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

**Semester Zimowy 2011/2012**

**Wykład**

# Modelowanie Nanostruktur

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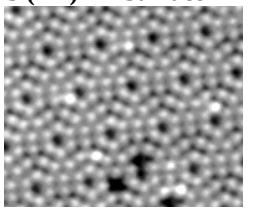
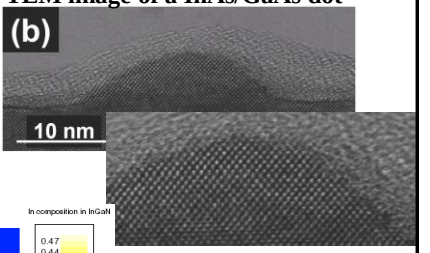
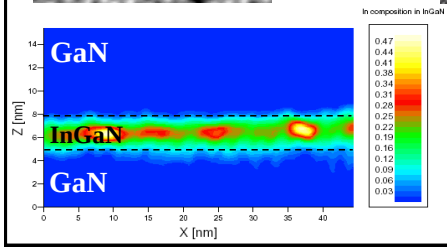
## Examples of Nanostructures

**Si(111)7×7 Surface**



**TEM image of a InAs/GaAs dot**




**HRTEM image: segregation of Indium in GaN/InGaN Quantum Well**



**Lecture 12 –** *January 3rd, 2012*

# On theoretical concepts for modeling nanostructures –

## *the messages to take home*

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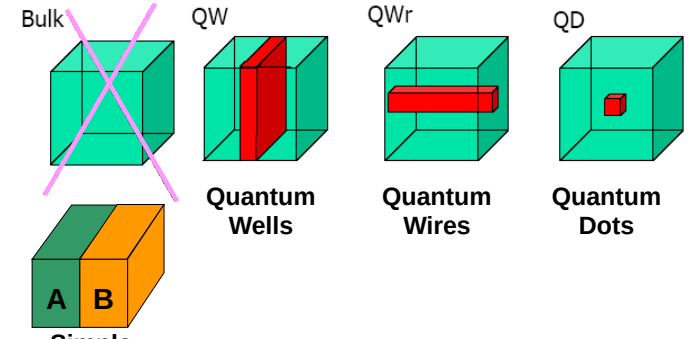
## Nanotechnology – Low Dimensional Structures




**Quantum Wells** | **Quantum Wires** | **Quantum Dots**

**Simple heterostructure**

# Continuum theory- Envelope Function Theory

## Envelope Function Theory – Effective Mass Equation

J. M. Luttinger & W. Kohn, Phys. Rev. B **97**, 869 (1955).

$$[\varepsilon(-i\vec{\nabla}) + U(\vec{r}) - \varepsilon]F_n(\vec{r}) = 0$$ **(EME)**

EME does not couple different bands

$$\psi(\vec{r}) = F_n(\vec{r})u_{n0}(\vec{r})$$

"True" wavefunction — **Envelope Function** — Periodic Bloch Function

- Special case of constant (or zero) external potential

$U(\vec{r}) = 0 \Rightarrow F_n(\vec{r}) = \exp(i\vec{k}\cdot\vec{r}) \Rightarrow \psi(\vec{r})$ **Bloch function**

- $U(z) \Rightarrow F_n(\vec{r}) = \exp[i(k_x x + k_y y)]F_n(z)$

## Electron in an external field

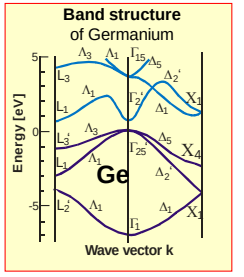
$$\left[\frac{\hat{\vec{p}}^2}{2m} + V(\vec{r}) + U(\vec{r})\right]\psi(\vec{r}) = \varepsilon\psi(\vec{r})$$

Periodic potential of crystal — Non-periodic external potential

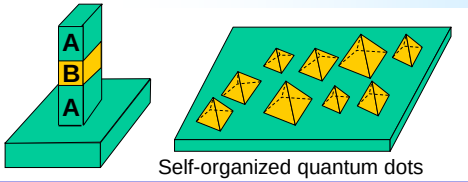
- Strongly varying on atomic scale
- Slowly varying on atomic scale

**Band Structure**

$U(\vec{r}) = 0 \Rightarrow \varepsilon_n(\vec{k}) \Rightarrow$




## Electron States in Quantum Dots




Self-organized quantum dots

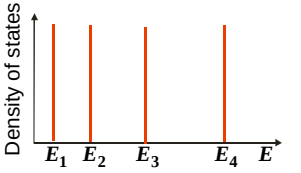
Electrons confined in all directions

$U(x,y,z)$

$$-\frac{\hbar^2}{2m^*}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)F_n(x,y,z) + U(x,y,z)F_n(x,y,z) = E_n F_n(x,y,z)$$

