Structure of matter, matter waves, atomic and molecular interactions.

As an example: atomic force microscopy and its macroscopic model.

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Relevant exam questions

8. Proofs of particle-wave duality in case of electron. Matter waves in free and bound state.

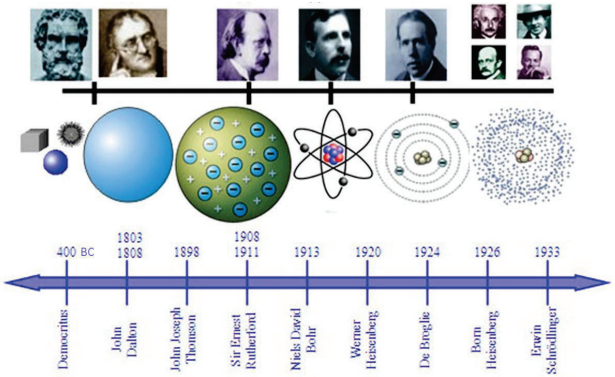
9. General description of atomic and molecular interactions.

10. Principles of atomic force microscopy (AFM), working modes, applications.

TB: pages 23-37

Atomic models

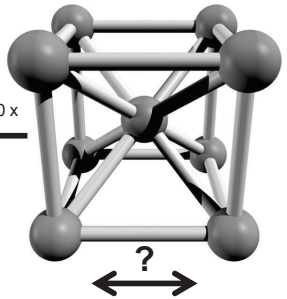
- **Democritus (~400 BC):** proposition of atomic structure
- **Dalton (1803):** stoichiometric law: elements consist of identical contituents
- **Thomson (1897):** discovery of electron (cathode rays)
- **Rutherford (1909-1911):** nucleus (nucleons: p^+ and n_0) and electrons
- **Bohr (1913):** discrete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



How are stable structures created/formed?

macroscopic scale: Atomium

165 000 000 000 x



nanoworld: face-centered cubic lattice of Fe

Governing principle:

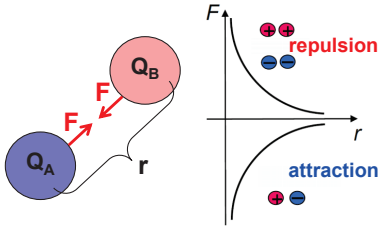
consequence: DISORDER — **repulsive interaction** ⟷ **attractive interaction** — consequence: ORDER

Fundamental interactions in physics

Interaction type	Binding particle	Range (m)	Relative strength
gravitation	every particle	infinite (~1/r²)	10^{-40}
electromagnetic (Coulomb)	charged particles	infinite (~1/r²)	10^{-2}
strong nuclear	nucleons	10^{-15}	1
weak nuclear	every particle	10^{-18}	10^{-13}

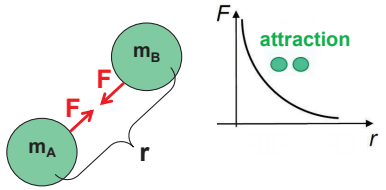
Coulomb-interaction

$$F_C = k \cdot \frac{Q_A \cdot Q_B}{r^2} \qquad k = 9 \cdot 10^9 \frac{Nm^2}{C^2}$$

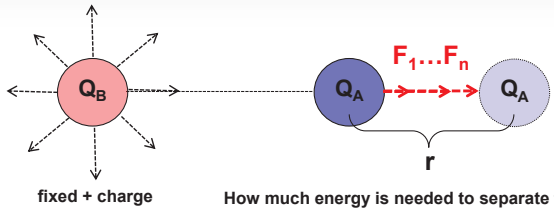


Gravitation

$$F_g = G \cdot \frac{m_A \cdot m_B}{r^2} \qquad G = 6{,}67 \cdot 10^{-11} \frac{m^3}{kg \cdot s^2}$$



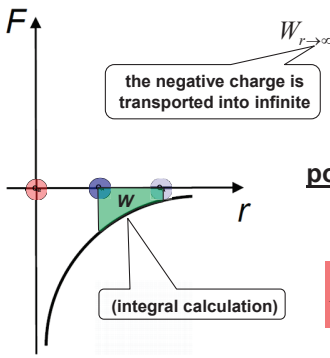
Electric potential energy (E_{pot})



How much energy is needed to separate the - charge?

