Modelowanie Nanostruktur

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Wykład

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Teoria Fukcjonalu Gęstości
Coarse-graining
Metoda ciasnego wiązania
(Tight-binding method)
Zastosowanie dla grafenu

Kohn – Sham realization of the Density Functional Theory – key to:
• computational materials science
• modeling of complex nanostructures

Materials Science – Basic Problem:
N electrons in an external potential

Materials are composed of nuclei \( \{ Z, M, \bar{R} \} \) and electrons \( \{ \bar{r} \} \)
the interactions are known

\[
H = -\sum_i \frac{\hbar^2 \nabla_i^2}{2m} + \sum_{i,\alpha} \frac{-Z_\alpha e^2}{|\bar{R}_\alpha - \bar{r}_i|} + \frac{1}{2} \sum_{i,j} \frac{e^2}{|\bar{r}_i - \bar{r}_j|} + \left( \frac{1}{2} \sum_{\alpha,\beta} \frac{Z_\alpha Z_\beta e^2}{|\bar{R}_\alpha - \bar{R}_\beta|} \right)
\]

\[
V_{ext} = \sum_i V_{ext}(\bar{r}_i)
\]
\[
V_{ext}(\bar{r}) = \sum_\alpha \frac{-Z_\alpha e^2}{|\bar{r} - \bar{R}_\alpha|}
\]
DFT- The Kohn- Sham Method


System of interacting electrons with density $\rho(\vec{r})$

System of non-interacting electrons with the same density $\rho(\vec{r})$

"Real" system $E[\rho] = \int d\vec{r} \rho(\vec{r}) \left[ T[\rho] + U[\rho] + E_x[\rho] + E_c[\rho] \right]$

"Fictitious" or Kohn-Sham reference system $E[\rho] = \int d\vec{r} \rho(\vec{r}) \left[ T[\rho] + U[\rho] + E_x[\rho] + E_c[\rho] \right]$

Total energy functional

- $E[\rho] = \int d\vec{r} v_{\text{ext}}(\vec{r}) \rho(\vec{r}) + T[\rho] + U[\rho] + E_x[\rho] + E_c[\rho]$

- $T[\rho] = \frac{1}{2} \sum_i \int d\vec{r} \sum_j d\vec{r}' \phi_i(\vec{r}) \phi_j^*(\vec{r}') \phi_j(\vec{r}')$

- $E_c[\rho] = \frac{1}{2} \sum_i \int d\vec{r} \sum_j d\vec{r}' \phi_i(\vec{r}) \left( \sum_j \frac{\phi_j(\vec{r}) \phi_j^*(\vec{r}')}{|\vec{r} - \vec{r}'|} \right) \phi_j(\vec{r}')$

Density Functional Theory (DFT) in Kohn-Sham realization

- Idea: consider electrons as independent particles moving in an effective potential

This reduction is rigorously possible!
The Kohn-Sham Method

- Kohn-Sham equations with local potential

\[ \psi_{\alpha}(\vec{r}) = e^{-\sum \frac{Z_i}{|\vec{r} - \vec{R}_i|}} \]

\[ \psi_{\alpha}(\vec{r}) = \frac{\delta E_\alpha}{\delta \rho} \]

\[ \nabla \cdot \mathbf{F} = \rho \]

These equation are nonlinear and must be solved iteratively (self-consistently)

Solution of the Kohn-Sham Equations - Methods

- Expansion of the Kohn-Sham orbitals in a basis \( \{ \chi_{\alpha k}^{\ell}(\vec{r}) \} \)

\[ \varphi_{nk}(\vec{r}) = \sum_{\alpha,\beta} c_{nk,\alpha,\beta} \chi_{\alpha k}^{\ell}(\vec{r}) \]

- Plane waves and pseudopotential
- Linearized Muffin Tin Orbital (LMTO) Method
- Linearized Augmented Plane Wave (LAPW) Method
- Projector Augmented Waves (PAW) Method
  - takes into account core electrons and keeps simultaneously valence functions smooth
  - state-of-the-art in the pseudopotential based methods

The Kohn-Sham Method – 'Aufbau' principle

How to calculate one particle density?

