Structure of matter. Matter wave. Atomic and molecular interactions. Atomic force microscopy.

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Early atomic models

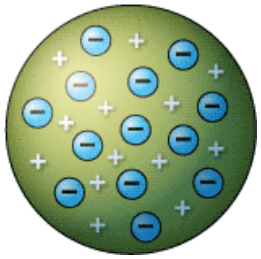
Democritus (460-370 BC)
Matter composed undivisible particles ("atomos").

John **Dalton** (1766-1844)
A given element composed of identical, undivisible atoms.

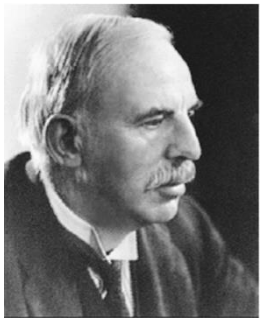
Dalton's atom

Joseph John **Thomson** (1856-1940)
Discovery of the electron.

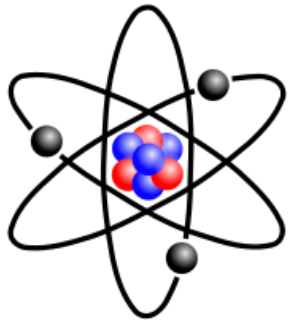
Cathode ray (electron beam) in vacuum tube.



"Plum pudding" atomic model



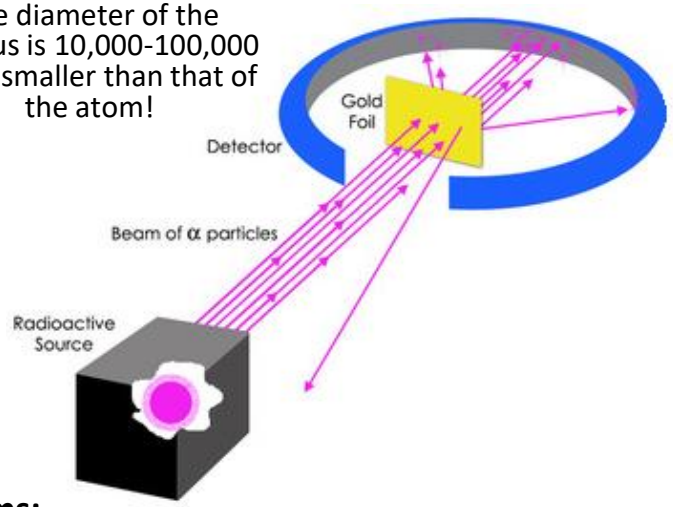
Ernest **Rutherford** (1871-1937)



Rutherford's atomic model: miniature planetary system

Rutherford experiment

The diameter of the nucleus is 10,000-100,000 times smaller than that of the atom!



Problems:

- unstable atom
- electrons: centripetal acceleration - light emission -energy loss - falling into the nucleus

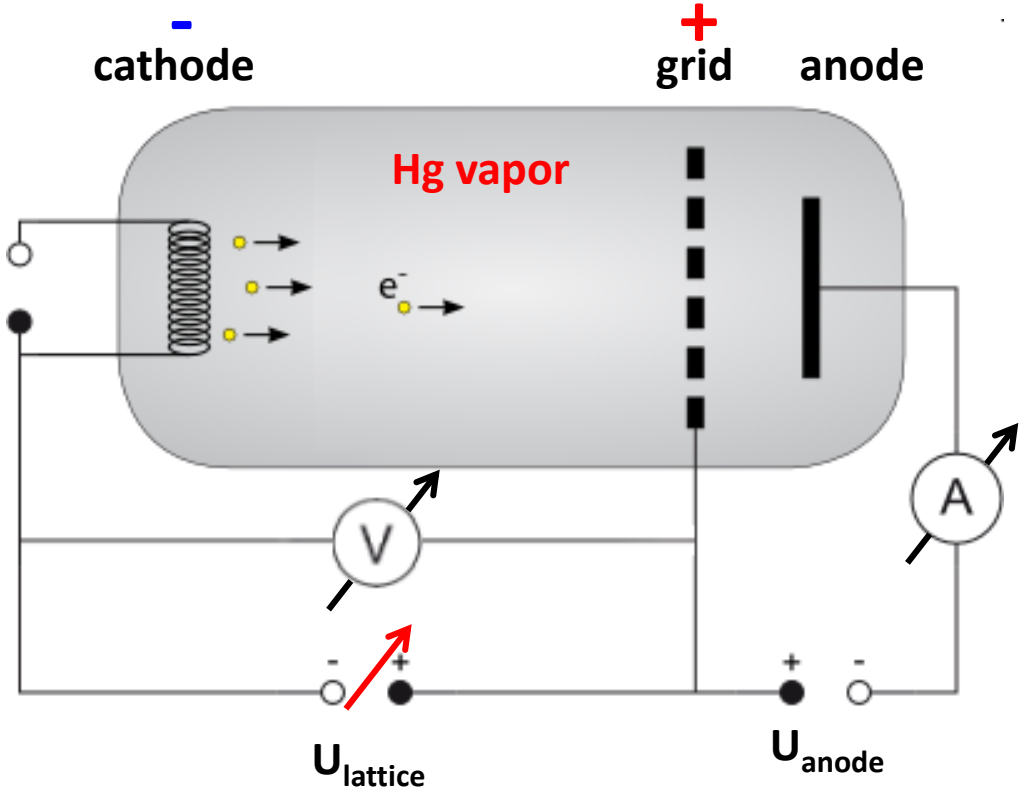
Energy of the atom changes in discrete steps

