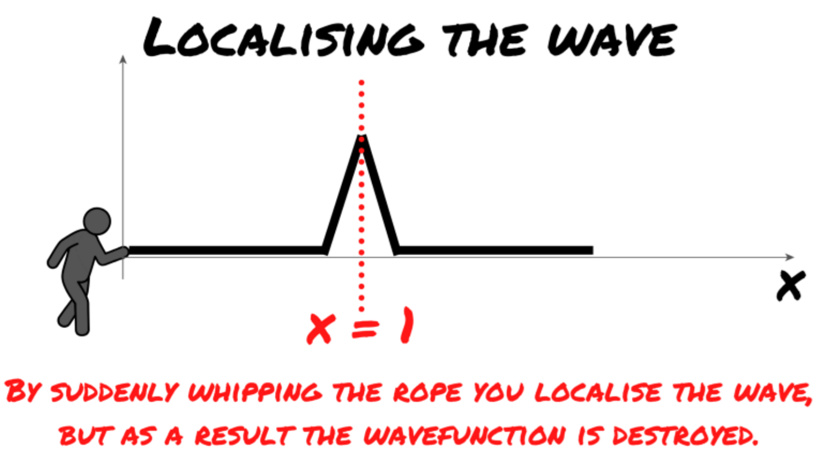
- **ψ^2: correlates to the probability density of finding an electron within an orbital**

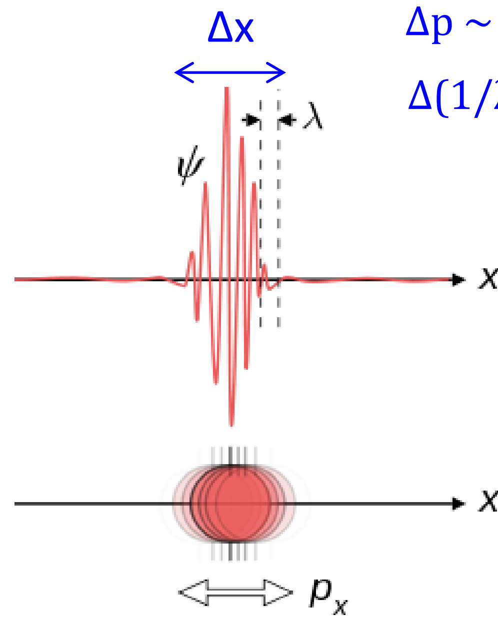


The electron bound in an atom

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







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

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

The Heisenberg uncertainty relation

the uncertainty of the momentum (Δp) :

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

$$\Delta E \cdot \Delta t \geq \frac{h}{4\pi}$$

Δt: uncertain, so E can be certain: **discrete energy levels for bound electron**

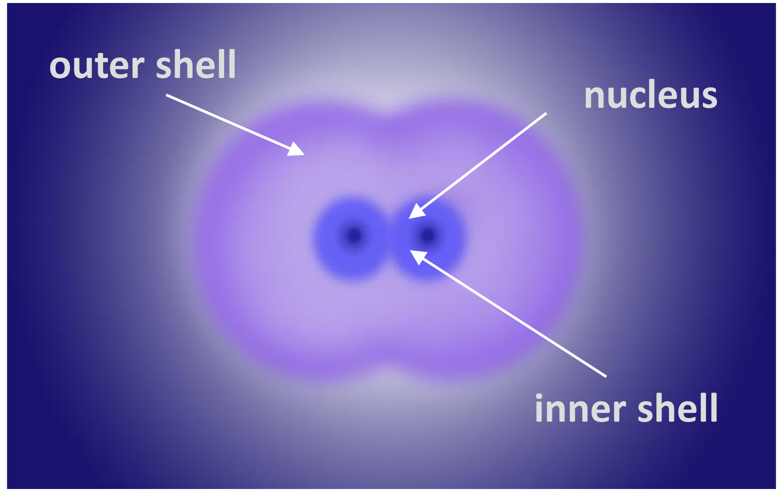
Atomic interactions

short range

interaction:

repulsion between nuclei

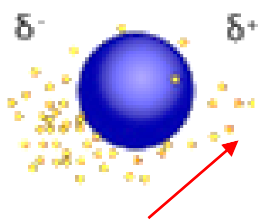
(electron cloud overlap)

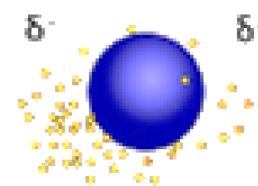


long range

interaction:

coulombic attraction

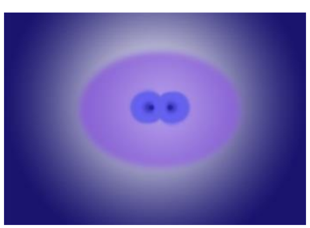


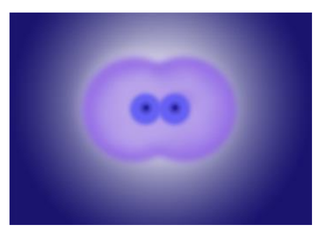


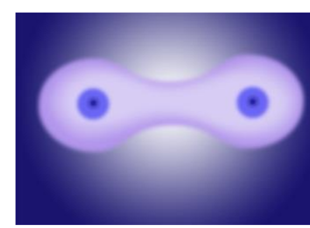
repulsion
(inner shells and nuclei)

equilibrium
attraction = repulsion

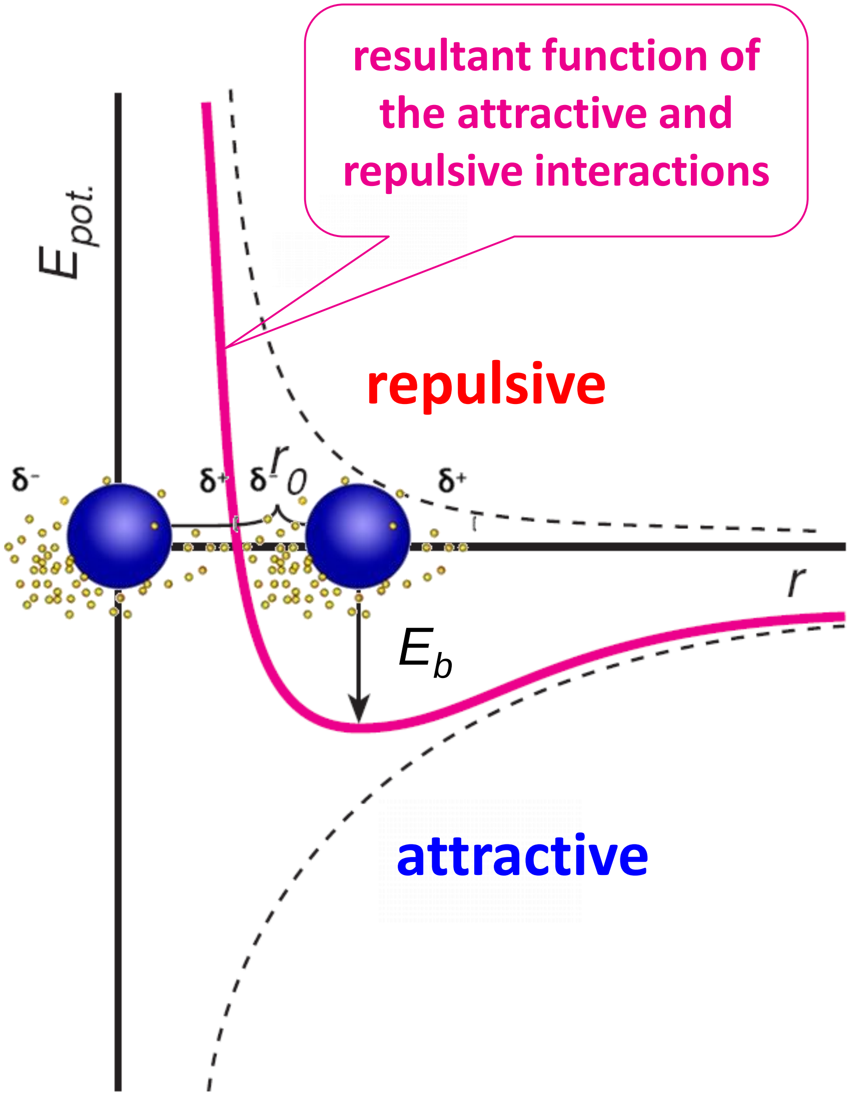
attraction
(outer shells)