- LUMO
- \( E_{N+1} \)
  - unoccupied

- HOMO
- \( E_N \)
  - occupied

- \( E_2 \)
- \( E_1 \)

Total energy

\[ E_{\text{tot}}(\{ \vec{R}_\alpha \}) = E_{\text{el}}(\{ \vec{R}_\alpha \}) + E_{\text{ion}}(\{ \vec{R}_\alpha \}) \]

Forces on ions

\[ \mathbf{F}_\alpha = -\frac{\partial E_{\text{tot}}}{\partial \vec{R}_\alpha} = -\nabla_{\vec{R}_\alpha} E_{\text{tot}} \]

Equilibrium: \( \forall \alpha \mathbf{F}_\alpha = 0 \)

Dynamics: \( M_\alpha \ddot{\vec{R}}_\alpha = \mathbf{F}_\alpha \)
Solution of the Kohn-Sham Equations

- Direct methods on a mesh in \( r \)-space
- Expansion of the Kohn-Sham orbitals in a basis \( \{ \chi_{\alpha}^{(k)}(r) \} \)

\[
\sum_{\alpha} \left[ \langle \chi_{\alpha}^{(k)} \left| \frac{-\hbar^2}{2m} \nabla^2 + V_{\text{KS}}(r) \right| \chi_{\alpha}^{(k)} \rangle - \varepsilon_{\alpha}(k) \left\langle \chi_{\alpha}^{(k)} \right| \chi_{\alpha}^{(k)} \rangle \right] c_{\alpha}^{(n,k)} = 0
\]

Eigenvalue problem \( \det[H_{aa}^{(k)} - \varepsilon_{a}(k)S_{aa}^{(k)}] = 0 \)

Bandstructure

First (convincing) LDA Calculations: Stability of crystals and pressure induced phase transitions


Cohesive energies in semiconductors

Comparison of LDA, EXX, and HF Methods

- Cohesive energy = Energy of free (separated) atoms – Energy of solid
- Cohesive energy = \( \langle \rho \rangle \) Binding energy

LDA – overestimates (LDA world is smaller than the real one)
HF – underestimates,
EXX – gives excellent cohesive energies in semiconductors

DFT – Calculation of the equation of state and elastic constants

- Equation of state - \( E_{\text{tot}}(V) \) or \( P(V) \)
- \( V_0, B_0, B'_0 \)
- Elastic constants

Energy of the strained system

Interesting prediction: Under high hydrostatic pressure and in low temperature silicon becomes superconducting!
Later on confirmed experimentally

**Cohesive Energy**

**First** (convincing) LDA Calculations: Stability of crystals and pressure induced phase transitions


First (convincing) LDA Calculations: Stability of crystals and pressure induced phase transitions

LDA calculations in semiconductors

Valence bands for GaAs as determined from angle-resolved photoemission experiments and pseudopotential theory

- LDA gives very good description of the occupied s-p valence bands (4s & 4p) in semiconductors
- Various methods of solving Kohn-Sham equations give very similar results

Fundamental band gaps in semiconductors:
Local Density Approximation & Exact Exchange

Fundamental Band Gaps

DFT - further developments required

Density functional theory has revolutionized the way scientists approach the electronic structure of atoms, molecules, and solid materials in physics, chemistry, and materials science. We are not at the end of this way!
Large scale modeling - Coarse-Graining

- For large scale modeling, one may introduce alternative approaches using simplified coarse-grained models (lattice gas models).
- These models can be treated with the methods used commonly in statistical mechanics such as:
  - mean-field theory,
  - the cluster variation method (CVM),
  - Monte Carlo methods.
- Question: how to provide a link between atomistic calculations (ab initio, classical potentials) and the potential parameters suitable for coarse-grained models.

What to do with large systems?