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

$F = ?$ changes continuously!



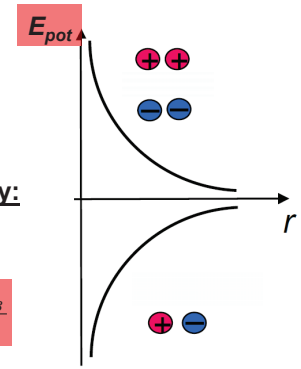
$$W_{r \to \infty} = -k \cdot \frac{Q_A \cdot Q_B}{r}$$

the negative charge is transported into infinite

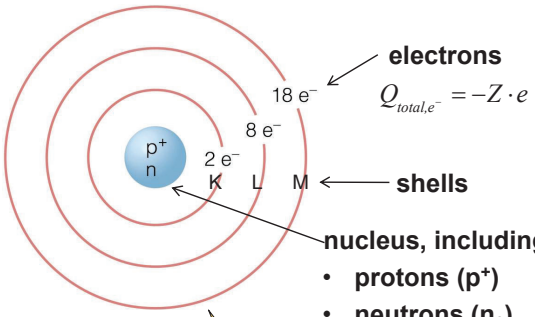
Electric potential energy:

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

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



Structure of the Atom



electrons

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

shells

nucleus, including:

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

nucleons

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

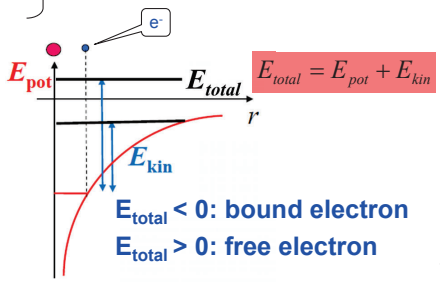
Z: atomic number = number of protons

N: neutron number

A: mass number = Z+N

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

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

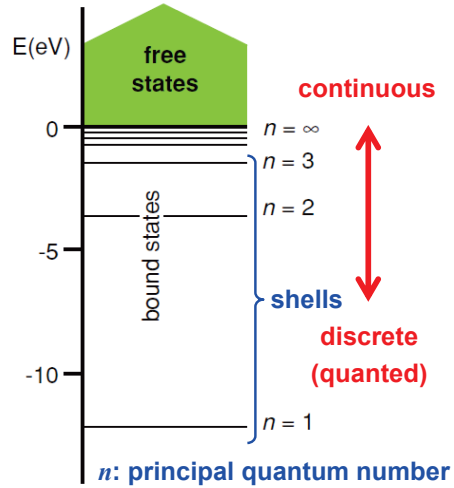


$$E_{total} = E_{pot} + E_{kin}$$

$E_{total} < 0$: bound electron

$E_{total} > 0$: free electron

The energy states of the electron

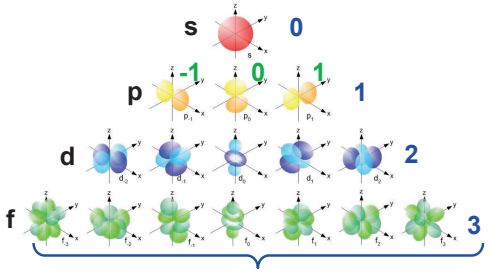


n: principal quantum number

an electron's possible energy levels in the Hydrogen atom

l: azimuthal quantum number

m: magnetic quantum number



subshells

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

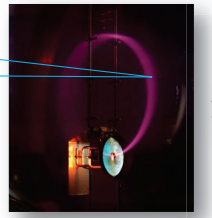
see light emission measurement

- 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



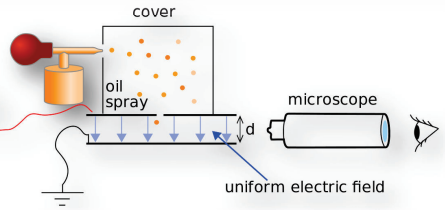
particle

wave

mass

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

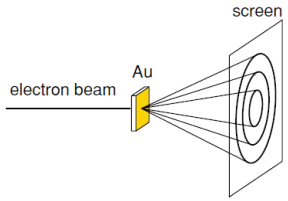
$m_e = 9.1*10^{-31}$ kg



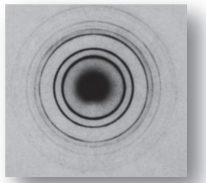
charge

(Millikan, 1910)