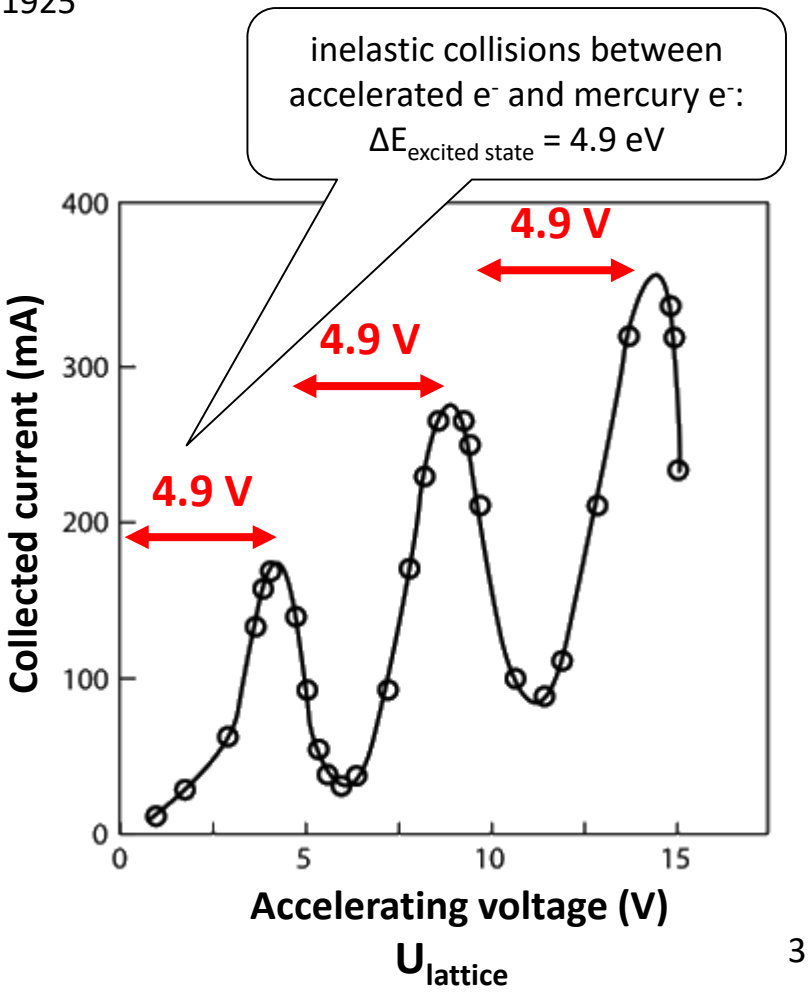

James Franck


Gustav Hertz

Franck-Hertz experiment

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





Bohr model of atom

Niels Bohr
(1885-1962)

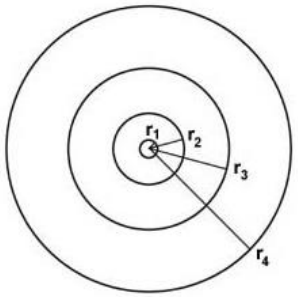
Bohr's postulates

1. Quantum condition:

- The electrons of an atom are on given orbits.
- On the given orbit the electron does not emit radiation, its energy is constant.
- The angular momentum (L) of the orbital electron is an integer multiple of h/2π:

$$L = mvr = n\frac{h}{2\pi}$$

n= principal quantum number. The radii of the orbits can be calculated. The radius of the first orbit is r_1 = 5,3 10^{-11} m ("Bohr-radius"). The radii of the further orbits are: $r_n = n^2 r_1$



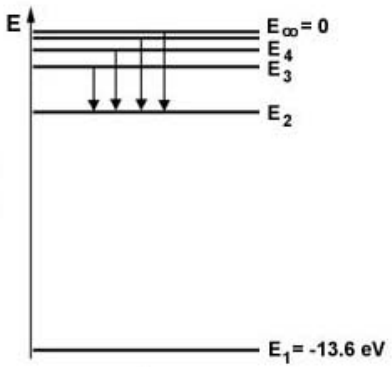
Bohr model of the hydrogen atom

2. Frequency condition:

- The atom radiates (i.e., emits light) only if the electron "jumps" from one orbit to the other.
- Energy of the radiation is the difference between the orbit energies:

$$E_{photon} = h \cdot f = E_2 - E_1$$

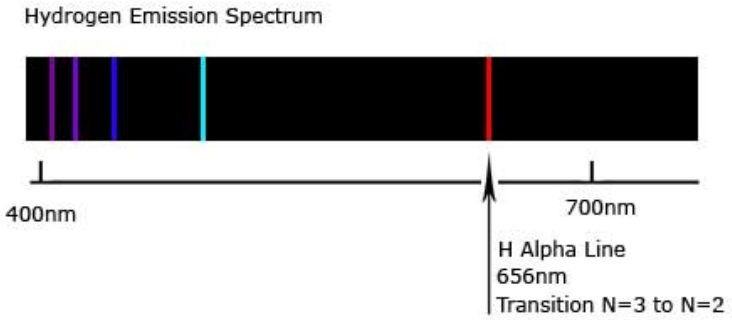
The orbit energies can be calculated. Energy of the first orbit is E_1=-13.6 eV.