**Density of states for zero dimensional (0D) electrons (artificial atoms)**

$$G^{(0D)}(E) = \sum_\nu \delta(E - E_\nu)$$



## Calculation of the strain tensor

**Elastic energy** $E = \frac{1}{2}\int C_{ijkl}(\vec{x})\varepsilon_{ij}(\vec{x})\varepsilon_{kl}(\vec{x})d\vec{x}$

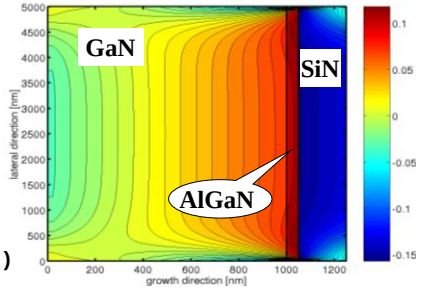
Minimization of elastic energy gives the strain distribution $\varepsilon_{kl}(\vec{x})$

It corresponds to $\frac{\partial \sigma_{ij}}{\partial x_i} = 0$

$\sigma_{ij} = C_{ijkl}\varepsilon_{kl}$

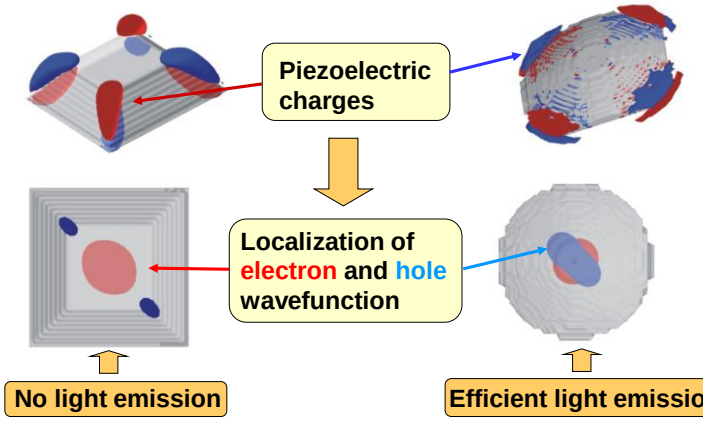
**Hook's Law**

**Strain Map**




**(for GaN/AlGaN HEMT )**

## Dot shape and piezoelectric charges




## 3D nano-device simulator - nextnano$^3$

**Simulator for 3D semiconductor nano-structures:**

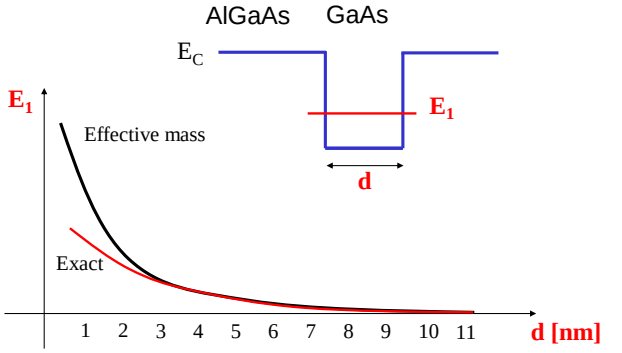
- Si/Ge and III-V materials
- Flexible structures & geometries
- Fully quantum mechanical
- Equilibrium & nonequilibrium

**Calculation of electronic structure :**

- 8-band kp-Schrödinger+Poisson equation
- Global strain minimization
- Piezo- and pyroelectric charges
- Exciton energies, optical matrix elements,...

**Calculation of current only close to equilibrium with new approach**

## How good is effective mass aprox. ?




- **Atomistic details sometimes matter !**

## Farsightedness (hyperopia) of the Standard k·p Model

Alex Zunger, phys. stat. sol. (a) **190,** 467 (2002)

The use of a small number of bands in conventional ***k·p*** treatment of nanostructures leads to "farsightedness" (hyperopia),

- detailed atomistic symmetry is not seen,
- only the global landscape symmetry is noted,

➡ the real symmetry is confused with a higher symmetry.

