Chair of Condensed Matter Physics
Institute of Theoretical Physics
Faculty of Physics, Universityof Warsaw

Semester Zimowy 2011/2012

Wykład

Modelowanie Nanostruktur

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Kohn – Sham realization of the Density Functional Theory – key to

- computational materials science
- modeling of complex nanostructures

Modelowanie Nanostruktur, 2011/2012
Jacek A. Majewski

Wykład 3 – *18 X 2011*

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

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

- **Materials are composed of nuclei** $\{Z_\alpha, M_\alpha, \vec{R}_\alpha\}$ **and electrons** $\{\vec{r}_i\}$

  ⇒ the interactions are known

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

Kinetic energy of electrons — **Electron-Nucleus interaction** — **Electron-Electron interaction** — **Nucleus-Nucleus interaction**

External potential

$$V_{ext} = \sum_i v_{ext}(\vec{r}_i)$$

$$v_{ext}(\vec{r}) = \sum_\alpha \frac{-Z_\alpha e^2}{|\vec{r} - \vec{R}_\alpha|}$$

Density Functional Theory (DFT)

- **One particle density determines the ground state energy of the system for arbitrary external potential**

$$E[\rho] = \int d^3\vec{r}\,\rho(\vec{r})v_{ext}(\vec{r}) + F[\rho]$$

$$\boxed{E[\rho_0] = E_0}$$

ground state energy

ground state density

Total energy functional — **Kinetic energy** — **Exchange energy** — **Correlation energy**

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

External energy — **Classic Coulomb energy** — **unknown!!!**

DFT- The Kohn- Sham Method

W. Kohn and L. J. Sham, Phys. Rev. ***140****, A1133 (1965)*

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

"Real" system

$\rho(\vec{r})$ $\quad T[\rho]$

"Fictitious" or Kohn-Sham reference system

$T_S[\rho]$ $\quad \rho_S(\vec{r}) = \rho(\vec{r})$

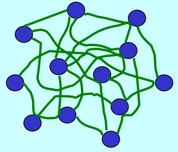
$$E[\rho] = \int d\vec{r}v_{ext}(\vec{r})\rho(\vec{r}) + T_S[\rho] + U[\rho] + E_x[\rho] + E_c[\rho]$$

unknown!!!

- $\rho(\vec{r}) = \sum_{i=1}^{N} \varphi^*_i(\vec{r})\varphi_i(\vec{r})$
- $T_s[\rho] = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\int d\vec{r}\varphi_i^*(\vec{r})\vec{\nabla}^2\varphi_i(\vec{r})$
- $E_x[\rho] = -\frac{1}{2}\sum_i \iint d\vec{r}d\vec{r}'\varphi_i^*(\vec{r})\left(\sum_j \frac{\varphi_j(\vec{r})\varphi_j^*(\vec{r}')}{|\vec{r}-\vec{r}'|}\right)\varphi_i(\vec{r}')$

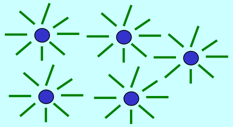
Density Functional Theory (DFT) in Kohn-Sham realization

Interacting particles



$\Psi(\vec{x}_1,\vec{x}_2,\ldots,\vec{x}_{10^{23}})$

Independent particles



$\varphi(\vec{x}_1)\varphi(\vec{x}_2)\ldots\varphi(\vec{x}_{10^{23}})$

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

This reduction is rigorously possible !

Density Functional Theory (DFT)

Approximations to the exchange & correlation

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

unknown!!!

- **Local Density Approximation (LDA)**

$$E_{xc}^{LDA}[\rho] = \int d\vec{r}\,\rho(\vec{r})\varepsilon_{xc}^{\mathrm{hom}}(\rho(\vec{r}))$$

- **Generalized Gradient Approximation (GGA)**

$$E_{xc}^{GGA}[\rho] = \int d\vec{r}\,f_{xc}(\rho(\vec{r}),\nabla\rho(\vec{r}))$$

The Kohn-Sham Method

- Kohn-Sham equations with local potential

$$\upsilon_H(\vec{r}) = \frac{\delta U}{\delta \rho} = \int d\vec{r}\,' \frac{\rho(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|} \qquad \frac{\delta E_x[\rho]}{\delta \rho} \qquad \frac{\delta E_c[\rho]}{\delta \rho}$$

$$\left[-\frac{\hbar^2}{2m}\vec{\nabla}^2 + \upsilon_{ext}(\vec{r}) + \upsilon_H(\vec{r}) + \upsilon_x(\vec{r}) + \upsilon_c(\vec{r})\right]\varphi_i(\vec{r}) = \varepsilon_i \varphi_i(\vec{r})$$

$$\upsilon_{ext}(\vec{r}) = -e^2 \sum_{s,n} \frac{Z_s}{|\vec{r} - \vec{\tau}_s - \vec{R}_n|}$$

$$\rho(\vec{r}) = \sum_{i=1}^{N} \varphi^*_i(\vec{r})\varphi_i(\vec{r})$$

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

Solution of the Kohn-Sham Equations - Methods

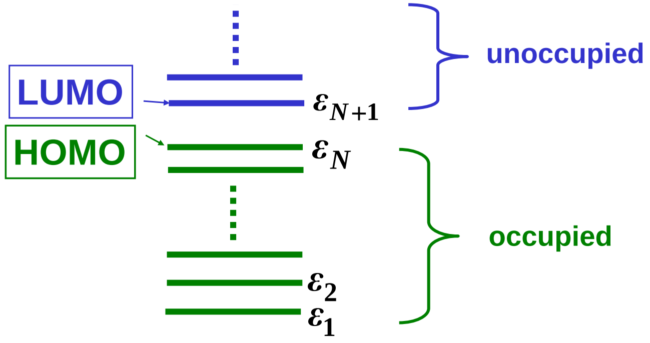
- Expansion of the Kohn-Sham orbitals in a basis $\{\chi_{\alpha\vec{k}}(\vec{r})\}$

$$\varphi_{n\vec{k}}(\vec{r}) = \mathcal{N} \sum_{\alpha} c_\alpha(n,\vec{k})\chi_{\alpha\vec{k}}(\vec{r})$$

- Plane waves and pseudopotential
- Linearized Muffin Tin Orbital (LMTO) Method
- Linearized Augnented Plane Wave (LAPW) Method
- Projector Augnented 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?