Energy levels in the H-atom

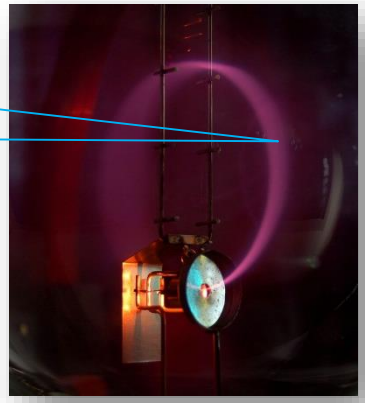
Significance

- The model explained the spectra of the hydrogen atom. But only that of the hydrogen atom.
- Emission spectroscopy
- (Laser)



Particle-wave duality of the electron

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



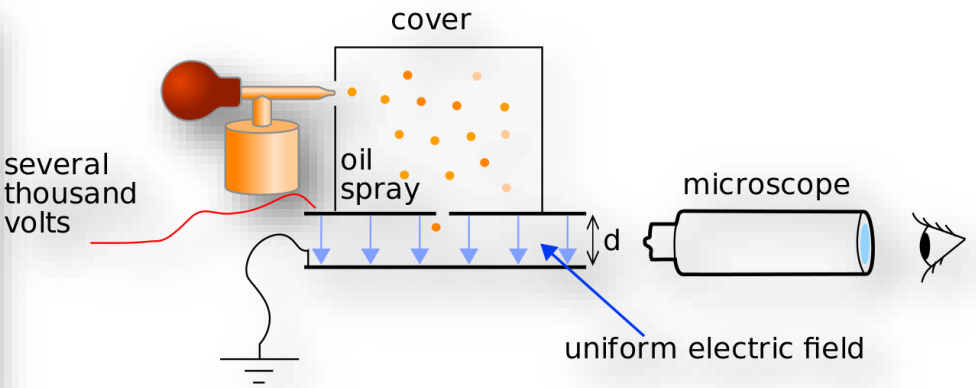
particle

wave

mass

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

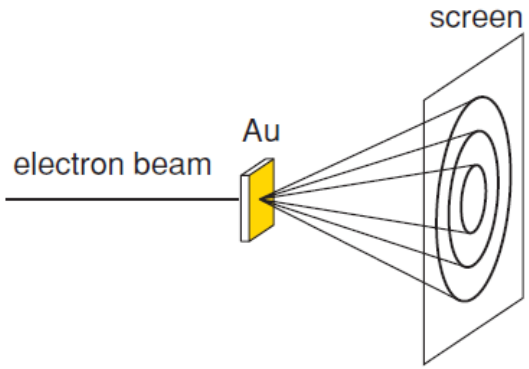
$m_e = 9.1 \cdot 10^{-31}$ kg



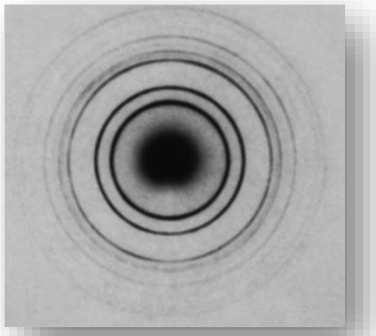
charge

(Millikan, 1910)

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



Davisson and Germer, 1927



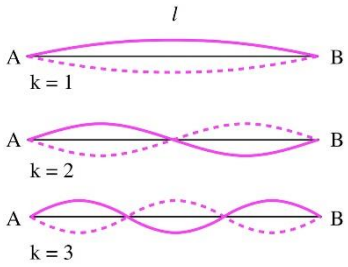
diffraction of fast electrons through a gold foil

Clinton Joseph Davisson (1881 –1958)

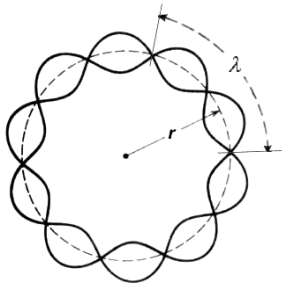
Lester Halbert Germer (1896–1971)

The electron as a wave

Quantized behavior in the **stationary waves of a stretched string**



$$l = k\frac{\lambda}{2}$$



Atomic electron as a standing wave

Quantum condition:

$$2\pi r = n\lambda = n\frac{h}{mv}$$

Propagation law of electron waves

Erwin **Schrödinger** (1887-1961)

Ψ (psi) wavefunction

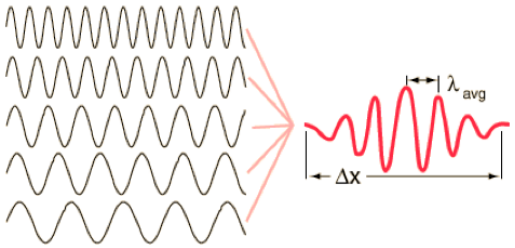
- [**Ψ(x,t)**]: gives the **amplitude of the electron wave** as a function of position (x) and time (t). Allows calculation of electron energies.
- **Ψ^2**: gives the **probability of finding the electron**.
- For a free electron Ψ is a sine wave: momentum is precisely known (p=h/λ), but position (x) entirely unknown.

Wavefunction of freely moving particle (potential energy = 0)

Uncertainty principle

Werner **Heisenberg** (1901-1976)

To localize the wave, we need to superimpose waves of different wavelength (λ) (interference):



Upon spreading λ (Δλ), localization will be more certain (Δx decreases), but it also spreads the momentum values (Δp increases), thereby increasing the uncertainty of determining momentum:

$$\Delta x \cdot \Delta p \geq \frac{h}{2\pi}$$

Matter waves

Einstein: mass-energy equivalence

$$E = mc^2$$

Planck: law of radiation

$$E = hf$$

Maxwell: speed of light

$$c = \lambda f$$

Louis-Victor-Pierre-Raymond, 7th duc **de Broglie** (1892-1987)

