Introduction to band structures

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March 2025

POLISH NATIONAL AGENCY
FOR ACADEMIC EXCHANGE

Hückel theory: basics

- Linear combination of atomic orbitals as in HF but simplified
- One identical atomic orbital at each center (here: 2p-orbital $\perp$ to molecular plane)
- Parametrize the integrals $S_{\mu\nu} = \delta_{\mu\nu}$
  $H_{\mu\nu} = \alpha\delta_{\mu\nu}$ and $H_{\mu\nu} = \beta$ if μ and ν neighbours
  α is the negative ionization potential of the atomic orbital
  β is the hopping integral (negative energy)
- Ethylen

$$H = \begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix} = \alpha \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \beta \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \alpha 1 + \beta T$$

- T topological matrix contains the structural information
- Solve $HC = \epsilon C$ to obtain orbitals and orbital energies

Hückel theory: ring with N atoms

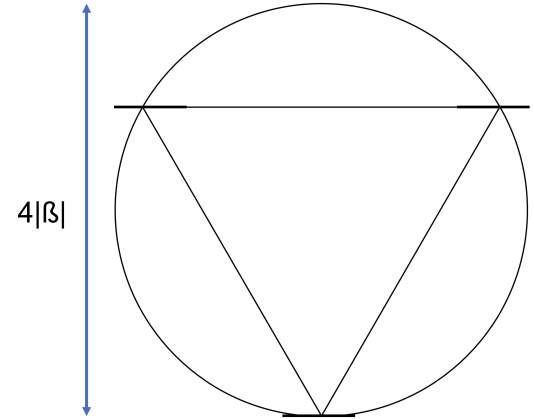
- Most famous example for Hückel theory: Bonding situation in benzene
- Topological matrix for rings $T = \begin{pmatrix} 0 & 1 & 0 & 0 & \cdots & 0 & 1 \\ 1 & 0 & 1 & 0 & \cdots & 0 & 0 \\ 0 & 1 & 0 & 1 & \cdots & 0 & 0 \\ \vdots & & \vdots & & & \vdots & \\ 1 & 0 & 0 & 0 & \cdots & 1 & 0 \end{pmatrix}$
- Ring closure: $T_{1N} = T_{N1} = 1$
- Each atom has two neighbours, identical interactions, correct symmetry.
- Analytical solutions available.
- The finite rings have the point group symmetry C_n, rotation around the axis.

Hückel rings: 3 atoms

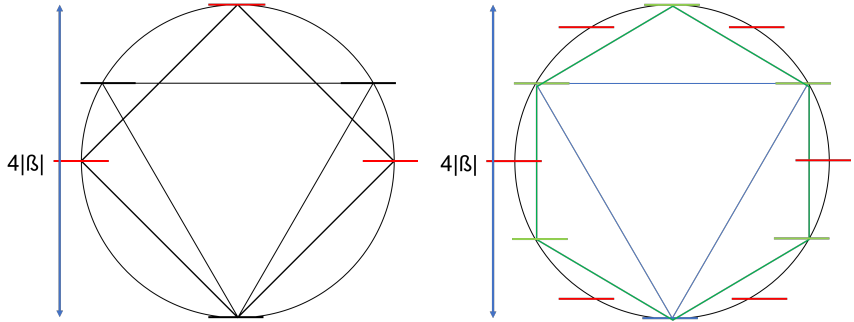
$$H = \begin{pmatrix} \alpha & \beta & \beta \\ \beta & \alpha & \beta \\ \beta & \beta & \alpha \end{pmatrix}$$

Solve Hückel equation
$\epsilon_0 = \alpha - 2\beta$ and $\epsilon_{+1/-1} = \alpha + \beta$

Orbitals
$\varphi_0 = \frac{1}{\sqrt{3}}(\chi_0 + \chi_1 + \chi_{-1})$
$\varphi_1 = \frac{1}{\sqrt{2}}(\chi_1 - \chi_{-1})$
$\varphi_{-1} = \frac{1}{\sqrt{6}}(2\chi_0 - \chi_1 - \chi_{-1})$