Polyelectrolyte problem: ions around DNA

Atomistic DFT calculations not really possible to sample distances 30 – 40 Å from DNA

Water molecule

Na⁺

Coarse-grained model for ions around DNA

All-atom model

Coarse-grained model
Coarse-grained model for ions around DNA

- Ions interacting with DNA by effective solvent-mediated potentials
- Different potentials for various parts of DNA
- No explicit water
- Density profile and integral charge

Lipid bilayer in water

Picture contains 50000 atoms

Minimal, reasonable piece of bilayer for atomistic calculations

72 lipids + at least 20 H_2O per lipid = 13000 atoms

Another example: Coarse-grained lipid model

All-atom model
118 atoms

Coarse-grained model
10 sites

Tight-binding method
The Kohn-Sham Method – The Kohn-Sham Equations

- Schrödinger-like equations with local potential

\[
\frac{\hbar^2}{2m} \nabla^2 \psi_{\text{ext}}(\vec{r}) + v_{\text{ext}}(\vec{r}) + v_{\text{nl}}(\vec{r}) + v_{\text{l}}(\vec{r}) + v_{\text{c}}(\vec{r}) \psi_n(\vec{r}) = \varepsilon_n \psi_n(\vec{r})
\]

- These equations are nonlinear and must be solved iteratively (self-consistently)

LCAO (Linear Combination of Atomic Orbitals)

\[
\varphi_n(\vec{r}) = \sum_{\alpha} a^{\alpha}_n \varphi^{\alpha}_n(\vec{r} - \vec{R}_\alpha)
\]

- 'Atomic' Kohn-Sham orbitals
- All atoms in the system

Kohn-Sham orbitals in periodic systems

\[
\varphi_{\alpha}(\vec{r}) = \sum_{n} e^{i \vec{K} \cdot \vec{R}_n} \chi_{\alpha}(\vec{r} - \vec{R}_n)
\]

- Basis atoms
- Primitive translations

\[
\{ \chi_{\alpha} \} - \text{fulfill Bloch's theorem}
\]

Problems
- Minimal Basis, i.e., one orbital per electron, is not sufficient
- Results depend on the chosen basis

Tight-Binding Formalism

- Hamiltonian matrix elements and overlap integrals are treated as empirical parameters
- Mostly, orthonormality of orbitals is assumed
- Huge spectrum of applications
- Qualitative insight into physics and semi-quantitative results

Tight-Binding Hamiltonian

\[ H = \sum_{ia} \epsilon_{ia} c_{ia}^\dagger c_{ia} + \sum_{ai,\beta j} t_{ia,j\beta} c_{ia}^\dagger c_{j\beta} \]

- **On-site energies** are not atomic eigenenergies. They include on average the effects of neighbors.

Problem: **Transferability**

*E.g.*, Si in diamond lattice (4 nearest neighbors) & in fcc lattice (12 nearest neighbors)

- Dependence of **the hopping energies** on the distance between atoms

Tight-Binding Formalism – Overlap Integrals

- In the general case orbitals will not be an orthonormal set and we define the **overlap integrals** as

\[ S_{i\alpha j\beta} = \langle i\alpha | j\beta \rangle = \int \phi_{i\alpha}^* \phi_{j\beta} \, d\mathbf{r} \]

- In orthogonal-TB schemes \( S \) reduces to the unit matrix.

One needs to solve

\[ \sum_{j\beta} (H_{i\alpha j\beta} - \epsilon S_{i\alpha j\beta}) c_{j\beta} = 0 \]

**Parameters to be determined**

- Semiempirical Tight-Binding Method

Tight-Binding Formalism – Parameters

- The TB parameters:
  - on-site,
  - hopping
  - (overlap integrals)

are usually determined empirically by fitting TB energies (eigenvalues) to the \textit{ab initio} (experimental) ones.

- One could also try to calculate them directly by performing the same calculation for a localized basis set exactly.