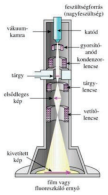
$e = -1.6*10^{-19}$ C



Davisson and Germer, 1927

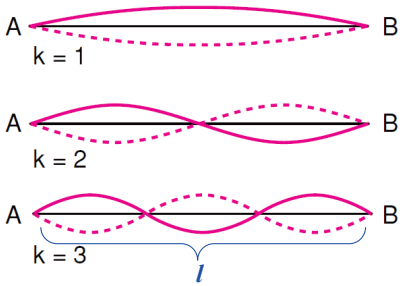


diffraction of fast electrons through a gold foil



electron microscope (revision)

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!

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

λ: wavelength of the matter wave

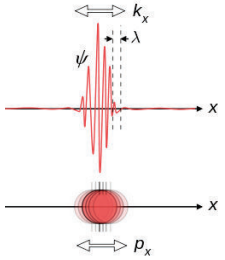
De Broglie, 1923

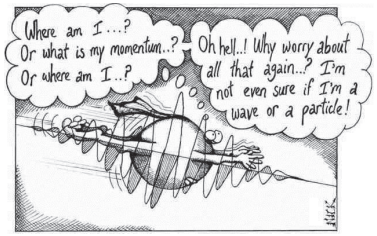
The state function of the electron:

$\psi(x,t)$

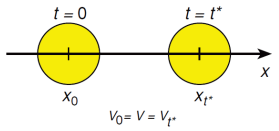
(Schrödinger)

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

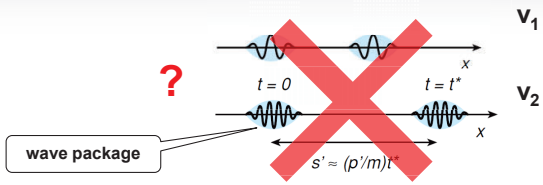




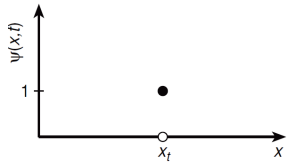
The propagation law of free electrons



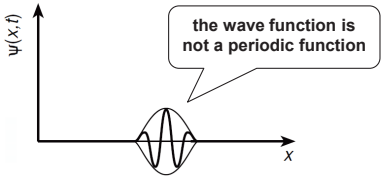
state of motion in classical mechanics



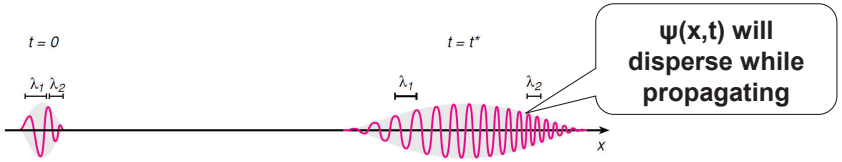
slower and faster propagation of an electron



position of a classical object can be determined exactly

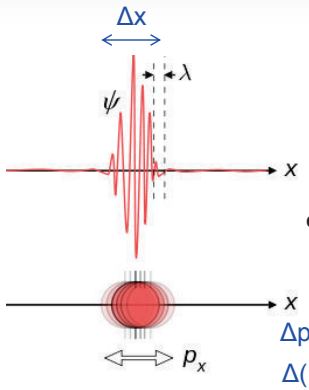


the state function of the electron

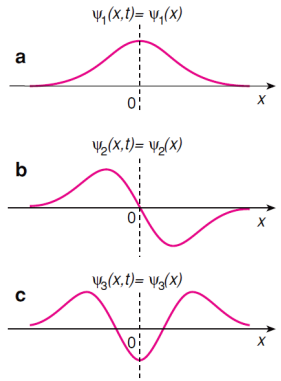


The electron bound in an atom

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



deformed state function



"one-dimensional H-atom"