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

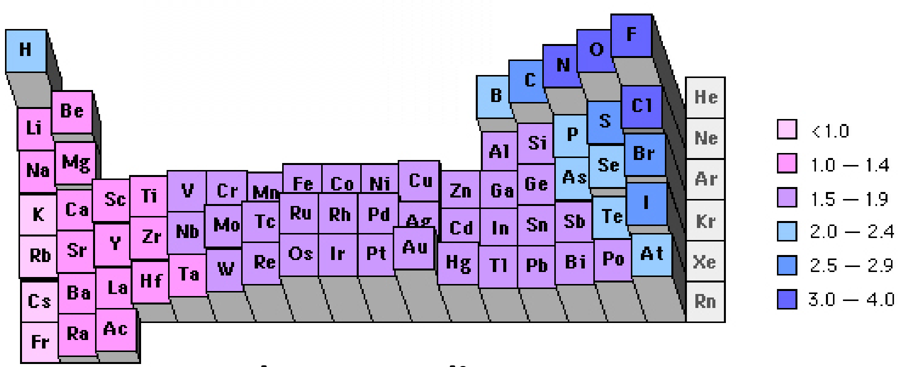
„tendency of an atom to attract electrons"

- **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, $E_b > 1eV$

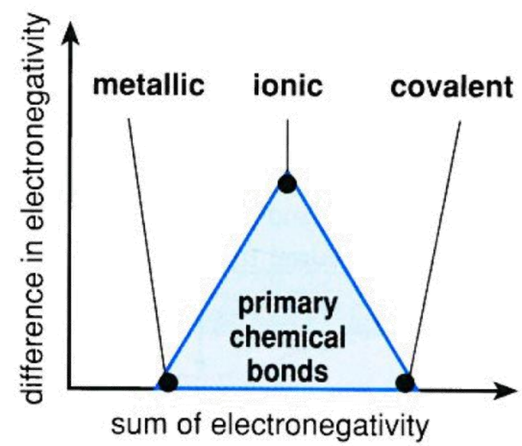
type depends from **electronegativity (EN)**

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

ionization energy | electron-affinity

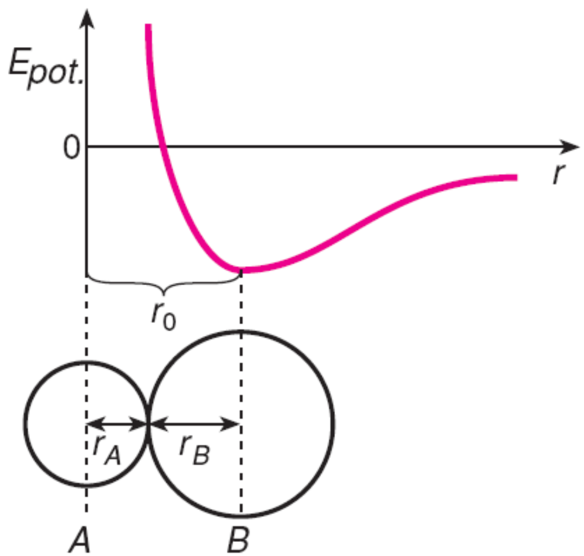


EN values according to Pauling

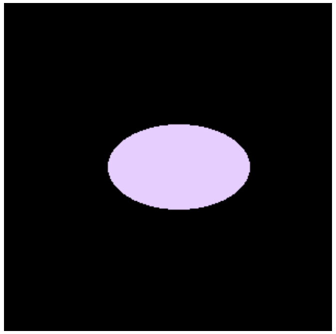


Secondary bonds 1

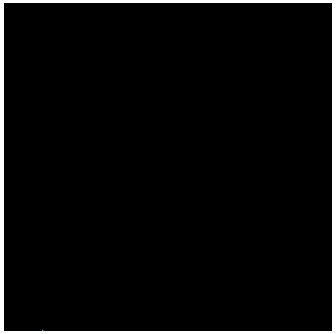
- **Van der Waals:** between two apolar atoms (without permanent dipole moment) where a temporarily created dipole interacts with an apolar molecule or atom thus converting it into a dipole **(induced dipole)**
    - **Van der Waals radius: $r_0=r_A+r_B$**
    - **Intermolecular or intramolecular**
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



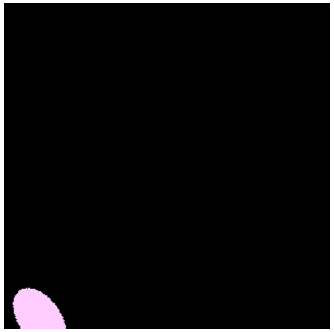
fluctuation



ion-dipole

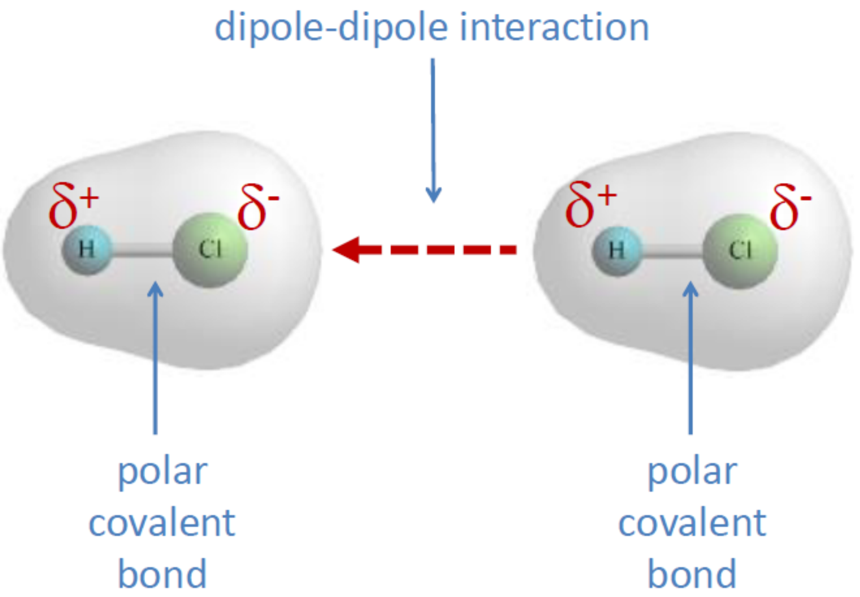


induced dipole



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)



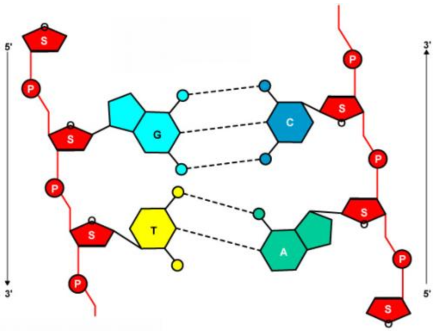
$$E_{attraction} = p * E$$

p: dipole momentum ($p = Q*d$)

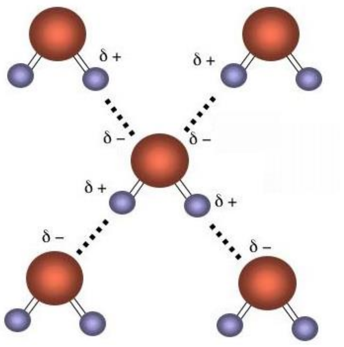
E: electric field strength generated by the surrounding partners

Secondary bonds 3

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

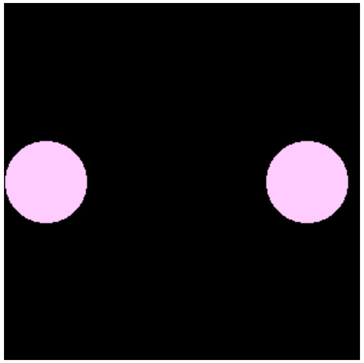


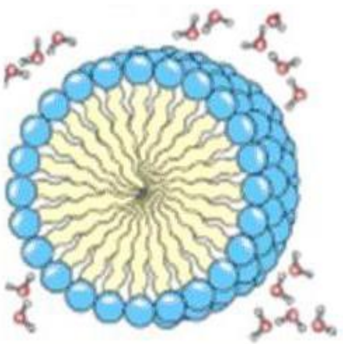
DNA



water

- **<u>Hydrophobic interaction:</u>** 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)