- Number of important symmetry-mandated physical couplings are unwittingly set to zero
- These are often introduced, after-the-fact, "by hand", via an ansatz.
- **In atomistic theories of nanostructures, the physically correct symmetry is naturally forced upon us by the structure itself.**

## Atomistic methods for modeling of nanostructures

- ***Ab initio* methods** (up to few hundred atoms)
- **Semiempirical methods** (up to 1M atoms)
  - Empirical Pseudopotential
  - **Tight-Binding Methods**

## What about realistic nanostructures ?

Inorganics

**3D** (bulks) : **1-10** atoms in the unit cell

**2D** (quantum wells): **10-100** atoms in the unit cell

**1D** (quantum wires): **1 K-10 K** atoms in the unit cell

**0D** (quantum dots): **100K-1000 K** atoms in the unit cell

Organics

**Nanotubes, DNA**: **100-1000** atoms (or more)

## *Ab initio* = Density Functional Theory Based Methods

## Density Functional Theory (DFT)

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

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

$E[\rho_0] = E_0$ — 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!!!

## The Kohn-Sham Method

- **Kohn-Sham equations with local potential**

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

$$\left[-\frac{\hbar^2}{2m}\vec{\nabla}^2 + v_{ext}(\vec{r}) + v_H(\vec{r}) + v_x(\vec{r}) + v_c(\vec{r})\right]\varphi_i(\vec{r}) = \varepsilon_i\varphi_i(\vec{r})$$

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

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

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

## 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)**

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

- **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 –Total Energy & Forces

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

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 - Methods

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

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

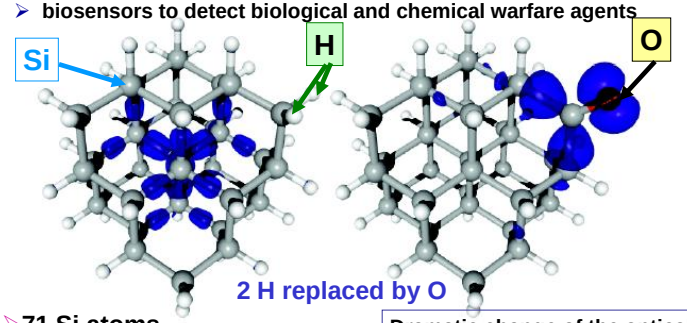
- **Plane waves and pseudopotential** $\chi_{\vec{G}}(\vec{r}) = exp(i\vec{G}\cdot\vec{r})$
- **Linear combination of atomic orbitals (LCAO)**
- **Discretization in real space** $\chi_i(\vec{r}) = \delta(\vec{r} - \vec{r}_i)$

Local in space – suitable for transport

# Tight-Binding methods

## DFT for silicon nanostructures

**Silicon nanoparticles (clusters, dots)**
- **optoelectronic materials on silicon basis**
- **biosensors to detect biological and chemical warfare agents**




2 H replaced by O

- **71 Si atoms 'passivated' by hydrogens**
- **Electrons are in the center of the dot**

**Dramatic change of the optical properties (wavelength) of the silicon nanostructure**

*G. Gali & F. Gygi, Lawrence Livermore National Laboratory*

## 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

## Tight-Binding Hamiltonian

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

**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**

## Why Tight-Binding ?

- Allows us to describe the band structure over the entire Brillouin zone
- Relaxes all the approximations of Envelope Function approaches
- Allows us to describe thin layer perturbation (few Å)
- Describes correctly band mixing
- Gives atomic details
- The computational cost is low
- It is a real space approach
- Molecular dynamics
- Scalability (from empirical to ab-initio)

## Scalability of TB approaches

### Empirical Tight-Binding

Hamiltonian matrix elements are obtained by comparison of calculated quantities with experiments or *ab initio* results.
**Very efficient, poor transferability**.

### Semi-Empirical Hartree-Fock

Methods used in the chemistry context (INDO, PM3 etc.).
Medium transferability.

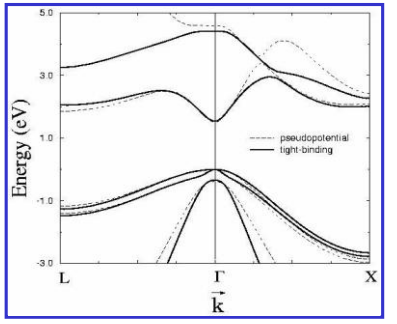
### Density Functional based Tight-Binding (DFTB, FIREBAL, SIESTA)

DFT local basis approaches provide transferable and accurate interaction potentials.
The numerical efficiency of the method allows for molecular dynamics simulations in large super cells, containing several hundreds of atoms.