Δp~Δ(1/λ)

Δ(1/λ) ≥ 1/Δx

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

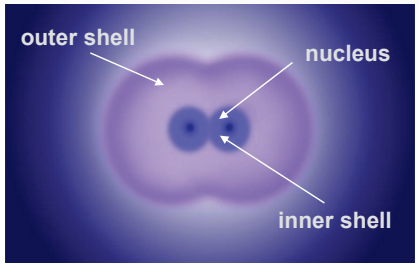
$$\Delta x \cdot \Delta p \geq h$$

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

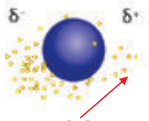
Δt: uncertain, so E can be certain: discrete energy levels

Atomic interactions

short range interaction: repulsion between nuclei
(electron cloud overlap)

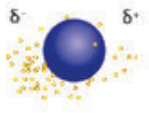


long range interaction: coulombic attraction

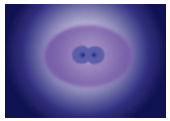


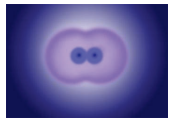
repulsion
(inner shells and nuclei)

equilibrium
attraction = repulsion

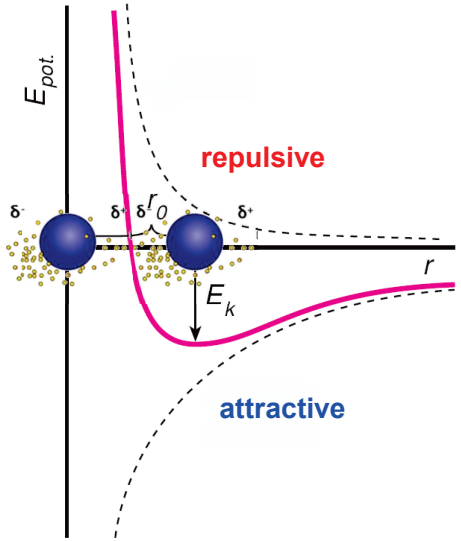


attraction
(outer shells)





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_k: binding energy

Primary bonds

intramolecular		intermolecular
strong	⟷	weak
primary		secondary

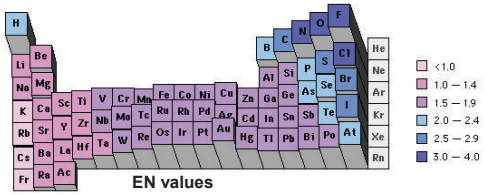
- **covalent:** common electron state around the participating nuclei
- **(metallic bond:** multi-atomic system**)**
- **electrostatic**
  - **ionic bond:** Coulomb-forces between ions
  - **dipole type charge distribution**

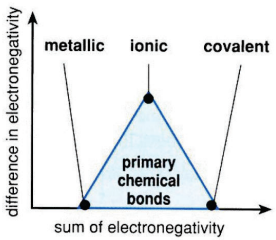
type depends from
electronegativity (EN)

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

ionization energy

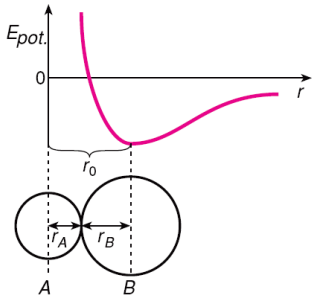
electron-affinity



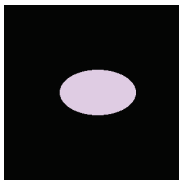


Secondary bonds 1

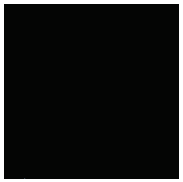
- **Van der Waals:** between atoms without permanent dipole moment (apolar)
  - temporarily created dipole interacts with an apolar molecule or atom thus converting it into a dipole **(induced dipole)**
  - **Van der Waals radius: $r_0=r_A+r_B$**



