PHOT 301: Quantum Photonics

LECTURE 25

Michaël Barbier, Fall semester (2024-2025)

QUANTUM MECHANICS OF MATTER

TYPES OF MATTER

- Materials:
  - single atoms,
  - molecules,
  - crystalline materials,
  - amorphous materials
- Materials can consist of many atoms

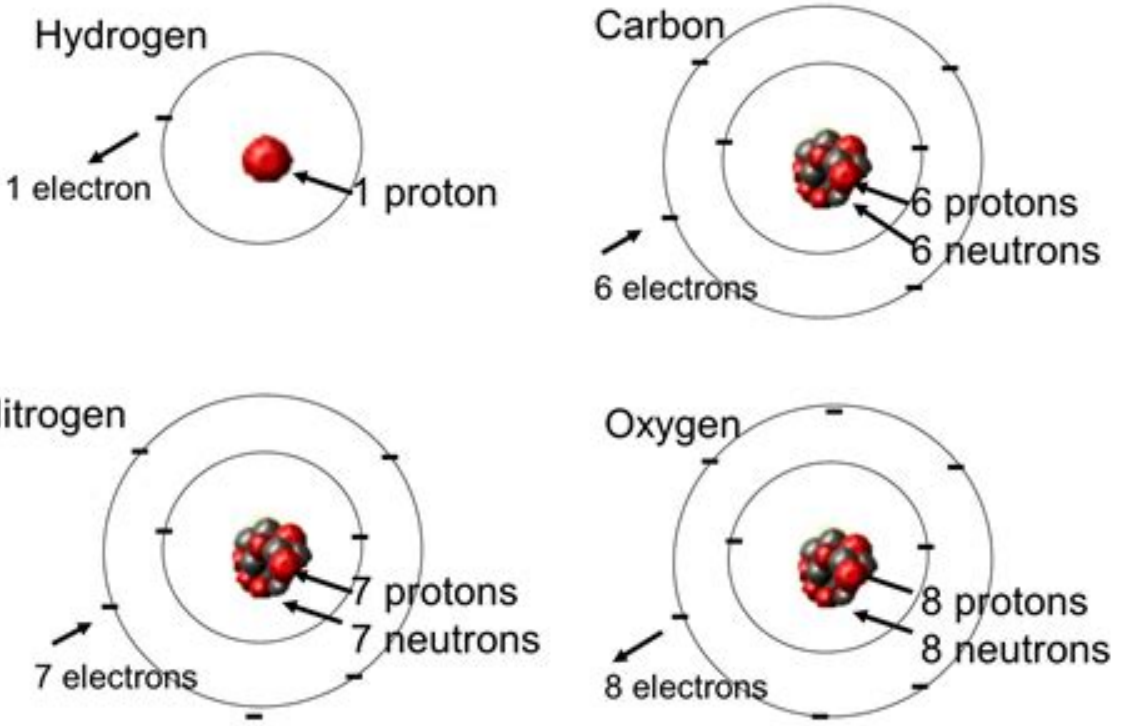
Classical description of matter:

- Continuum approximation: volumes with properties
  - Electric/heat conductivity
  - Elasticity, mass, etc.

How can we describe matter with *Quantum mechanics*?