The Kohn-Sham Method –Total Energy & Forces

$$E[\rho] = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\int d\vec{r}\varphi_i^*(\vec{r})\vec{\nabla}^2\varphi_i(\vec{r}) + U[\rho] + E_x[\rho] + E_c[\rho] + \int d\vec{r}\upsilon_{ext}(\vec{r})\rho(\vec{r})$$

total electronic energy in the field of ions

Energy of ions

$$E_{ion} = \frac{1}{2}\sum_{\alpha,\beta}\frac{Z_\alpha Z_\beta}{|\vec{R}_\alpha - \vec{R}_\beta|}$$

Total energy

$$E_{tot}(\{\vec{R}_\alpha\}) = E_{el}(\{\vec{R}_\alpha\}) + E_{ion}(\{\vec{R}_\alpha\})$$

Forces on ions

$$\vec{F}_\alpha = -\frac{\partial E_{tot}}{\partial \vec{R}_\alpha} = -\nabla_{\vec{R}_\alpha} E_{tot}$$

Equilibrium: $\forall_\alpha \vec{F}_\alpha = 0$

Dynamics: $M_\alpha \ddot{\vec{R}}_\alpha = \vec{F}_\alpha$

Solution of the Kohn-Sham Equations

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

$$\varphi_{n\vec{k}}(\vec{r}) = \mathbb{N}\sum_{\alpha} c_{\alpha}(n,\vec{k})\chi_{\alpha\vec{k}}(\vec{r})$$

$$\boxed{\left[\sum_{\alpha'} \left\langle \chi_{\alpha\vec{k}} \,\middle|\, -\frac{\hbar^2}{2m}\vec{\nabla}^2 + \upsilon_{KS}(\vec{r}) \,\middle|\, \chi_{\alpha'\vec{k}} \right\rangle - \varepsilon_n(\vec{k})\left\langle \chi_{\alpha\vec{k}} \,\middle|\, \chi_{\alpha'\vec{k}} \right\rangle\right] c_{\alpha'}(n,\vec{k}) = 0}$$

Hamiltonian matrix elements

Overlap integrals

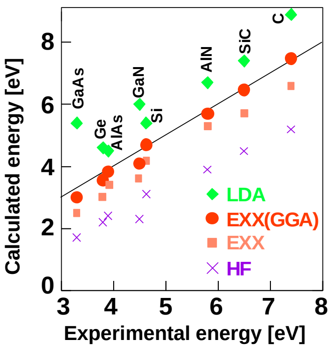
$$\boxed{[H_{\alpha\alpha'}(\vec{k}) - \varepsilon_n(\vec{k})S_{\alpha\alpha'}(\vec{k})]c_{\alpha'}(n,\vec{k}) = 0}$$

Eigenvalueproblem $\det[H_{\alpha\alpha'}(\vec{k}) - \varepsilon_n(\vec{k})S_{\alpha\alpha'}(\vec{k})] = 0$

➡ $\varepsilon_n(\vec{k})$ **Bandstructure**

Cohesive energies in semiconductors Comparison of LDA, EXX, and HF Methods

Cohesive Energy

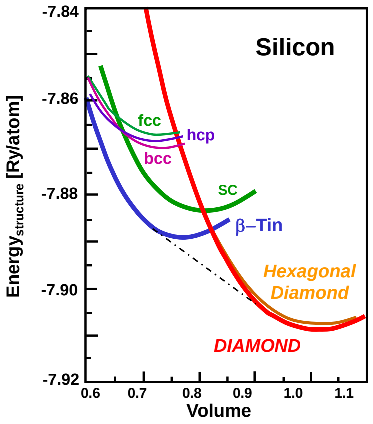


Cohesive energy =
Energy of free (separated) atoms –
Energy of solid

Cohesive energy = ***-- Binding energy***

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

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



M. T. Yin & M. L. Cohen,
*Phys. Rev. B **26**, 5668 (1982)*

$$\boxed{P_{transition} = \frac{E_{tot}^{(1)}(V_t^{(1)}) - E_{tot}^{(2)}(V_t^{(2)})}{V_t^{(2)} - V_t^{(1)}}}$$

$$P = -\frac{\partial E}{\partial V}$$

Interesting prediction:
Under high hydrostatic pressure and in low temperature silicon becomes superconducting !

