Faculty of Physics,
University of Warsaw

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Lecture

Modeling of Nanostructures and Materials

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Modeling of Nanostructures and Materials *Jacek A. Majewski*

Lecture 13 – *June 2, 2014*

Continuous Methods for Modeling of Nanostructures

- k.p method, effective mass approximation, EFT
- Shallow donors and acceptors
- Quantum wells, wires, and dots
- Self-consistent solution

Ab initio theory of Valence Band Offsets

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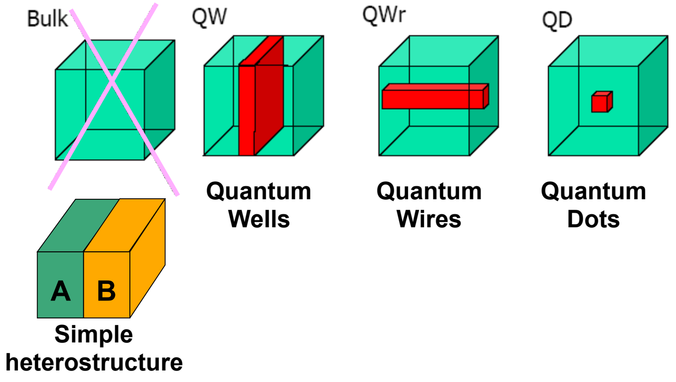
Nanotechnology – Low Dimensional Structures

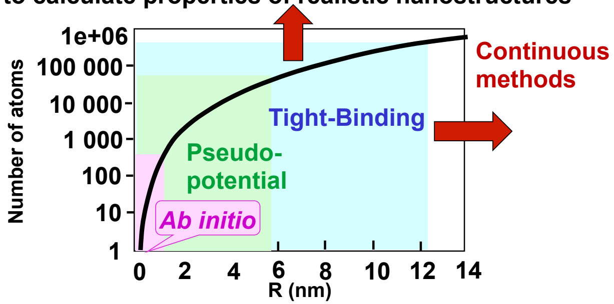


Atomistic methods for modeling of nanostructures

- *Ab initio* methods (up to few hundred atoms)
- **Semiempirical methods** (up to 1M atoms)
  - (Empirical Pseudopotential)
  - Tight-Binding Methods
- Continuum Methods
  (e.g., effective mass approximation)

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.

Continuum theory-
Envelope Function Theory
k.P Method

Electron in an external field

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

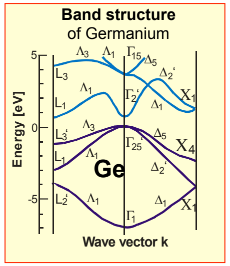
Periodic potential of crystal

Non-periodic external potential

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

Band Structure

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



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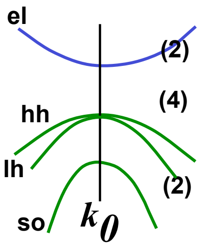
k.P method for the band structure calculations

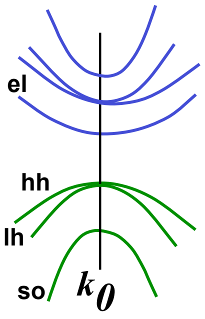
$$\hat{H}=\frac{\hat{\vec{p}}^2}{2m}+V(\vec{r})$$



Valence (6) and conduction bands (2) around k=0 (Γ) point are basis for **8x8 k.p** band model

Band structure known in k_0,

computed for k-points closed to k_0



14x14 k.p

Envelope Function Theory- Degenerate Bands

- Matrices obtained from k.p method, (e.g., 8 band k.p method)

$$\hat{H}_{ab} = D_{ab}^{(0)} + \sum_{\mu=1}^{3} D_{ab}^{(1)\mu} k_\mu + \sum_{\mu=1}^{3}\sum_{\nu=1}^{3} D_{ab}^{(2)\mu\nu} k_\mu k_\nu$$

  - Periodic potential hidden in the parameters of the Hamiltonian matrix
  - Parameters of the Hamiltonian determined on the basis of the perturbation theory verified by experimental results

8 band k.p Method

- The most "popular" form of the k.p Method
- Hamiltonian matrices in both bases used in the calculations
- 8 x 8 matrix easily handled numerically
- For analytical purposes one must take further simplifications

  E. O. Kane, *"The k.p Method"*, Semiconductors and Semimetals,
  Vol. 1, eds. R. K. Willardson and A. C. Beer,
  (Academic Press, San Diego, 1966), p. 75.