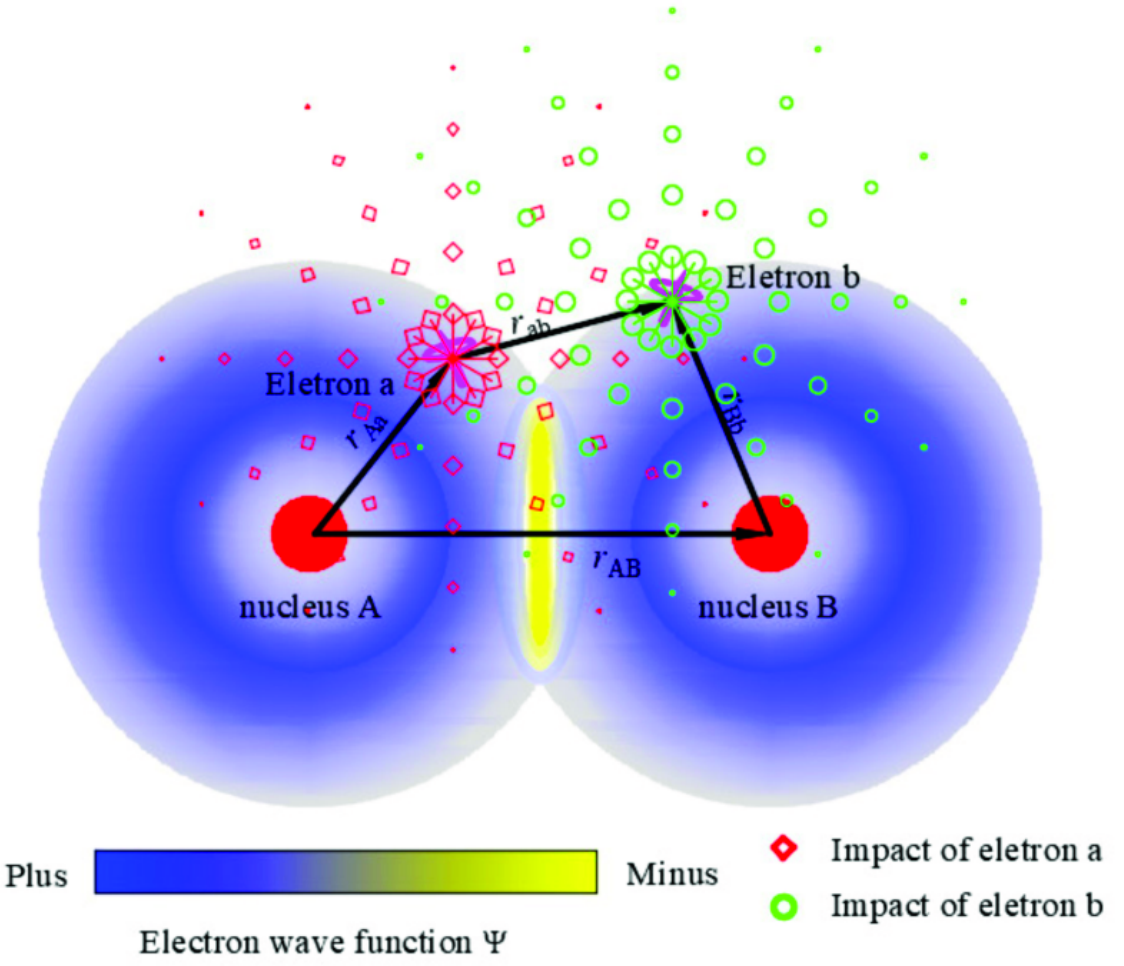
MATTER: SINGLE ATOMS

- Materials:
  - single atoms,
  - molecules,
  - crystalline materials,
  - amorphous materials
- Materials consist of many atoms



MATTER: MULTIPLE ATOMS

- Materials:
  - single atoms,
  - molecules,
  - crystalline materials,
  - amorphous materials
- Materials can consist of many atoms
- Describing electrons in matter:
  - (Relative) positions of the nuclei
  - Positions of the electrons
  - Interactions between all nuclei and all electrons