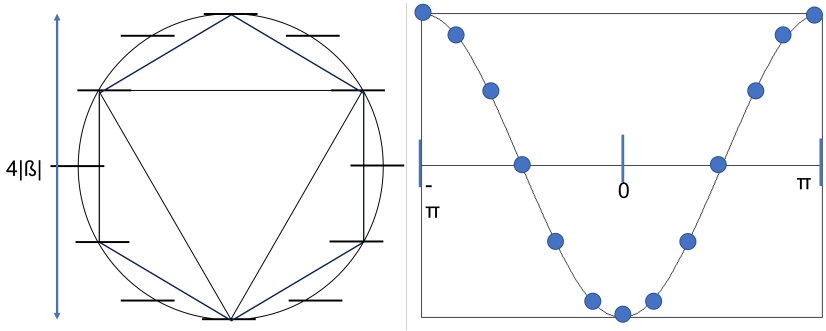


Hückel rings



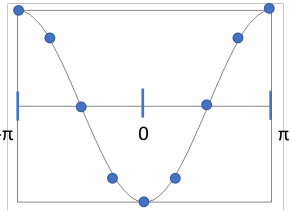
- Frost Musulin diagram
  draw a circle with radius 2β and position the ring with an atom at the bottom
- Orbital energies correspond to the position of the edges

Hückel rings to band structure



- Orbital energies
  $\epsilon_j = \alpha + 2\beta \cos \frac{2\pi j}{N}$ with $j =]-\frac{N}{2}, \frac{N}{2}], j \in \mathbb{Z}$ draw a circle with radius 2β and position the ring with an atom at the bottom
- With increase of N more and more orbitals are added. Gets continuous for $N \to \infty$

Hückel rings to band structure: continued

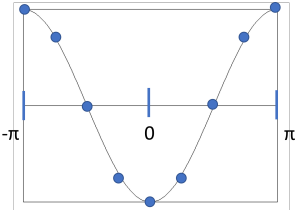


Orbitals

$$\varphi_j = \sum_{m=-\frac{N}{2}}^{\frac{N}{2}} \exp\left(\frac{\mathrm{i}2\pi jm}{N}\right)\chi_m$$

- Bloch orbitals
- $\varphi_j = \varphi^*_{-j}$ are conjugate complex pairs with $\epsilon_j = \epsilon_{-j}$.
- j defines the phase structure of the Bloch orbital (k-space symmetry)
- φ_0 has the same phase in every cell. Γ-point in k-space

1D band structure



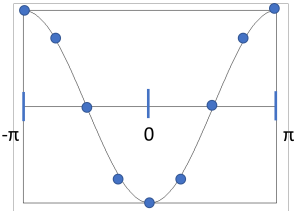
Orbitals

$$\varphi_j = \sum_{m=-\frac{N}{2}}^{\frac{N}{2}} \exp\left(\frac{\mathrm{i}2\pi jm}{N}\right)\chi_m$$

- For $N \to \infty$ continuous band and each Bloch orbital is an infinite sum
- Define continuous index $k \in [-\frac{\pi}{a}, \frac{\pi}{a}]$, a is the lattice constant in a 1D chain.

$$\varphi_k = \sum_{m=-\infty}^{\infty} \exp(\mathrm{i}km)\chi_m$$

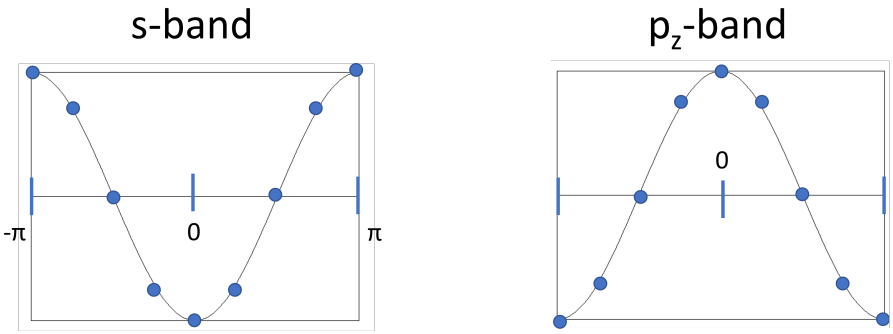
Born-von Karman periodic boundary conditions