- One author – one notation

  e.g., Luttinger parameters

$$\gamma_1 = -\frac{2m}{3h^2}(L+2M) - 1$$

$$\gamma_2 = -\frac{m}{3h^2}(L-M)$$

$$\gamma_3 = -\frac{m}{3h^2}N$$

- Crystal potential hidden in the parameters of the k.p matrix

Electron in an external field

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

Periodic potential of crystal

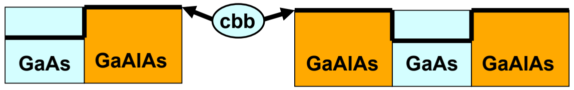
- Strongly varying on atomic scale

Non-periodic external potential

- Slowly varying on atomic scale

Which external fields ?

- Shallow impurities, e.g., donors $U(\vec{r}) = -\frac{e^2}{\kappa|\vec{r}|}$
- Magnetic field B, $\vec{B} = curl\vec{A} = \vec{\nabla}\times\vec{A}$
- Heterostructures, Quantum Wells, Quantum wires, Q. Dots



- Does equation that involves the effective mass and a slowly varying function exist ? $\left(\frac{\vec{p}^2}{2m^*} + U(\vec{r})\right)F(\vec{r}) = \varepsilon F(\vec{r})$ $F(\vec{r}) = ?$

Envelope Function Theory – Effective Mass Equation

Envelope Function Theory- Degenerate Bands

- Matrices obtained from k.p method, (e.g., 8 band k.p method)

$$\hat{\hat{H}}_{ab} = D_{ab}^{(0)} + \sum_{\mu=1}^{3} D_{ab}^{(1)\mu} k_\mu + \sum_{\mu=1}^{3}\sum_{\nu=1}^{3} D_{ab}^{(2)\mu\nu} k_\mu k_\nu$$

Periodic potential hidden in the parameters of the Hamiltonian matrix

- The effect of non-periodic external potential can be described by a system of differential equations for the envelope functions

$$\boxed{\begin{aligned}\sum_{b=1}^{s}[\sum_{\mu=1}^{3}\sum_{\nu=1}^{3} D_{ab}^{(2)\mu\nu}(-i\nabla_\mu)(-i\nabla_\nu) + \\ + \sum_{\mu=1}^{3} D_{ab}^{(1)\mu}(-i\nabla_\mu) + D_{ab}^{(0)} + U(\vec{r})\delta_{ab}]F_b(\vec{r}) = \varepsilon F_b(\vec{r})\end{aligned}}$$

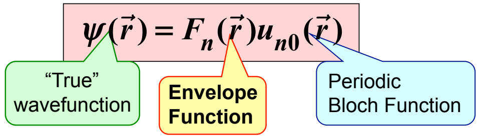
- Wave function $\psi(\vec{r}) = \sum_{b=1}^{s} F_b(\vec{r}) u_{b0}(\vec{r})$
- Basis theory for studies of low dimensional systems

Envelope Function Theory – Effective Mass Equation

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

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

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

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

Envelope Function Theory - Applications

a) Magnetic field

- Minimal coupling principle for full Hamiltonian $\hat{\vec{p}} \to \hat{\vec{p}} - \frac{e}{c}\vec{A}(\vec{r})$
- In effective Hamiltonian $k_\mu \to -i\nabla_\mu - \frac{e}{c}A_\mu(\vec{r})$
- Non-degenerate case - conduction band electrons

$[\varepsilon(-i\vec{\nabla} - \frac{e}{c}\vec{A}(\vec{r})) - \varepsilon]F_n(\vec{r}) = 0 \Longrightarrow$ Landau levels

- Degenerate case of valence band

$$\sum_{b=1}^{s}[D_{ab}^{\mu\nu}(-i\nabla_\mu - \frac{e}{c}A_\mu(\vec{r}))(-i\nabla_\nu - \frac{e}{c}A_\nu(\vec{r}))]F_b(\vec{r}) = \varepsilon F_b(\vec{r})$$

b) Donors in semiconductors

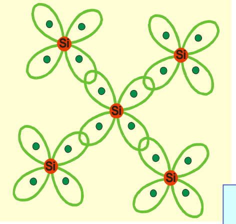
c) Low dimensional semiconductor structures

Modeling of Nanostructures with EMT (EFT)

Envelope Function Theory- Donors in semiconductors

Shallow impurities and doping in semiconductors

- **Donors in Elemental Semiconductor**



Pentavalent Donor impurity (e.g., P, As, Sb) = Silicon-like + Electron & positive ion

The attractive potential $U(\vec{r}) = \frac{-e^2}{\varepsilon|\vec{r}|}$

Coulombic attraction !