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

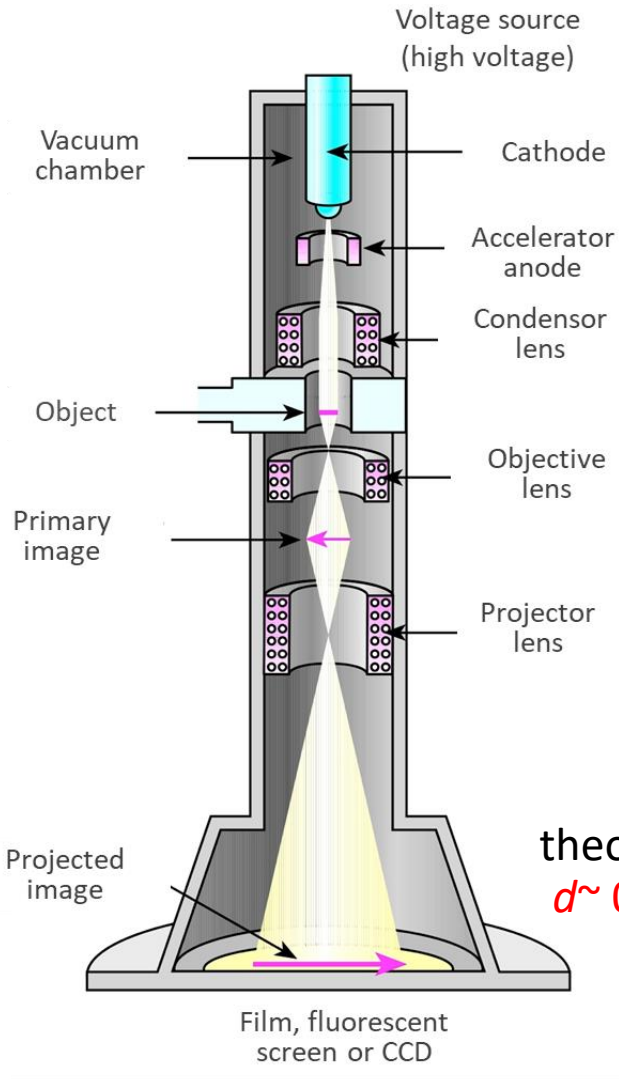
Momentum of particle (or photon!):

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

Wavelength of particle ("de Broglie wavelength"):

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

Transmission electron microscope (TEM)



Resolution:

$$d = \frac{\lambda}{\alpha}$$

d=smallest resolved distance

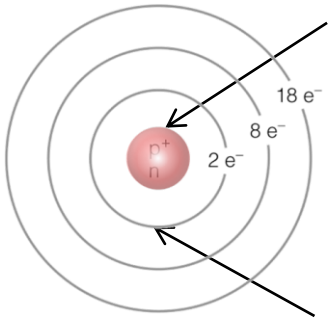
λ="de Broglie" wavelength

α=angle between the optical axis and the direction of the magnetic field

theoretical resolution:

d~ 0,005 nm (=5 pm)

Atom: Quantum mechanical model



nucleus, including:

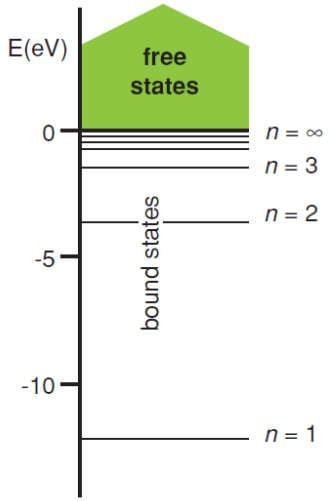
- protons (p^+)
- neutrons (n_0)

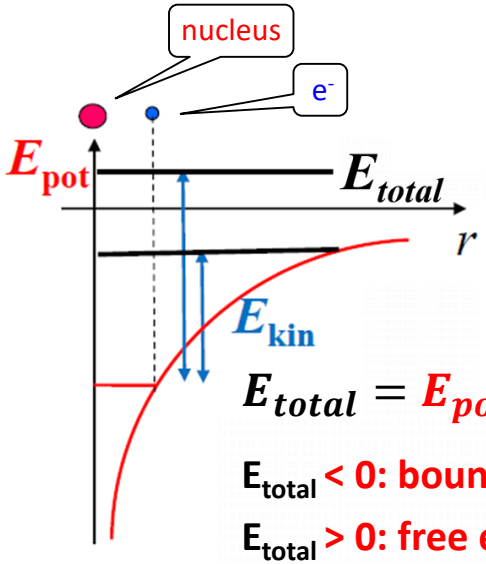
$$Q_{total,nucl} = Z \cdot e$$

electrons

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

Z: atomic number





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

E_{total} < 0: bound electron

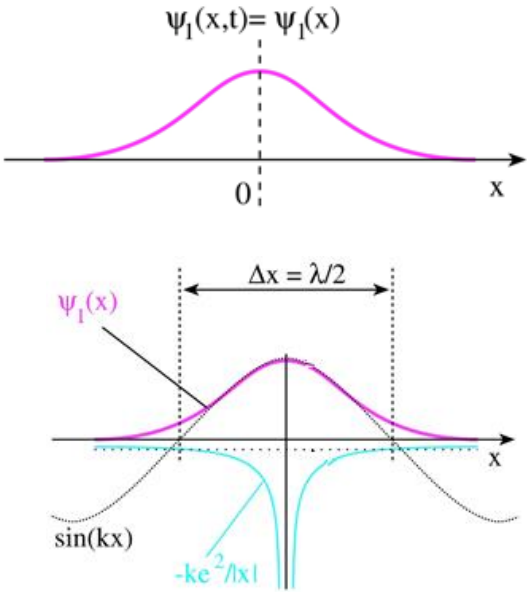
E_{total} > 0: free electron

Quantum mechanics

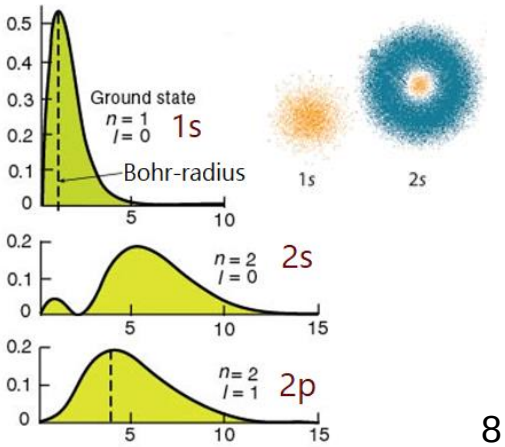
1. describes the states of the electron
(one state → one wavefunction, Ψ)

2. calculates the electron's most probable location (orbital, r) and energy (E)

In the atom, Coulombic attraction determines the potential energy.