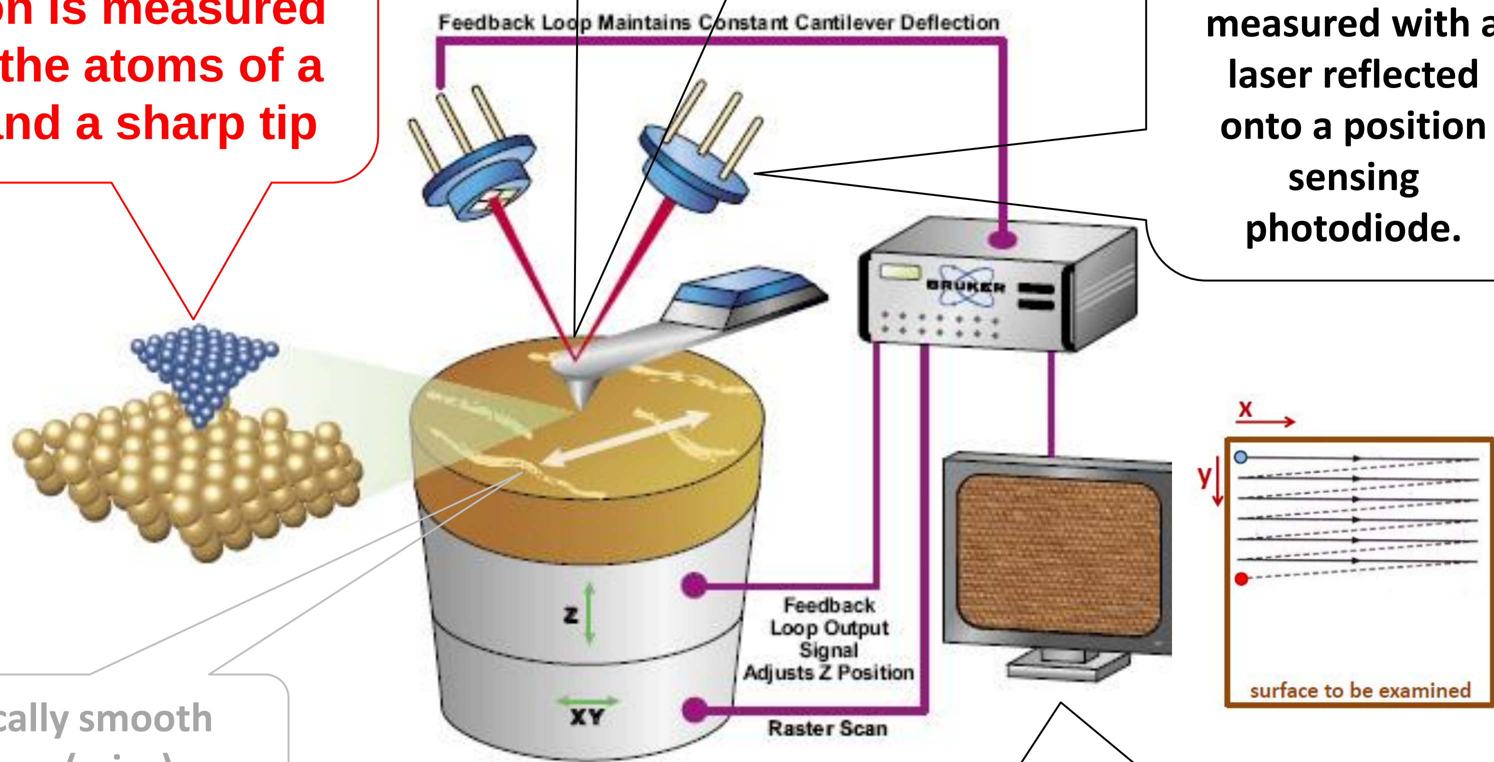
lipids in water

Atomic force microscope (AFM)

1. Van der Waals interaction is measured between the atoms of a sample and a sharp tip

2. The tip is deflected due to the Van der Waals forces.

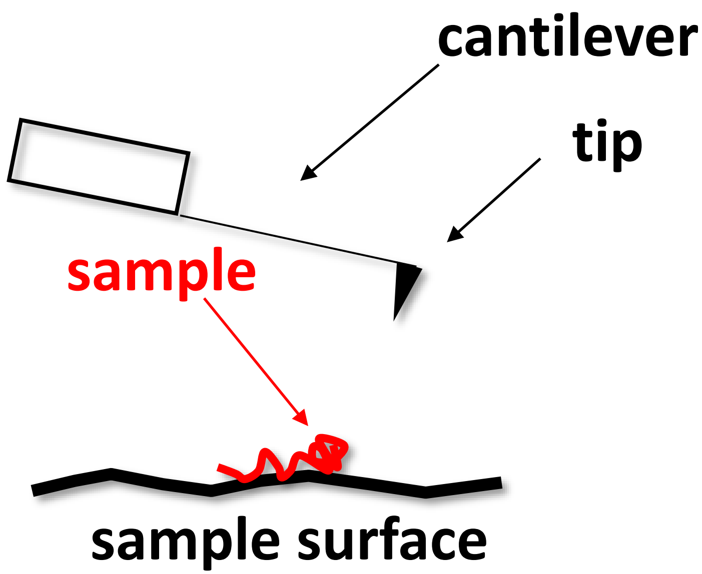
3. The deflection is measured with a laser reflected onto a position sensing photodiode.

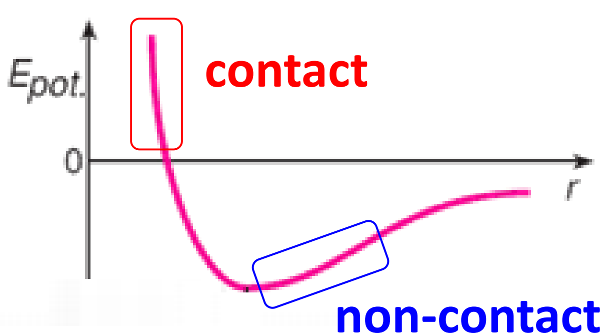


atomically smooth surface (mica)

4. The cantilever is scanned in X-Y-Z directions: atomic resolution with raster scan.

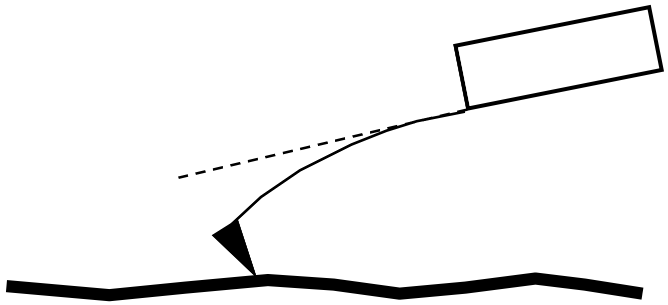
AFM operating modes



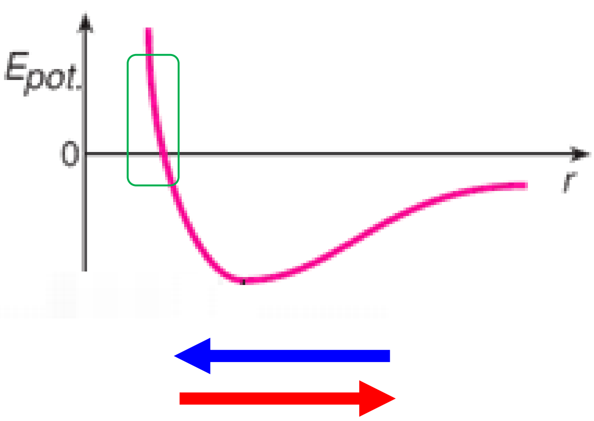


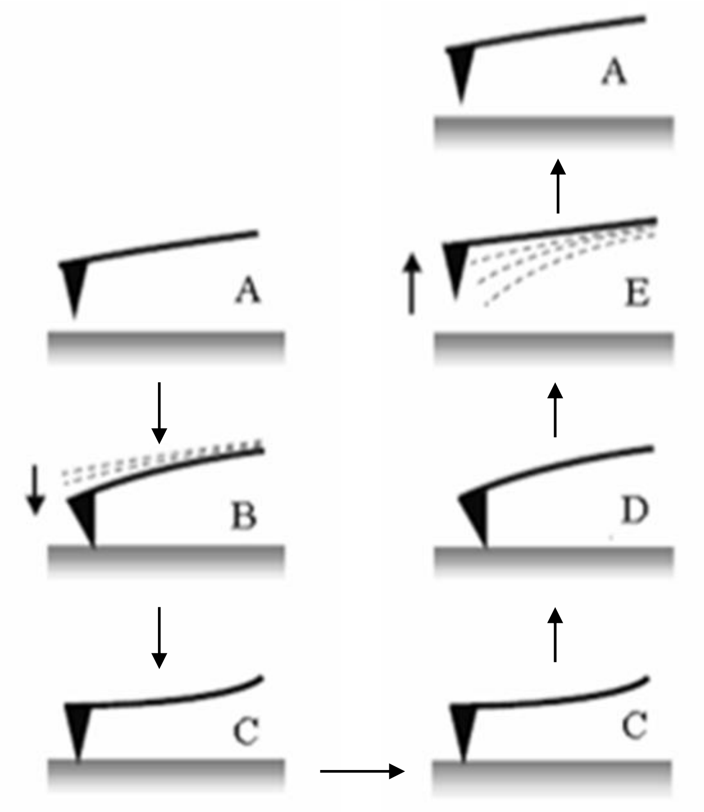
- **Contact:** the tip touches the surface, the **deflection of the cantilever** (i.e. the force exerted on the sample by the tip) is held **constant**.
  - **Z-feedback** system: deflection is maintained at a constant value (setpoint) by lifting or lowering the cantilever.
  - **topography data** (i.e.: 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