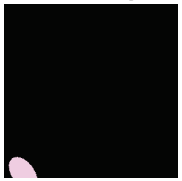
fluctuation



ion-dipole

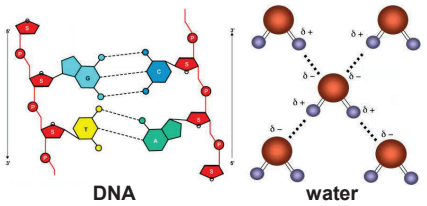


induced dipole

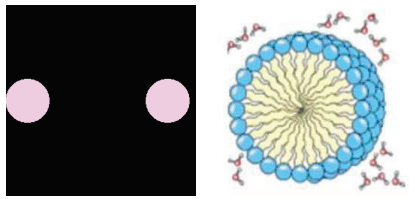


Secondary bonds 2

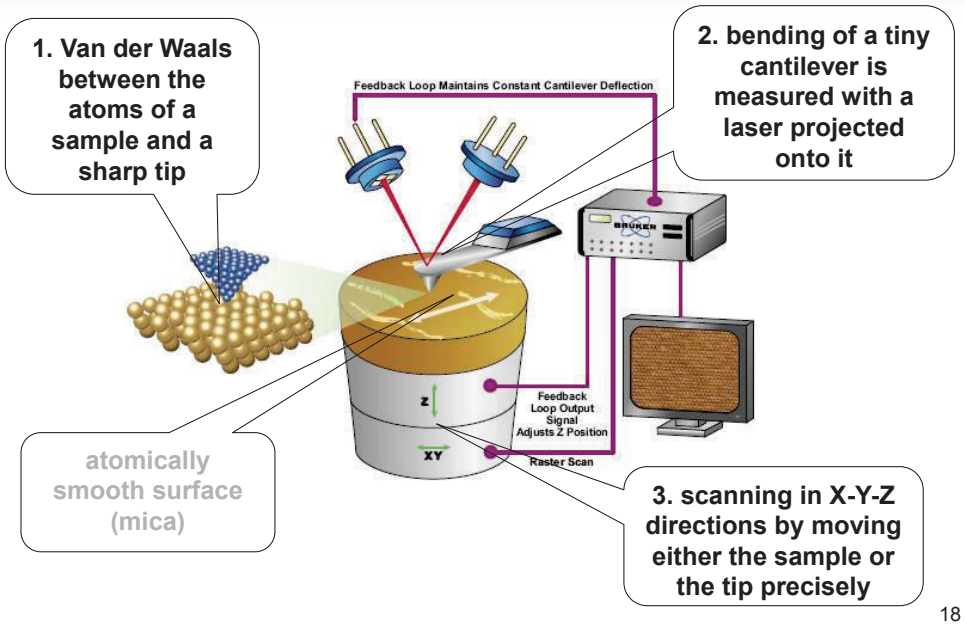
- **H-bond**: the H-atom interbridges 2 other atoms (F, O, N) of high electronegativity
  - **r ~ 0.23-0.35 nm**
  - **E ~ 0.2 eV**



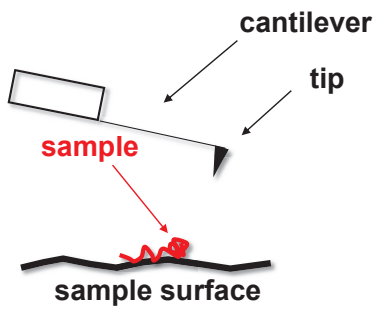
- **hydrophobic interaction:** weak Van der Waals interaction, but thermal motion (kT~0.025 eV) would disrupt the system
  - ordered water molecules exclude the apolar structures (minimized contact surface)

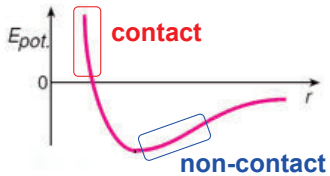


Atomic force microscope (AFM)