Probability of finding the electron in the atom:



Quantum numbers

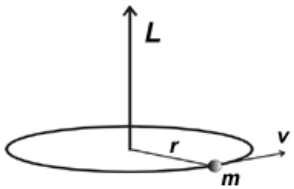
name	symbol	orbital meaning	range of values	value example
principal quantum number	n	shell	$1 \leq n$	$n = 1, 2, 3...$
azimuthal quantum number (angular momentum)	ℓ	subshell	$(0 \leq \ell \leq n-1)$	for $n = 3$: $\ell = 0, 1, 2\ (s, p, d)$
magnetic quantum number, (projection of angular momentum)	m_ℓ	energy shift	$-\ell \leq m_\ell \leq \ell$	for $\ell = 2$: $m_\ell = -2, -1, 0, 1, 2$
spin projection quantum number	m_s	spin	$-\frac{1}{2}, \frac{1}{2}$	for an electron, either: $-\frac{1}{2}, \frac{1}{2}$

1. Energy

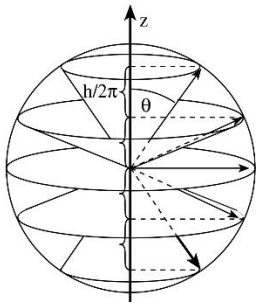
Energy of the electron in a given quantum state

2. Angular momentum

absolute value



direction



3. Spin

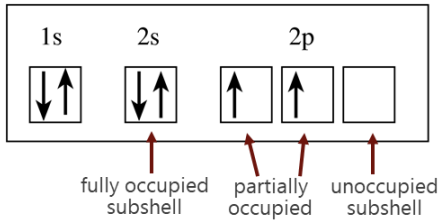
intrinsic angular momentum and magnetic momentum

Pauli's exclusion principle

- Each quantum state can be occupied by a single electron.
- Within an atom there cannot be two electrons for which all four quantum numbers are identical.

Hund principle

- Order of filling up the quantum states.
- For a given electron configuration, the state with maximum total spin has the lowest energy.

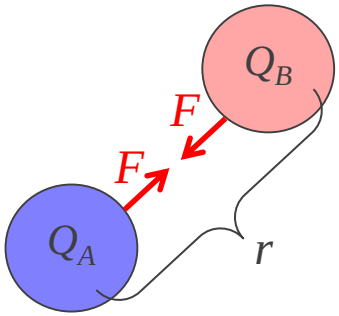


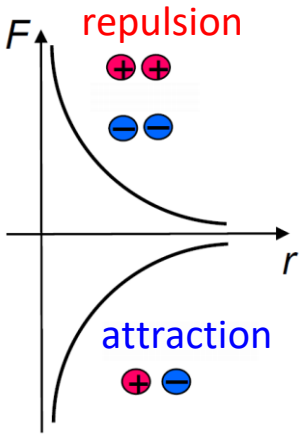
When assigning electrons to orbitals, an electron first seeks to fill all the orbitals with similar energy.

Molecules: fundamental interactions in physics

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

Coulomb-interaction

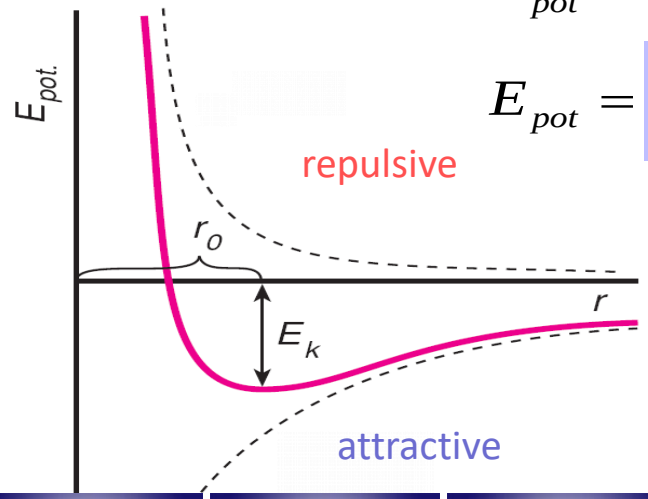




$$F_C = k \cdot \frac{Q_A \cdot Q_B}{r^2}$$

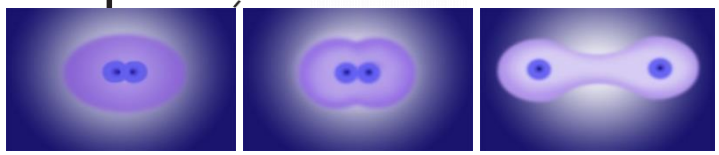
$$E_{pot} = E_{attraction} + E_{repulsion}$$

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



A, B: constants that depend on the interaction and the atoms

n (attraction) < *m* (repulsion)



r_0: binding distance

E_k: binding energy

Primary bonds

„tendency of an atom to attract electrons"