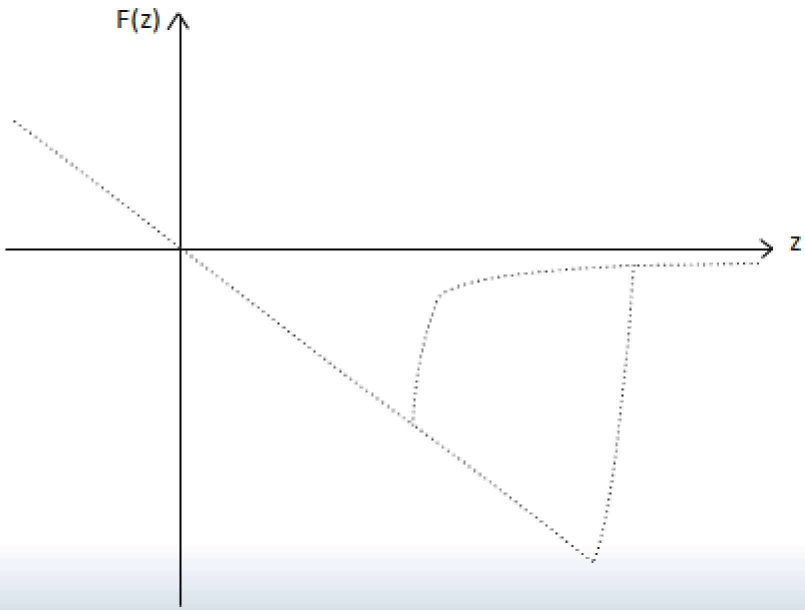


approaching the surface

leaving the surface

Contact mode AFM

Force-displacement curve



This is a force-displacement curve, showing the change in the force acting on the tip as it approaches and withdraws from the surface.

The horizontal axis is the extension of the piezo in the z-direction.

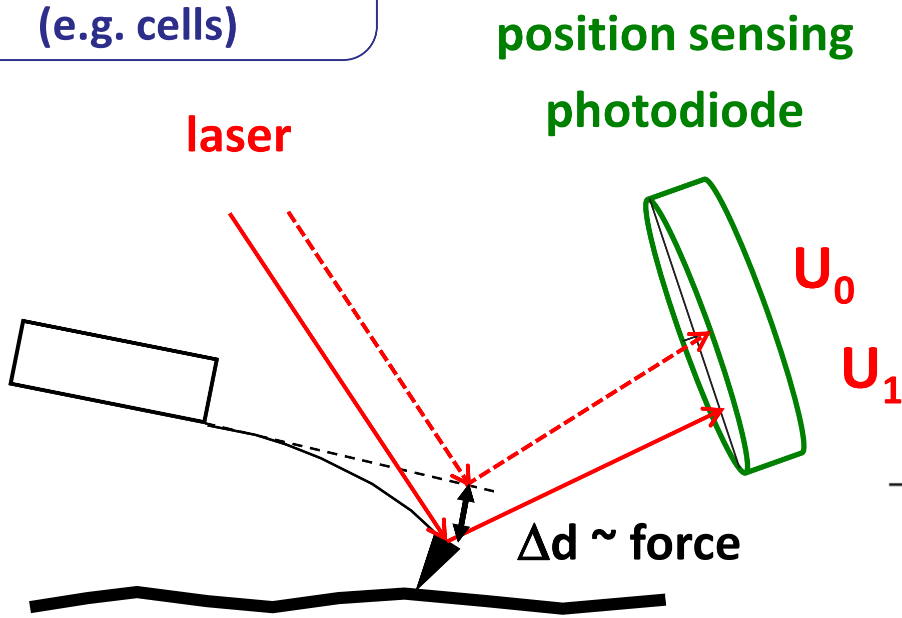
The y-axis is the force experienced by the cantilever. Since force is calculated from Hooke's law: $F = -kx$, the y-axis can also be considered as cantilever deflection.

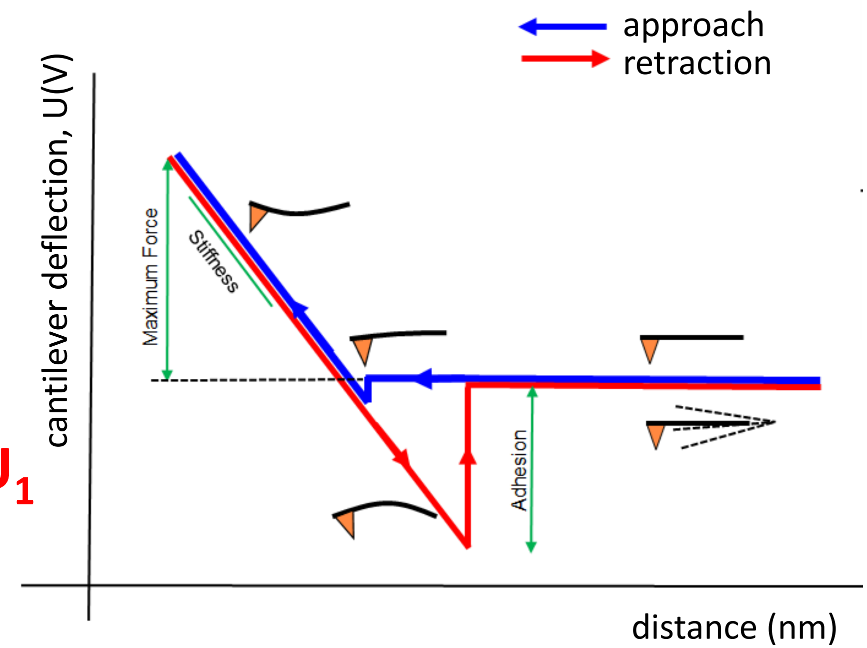
Start

www.doitpoms.ac.uk

Contact mode AFM

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





$F = D \cdot \Delta d$

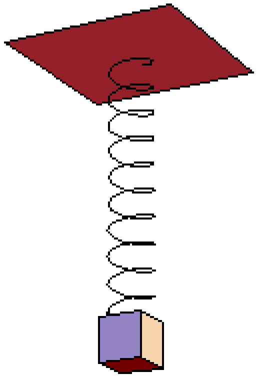
Δd: deflection

D: spring constant

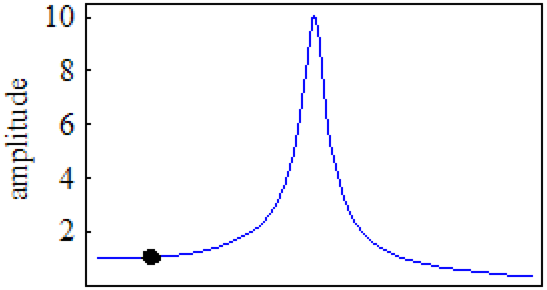
force / elasticity measurement on biological samples

Resonance

<u>Resonance:</u> 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.