## The $sp^3s^*$ Hamiltonian

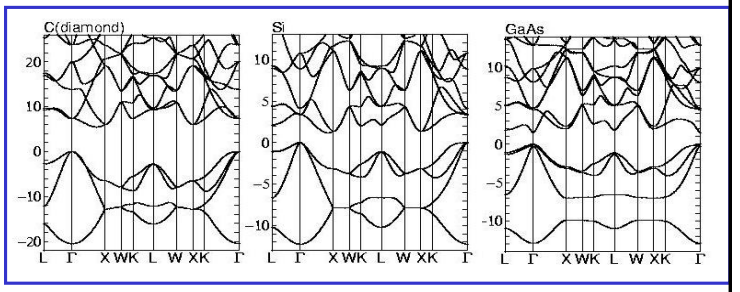
[Vogl et al. J. Phys. Chem Sol. 44, 365 (1983)]

In order to reproduce both valence and conduction band of covalently bounded semiconductors a $s^*$ orbital is introduced to account for high energy orbitals (*d*, *f* etc.)



# The $sp^3d^5s^*$ Hamiltonian

**Many parameters, but works quite well !**



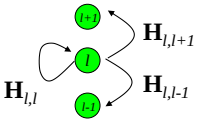

# Tight-binding for quantum wells (1)

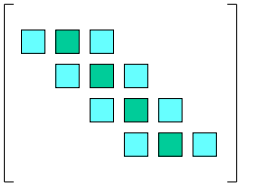
Schroedinger equation

$$\langle m\alpha;\mathbf{k}_{//}|H-E|\psi_{\mathbf{k}_{//}}\rangle=0 \quad \text{Matrix form} \quad \sum_{m=-M}^{M}\mathbf{H}_{l,l+m}\mathbf{C}_{l+m}=E\mathbf{C}_l$$

where M is the number of interacting planes

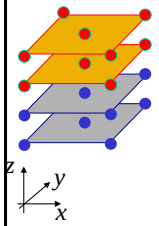
For M=1 we have:




$\mathbf{H}=$ 

…**but boundary conditions ?**

# Tight-binding for quantum wells (1)




For a quantum well and similar 2D heterojunctions, the symmetry is broken in one direction, thus the Bloch theorem cannot apply in this direction.

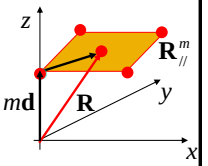
We define the Bloch sums in the m-th atomic plane

$$|m\alpha;\mathbf{k}_{//}\rangle=\frac{1}{\sqrt{N}}\sum_{\mathbf{R}_{//}^m}e^{i\mathbf{k}_{//}\cdot\mathbf{R}_{//}^m}|\mathbf{R}\alpha\rangle$$

LCAO wavefunction

$$|\psi_{\mathbf{k}_{//}}\rangle=\sum_{\text{planes},\,m}\ \sum_{\text{orbitals},\,\alpha}C_{m\alpha}(\mathbf{k}_{//})|m\alpha;\mathbf{k}_{//}\rangle$$

In this case the number of *C*'s is related to the number of planes



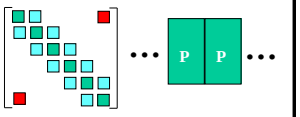

$$\mathbf{R}=m\mathbf{d}+\mathbf{R}_{//}^m$$

# Tight-binding for quantum wells (3)

## Boundary conditions

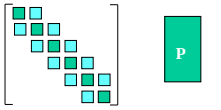
**Periodic**

After P planes the structure repeats itself.
Suitable for superlattices

$\mathbf{H}=$ 


**Finite chain**

After P planes the structure ends.
Suitable for quantum wells.

$\mathbf{H}=$ 


**Open boundary conditions**

After P planes there is a semiinfinite crystal.
Suitable for current calculations.

## Where do we put the atoms ?

To describe the electronic and optical properties of a nanostructure we need to know where the atoms are.

1) We know "a priori" where the atoms are
(for example X-ray informations)

2) We need to calculate the atomic positions

- Quantum calculation (DFTB, SIESTA)
- Continuum theory – elasticity theory
- Valence Force Field (Keating model & extensions)
- Aditional Repulsive terms added to TB Hamiltonian

➡ **T-B molecular dynamics**

$$M_l \ddot{\boldsymbol{R}}_l = -\frac{\partial}{\partial \boldsymbol{R}_l} E(\{\boldsymbol{R}_l\}, \{c^i_{l\alpha}\})$$

