# Theoretical methods of surface and solid state chemistry

**Surface chemistry** is a branch of chemistry related to the study of the chemical and phase structure of the surface and its influence on the properties of solids, with chemical reactions on the surface of solids.

**Solid-state chemistry** is a branch of chemistry that studies various aspects of solid-phase substances, in particular, their synthesis, structure, properties, applications, etc. The objects of her research are crystalline and amorphous, inorganic and organic substances.

# Theoretical methods of solid state chemistry

Quantum chemistry and molecular dynamics
Thermodynamics of a solid state
Chemical kinetics

The main goal of the theoretical calculations is to establish the “structure-property” relationships in various molecular systems and to implement the strategies for the directed design of new materials on this basis.

The basis of the theoretical calculations of the chemical structure of solids - methods of quantum chemistry of solids and statistical thermodynamics of complex systems.

# Quantum chemistry of solid state

**Topic 1. Electrical conductivity of solid bodies.**

**One-electron approximation (Hückel method) and band theory of solids. Electric and magnetic properties from the point of view of band theory**

**Topic 2. Multi-electron models in the quantum chemistry of nanostructured materials: Valence bond method, Heisenberg and Hubbard models. Lieb theorem and magnetic structure of solids.**

**Topic 3. Theoretical modeling of thermodynamic properties of solids. Low-temperature thermodynamics of nanomaterials.  Transfer matrix method.**

# One-electron methods in solid state theory

## The method of molecular orbitals

### Orbital approximation:

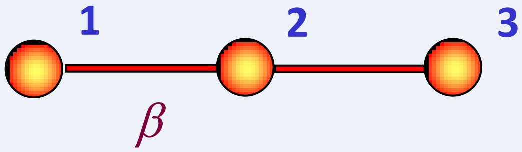
$$\Psi(1,2,\cdots N)=\Psi_1(1)\Psi_2(2)\cdots\Psi_N(N)$$

**A molecular orbital is the space area where an electron is most likely to be in the electric field of the atoms that make up the molecule**

$$\Psi_n=\sum_{k=1}^{N}a_{k,n}\varphi_k$$

# The allylic radical in Hückel method

$C_3H_5$



$$\left\{\begin{aligned} \alpha\, a_{1,n} + \beta\, a_{2,n} &= \varepsilon_n\, a_{1,n} \\ \alpha\, a_{2,n} + \beta\, a_{1,n} + \beta\, a_{3,n} &= \varepsilon_n\, a_{2,n} \\ \alpha\, a_{3,n} + \beta\, a_{2,n} &= \varepsilon_n\, a_{3,n} \end{aligned}\right. \Rightarrow \begin{vmatrix} \alpha-\varepsilon & \beta & 0 \\ \beta & \alpha-\varepsilon & \beta \\ 0 & \beta & \alpha-\varepsilon \end{vmatrix} = 0$$

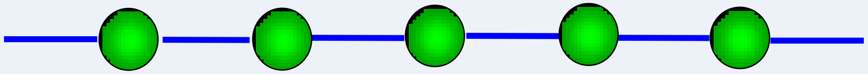
$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0 \Rightarrow x\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} - \begin{vmatrix} 1 & 0 \\ 1 & x \end{vmatrix} = 0 \Rightarrow x^3 - 2x = 0$$

$$x = \frac{\alpha-\varepsilon}{\beta}$$

$$x = 0,\ \pm\sqrt{2} \rightarrow \varepsilon = \alpha,\ \alpha \pm \sqrt{2}\beta$$

$$x = 0 : a_2 = 0,\quad x = \pm\sqrt{2} : a_2 = \pm 1/\sqrt{2}$$

# Energy spectrum of polyacetylene

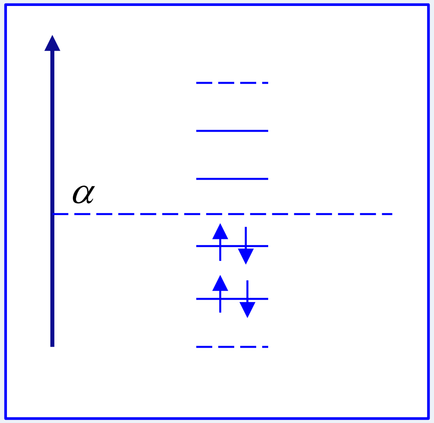


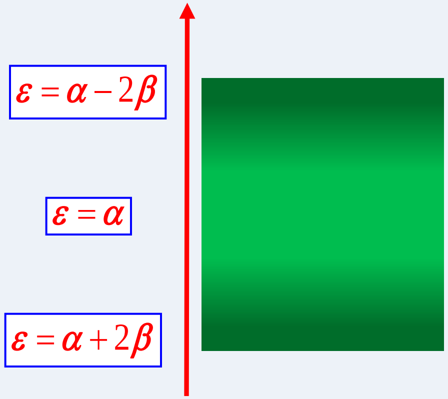
$$\begin{cases} (\alpha-\varepsilon)a_1+\beta a_2+\beta a_N=0 \\ \beta a_1+(\alpha-\varepsilon)a_2+\beta a_3=0 \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ \beta a_1+\beta a_{N-1}+(\alpha-\varepsilon)a_N=0 \end{cases}$$

**Use of translational symmetry**

$$\varphi_n=\sum_{m=1}^{N}a_{m,n}f_m, \quad a_{m,n}=\frac{1}{\sqrt{N}}\exp\left(i\frac{2\pi}{N}mn\right)$$

$$\varepsilon_n=\alpha+2\beta\cos\left(\frac{2\pi}{N}n\right), \quad n=1,2,\ldots N$$





# Ground state energy and low-energy excitations

**The sum over the filled states**

$$E_0 = N\alpha + 4\beta \sum_{|k|\le\frac{\pi}{2}} \cos(k)$$

$$E_0 = N\alpha + \frac{2\beta N}{\pi}\int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \cos(k)\,dk = N\left(\alpha + \frac{4\beta}{\pi}\right)$$

**The energy of one electron moving in the field of an ion chain: the quasi-particle nature of low-energy excitations**

$$\lambda = \alpha + 2\beta\cos(k) = \alpha + 2\beta - \beta\left(\frac{2\pi a}{L} l\right)^2, \quad l = 0, 1, 2 \ldots << N$$

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi(x)}{(dx)^2} = \lambda\Psi(x) \to \lambda = \frac{h^2 l^2}{2mL^2}$$

$$m = \frac{\hbar^2}{2|\beta|\,a^2}$$