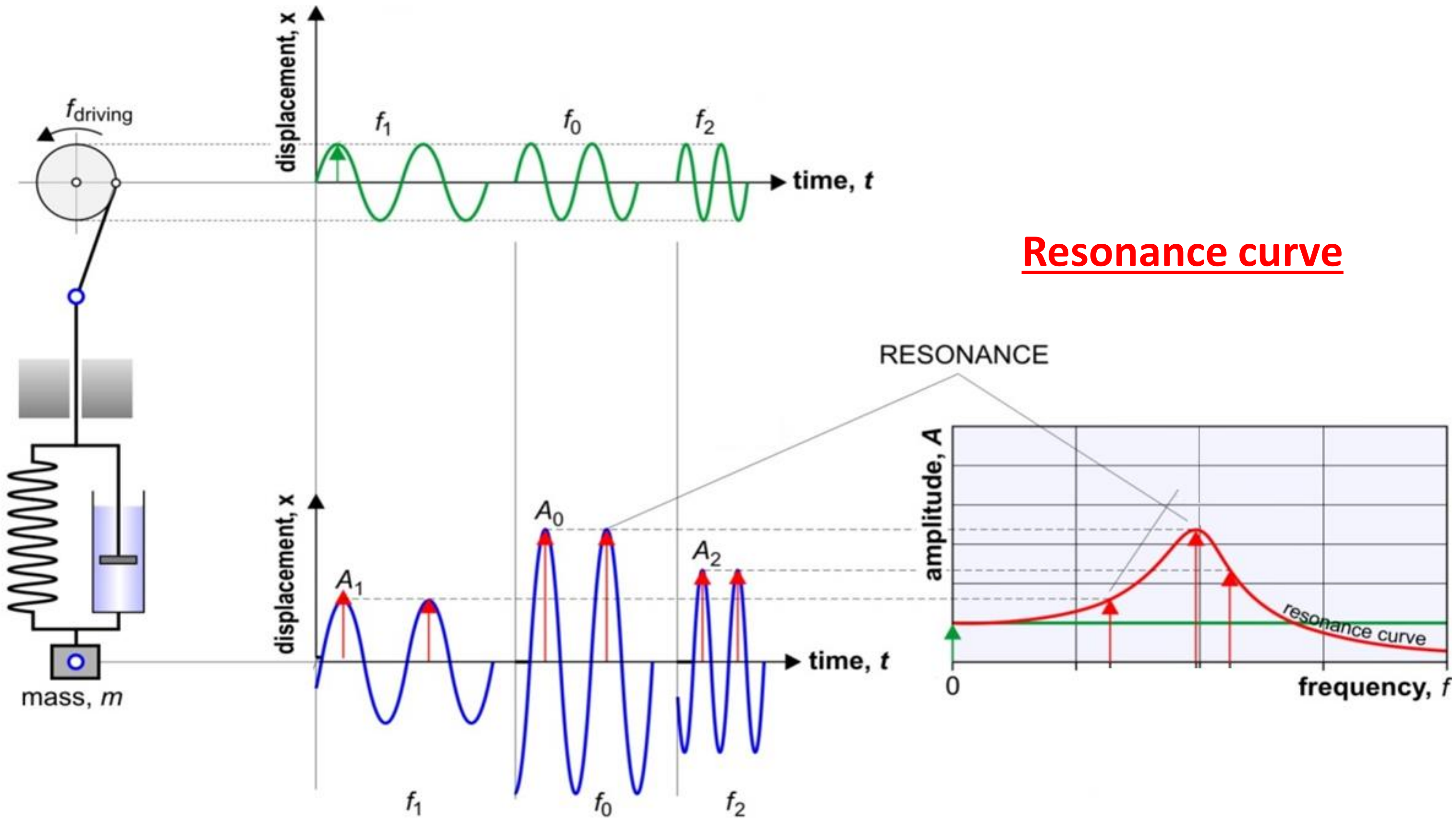


Driven oscillation

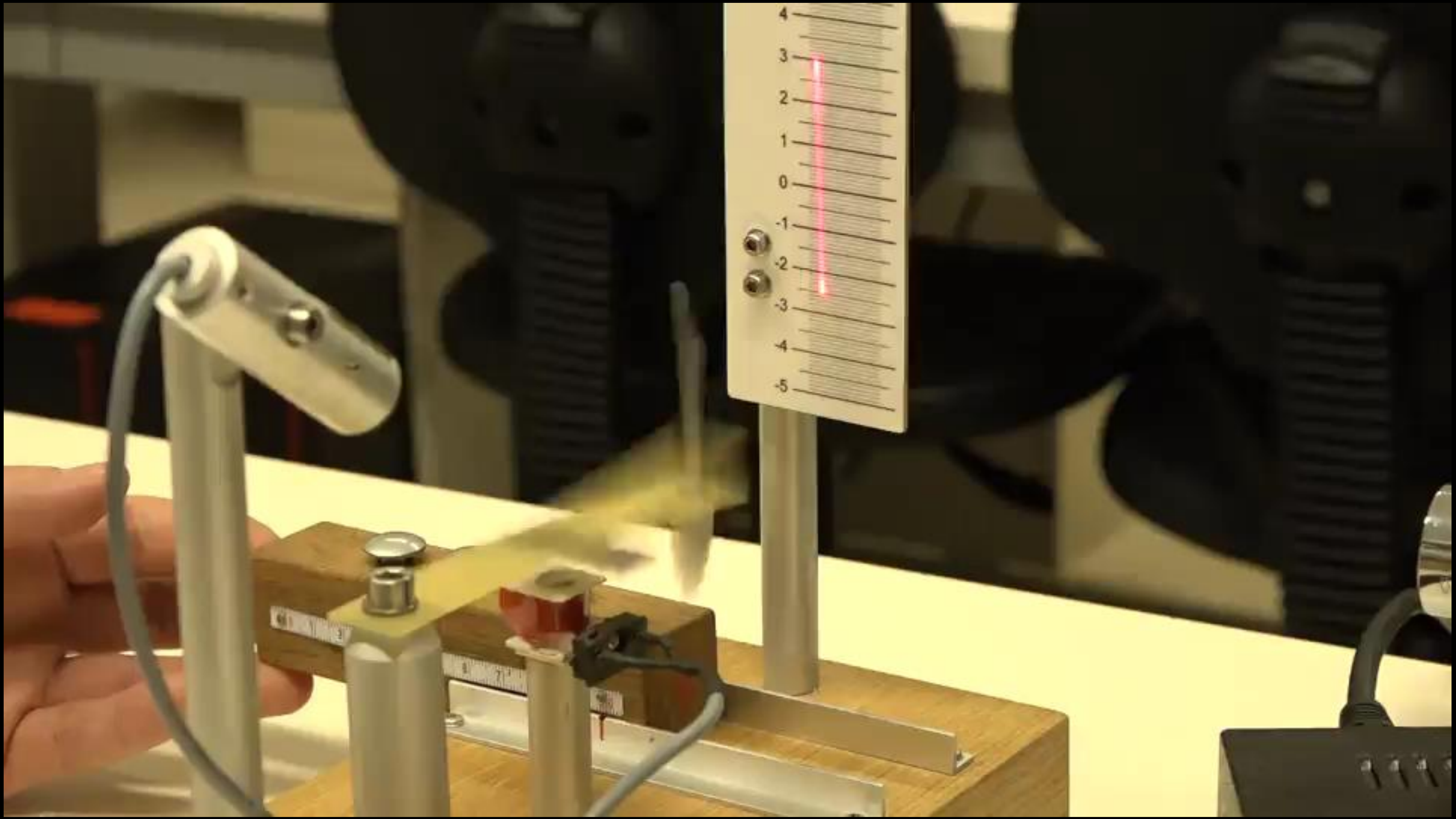


Non-contact/oscillating mode AFM

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.