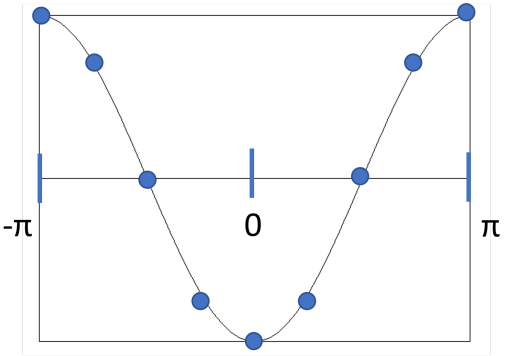
- For continuous k orbitals and electrons cannot easily be counted
- Define a large number of atoms N and assume periodic boundary conditions after that number of atoms
- Number of atoms defines a grid of equidistant k-points
- Number of atoms defines the number of electrons
- Works as in the rings and can be extended to 2D and 3D

$$k = \frac{\pi j}{aN}, j \in]-\frac{N}{2}, \frac{N}{2}], j \in \mathbb{Z}$$

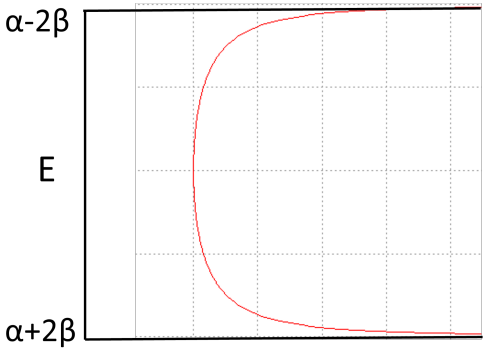
Form of the bands



Density of states



Band structure

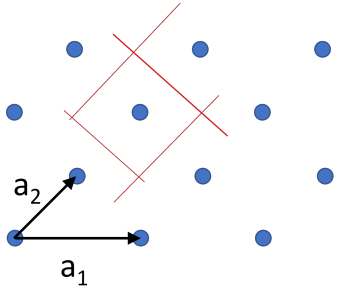


Density of states D(E)

$$D(\epsilon) = \frac{dk}{d\epsilon} = \frac{-1}{\sqrt{1 - \left(\frac{\epsilon-\alpha}{2\beta}\right)^2}2\beta}$$

Solids: Bravais lattice and 1st Brillouin zone

Bravais lattice 2D



Bravais lattice 1D

1. Brillouin-Zone

A Bravais lattice consists of an infinite number of discrete points and looks the same from whatever lattice point you view it.
The first Brillouin zone is the region closer to a chosen lattice point than to any other lattice point.

Solids: Reciprocal lattice

- All lattice points of a Bravais lattice are given by the lattice vectors a_1, a_2, a_3 as $R = n_1 a_1 + n_2 a_2 + n_3 a_3, n \in \mathbb{Z}$
- Then the lattice vectors of the reciprocal lattice b_1, b_2, b_3 are defined as

$$a_i b_j = 2\pi \delta_{ij}$$

- And the lattice points of the reciprocal lattice by $K = l_1 b_1 + l_2 b_2 + l_3 b_3, l \in \mathbb{Z}$
- All plane waves of the form $\exp(Kr)$ have the periodicity of the real lattice. $\exp(K(R + r)) = \exp(Kr)$
- The eigenfunctions of an electron in a periodic potential $V(r + R) = V(r)$, are Bloch orbitals $\varphi_k(r) = u_k(r) \exp(ikr)$.
- $u_k(r) = u_k(r + R)$ has the periodicity of the lattice and $\exp(ikr)$ gives the phase of the orbitals

Summary: Comparison of Hückel rings and band structure

Similarities

- The Hückel rings are a simplified model system. As in an infinite chain, each atom sees the same potential.
- Increasing the number of atoms in the ring, allows to move from discrete orbitals to a continuous band structure.
- The C_n symmetry corresponds to k-space symmetry, with similar degeneracies and orbital forms (Bloch orbitals).
- In praxis, periodic boundary conditions are assumed for the infinite chain (Born-von Karman).
- The density of states can be constructed.

Limitations of the model

- Only one dimension was considered.
- Only one orbital per atom.
- Interactions of different bands at the same k-point have to be considered.

See lecture on periodic Hartree-Fock