## 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 – The Total Energy

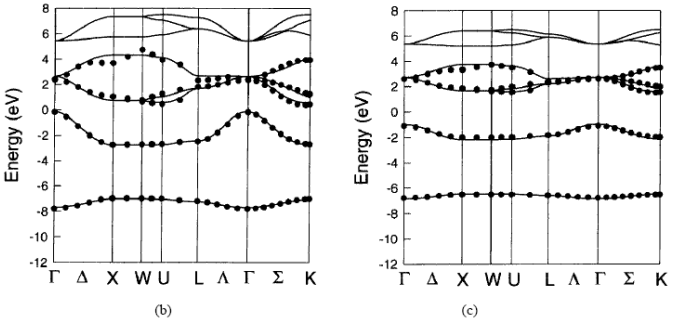
$$E = \sum_{k,n} \epsilon_n(k) + \sum_{l=2}^{N} \sum_{l'=1}^{l-1} E_{rep}(|\boldsymbol{R}_l - \boldsymbol{R}_{l'}|) + U \sum_{l=1}^{N} (q_l - q_l^0)^2$$

**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***

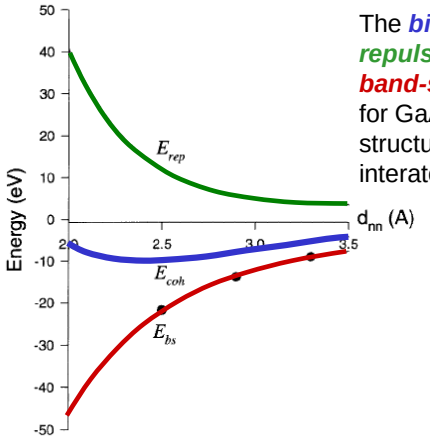
**Typical** $U \sim 1eV$

## Tight-Binding Formalism – 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

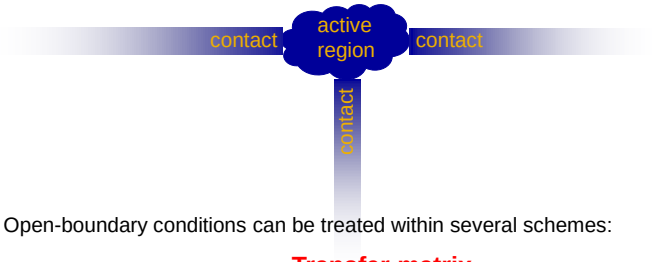
## Tight-Binding Formalism – The Total Energy




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.

## Boundary conditions for transport

The transport problem is: active region where symmetry is lost + contact regions (semi-infinite bulk)




Open-boundary conditions can be treated within several schemes:

- **Transfer matrix**
- **Green Functions**

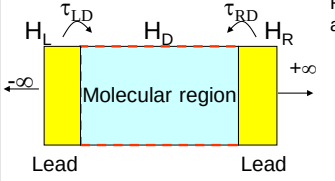
These schemes are well suited for localized orbital approach like TB

## 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**

## Device description: Green Function Approach




Retarded (r) and advanced (a) Green functions are defined as follow (matrix notation)

$$\left[(E \pm i\eta)\mathbf{I} - \mathbf{H}\right]\mathbf{G}^{r,a} = \mathbf{I}$$

Let us write H and G in a block form

$$\mathbf{H} = \begin{bmatrix} H_L & \tau_{LD} & 0 \\ \tau_{DR} & H_D & \tau_{DR} \\ 0 & \tau_{RD} & H_R \end{bmatrix} \qquad \mathbf{G} = \begin{bmatrix} G_L & G_{LD} & G_{LR} \\ G_{DL} & G_D & G_{DR} \\ G_{RL} & G_{RD} & G_R \end{bmatrix}$$

With these definitions and considering that $\left[(E \pm i\eta)\mathbf{I} - \mathbf{H}_{L,R}\right]g_{L,R} = \mathbf{I}$

defines the Green function $g_{L,R}$ of the semi-infinite lead (which can be easily calculated)

$$G_D = \left(E - H_D - \Sigma_L - \Sigma_R\right)^{-1}$$

$$\Sigma_L = \tau_{DL} g_L \tau_{LD} \qquad \Sigma_R = \tau_{DR} g_R \tau_{RD}$$ Self-energy

$$\Gamma_{L,R} = i\left[\Sigma^r_{L,R} - \Sigma^a_{L,R}\right]$$

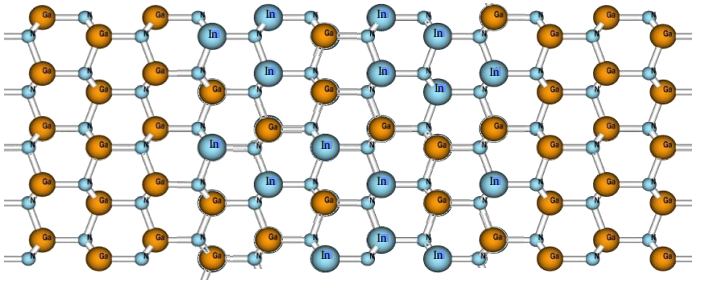
$$T = tr\left(\Gamma_L G^r_D \Gamma_R G^a_D\right)$$ **Transmission coefficient**