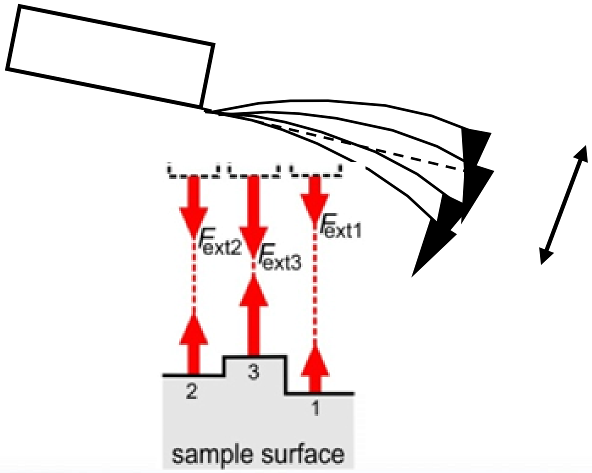


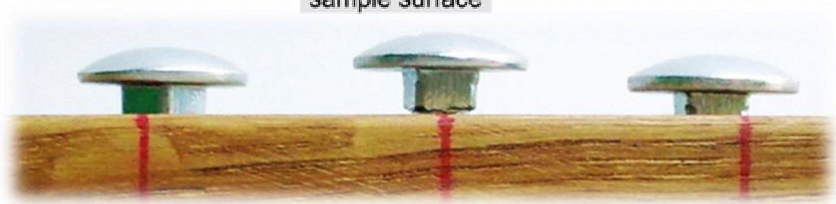
Non-contact/oscillating mode AFM model

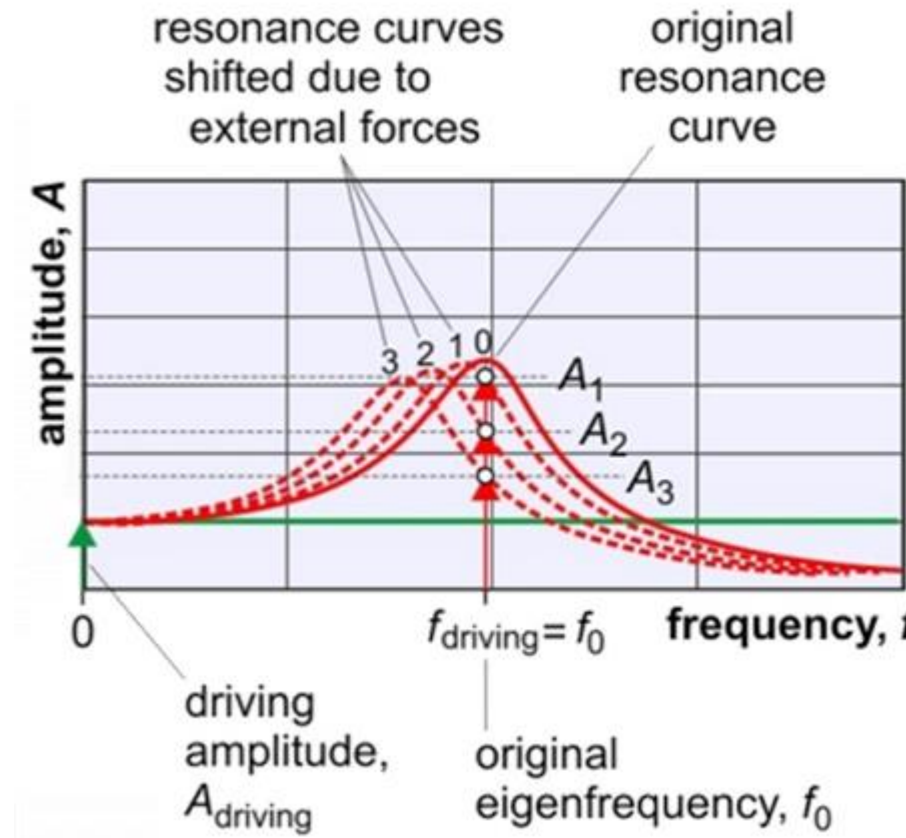


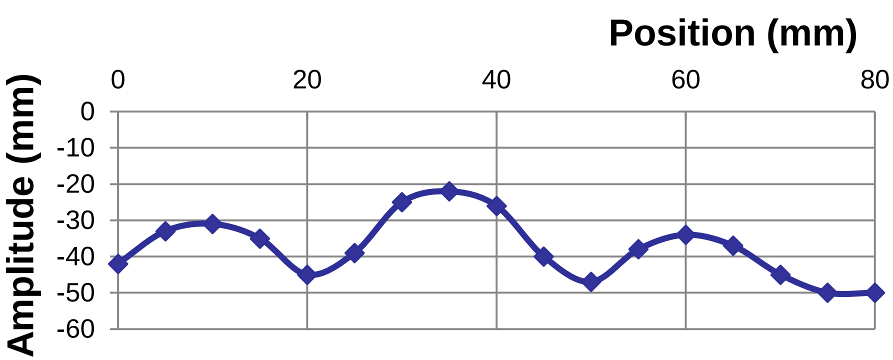
N.B.: magnetic interaction models the Van der Waals forces

Non-contact/oscillating mode AFM





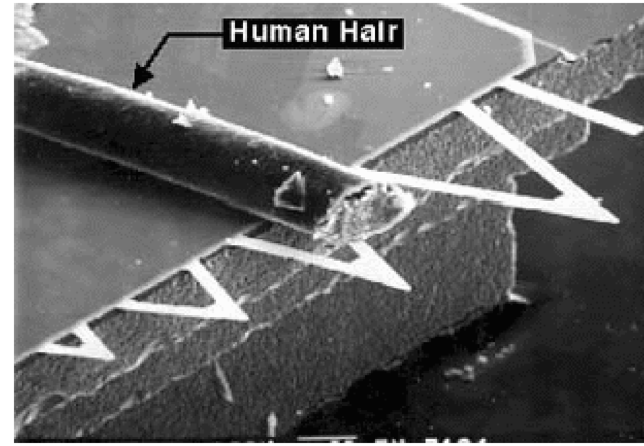


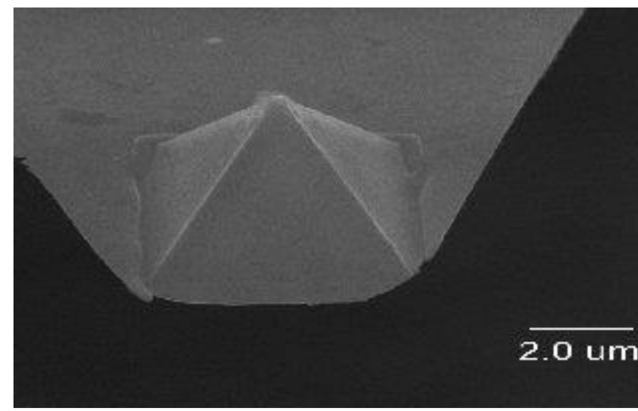


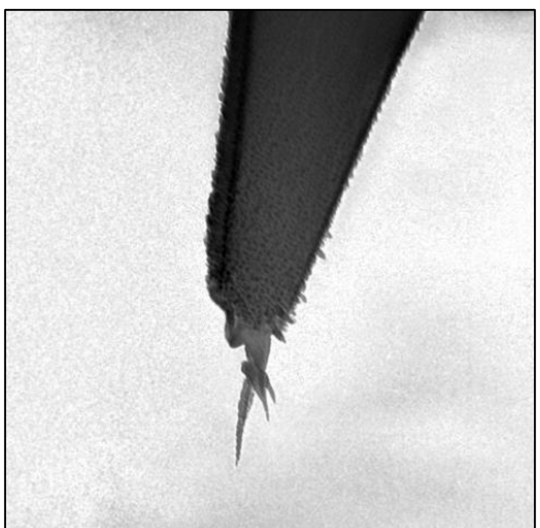
$$f_0 = \frac{1}{2\pi}\sqrt{\frac{D}{m}}$$

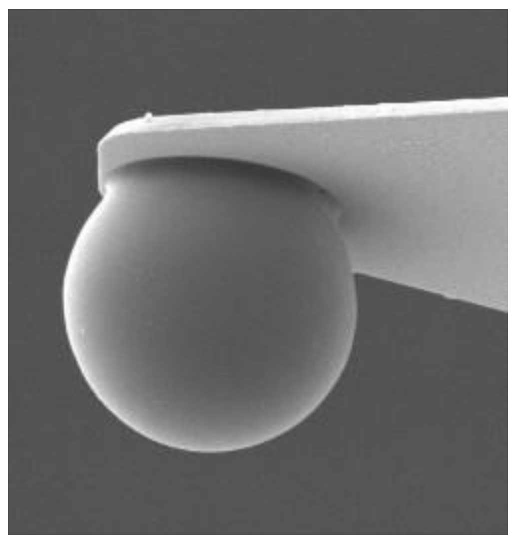
Cantilevers

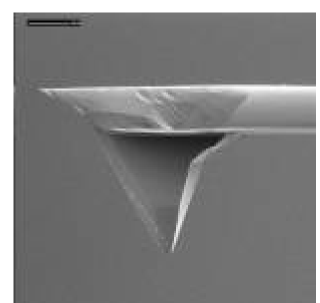
- **Material: mainly silicon nitride**
- **Tip radius: 0.1 nm - 100 µm**
- **Spring constant ~ 0.1 - 10 N/m**
- **f_o ~ 50-500 kHz**