Later on confirmed experimentally

DFT – Calculation of the equation of state and elastic constants

- **Equation of state -** $E_{tot}(V)$ **or** $P(V)$

➡ V_0 B_0 B_0'

- **Elastic constants**

Energy of the strained system

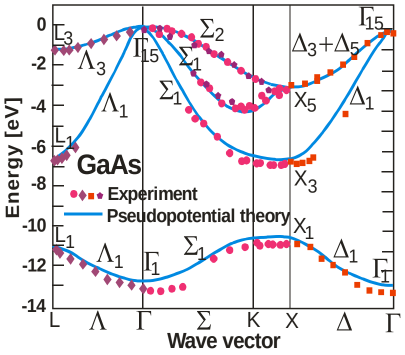
$$\boxed{\rho_0 E(\eta) = \frac{1}{2!}\sum_{i,j=1,6} c_{ij}\eta_i\eta_j + \frac{1}{3!}\sum_{i,j,k=1,6} c_{ijk}\eta_i\eta_j\eta_j + \ldots}$$

Second order Elastic constants

Third order Elastic constants

LDA calculations in semiconductors

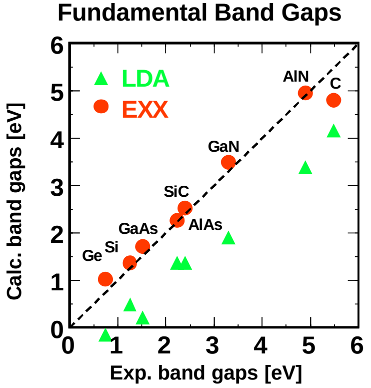
Valence bands for GaAs as determined from angle-resolved photoemission experiments and pseudopotential theory



- **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

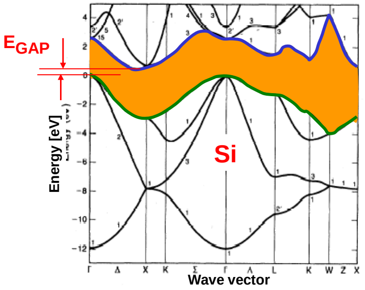


- **EXX Method leads to Kohn-Sham gaps that agree very well with experiment**

➡ Large part of the error in the fundamental gaps is connected to the approximated functionals (LDA, GGA)

LDA calculations in semiconductors – Energy gap

Band structure of diamond silicon



$E_{GAP} = E_{LUMO} - E_{HOMO}$
Too small by factor of 2

- For all semiconductors and insulators, LDA (GGA) give energy gaps that are 40%-70% of experimental gaps

Kohn-Sham gap

$$E^{KS}_{Gap} = \varepsilon^{KS}_{cbb} - \varepsilon^{KS}_{vbt}$$

$$E^{KS}_{Gap} = \varepsilon^{KS}_{N+1}(N) - \varepsilon^{KS}_{N}(N)$$

- Relation of the Kohn-Sham gap to the ***quasi-particle energy*** (change of system energy caused by adding a particle) ?
- Is the Kohn-Sham gap generally wrong, for description of one particle excitations ?
- Does the error is caused by the approximation of the functionals ?

"**The band gap problem**"

DFT - further developements 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!

Coarse-graining & effective approaches

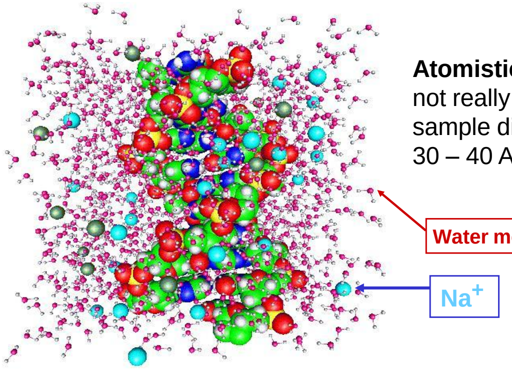
Large scale modeling - Coarse-Graining

- 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?

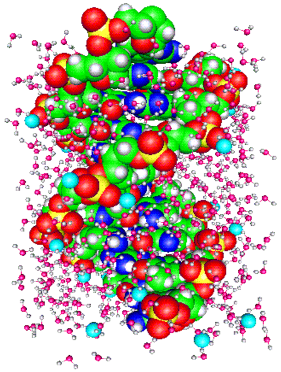
Polyelectrolyte problem: ions around DNA

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

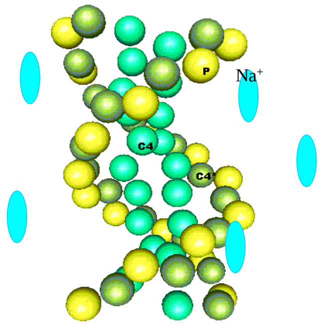


Coarse-grained model for ions around DNA

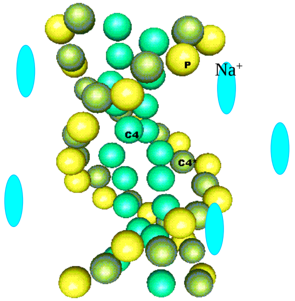
All-atom model



Coarse-grained model

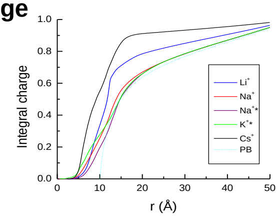


Coarse-grained model for ions around DNA

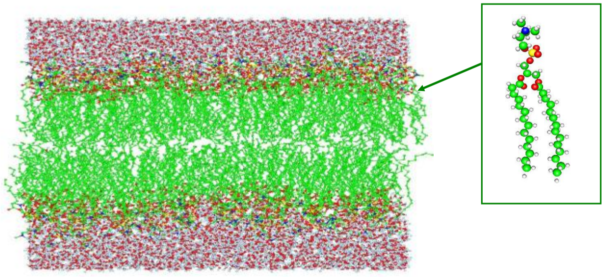


- Ions interacting with DNA by effective solvent-mediated potentials
- Different potentials for various parts of DNA
- No explicit water

→ density profile and integral charge



Lipid bilayer in water

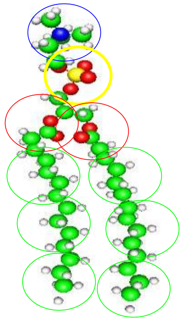


Picture contains 50000 atoms

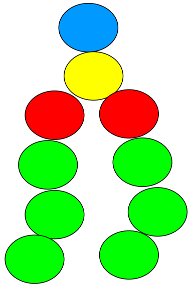
Minimal, reasonable piece of bilayer for **atomistic calculations**