$$G = \frac{2e^2}{\hbar} T$$ **Conductance**

# Tight-Binding method Applications

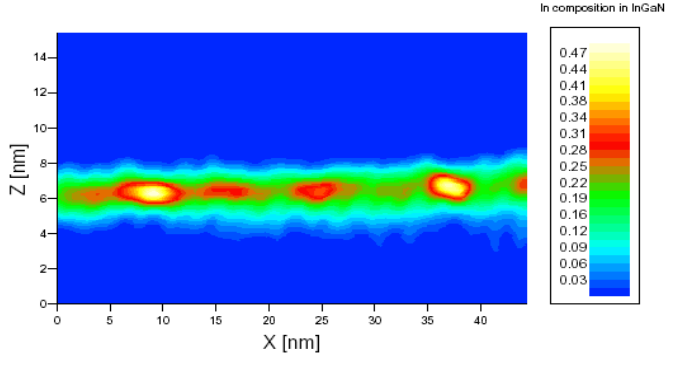
- Optical properties of GaN/InGaN QWs
- Simulations of reactive collisions in biased CNT

## Indium fluctuations

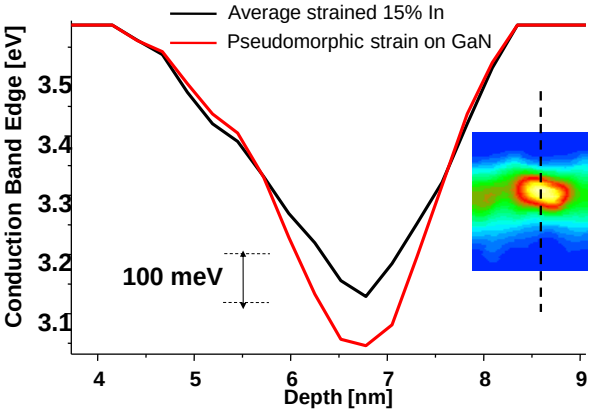



- **Indium** fluctuations are obtained from experimental results
- **Tight-binding** **calculations with 100 000 atoms**

## Indium fluctuations in InGaN/Gan QWs



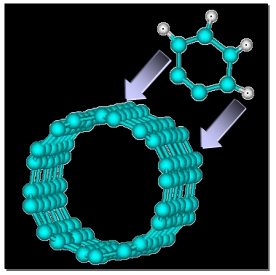

## Conduction Band Edge Profile

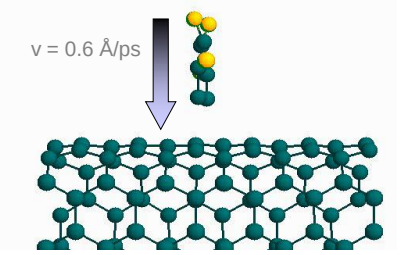



- **Typical photoluminescence results exhibit two peaks**

## Green's Function + Molecular dynamics
## Carbon Nanotubes

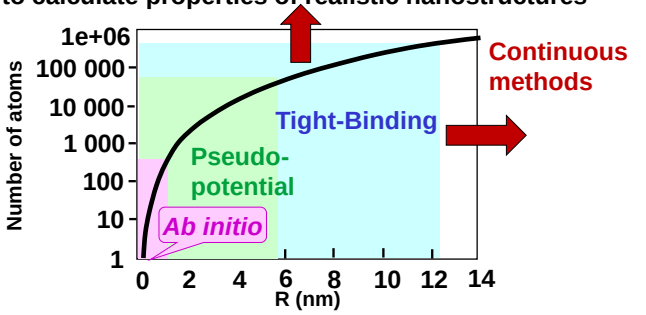
- **Molecular Dynamics** simulations of a reactive collision of a biased nanotube (V=100mV) and benzene
- **Current** flowing in the nanotube calculated at each MD step