The dielectric constant of the semiconductor

- **Donors in III-V semiconductors**
  Group IV elements (e.g., Si, Ge) substituting cations (e.g., Al, Ga)
- **Acceptors**
  Elements of group III (e.g., Al, Ga) substituting an element of group IV (e.g., Si, Ge)

Envelope Function Theory- Shallow impurities

- **Shallow impurities (donors and acceptors) can be described by the Coulombic potential $U(r)$**

$$\hat{H} = \frac{\hat{\vec{p}}^2}{2m} + V_{crystal}(\vec{r}) + U(\vec{r})$$

- **Which band (bands) should be considered in the EFT?**
- **Acceptors in semiconductors**
  Six valence bands around $k_0 = 0$

$$\Psi = \sum_{i=1}^{6} u_{vi0}(\vec{r}) F_{vi}(\vec{r})$$

$$\sum_{j'=1}^{6} [D_{jj'}^{(2)\alpha\beta}(-i\nabla_\alpha)(-i\nabla_\beta) + D_{jj'}^{(0)} + U(r)\delta_{jj'}] F_{j'}(\vec{r}) = EF_j(\vec{r})$$

Analytical solution is quite difficult, even when approximation techniques are used.

- **Donors in Silicon (Germanium)**
  For Silicon, there are six equivalent conduction band minima along Δ axis

$$\left[-\frac{\hbar^2}{2}\left(\frac{2\nabla_t^2}{m_t^*} + \frac{2\nabla_l^2}{m_l^*}\right) - \frac{e^2}{\varepsilon|\vec{r}|}\right] F_c(\vec{r}) = (E - \varepsilon_{c0}) F_c(\vec{r})$$

"Elliptically deformed hydrogen problem "

Envelope Function Theory- Donors in III-V semiconductors

- **Donors in the III-V semiconductors**
  Single conduction band around $k_0 = 0$

$$\varepsilon_c(\vec{k}) = \varepsilon_{c0} + \frac{\hbar^2}{2m^*}\vec{k}^2$$

$$\Psi = u_{c0}(\vec{r}) F_c(\vec{r})$$

$$\left[-\frac{\hbar^2}{2m^*}\vec{\nabla}^2 - \frac{e^2}{\varepsilon|\vec{r}|}\right] F_c(\vec{r}) = (E - \varepsilon_{c0}) F_c(\vec{r})$$

Hydrogen atom problem

$E - \varepsilon_{c0}$ **- is the impurity energy with respect to the conduction band edge**

- $m \to m^*$
- **Coulomb potential reduced by $1/\varepsilon$**

The energy solutions for this problem are:

$$E - \varepsilon_{c0} = -\frac{e^4 m^*}{2\varepsilon^2 \hbar^2}\frac{1}{n^2} \quad \text{for } n = 1, 2, \ldots$$

- **Ground state energy level:** $E_d = \varepsilon_{c0} - Ry^*$ $\quad Ry^* = Ry\left(\frac{1}{\varepsilon}\right)^2 \frac{m^*}{m}$

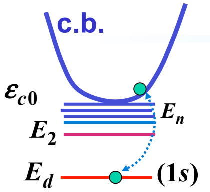
$$1Ry = \frac{\hbar^2}{2ma_B^2} \qquad a_B = \frac{\hbar^2}{me^2}$$

Effective Rydberg

- **The wavefunction of the ground state is** $F_c(r) = \frac{1}{\sqrt{\pi a^{*3}}} e^{-r/a^*}$

Donor effective Bohr radius $a^* = \frac{\varepsilon\hbar^2}{m^* e^2} = a_B \varepsilon \frac{m}{m^*}$

Envelope Function Theory- Donors in III-V semiconductors



Effective mass theory (+ EFT) predicts that the energy levels of shallow impurities are independent of the specific donor or acceptor

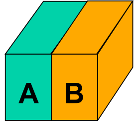
	$E_d(1s)[meV]$	**Experiment** *[meV]*
GaAs	**5.72**	**Si_{Ga} – 5.84** **Ge_{Ga} – 5.88** **S_{As} – 5.87** **Se_{As} – 5.79**
InSb	**0.6**	**Te_{Sb} - 0.6**
CdTe	**11.6**	**In_{Cd} – 14** **Al_{Cd} - 14**

Thermal ionization of shallow impurities is very easy !