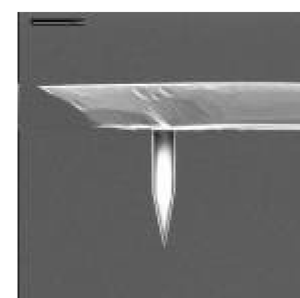




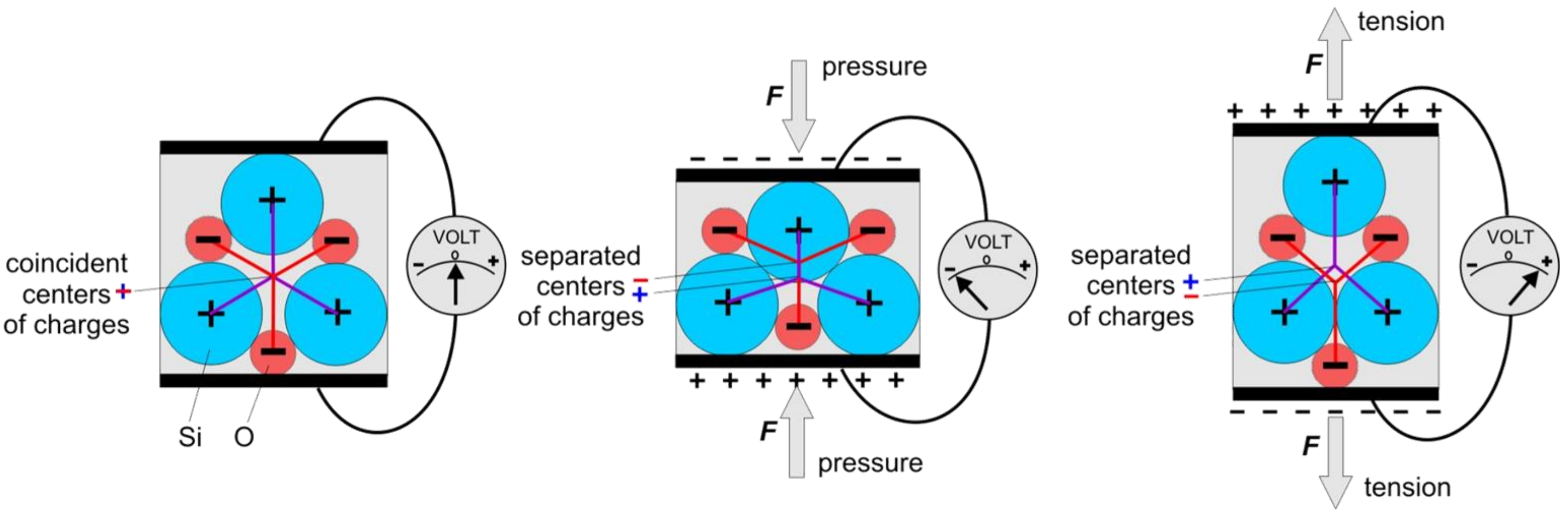








Principle of X-Y-Z raster scanning: piezoelectricity



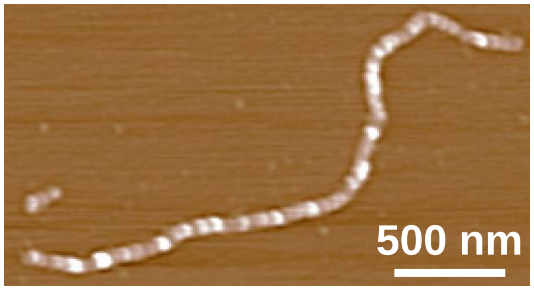
- **direct piezoelectric effect: deformation → voltage**
- **inverse piezoelectric effect: voltage → deformation**
- **X, Y, Z axis piezo: e.g. 150 V → 40 µm**

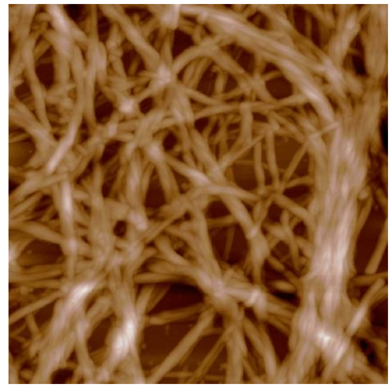
0.1-nm-accuracy possible

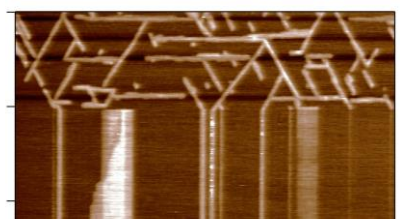
AFM - properties

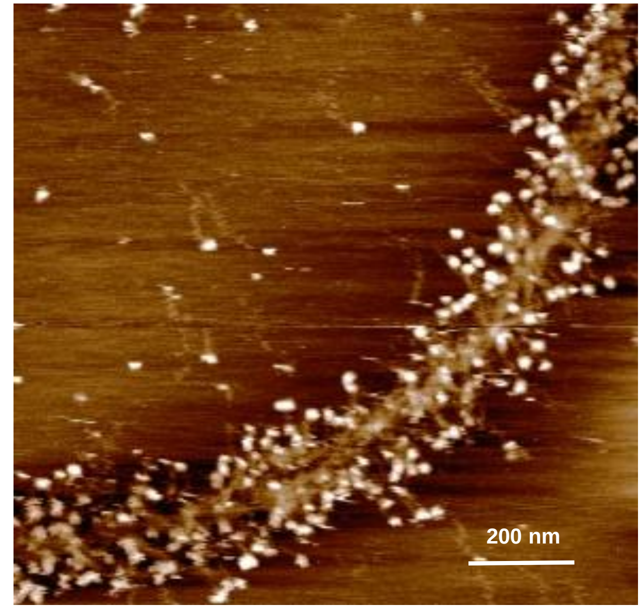
- **Main advantages:**
  - 3D surface profile.
  - Images are collected with ~10 pm vertical and somewhat worse horizontal resolution.
  - Any surfaces (conductors, insulators and semiconductors) can be imaged.
  - Works in ambient air, special gas or in fluid environment as well.
  - Usually does not 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.

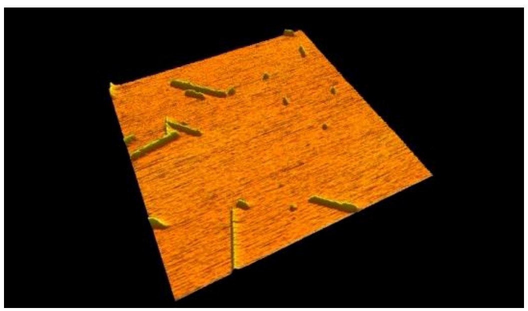
Images recorded in our lab at the Department

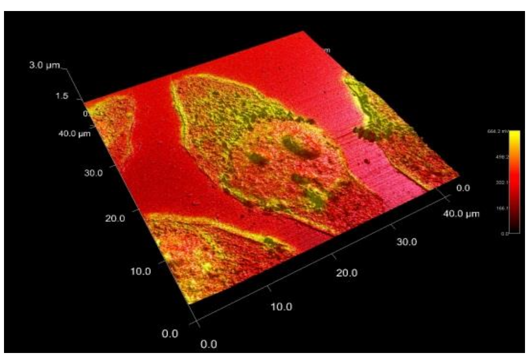


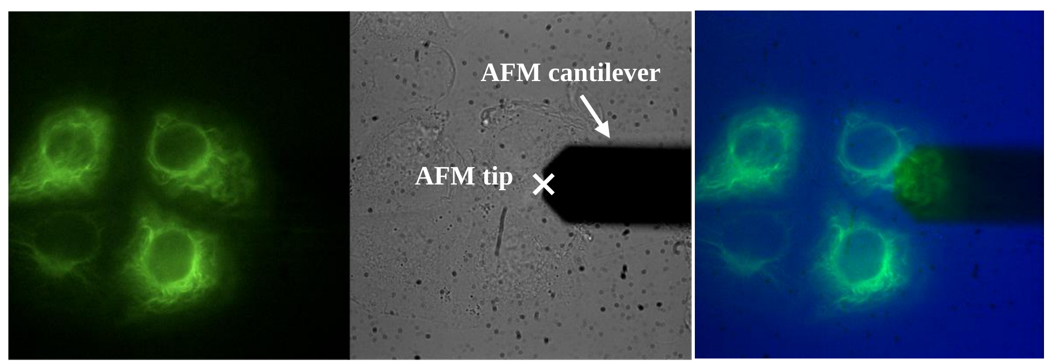










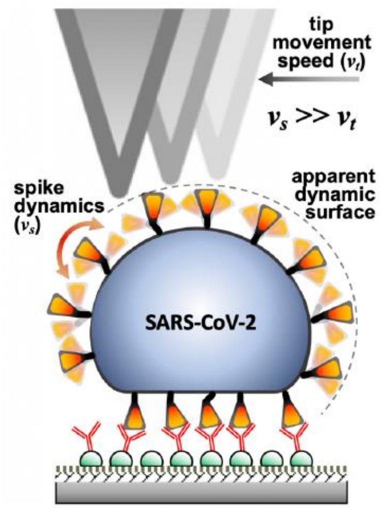


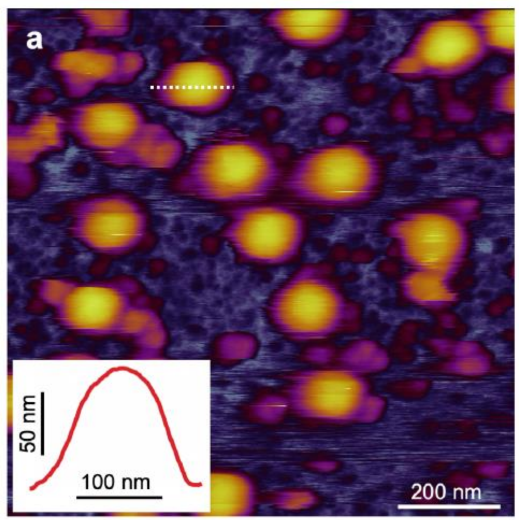
Native SARS-CoV-2 imaged in our lab

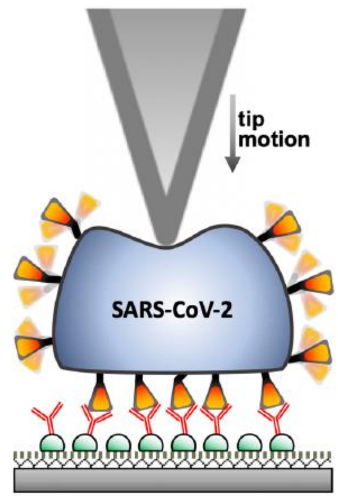
Topography, spike dynamics and nanomechanics of individual native SARS-CoV-2 virions