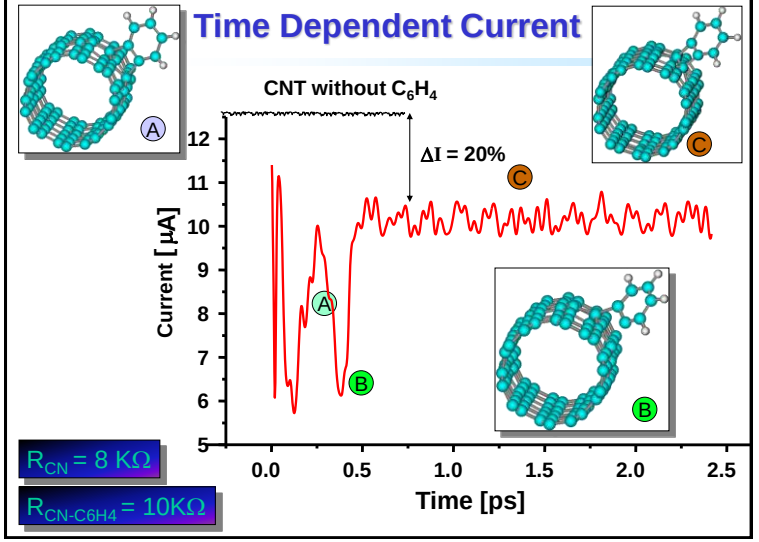

## Atomistic vs. Continuous Methods

- **Microscopic approaches can be applied to calculate properties of realistic nanostructures**




Number of atoms in a spherical Si nanocrystal as a function of its radius R.
Current limits of the main techniques for calculating electronic structure.
Nanostructures commonly studied experimentally lie in the size range 2-15 nm.

## Time Dependent Current




## Conclusions – TB Approaches

- can range from empirical to *ab-initio,*
- avoid all the Envelope Function approximations,
- Green-Function or Transfer matrix techniques can be easily implemented to calculate electronic transport,
- molecular dynamics and current calculations can be coupled together.

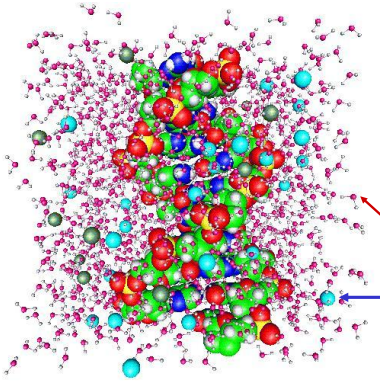
# Coarse-graining & effective approaches

## 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?

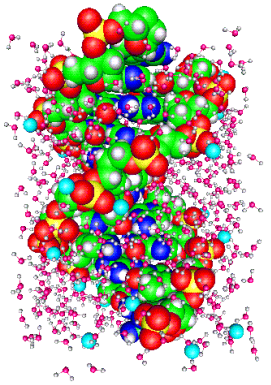
**Polyelectrolyte problem: ions around DNA**



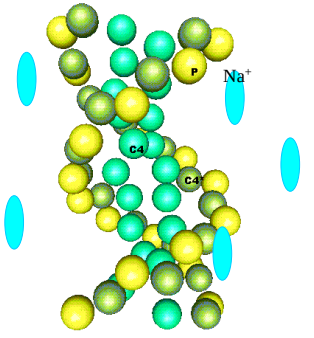

**Atomistic DFT calculations**
not really possible to sample distances
30 – 40 A from DNA

## Coarse-grained model for ions around DNA

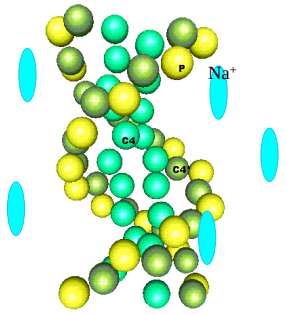
**All-atom model**



**Coarse-grained model**

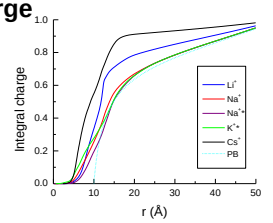


## Coarse-grained model for ions around DNA

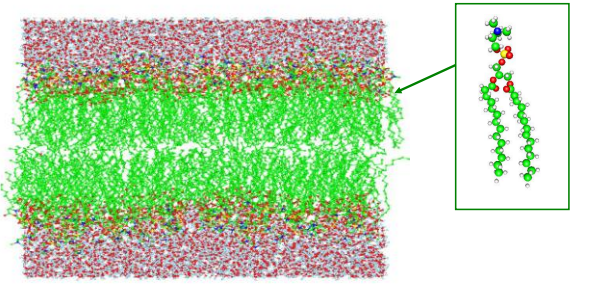



- Ions interacting with DNA by effective solvent-mediated potentials
- Different potentials for various parts of DNA
- No explicit water

⇒ density profile and integral charge




## Lipid bilayer in water

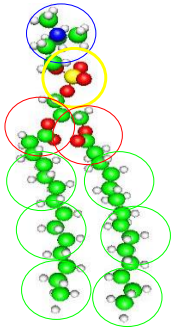


Picture contains 50000 atoms

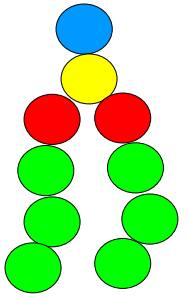
Minimal, reasonable piece of bilayer for **atomistic calculation**