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

$$\upsilon_H(\vec{r}) = \frac{\delta U}{\delta \rho} = \int d\vec{r}\,' \frac{\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}$$

$$\frac{\delta E_x[\rho]}{\delta \rho} \qquad \frac{\delta E_c[\rho]}{\delta \rho}$$

$$\left[-\frac{\hbar^2}{2m}\vec{\nabla}^2 + \upsilon_{ext}(\vec{r}) + \upsilon_H(\vec{r}) + \upsilon_x(\vec{r}) + \upsilon_c(\vec{r})\right]\varphi_i(\vec{r}) = \varepsilon_i \varphi_i(\vec{r})$$

$$\upsilon_{ext}(\vec{r}) = -e^2 \sum_{s,n} \frac{Z_s}{|\vec{r}-\vec{\tau}_s-\vec{R}_n|}$$

$$\rho(\vec{r}) = \sum_{i=1}^{N} \varphi^*_i(\vec{r})\varphi_i(\vec{r})$$

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

Tight-Binding Formalism

$$\varphi_n(\vec{r}) = \sum_{\alpha,i} c_n^{\alpha i} \chi_{\alpha i}(\vec{r})$$

index of orbital

index of atom

$\{\chi_{\alpha i}\}$ orthogonal set of functions

➡ NOT ATOMIC ORBITALS !

$$\varepsilon_n = <\varphi_n | H | \varphi_n> = \sum_{i\alpha}\sum_{j\beta} (c_n^{\alpha i})^* c_n^{\beta j} < i\alpha | H | j\beta >$$

Tight –binding Hamiltonian

$$H = \sum_{\alpha i} \varepsilon_{i\alpha} | i\alpha >< i\alpha | + \sum_{\alpha i, \beta j} t_{i\alpha, j\beta} | i\alpha >< j\beta |$$

on-site

hoping TB-parameters

LCAO (Linear Combination of Atomic Orbitals)

$$\varphi_n(\vec{r}) = \mathbb{N} \sum_{\alpha} c_{\alpha n} \phi_\alpha^{at}(\vec{r} - \vec{X}_\alpha)$$

All atoms in the system

ϕ_α^{at} - ‘Atomic’ Kohn-Sham orbitals:

$$[\frac{\hat{\vec{p}}^2}{2m} + \upsilon_{KS}^{at}]\phi_\alpha^{at} = \varepsilon_\alpha^{at}\phi_\alpha^{at}$$

Kohn-Sham orbitals in periodic systems

$$\varphi_{n\vec{k}}(\vec{r}) = \mathbb{N} \sum_{\alpha} c_\alpha(n,\vec{k}) \chi_{\alpha\vec{k}}(\vec{r})$$

$$\chi_{\alpha\vec{k}}(\vec{r}) = \sum_{\vec{R}_l} e^{i\vec{k}\cdot\vec{R}_l} \phi_\alpha^{at}(\vec{r} - \vec{R}_l - \vec{\tau}_{s(\alpha)})$$

$\{\vec{\tau}_s\}$ Basis atoms

$\{\vec{R}_l\}$ Primitive translations

$\{\chi_{\alpha\vec{k}}\}$ - fulfill Bloch’s theorem $\chi_{\alpha\vec{k}}(\vec{r} + \vec{R}_n) = e^{i\vec{k}\cdot\vec{R}_n}\chi_{\alpha\vec{k}}(\vec{r})$

Problems

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

LCAO - Semiempirical Tight-Binding Method

- Hamiltonian matrix elements $\langle \phi_\alpha | \hat{H} | \phi_{\alpha'} \rangle \equiv H_{\alpha\alpha'}$
  and overlap integrals $\langle \phi_\alpha | \phi_{\alpha'} \rangle \equiv S_{\alpha\alpha'}$
  are treated as empirical parameters
- Mostly, orthonormality of orbitals is assumed, $S_{\alpha\alpha'} = \delta_{\alpha\alpha'}$
- Huge spectrum of applications
- **Qualitative insight into physics and semi-quantitative results**

W. A. Harrison, “Electronic Structure and the Properties of Solids The Physics of the Chemical Bond”, Freeman & Comp. (1980)

Tight-Binding Hamiltonian

$$H=\sum_{\alpha i}\varepsilon_{i\alpha}c^{\dagger}_{i\alpha}c_{i\alpha}+\sum_{\alpha i,\beta j}t_{i\alpha,j\beta}c^{\dagger}_{i\alpha}c_{j\beta}$$

creation & anihilation operators

- *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 – Parameters

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

  are usually determined empirically by fitting TB energies (eigenvalues) to the *ab initio* (experimantal) ones.
- One could also try to calculate them directly by performing the same calculation for a localized basis set exactly
  e.g., F. Liu, Phys. Rev. B 52, 10677 (1995)
- 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

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.