AFM operating modes

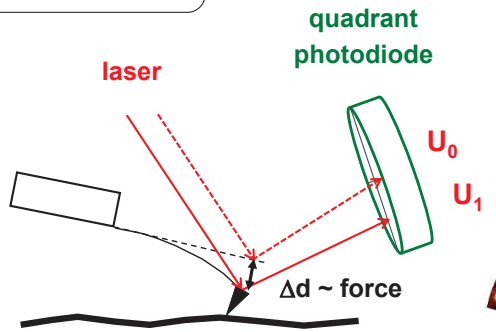




- **contact:** the tip touches the surface: cantilever deflection relates to the surface topography
- **non-contact:** the tip is being oscillated without contact with the surface: amplitude and resonant frequency changes
- **oscillating:** the cantilever is being oscillated near its resonant frequency

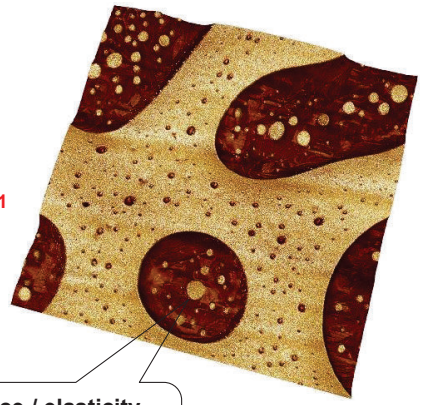
Contact mode AFM

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



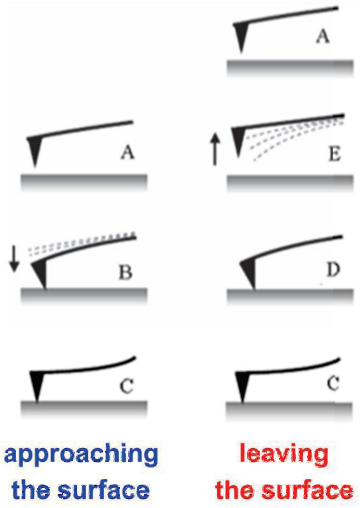
F = force = D Δd

Δd: deflection
D: spring constant



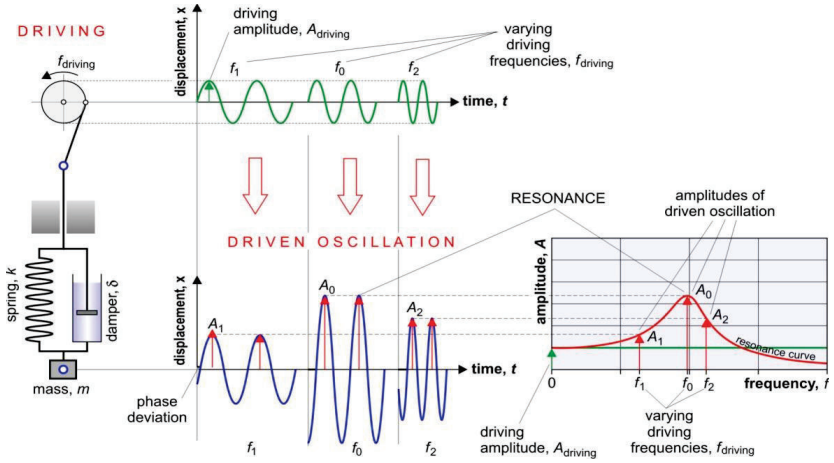
force / elasticity measurement on biological samples