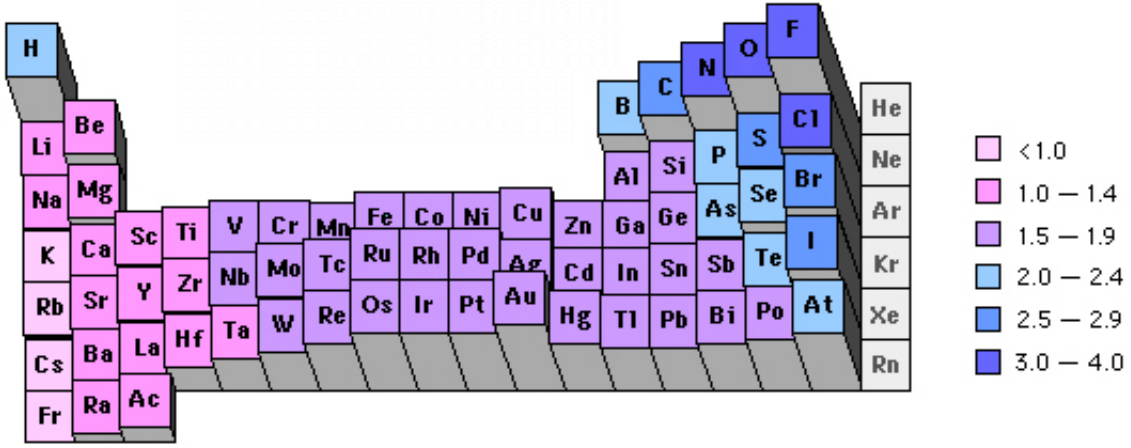
- **covalent:** common electron state around the participating nuclei, strong: $E_b > 1eV$
- **metallic bond:** multi-atomic system, $E_b > 1eV$
- **ionic bond:** Coulomb-forces between ions, $E_b > 1eV$

type depends from electronegativity (EN)

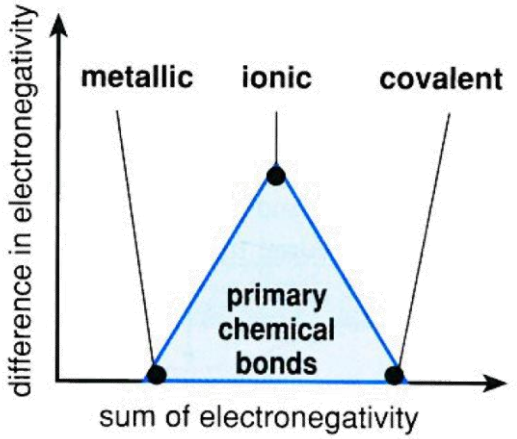
$$EN = |E_i| + |E_{ea}|$$

ionization energy

electron-affinity

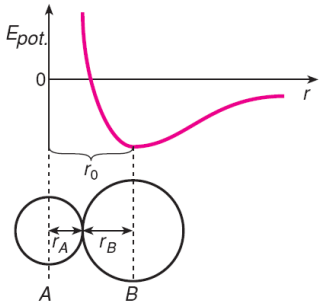


EN values according to Pauling

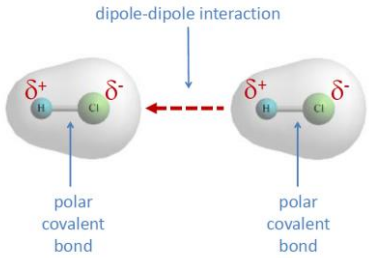


Secondary bonds

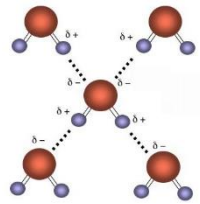
- **Van der Waals:** between two apolar atoms (without permanent dipole moment) where a temporarily created dipole interacts with an apolar molecule or atom thus converting it into a dipole (induced dipole)
  - Van der Waals radius: $r_0 = r_A + r_B$
  - Intermolecular or intramolecular
  - Important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



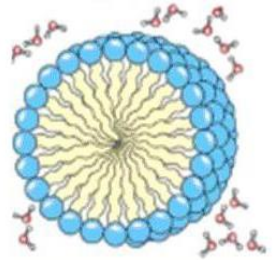
- **Dipole-dipole interaction:** constant charge distribution is present in a (given part of a) molecule
  - partially (+) and (-) segments are held together by electrostatic interactions (Coulomb-forces)
  - intra-/intermolecular
  - weak interaction (E_b = 0.003-0.02 eV)



- **H-bond:** H-atom interbridges two other atoms (F, O, N) of high electronegativity
  - r ~ 0,23 - 0,35 nm
  - E_b ~ 0,2 eV



- **Hydrophobic interaction:** weak Van der Waals interaction (Eb = 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)