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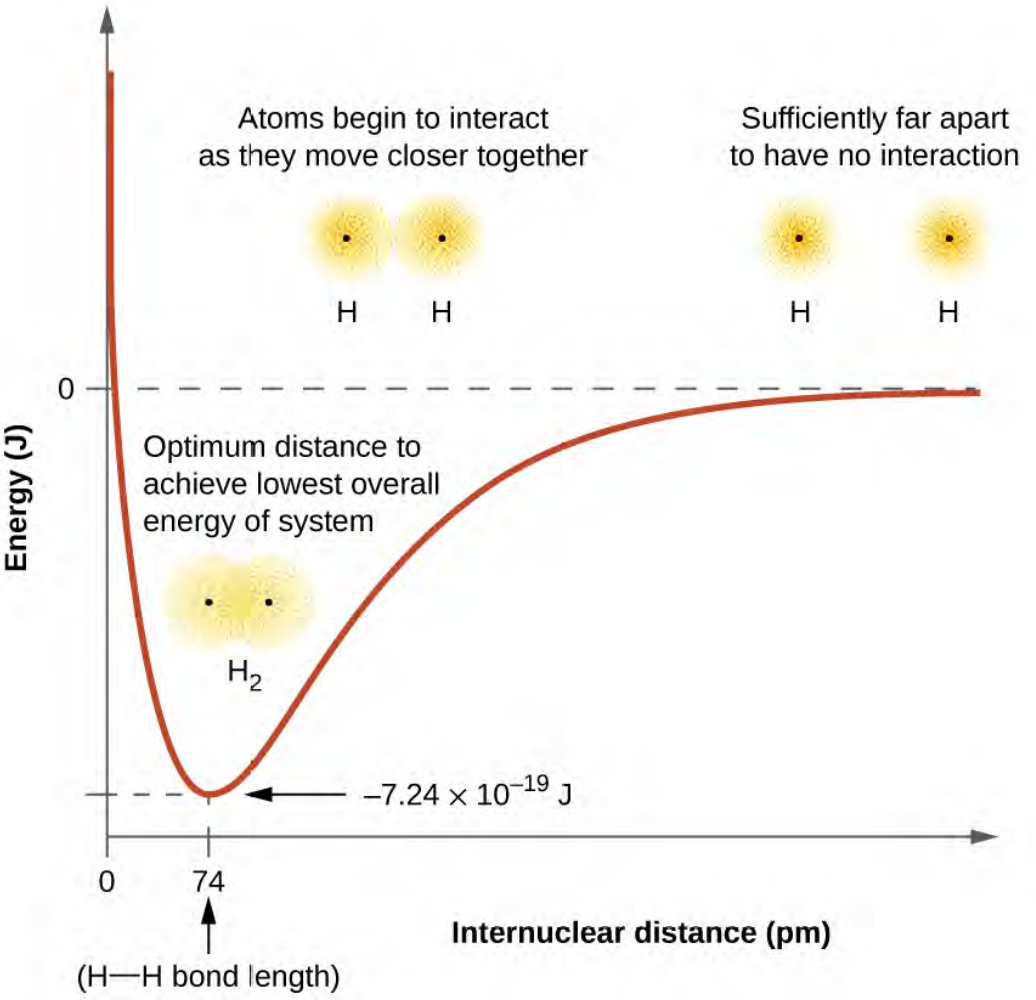
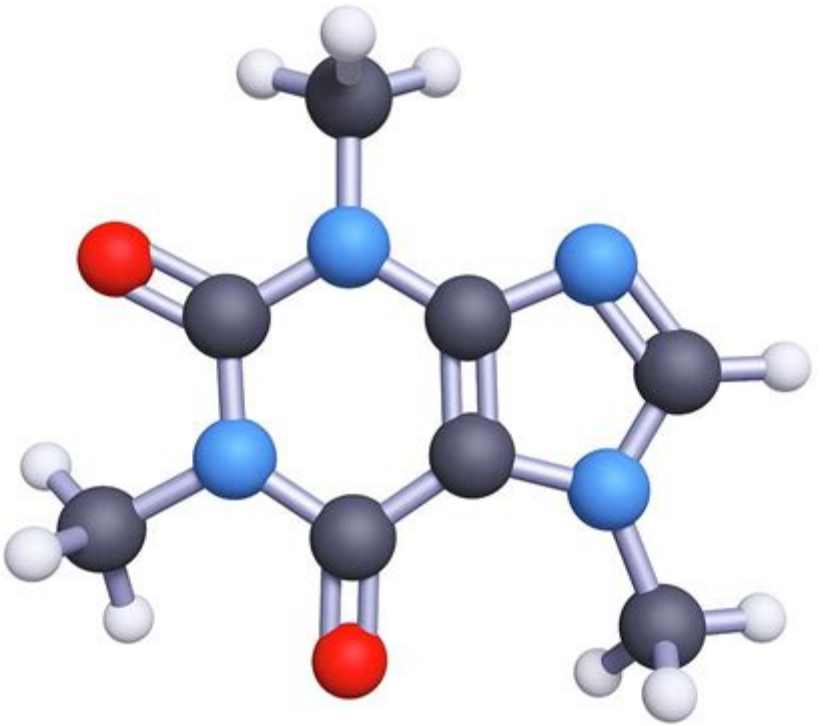


MATTER: MOLECULES

- Materials:
  - single atoms,
  - molecules,
  - crystalline materials,
  - amorphous materials

- **Covalent** bonds
- Electronic interactions
- Configuration in space
- Vibrations