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

## Another example: Coarse-grained lipid model

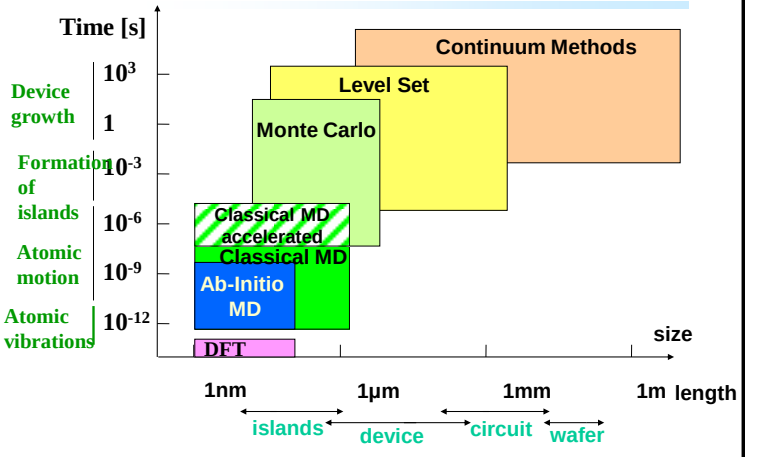


All-atom model
118 atoms



Coarse-grained model
10 sites

## Hierarchy of Theoretical Approaches



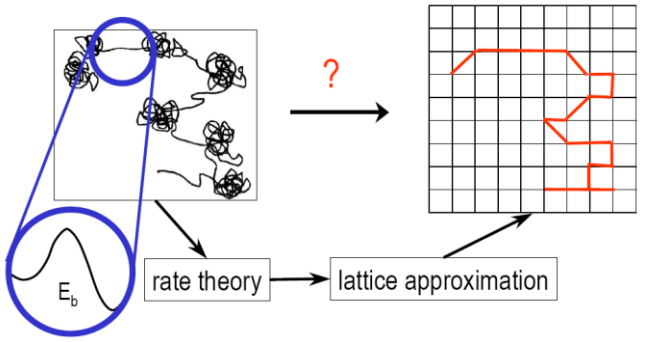
## Kinetic Monte Carlo a tool for simulation of growth processes

## Simulation of growth processes – Kinetic Monte Carlo (KMC)

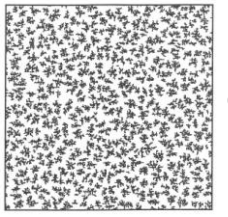
- Modeling crystal growth with the KMC method allows one to cover experimentally relevant growth times and system sizes, since each event on the surface is just described by a single quantity—the transition rate—rather than by modeling the full reaction path including atomic geometries and energies

➡ **Bridging of length and time scales**

## From Molecular Dynamics to Kinetic Monte Carlo



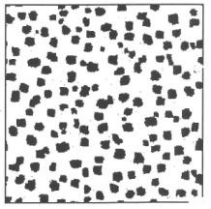

## KMC Simulations: Effect of Nearest Neighbor Bond Energy $E_N$



**KMC Simulations**

**Large $E_N$:** Irreversible Growth

**Small $E_N$:** Compact Islands

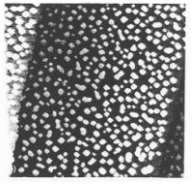


**Experimental Data**

**Au/Ru(100)**

Hwang et al., PRL 67 (1991)

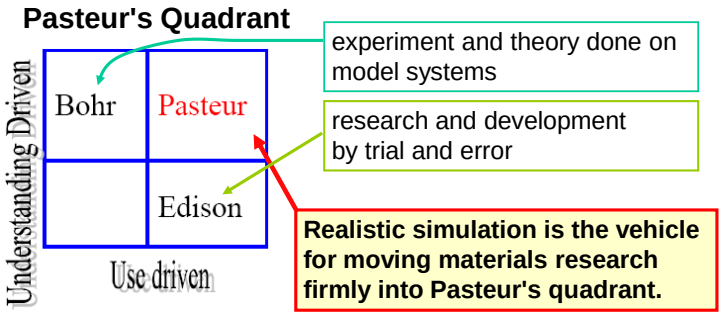
**Ni/Ni(100)**



Kopatzki et al., Surf.Sci. 284 (1993)

## Computational Materials Science: A Scientific Revolution about to Materialize

- Due to the complexity of materials systems, progress has necessarily proceeded either within the Bohr quadrant or Edison's quadrant




# Thank you!