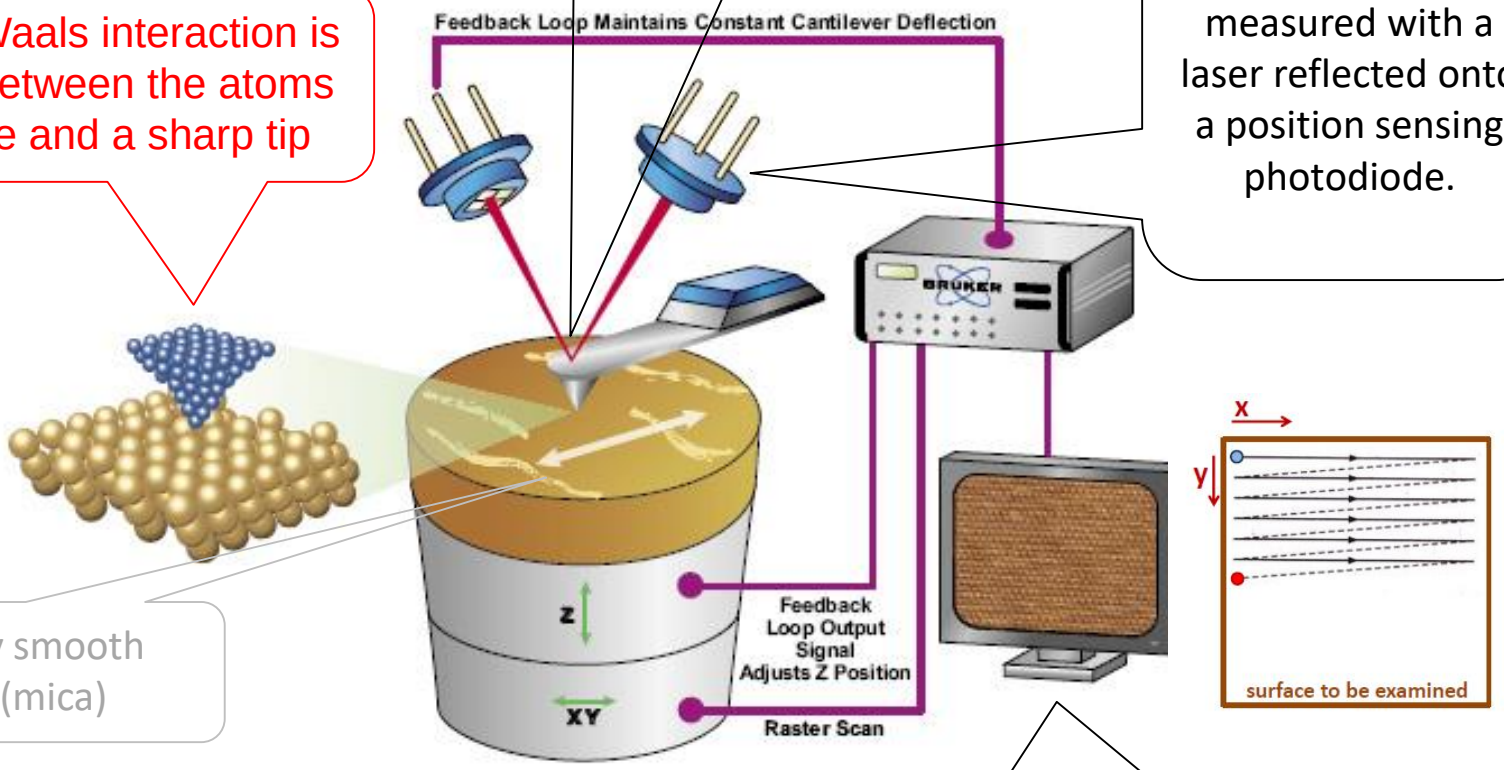


Atomic force microscope (AFM)

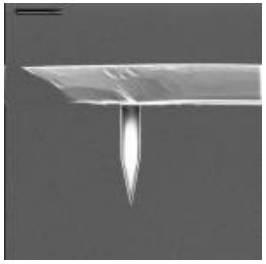
1. Van der Waals interaction is measured between the atoms of a sample and a sharp tip

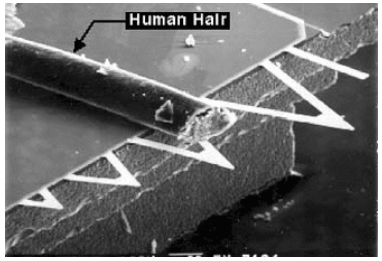
2. The tip is deflected due to the Van der Waals forces.

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



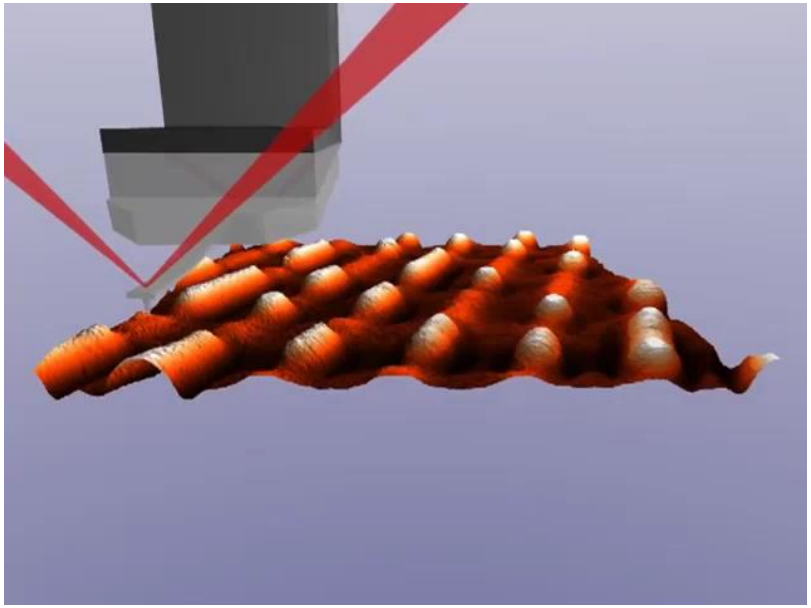
atomically smooth surface (mica)