Contact mode AFM

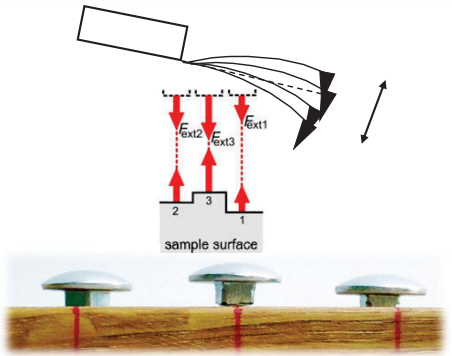


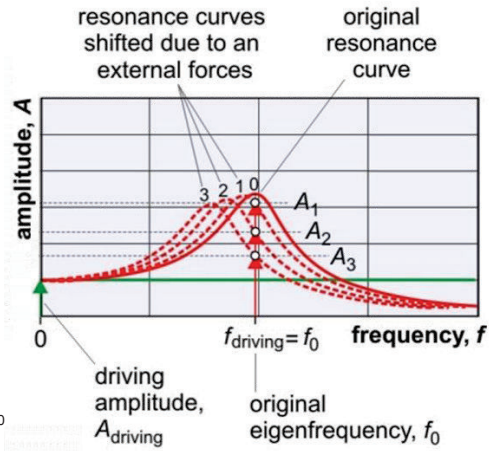
Oscillating mode AFM

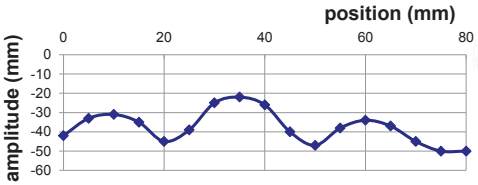
Resonance: a driven oscillation occurring when the oscillatory system is exposed to a driving force with a frequency close to its eigenfrequency. Amplitudes may become extremely large.



Oscillating mode AFM



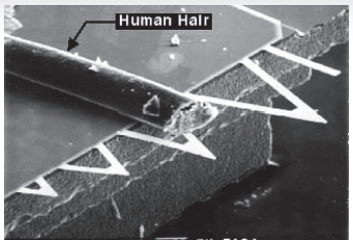


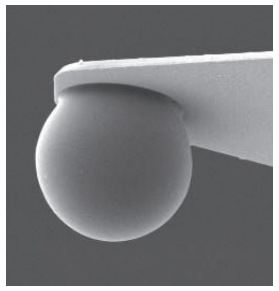


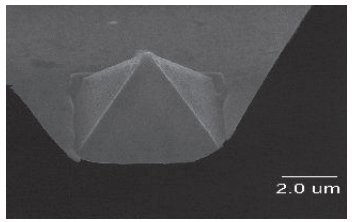
$$f_0 = \frac{1}{2\pi}\sqrt{\frac{D}{m}}$$

Cantilevers

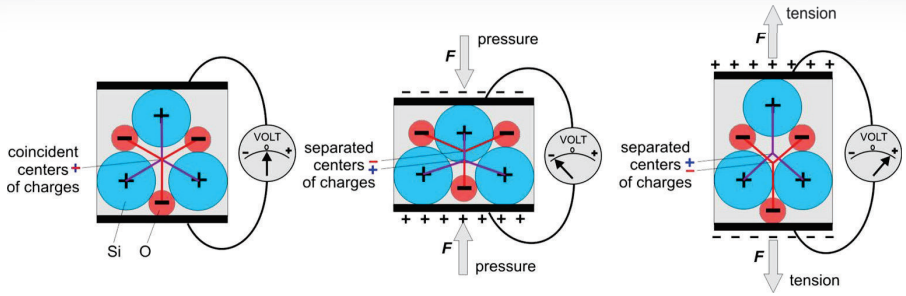
- **material: mainly silicon nitride**
- **tip radius: 0.1 nm- 100 µm**
- **spring constant ~ 0.1-10 N/m**
- **f_o ~ 50-500 kHz**