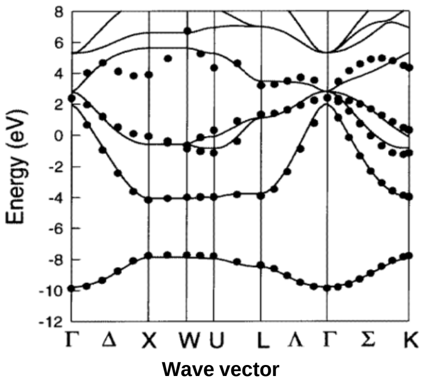
One needs to solve $\sum_{j\beta}(\underset{\uparrow}{H_{i\alpha j\beta}}-\epsilon \underset{\uparrow}{S_{i\alpha j\beta}})c_{j\beta}=0$

Parameters to be determined

➡ Semiempirical Tight-Binding Method

Tight-Binding Formalism – Parameters

Fitting the *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

$$H = \sum_{\alpha i} \varepsilon_{i\alpha} c^{\dagger}_{i\alpha} c_{i\alpha} + \sum_{\alpha i,\beta j} t_{i\alpha, j\beta} c^{\dagger}_{i\alpha} c_{j\beta}$$

- 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

P. W. Anderson, Phys. Rev. Lett. **21**, 13 (1968)
Phys. Rev. **181**, 25 (1969)

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

- The expression for the pseudo-Hamiltonian of atom i

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

- 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

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

Calculations for systems with distorted lattice

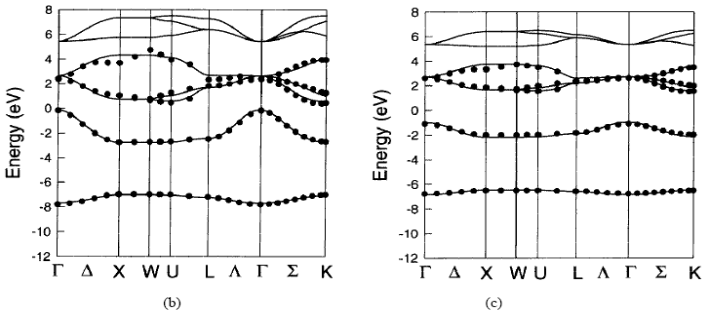
The dependence of the hopping integrals on the inter-atomic distance

- **Harrison's ~d^{-2} dependence**
- **Exponential dependence** $t = t_0 \, exp(-\beta r)$
- $t_{\alpha\beta}(R_{ij}) = t_{\alpha\beta}(r_0) f(R_{ij})$

$$f(r) = \begin{cases} \left(\frac{r_0}{r}\right)^{n} exp\left\{ n\left[-\left(\frac{r}{r_c}\right)^{n_c} + \left(\frac{r_0}{r_c}\right)^{n_c} \right] \right\} & r < r_1 \\ c_0 + c_1(r - r_1) + c_2(r - r_2)^2 + c_3(r - r_2)^3 & r \geq r_1 \end{cases}$$

C. Xu *et al.*, J. Phys. Condens. Matter 4, 6047 (1992)

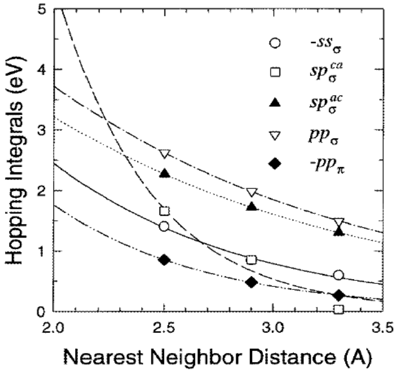
Tight-Binding Formalism – Dependence of the hopping integrals on atomic distance



LDA (●) and tight-binding (———) 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.

Y. P. Feng, C. K. Ong, H. C. Poon and D. Tomanek, J. Phys.: Condens. Matter 9, 4345 (1997).

Tight-Binding Formalism – Band Energy

$$\boxed{U_{\mathrm{band}} = 2\sum_{\mathrm{occ}} \epsilon_s = 2\sum_s n_s \epsilon_s}$$

- **This energy term is called the *band energy*, and is usually attractive and responsible for the cohesion.**

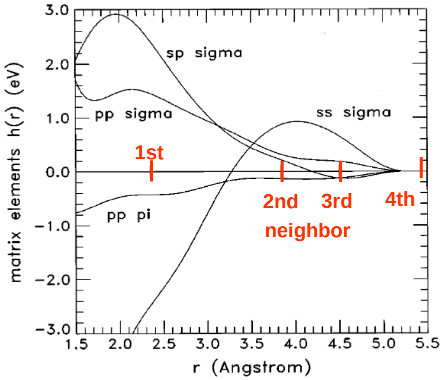
- **In fact, if atoms get closer their overlap increases, the range of the eigenvalues increases and, since only the lowest energy states are occupied, the energy decreases (bonding increases).**

➡ **"Real" description of solids requires repulsive term (to prevent colaps)**

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

Highly optimized tight-binding model of silicon

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



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.

T. J. Lenosky et al., Phys. Rev. B 55, 1528 (1996)

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**

$$\boxed{E = U_{\mathrm{rep}} + U_{\mathrm{band}}}$$

an empirical repulsive energy term

Tight-Binding Formalism – The Repulsive Energy

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

$$\boxed{U_{\rm rep} = \frac{1}{2} \sum_{ij} v_R(r_{ij})}$$

but many-body expressions such as

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

(where g is a non-linear embedding function, which can be fitted by a polynomial) have also been proposed.

Φ has similar dependence on the R_{ij} as hopping integrals

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 *ab initio* calculations, and the tight-binding band-structure energy**
- **Several crystallographic phases of a material are usually used**

➡ Structure independent parametrization of the repulsive terms

Tight-Binding Formalism – The Total Energy

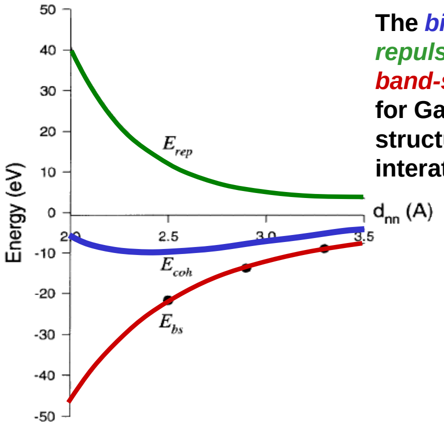
$$\boxed{E = \sum_{k,n} \epsilon_n(k) + \sum_{l=2}^{N} \sum_{l'=1}^{l-1} E_{rep}(|\boldsymbol{R}_l - \boldsymbol{R}_{l'}|) + U \sum_{l=1}^{N} (q_l - q_l^0)^2}$$