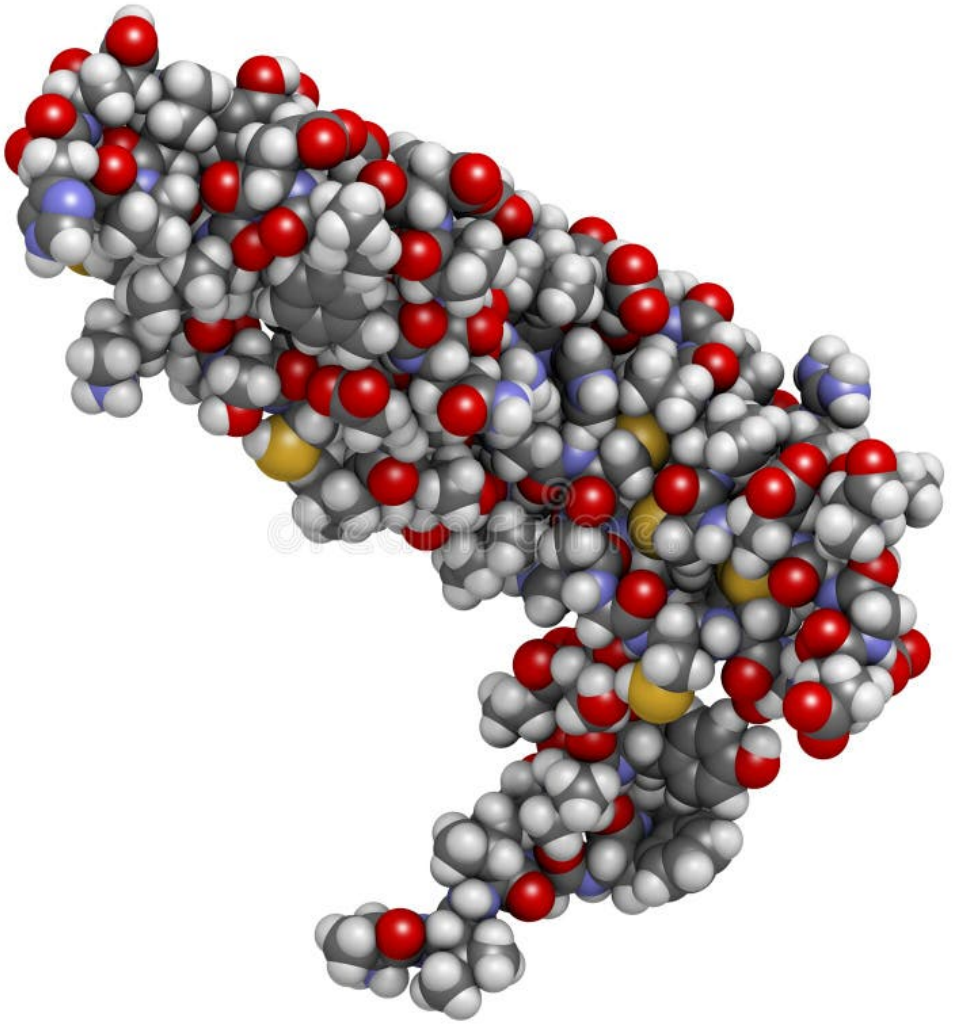
Molecules consist of multiple atoms:



Caffeine
$C_8H_{10}N_4O_2$

MATTER: LARGE MOLECULES

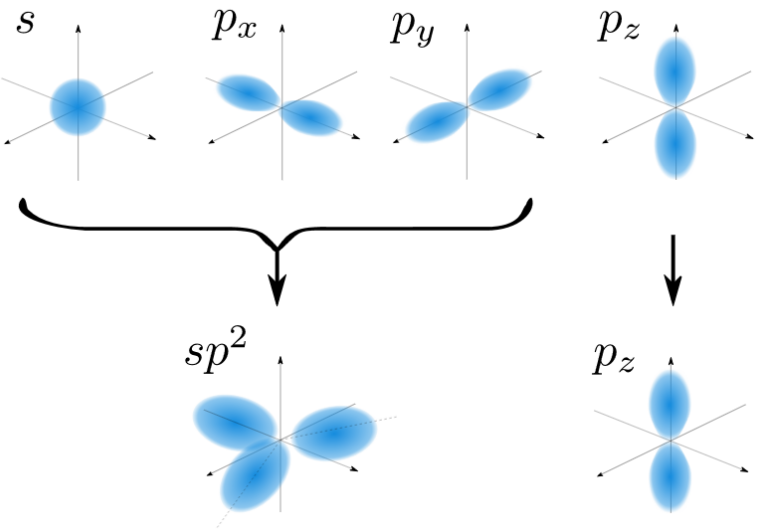
- Materials:
  - single atoms,
  - molecules,
  - crystalline materials,
  - amorphous materials