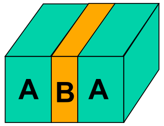
- **Experimental values are generally lower than EMT predictions**
- **Near the core, the impurity potential is not purely Coulombic and the simple model of screening (via the dielectric constant) is not suitable**
  → **Rather large *chemical shift* for the ground state energies**
- Energies of the excited states are nearly independent of the specific donor
- **The donor Bohr radius ~ 100 A (typical lattice constant 5.4 – 6.5 A)**

Envelope Function Theory- Electrons in Quantum Structures

Simple heterostructures



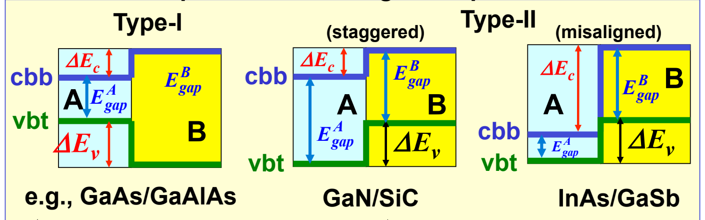
Quantum Wells



- A heterostructure is formed when two different materials (A & B) are joined together
- Modern materials growth techniques lead to heterostructures of extremely abrupt interfaces with interfacial thicknesses approaching only one atomic monolayer
- Heterostructures of great technological importance include: SiO_2/Si, GaAs/AlGaAs, GaInAs/InP, GaSb/AlSb, GaN/AlN, GaInN/GaN, etc.
- The major goal of the fabrication of heterostructures is the controllable modification of the energy bands of carriers
- The energy band diagrams for semiconductor heterostructures ?

Envelope Function Theory- Electrons in Quantum Structures

Various possible band-edge lineups in heterostructure

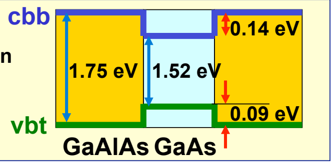


e.g., GaAs/GaAlAs GaN/SiC InAs/GaSb

ΔE_v - Valence Band Offset (VBO) ΔE_c - Conduction band offset

VBO' s can be only obtained either from experiment or ab-initio calculations

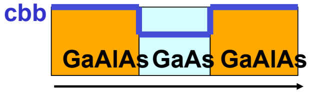
Band lineup in GaAs / GaAlAs Quantum Well with Al mole fraction equal 20%



Envelope Function Theory- Electrons in Quantum Wells

Effect of Quantum Confinement on Electrons

- Let us consider an electron in the conduction band near Γ point



Growth direction (z – direction)

$$\varepsilon_c(\vec{k}) = \varepsilon_{c0} + \frac{\hbar^2}{2m^*}\vec{k}^2$$

Potential $U(\vec{r})$?

$$U(\vec{r}) = U(z) = \begin{cases} \varepsilon_{c0} & z \in \text{GaAs} \\ \varepsilon_{c0} + \Delta E_c & z \in \text{GaAlAs} \end{cases}$$

$U(\vec{r})$ is constant in the xy plane

Effective Mass Equation for the Envelope Function F

$$-\frac{h^2}{2m^*}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)F(x,y,z) + U(z)F(x,y,z) = EF(x,y,z)$$

Separation Ansatz $F(x,y,z) = F_x(x)F_y(y)F_z(z)$

$$-\frac{h^2}{2m^*}\left(\frac{\partial^2 F_x}{\partial x^2}F_yF_z + \frac{\partial^2 F_y}{\partial y^2}F_xF_z + \frac{\partial^2 F_z}{\partial z^2}F_xF_y\right) + U(z)F_xF_yF_z = EF_xF_yF_z$$

Effective Mass Equation of an Electron in a Quantum Well

$$-\frac{h^2}{2m^*}\left(\frac{\partial^2 F_x}{\partial x^2}F_yF_z + \frac{\partial^2 F_y}{\partial y^2}F_xF_z + \frac{\partial^2 F_z}{\partial z^2}F_xF_y\right) + U(z)F_xF_yF_z = EF_xF_yF_z$$

$$E = E_x + E_y + E_z$$

$$-\frac{h^2}{2m^*}\frac{\partial^2 F_x}{\partial x^2}F_yF_z = E_xF_xF_yF_z \qquad -\frac{h^2}{2m^*}\frac{\partial^2 F_y}{\partial y^2}F_xF_z = E_yF_xF_yF_z$$

$$-\frac{h^2}{2m^*}\frac{\partial^2 F_z}{\partial z^2}F_xF_y + U(z)F_xF_yF_z = E_zF_xF_yF_z$$

$$-\frac{h^2}{2m^*}\frac{\partial^2 F_x}{\partial x^2} = E_xF_x \quad \Rightarrow F_x \sim e^{ik_xx}, \quad E_x = \frac{h^2}{2m^*}k_x^2$$

$$-\frac{h^2}{2m^*}\frac{\partial^2 F_y}{\partial y^2} = E_yF_y \quad \Rightarrow F_y \sim e^{ik_yy}, \quad E_y = \frac{h^2}{2m^*}k_y^2$$

$$-\frac{h^2}{2m^*}\frac{\partial^2 F_{zn}}{\partial z^2} + U(z)F_{zn} = E_{zn}F_{zn}$$