- Simple version of the TB method – universal parameters

  *W. Harrison, Electronic structure and the properties of solids* (Dover, New York, 1980)

  - not very transferable and not accurate enough
  - allow to extract qualitative physics

- Fitting the \textit{ab initio} band structure

**LDA (●) and tight-binding (———)**

band structures for GaAs

in the zinc-blende structure
Tight-Binding Formalism – Physical meaning of the on-site energies

\[ H = \sum_{\alpha i} \varepsilon_{\alpha i} c_{\alpha i}^\dagger c_{\alpha i} + \sum_{\alpha i, \beta j} t_{\alpha i, \beta j} c_{\alpha i}^\dagger c_{\beta j} \]

- Anderson has shown that there exists a pseudoatomic Hamiltonian that has as its eigenstates the basis states \( |i\alpha > \), but this Hamiltonian is not an atomic one and depends yet again on neighboring atoms.

\[ H_i |i\alpha >= (T + V_i + \sum_{j \neq i, \beta} V_j - |j\beta > < j\beta |V_j i\alpha >= \varepsilon_{i\alpha} |i\alpha > \]

- Similar procedure to the construction of the pseudopotential


Tight-Binding Formalism – Dependence of the hopping integrals on atomic distance

- Calculations for systems with distorted lattice
- The dependence of the hopping integrals on the inter-atomic distance
- Harrison's \( -d^2 \) dependence
- Exponential dependence \( t = t_0 \exp(-\beta r) \)

\[ t_{\alpha \beta}(R_{ij}) = t_{\alpha \beta}(r_0) f(R_{ij}) \]

\[ f(r) = \left\{ \begin{array}{ll}
(r_0/r)^n \exp\left(-\frac{r}{r_1}\right) & r < r_1 \\
\left[1 + \frac{r_0}{r_0} \left( c_0 + c_1(r - r_1) + c_2(r - r_1)^2 + c_3(r - r_1)^3 \right) \right] & r \geq r_1
\end{array} \right. \]


Tight-Binding Formalism – Physical meaning of the on-site energies

- The expression for the pseudo-Hamiltonian of atom \( i \)

\[ H_i |i\alpha >= (T_i + V_i + \sum_{j \neq i} V_j - |j\beta > < j\beta |V_j i\alpha >= \varepsilon_{i\alpha} |i\alpha > \]

- In the pseudopotential one projects out core states
- Here one projects out the states of the neighboring atoms which overlap with the atomic basis function.
- This is where the dependence on the environment comes from in this atomic pseudo-Hamiltonian

LDA (•) and tight-binding (solid line) band structures for GaAs in the zinc-blende structure for two different bond lengths

(b) 2.9 Å, and (c) 3.3 Å
Tight-Binding Formalism – Dependence of the hopping integrals on atomic distance

Minimal sp basis used

Tight-binding hopping integrals with the functional dependence

\[ t = t_0 \exp(-\beta r) \]

(lines) as functions of the interatomic distance for GaAs in the zinc-blende structure. Optimum fits of the LDA band structure at selected nearest-neighbour distances are given by the data points.


Tight-Binding Formalism – Band Energy

\[ U_{\text{band}} = 2 \sum_{\text{o.c.c.}} \epsilon_s = 2 \sum \frac{n_s}{s} \epsilon_s \]

- This energy term is called the band energy, and is usually attractive and responsible for the cohesion.
- In fact, if atoms get closer their overlap increases, the range of the eigenvalues increases and, since only the lowest energy states are occupied, the energy decreases (bonding increases).

“Real” description of solids requires repulsive term (to prevent colaps)

Tight-Binding Formalism – The Total Energy

- However, the TB formalism shown above describes only bonding due to the outer electrons.
- If one brings two atoms close together, inner shells will start to overlap and bring additional energy (in the form of a strong repulsion) that is not included in the band energy term.
- The total energy will therefore be given as

\[ E = U_{\text{rep}} + U_{\text{band}} \]

an empirical repulsive energy term

Highly optimized tight-binding model of silicon

Matrix elements \( h_{ss}(r), h_{sp}(r), h_{pp}(r) & h_{pp}(r) \)

The matrix elements are defined whenever \( r \) is greater than 1.5 Å.

The distances corresponding to the first four neighbor shells in the diamond structure are marked by short vertical lines; each matrix element goes smoothly to zero between the third and fourth neighbor shells.