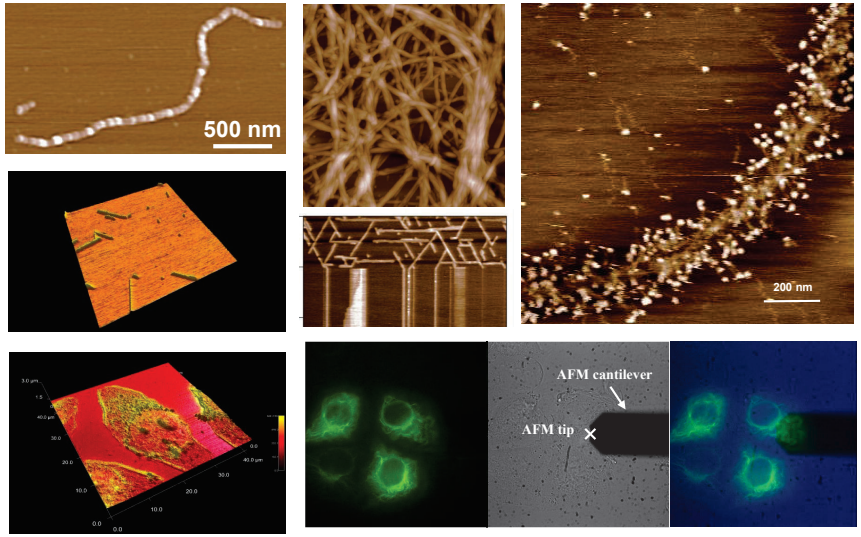
Principle of scanning: piezoelectricity



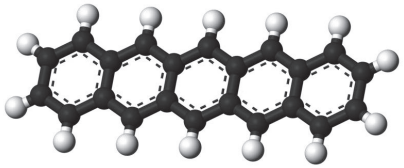
- direct piezoelectric effect: deformation → voltage
- inverse piezoelectric effect: voltage → deformation
- X, Y, Z axis piezo: e.g. 150 V → 40 µm

0.1-nm-accuracy possible

Images that were born in our lab…

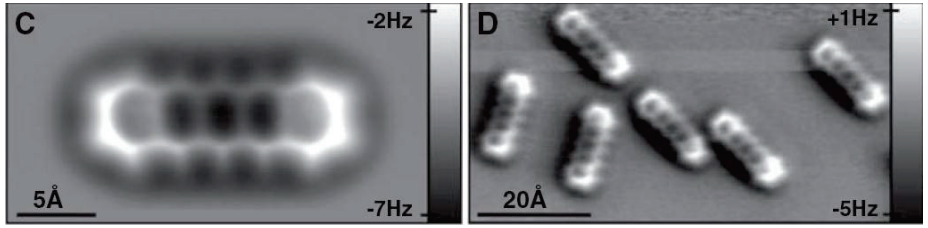


Pentacene molecule

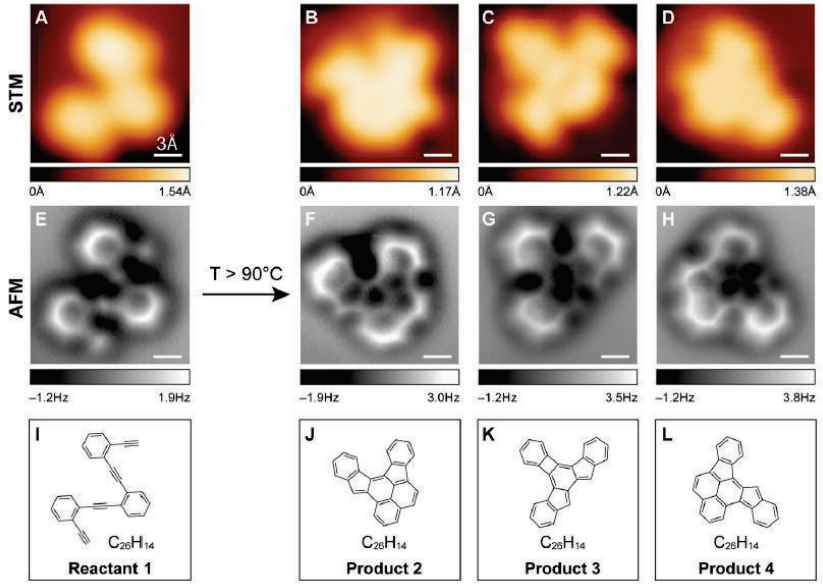


STM

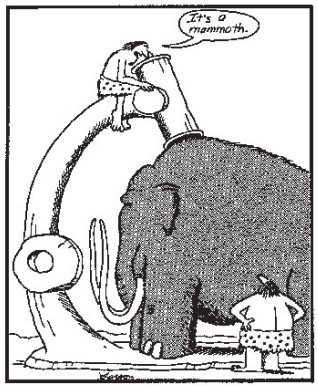
AFM (tip covered with CO)



Visualizing chemical reactions



Thank YOU for your attention!



Early microscope