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 → *Charge transfer energy***

Typical $U \sim 1eV$

Tight-Binding Formalism – The Total Energy



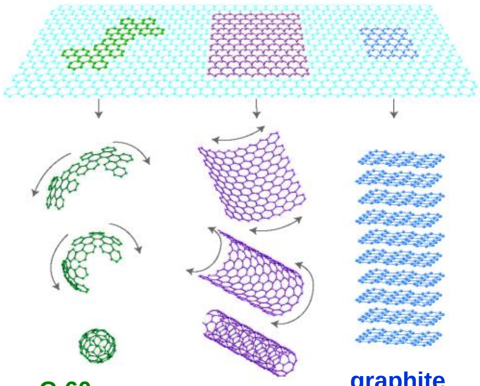
The *binding energy* (E_{coh}), *repulsive energy* (E_{rep}), and *band-structure energy* (E_{bs}) for GaAs in the zinc-blende structure, as functions of the interatomic distance.

Tight-binding method
Application: graphene

Graphene:
a sheet of carbon atoms

What is graphene?

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



- **Basis for:**

Bottom-up & Top-down nanosystems

fullerene ←→ **(dots - 0D)**

Carbon nanotubes ←→ **(q. wires – 1D)**

Graphene ←→ **(2D systems)**

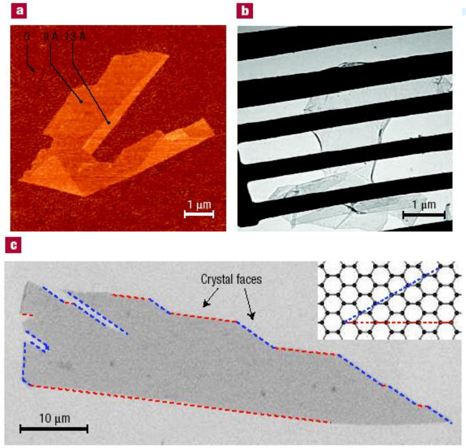
Does graphene exist?

- 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)

Samples of graphene



a) Atomic force microscopy

b) Transmission electron microscopy image

c) Scanning electron microscope image

Nobel Prize in Physics 2010

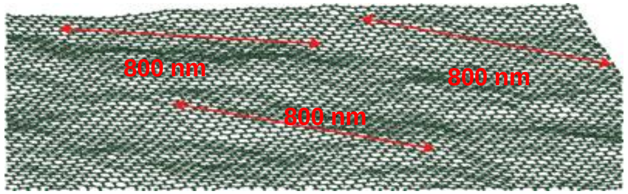
Andre Geim

Konstantin Novoselov

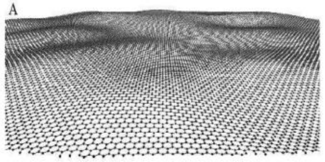
The Nobel Prize in Physics 2010 was awarded jointly to Andre Geim and Konstantin Novoselov *"for groundbreaking experiments regarding the two-dimensional material graphene"*

What stabilizes graphene?

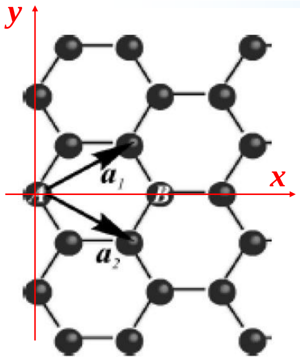
- **Possibly, 3-d rippling stabilizes crystal**



- Crumpling of graphene sheet – the main source of disorder



Graphene – a single sheet of C atoms



- **Two unit-cell vectors:**

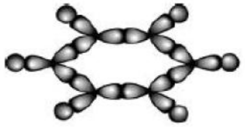
$$\vec{a}_1 = a(\frac{\sqrt{3}}{2}, \frac{1}{2})$$

$$\vec{a}_2 = a(\frac{\sqrt{3}}{2}, -\frac{1}{2})$$

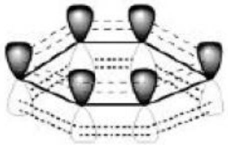
- **Two non-equivalent atoms A and B in the unit cell (two sublattices)**

$$a = \sqrt{3}d, d = 0.14nm$$

Tight-binding description of graphene



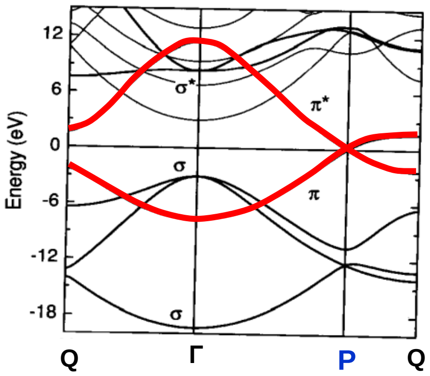
σ bonds – not considered in this model

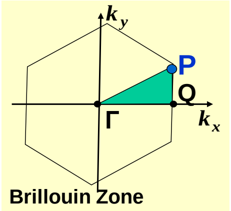


***π* bonds considered**

- **One p_z orbital pro atom**
- **Only couplings between nearest neighbors taken into account**