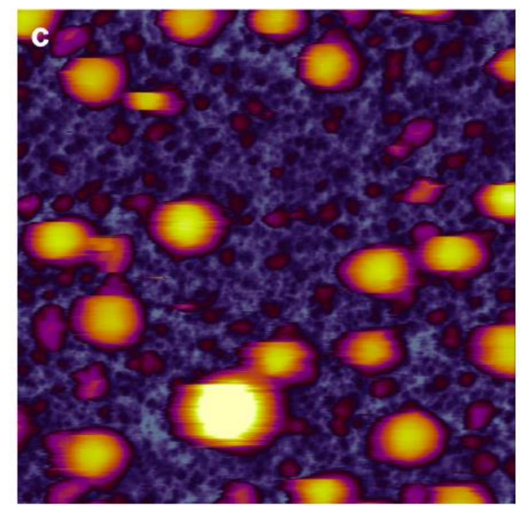
Bálint Kiss[1#], Zoltán Kis[2,3#], Bernadett Pályi[2], Miklós S.Z. Kellermayer[1*]

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

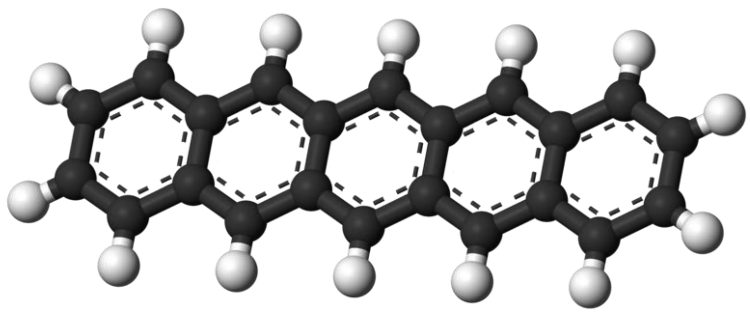




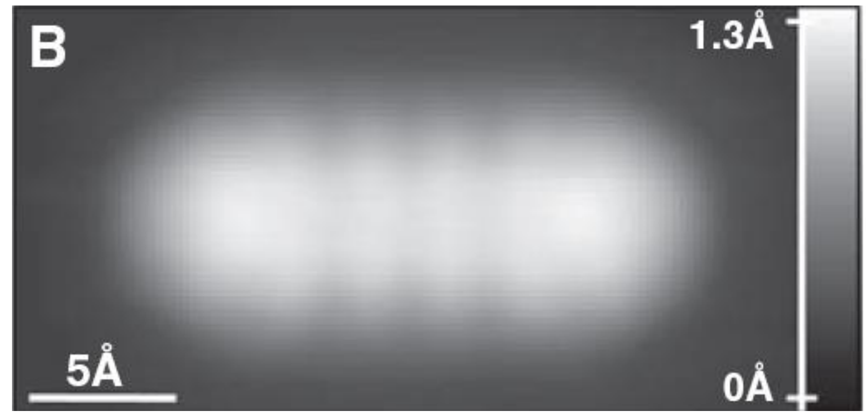




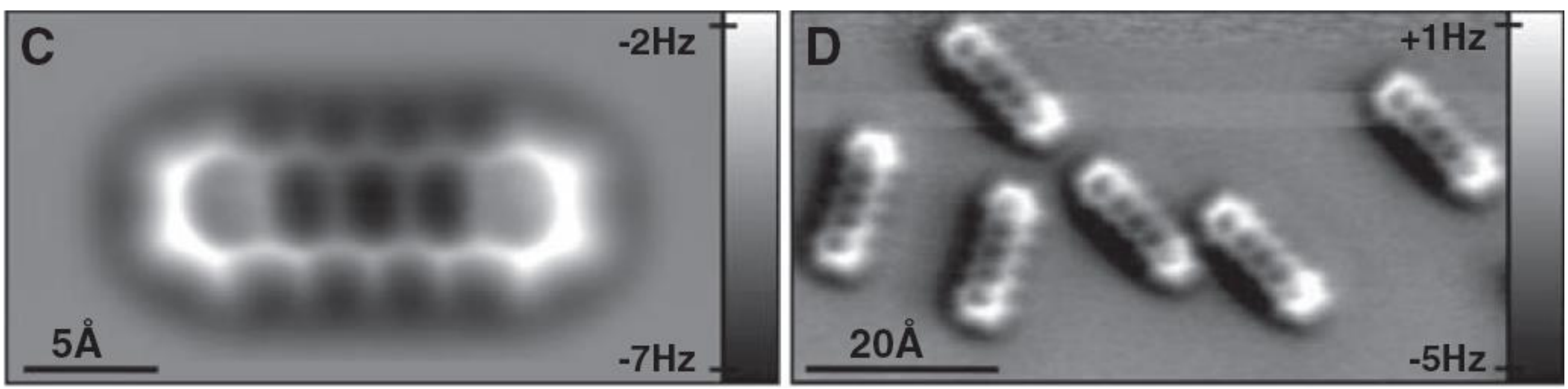
Pentacene molecule



electron current through the tip (STM)

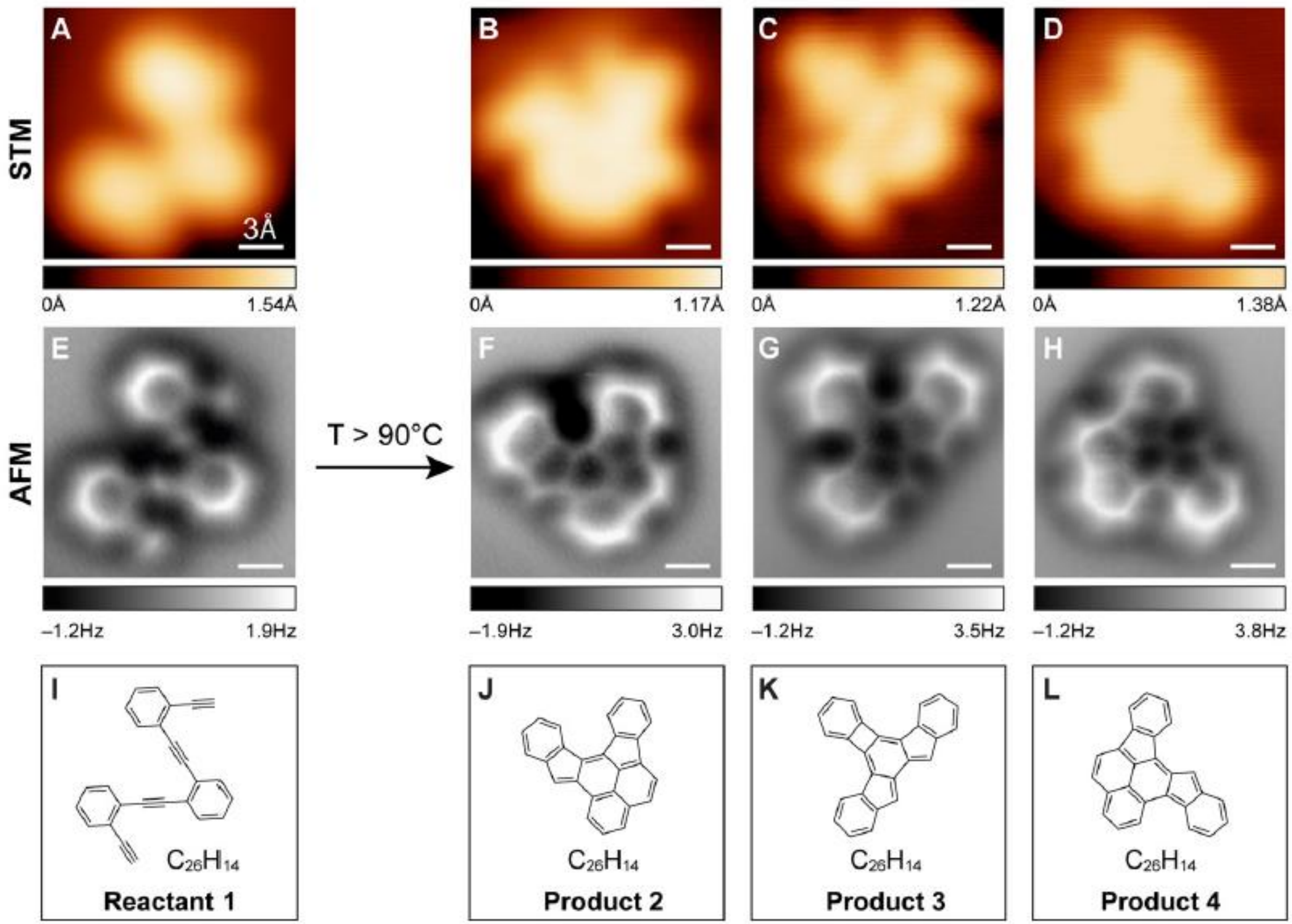


AFM images (tip covered with CO)



Nature Chemistry 1, 597 - 598 (2009)

Visualizing chemical reactions



Thank you

for your attention!