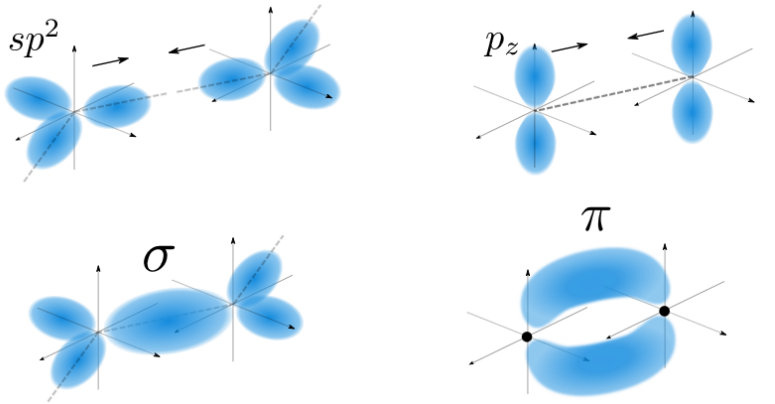
- Covalent bonds
- Electronic interactions
- **Configuration in space**
- Vibrations

COVALENT BONDS

- Superposition of orbitals: sp^2-**hybridization**
  - Orbitals in the plane
  - s-orbital is now symmetric with p-orbitals
- Improved orbital overlap/access to all electrons



- σ-**bonds**: Strong overlap between sp^2-hybridized orbitals
- π-**bonds**: Less overlap between p_z-orbitals but also in the plane



TIGHT-BINDING / LCAO

- Tight-binding method assumes electrons close to nuclei
- Wave functions are **Linear Combinations of Atomic Orbitals** (LCAO)
- Example of a molecule with two atoms:

$$\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V}_1 + \hat{V}_2$$

Eigenstates atomic orbitals:

$$(\frac{\hat{p}^2}{2m} + \hat{V}_1)|1\rangle = \varepsilon_0 \, |1\rangle$$
$$(\frac{\hat{p}^2}{2m} + \hat{V}_2)|2\rangle = \varepsilon_0 \, |2\rangle$$

TIGHT-BINDING / LCAO

Assume Linear Combination of Atomic Orbitals:

$$|\psi\rangle = \phi_1 |1\rangle + \phi_2 |2\rangle$$

with ϕ_j amplitude of jth atom orbital and $\langle 1|2\rangle = 0$

$$\hat{H}|\psi\rangle = E|\psi\rangle = \phi_1 E|1\rangle + \phi_2 E|2\rangle$$

Multiply to the left with bra's $\langle 1|$ and $\langle 2|$

$$E\phi_1 = \phi_1\langle 1|\hat{H}|1\rangle + \phi_2\langle 1|\hat{H}|2\rangle$$
$$E\phi_2 = \phi_2\langle 2|\hat{H}|1\rangle + \phi_2\langle 2|\hat{H}|2\rangle$$

This gives us a new *Hamiltonian*

$$\Longrightarrow \begin{pmatrix} \langle 1|\hat{H}|1\rangle & \langle 1|\hat{H}|2\rangle \\ \langle 2|\hat{H}|1\rangle & \langle 2|\hat{H}|2\rangle \end{pmatrix} \begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix} = E \begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix}$$

Lecture 25: Molecules and Tight-binding method

TIGHT-BINDING / LCAO

$$\Longrightarrow \begin{pmatrix} \langle 1|\hat{H}|1\rangle & \langle 1|\hat{H}|2\rangle \\ \langle 2|\hat{H}|1\rangle & \langle 2|\hat{H}|2\rangle \end{pmatrix} \begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix} = E \begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix}$$

- The diagonal elements $\langle j|\hat{H}|j\rangle = E_0$ represent the onsite energy
- The off-diagonal elements $\langle 1|\hat{H}|2\rangle = -t$ represent the hopping term

$$\Longrightarrow \begin{pmatrix} E_0 & -t \\ -t & E_0 \end{pmatrix} \begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix} = E \begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix}$$

- This eigenvalue equation has eigenvalues/eigenstates:

$$E_\pm = E_0 \mp t, \qquad \psi_\pm = \frac{1}{\sqrt{2}}(|1\rangle \pm |2\rangle)$$

Lecture 25: Molecules and Tight-binding method

TIGHT-BINDING

$$\begin{pmatrix} E_0 & -t \\ -t & E_0 \end{pmatrix} \begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix} = E \begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix}$$

$$E_\pm = E_0 \mp t$$

$$\psi_\pm = \frac{1}{\sqrt{2}}(|1\rangle \pm |2\rangle)$$