Electronic band structure of graphene



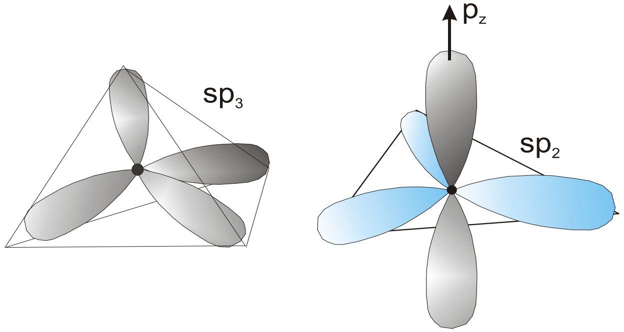


The band structure was calculated with a first-principles method

M. Machon, *et al.*, Phys. Rev. B **66**, 155410 (2002)

Covalent bonds between carbons

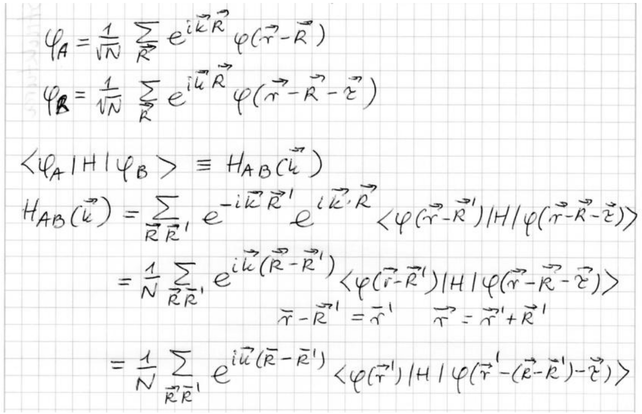
sp^3 and sp^2 hybrids



Tight-binding description of graphene

- $\begin{vmatrix} \varepsilon_p-\varepsilon(\vec{k}) & H_{AB}(\vec{k}) \\ H^*_{AB}(\vec{k}) & \varepsilon_p-\varepsilon(\vec{k}) \end{vmatrix} = 0 \quad \Rightarrow \quad \varepsilon(\vec{k})$
- $H_{AA} = H_{BB} = \varepsilon_p$
- $H_{AB}(\vec{k}) = \sum_{\vec{R}_n} exp(i\vec{k}\cdot\vec{R}_n) < \varphi_A(\vec{\tau}_A) \,|\, \hat{H} \,|\, \varphi_B(\vec{\tau}_B+\vec{R}_n) >$
- $H_{AB}(\vec{k}) = t[1+exp(i\vec{k}\cdot\vec{a}_1)+exp(i\vec{k}\cdot\vec{a}_2)]$
- $\varepsilon_p = 0$ (zero of energy)
- $\boxed{\varepsilon(\vec{k}) = \pm t\left(H_{AB}(\vec{k})H^*_{AB}(\vec{k})\right)^{1/2}}$

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



$$\varphi_A = \frac{1}{\sqrt{N}}\sum_{\vec{R}} e^{i\vec{k}\vec{R}}\varphi(\vec{r}-\vec{R})$$

$$\varphi_B = \frac{1}{\sqrt{N}}\sum_{\vec{R}} e^{i\vec{k}\vec{R}}\varphi(\vec{r}-\vec{R}-\vec{\tau})$$

$$\langle\varphi_A|H|\varphi_B\rangle \equiv H_{AB}(\vec{k})$$

$$H_{AB}(\vec{k}) = \sum_{\vec{R}\vec{R}'} e^{-i\vec{k}\vec{R}'}e^{i\vec{k}\cdot\vec{R}}\langle\varphi(\vec{r}-\vec{R}')|H|\varphi(\vec{r}-\vec{R}-\vec{\tau})\rangle$$

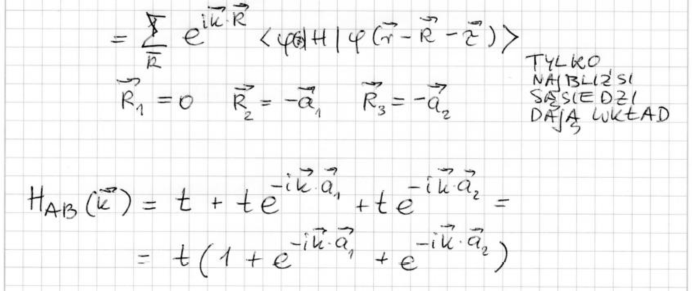
$$= \frac{1}{N}\sum_{\vec{R}\vec{R}'} e^{i\vec{k}(\vec{R}-\vec{R}')}\langle\varphi(\vec{r}-\vec{R}')|H|\varphi(\vec{r}-\vec{R}-\vec{\tau})\rangle$$

$$\vec{r}-\vec{R}' = \vec{r}' \qquad \vec{r} = \vec{r}'+\vec{R}'$$

$$= \frac{1}{N}\sum_{\vec{R}\vec{R}'} e^{i\vec{k}(\vec{R}-\vec{R}')}\langle\varphi(\vec{r}')|H|\varphi(\vec{r}'-(\vec{R}-\vec{R}')-\vec{\tau})\rangle$$

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

$H_{AB}(\vec{k}) =$



$$= \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}}\langle\varphi(0)|H|\varphi(\vec{r}-\vec{R}-\vec{\tau})\rangle$$

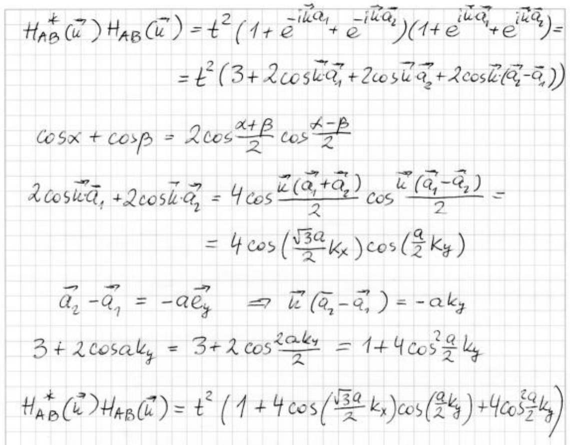
$$\vec{R}_1 = 0 \qquad \vec{R}_2 = -\vec{a}_1 \qquad \vec{R}_3 = -\vec{a}_2$$