Tight-Binding Formalism – The Repulsive Energy

In most cases this is modeled simply as a sum of two-body repulsive potentials between atoms:

\[ U_{\text{rep}} = \frac{1}{2} \sum_{ij} v_R(r_{ij}) \]

but many-body expressions such as

\[ U_{\text{rep}} = \sum_i g \left[ \sum_j \Phi(r_{ij}) \right] \]

(where \( g \) is a non-linear embedding function, which can be fitted by a polynomial) have also been proposed. \( \Phi \) has similar dependence on the \( R_{ij} \) as hopping integrals.

Tight-Binding Formalism – The Total Energy

\[ E = \sum_n \epsilon_n(k) + \sum_{l \neq l'} E_{\text{rep}}(|R_l - R_{l'}|) + U \sum_{l=1}^N (q_l - q_l^0)^2 \]

- Band structure energy
- Repulsive energy
- Charge transfer energy

The total repulsive energy contains ion–ion repulsion, exchange–correlation energy, and accounts for the double counting of electron–electron interactions in the band-structure energy term.

- The last term imposes an energy penalty on large inter-atomic charge transfers \( \Rightarrow \) Charge transfer energy

Typical \( U \sim 1eV \)

Tight-Binding Formalism – Parametrization of the repulsive term

- Using the interpolated hopping integrals, the tight-binding band-structure energy can be obtained for any geometry and inter-atomic distance.
- We then define the repulsive energy as the difference between the ‘exact’ binding energy, obtained using \( \text{ab initio} \) calculations, and the tight-binding band-structure energy.
- Several crystallographic phases of a material are usually used.

\[ \Rightarrow \] Structure independent parametrization of the repulsive terms

Tight-Binding Formalism – The Total Energy

The binding energy \( (E_{\text{coh}}) \), repulsive energy \( (E_{\text{rep}}) \), and band-structure energy \( (E_{\text{bs}}) \) for GaAs in the zinc-blende structure, as functions of the interatomic distance.
What is graphene?

- 2-dimensional hexagonal lattice of carbon
  - sp² hybridized carbon atoms
  - Among strongest bonds in nature

- Basis for:
  - C-60 (bucky balls)
  - nanotubes
  - graphite

Bottom-up & Top-down nanosystems

- fullerene ↔ (dots - 0D)
- Carbon nanotubes ↔ (q. wires – 1D)
- Graphene ↔ (2D systems)
Does graphene exist?

- In the 1930s, Landau and Peierls (later Mermin) showed that thermodynamics prevents the existence of 2-d crystals in free state.
- Melting temperature of thin films decreases rapidly with temperature -> monolayers generally unstable
- In 2004, experimental discovery of graphene - high quality 2-d crystal !!!

Andrey Geim (Manchester)

Nobel Prize in Physics 2010

Andre Geim  Konstantin Novoselov

The Nobel Prize in Physics 2010 was awarded jointly to Andre Geim and Konstantin Novoselov "for groundbreaking experiments regarding the two-dimensional material graphene"

Samples of graphene

What stabilizes graphene?

- Possibly, 3-d rippling stabilizes crystal
- Crumpling of graphene sheet – the main source of disorder
Graphene – a single sheet of C atoms

- Two unit-cell vectors:
  \[
  \vec{a}_1 = a \left( \frac{\sqrt{3}}{2}, \frac{1}{2} \right) \\
  \vec{a}_2 = a \left( \frac{\sqrt{3}}{2}, -\frac{1}{2} \right)
  \]
- Two non-equivalent atoms A and B in the unit cell (two sublattices)

\[
a = \sqrt{3}d, \quad d = 0.14\text{nm}
\]