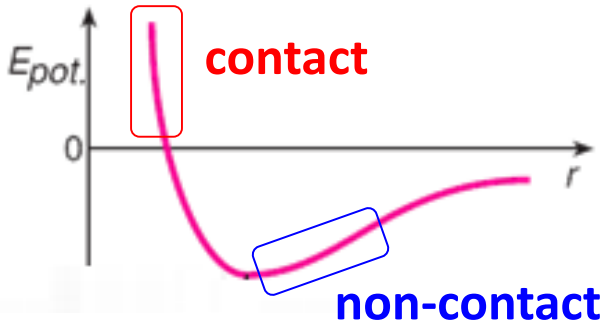




4. The cantilever is scanned in X-Y-Z directions: atomic resolution with raster scan.

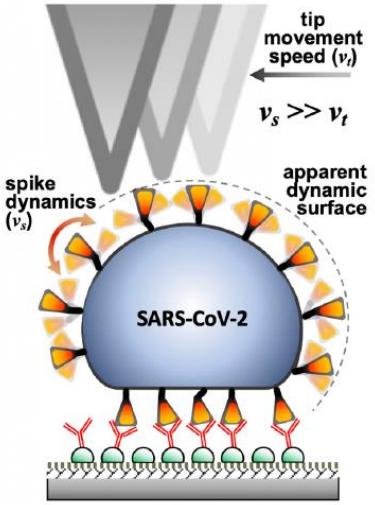
AFM operating modes

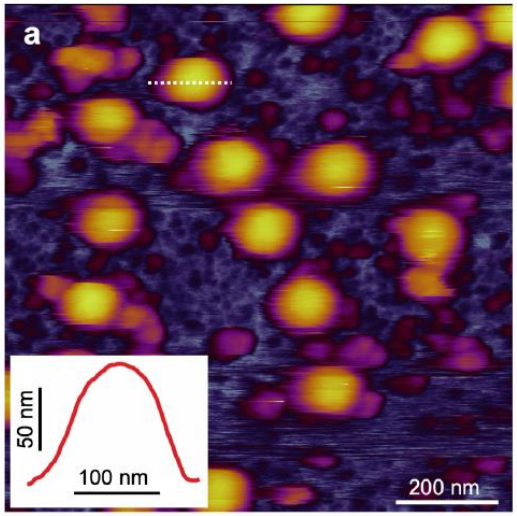


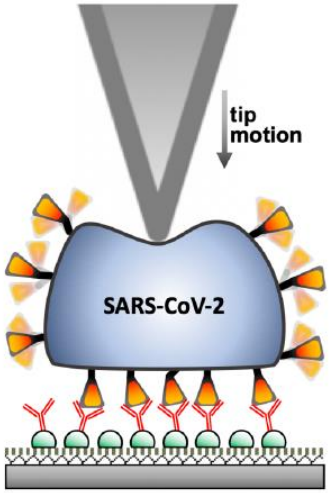


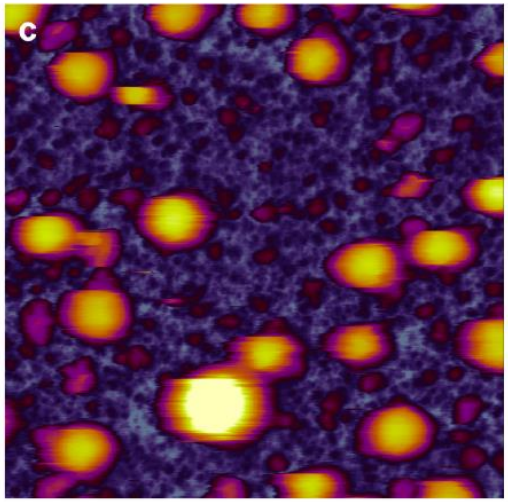
- **Contact:** the tip touches the surface, the **deflection of the cantilever** (i.e. the force exerted on the sample by the tip) is held **constant**.
  - **Z-feedback** system: deflection is maintained at a constant value (setpoint) by lifting or lowering the cantilever.
  - **topography data** (i.e.: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

Native SARS-CoV-2 imaged in our lab









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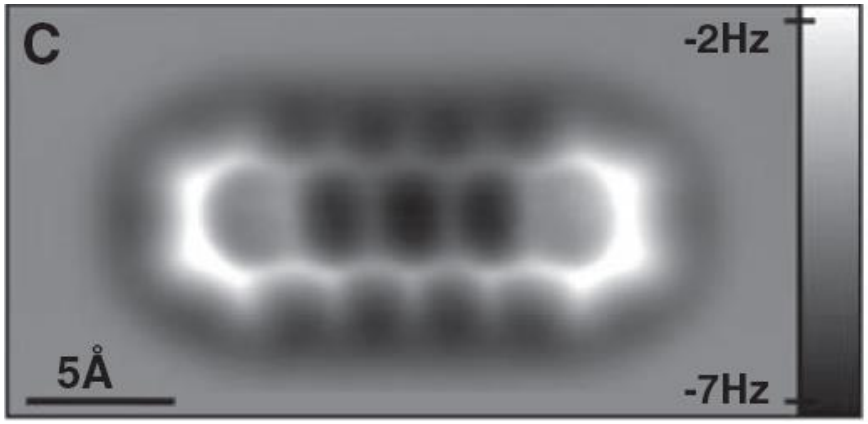
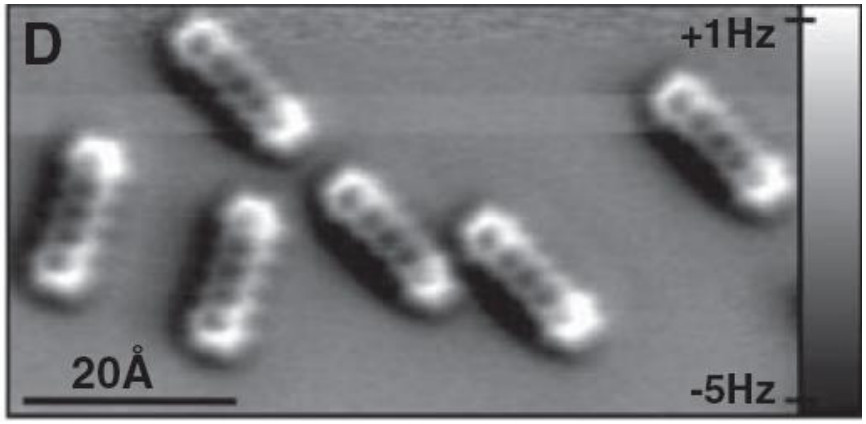
Pentacene molecule





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