TYLKO
NAJBLIŻSI
SĄSIEDZI
DAJĄ WKŁAD

$$H_{AB}(\vec{k}) = t + te^{-i\vec{k}\cdot\vec{a}_1} + te^{-i\vec{k}\cdot\vec{a}_2} =$$

$$= t(1+e^{-i\vec{k}\cdot\vec{a}_1}+e^{-i\vec{k}\cdot\vec{a}_2})$$

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



$$H^*_{AB}(\vec{k})H_{AB}(\vec{k}) = t^2(1+e^{-i\vec{k}\vec{a}_1}+e^{-i\vec{k}\vec{a}_2})(1+e^{i\vec{k}\vec{a}_1}+e^{i\vec{k}\vec{a}_2}) =$$

$$= t^2(3+2\cos\vec{k}\cdot\vec{a}_1+2\cos\vec{k}\cdot\vec{a}_2+2\cos\vec{k}\cdot(\vec{a}_2-\vec{a}_1))$$

$$\cos\alpha+\cos\beta = 2\cos\frac{\alpha+\beta}{2}\cos\frac{\alpha-\beta}{2}$$

$$2\cos\vec{k}\cdot\vec{a}_1+2\cos\vec{k}\cdot\vec{a}_2 = 4\cos\frac{\vec{k}(\vec{a}_1+\vec{a}_2)}{2}\cos\frac{\vec{k}(\vec{a}_1-\vec{a}_2)}{2} =$$

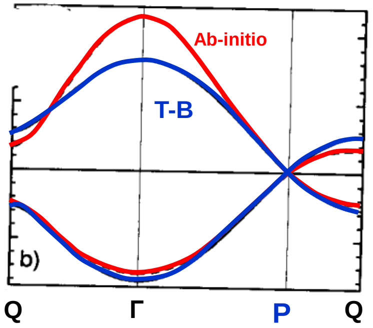
$$= 4\cos\left(\frac{\sqrt{3}a}{2}k_x\right)\cos\left(\frac{a}{2}k_y\right)$$

$$\vec{a}_2-\vec{a}_1 = -a\vec{e}_y \quad \Rightarrow \quad \vec{k}(\vec{a}_2-\vec{a}_1) = -ak_y$$

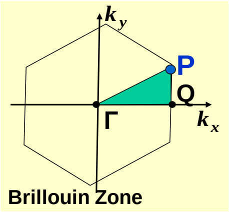
$$3+2\cos ak_y = 3+2\cos\frac{2ak_y}{2} = 1+4\cos^2\frac{a}{2}k_y$$

$$H^*_{AB}(\vec{k})H_{AB}(\vec{k}) = t^2\left(1+4\cos\left(\frac{\sqrt{3}a}{2}k_x\right)\cos\left(\frac{a}{2}k_y\right)+4\cos^2\frac{a}{2}k_y\right)$$

Nearest-neighbors tight-binding electronic structure of graphene



$\Gamma = (0,0,0)$
$Q = \frac{2\pi}{a}\left(\frac{1}{\sqrt{3}}, 0\right)$
$P = \frac{2\pi}{a}\left(\frac{1}{\sqrt{3}}, \frac{1}{3}\right)$

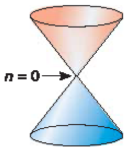


Hopping parameter

t = -2.7 eV

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*** (ligh cone), up to *eV* energy scales

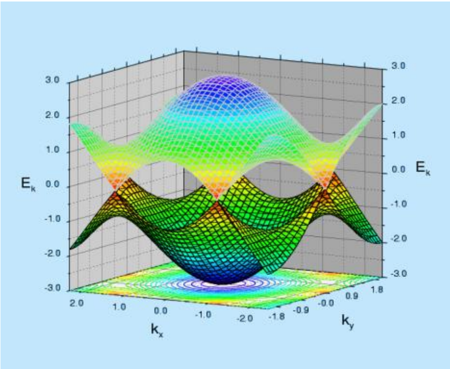
$$E(\vec{q}) = v_F |\vec{q}|$$

$$\vec{q} = \vec{k} - \vec{K}, v_F = 8 \times 10^5 \, m/\sec$$

- ***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.**

Tight-binding band structure of graphene

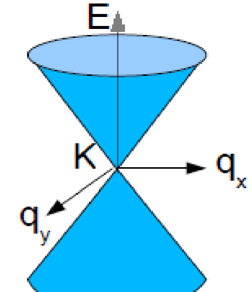
$$\varepsilon(\vec{k}) = \pm t \left\{ 1 + 4\cos^2\left(\frac{k_y a}{2}\right) + 4\cos\left(\frac{\sqrt{3} k_x a}{2}\right)\cos\left(\frac{k_y a}{2}\right) \right\}^{1/2}$$



Graphene is semi-metallic

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

Massless 2D Dirac Fermions



$$E = \pm v_F |q|$$

"light cone"

$$H_K = \begin{pmatrix} 0 & v_F(q_x - iq_y) \\ v_F(q_x + iq_y) & 0 \end{pmatrix}$$

- q = K - k
- 2x2 structure from 2 site unit cell => pseudo spin

$$H_K = v_F \begin{pmatrix} \sigma_x & \sigma_y \end{pmatrix} \begin{pmatrix} q_x \\ q_y \end{pmatrix}$$

Pseudo spin is projected on momentum
- σ parallel q <=> electron
- σ antiparallel q <=> hole

Intriguing Physics of Graphene