Electronic band structure of graphene

The band structure was calculated with a first-principles method

Covalent bonds between carbons

- \(\text{sp}^3\) and \(\text{sp}^2\) hybrids


Tight-binding description of graphene

- \(\sigma\) bonds – not considered in this model
- \(\pi\) bonds considered
- One \(p_z\) orbital per atom
- Only couplings between nearest neighbors taken into account
**Tight-binding description of graphene**

\[
\begin{align*}
|\varepsilon_p - \varepsilon(\vec{k})| &= 0 
\Rightarrow 
\varepsilon(\vec{k}) \\
|H_{AB}(\vec{k})| &= 0 
\Rightarrow 
\varepsilon(\vec{k})
\end{align*}
\]
- \( H_{AA} = H_{BB} = \varepsilon_p \)
- \( H_{AB}(\vec{k}) = \sum \exp(i\vec{k} \cdot \vec{R}_n) <\varphi_A(\vec{r}_A)|\hat{H}|\varphi_B(\vec{r}_B + \vec{R}_n)> \)
- \( H_{AB}(\vec{k}) = t[1 + \exp(i\vec{k} \cdot \vec{a}_1) + \exp(i\vec{k} \cdot \vec{a}_2)] \)
- \( \varepsilon_p = 0 \) (zero of energy)

- \( \varepsilon(\vec{k}) = \pm t\left(H_{AB}(\vec{k})H_{AB}^*(\vec{k})\right)^{1/2} \)

**Band structure of graphene – T-B metod (1)**

\[
\begin{align*}
\varphi_A &= \frac{1}{N} \sum_{\vec{R}} e^{i\vec{k} \cdot \vec{R}} \varphi(\vec{r} - \vec{R}) \\
\varphi_B &= \frac{1}{N} \sum_{\vec{R}} e^{i\vec{k} \cdot \vec{R}} \varphi(\vec{r} - \vec{R} - \vec{a}) \\
\langle \varphi_A \mid H \mid \varphi_B \rangle &= \sum_{\vec{R}_1 \vec{R}_2} e^{-i\vec{k} \cdot (\vec{R}_2 - \vec{R}_1)} \langle \varphi(\vec{r} - \vec{R}_2) \mid H \mid \varphi(\vec{r} - \vec{R}_1 - \vec{a}) \rangle \\
&= \frac{t}{N} \sum_{\vec{R}_1 \vec{R}_2} e^{i\vec{k} \cdot (\vec{R}_2 - \vec{R}_1)} \langle \varphi(\vec{r} - \vec{R}_2) \mid H \mid \varphi(\vec{r} - \vec{R}_1 - \vec{a}) \rangle
\end{align*}
\]

**Band structure of graphene – T-B metod (2)**

\[
H_{AB}(\vec{k}) =
\begin{cases}
\pm \frac{1}{\sqrt{2}} e^{i\vec{k} \cdot \vec{a}} |\varphi(\vec{k} - \vec{R})\rangle
\end{cases}
\]

**Band structure of graphene – T-B metod (3)**

\[
H_{ab}(\vec{k}) = t^2 \left( 1 + 4 \cos(2\pi/3) \right) e^{i\vec{k} \cdot \vec{a}}
\]
Nearest-neighbors tight-binding electronic structure of graphene

Hopping parameter $t = -2.7 \text{ eV}$

Tight-binding band structure of graphene

$\varepsilon(k) = \pm t \left\{ 1 + 4 \cos^2 \left( \frac{k_y a}{2} \right) + 4 \cos \left( \frac{\sqrt{3} k_y a}{2} \right) \cos \left( \frac{k_x a}{2} \right) \right\}^{1/2}$

Graphene is semi-metallic

Energy gap is equal zero only in one k-point (P-point)

Band structure of graphene - summary

- Graphene is semi-metallic
- Fermi energy is zero, no closed Fermi surface, only isolated Fermi points
- Close to corner points, relativistic dispersion (light cone), up to eV energy scales
  \[ E(\vec{q}) = v_F |\vec{q}| \]
  \[ \vec{q} = \vec{k} - \vec{K}, v_F = 8 \times 10^5 \text{ m/sec} \]
- Relativistic behavior comes from interaction with lattice potential of graphene, not from carriers moving near speed of light.
- Behavior ONLY present in monolayer graphene; disappears with 2 or more layers.

Massless 2D Dirac Fermions

Energy gap is equal zero only in one k-point (P-point)

$E = \pm v_F |\vec{q}|$

“light cone”

Intriguing Physics of Graphene