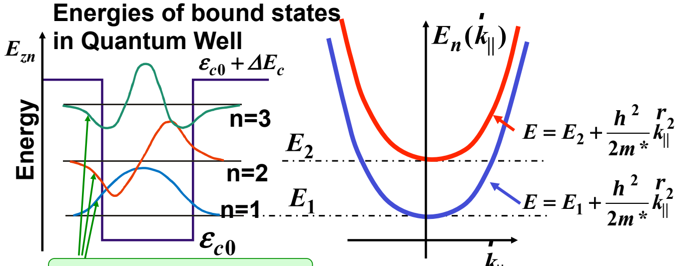
Conduction band states of a Quantum Well

$$F_{\vec{k}_\parallel}(\vec{r}_\parallel) = \frac{1}{A}\exp[i(k_x x + k_y y)] = \frac{1}{A}\exp(i\vec{k}_\parallel \cdot \vec{r}_\parallel)$$

$$\boxed{F_{n,\vec{k}_\parallel}(\vec{r}) = F_{\vec{k}_\parallel}(\vec{r}_\parallel)F_{zn}(z) = \frac{1}{A}\exp(i\vec{k}_\parallel \cdot \vec{r}_\parallel)F_{zn}(z)} \leftarrow F_{zn}(z)$$

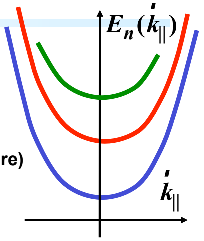
$$\boxed{E_n(\vec{k}_\parallel) = \frac{\hbar^2}{2m^*}\vec{k}_\parallel^2 + E_{zn}} \xleftarrow{E_{zn}} \boxed{-\frac{\hbar^2}{2m^*}\frac{\partial^2 F_{zn}}{\partial z^2} + U(z)F_{zn} = E_{zn}F_{zn}}$$

Energies of bound states in Quantum Well



Wave functions $F_{zn}(z)$

Conduction band states of a Quantum Well



- The confinement of electrons in one dimension results in the creation of energy subbands E_n, which contribute to the energy spectrum:

$$\boxed{E_n(\vec{k}_\parallel) = \frac{\hbar^2}{2m^*}\vec{k}_\parallel^2 + E_n}$$

E_n - Quantized energy associated with the transverse (perpendicular to the heterostructure) confinement.

- Two quantum numbers, one discrete n and another continuous $\vec{k}_\parallel$, are now associated with each electron subband
- At fixed n, the continuum range of $\vec{k}_\parallel$ spans the energy band, which Is usually referred to as a two-dimensional subband
- If electrons occupy only the lowest level, free motion of electrons is possible only in the x,y plane, i.e., in two directions.
  This system is referred to as a *two-dimensional electron gas (2DEG)*
- The behavior of a two-dimensional electron gas differs strongly from that of a bulk crystal.

Density of States of a Two-Dimensional Electron Gas

A special function known as the *density of states G(E)* that gives the number of quantum states $dN(E)$ in a small interval dE around energy E: $dN(E)= G(E)\, dE$

ν - the set of quantum numbers (discrete and continuous)
- corresponding to a certain quantum state

$$\boxed{G(E) = \sum_\nu \delta(E - E_\nu)}$$

Energy associated with the quantum state ν

Spin quantum number

Continuous two-dimensional vector

For 2DEG: $\nu = \{s, n, \vec{k}_\parallel\}$

A quantum number characterizing the transverse quantization of the electron states

$$\boxed{G(E) = 2\sum_{n,k_x,k_y}\delta[E - E_n - \frac{\hbar^2}{2m^*}(k_x^2 + k_y^2)]}$$

Density of States of a Two-Dimensional Electron Gas

$$\boxed{G(E) = 2\sum_{n,k_x,k_y}\delta[E - E_n - \frac{\hbar^2}{2m^*}(k_x^2 + k_y^2)]}$$

L_x, L_y - are the sizes of the system in x and y directions

$S = L_x L_y$ - the surface of the system $\sum_{k_x,k_y}(K) = \frac{L_x L_y}{(2\pi)^2}\iint dk_x dk_y (K)$

$$G(E) = 2\frac{L_x L_y}{(2\pi)^2}\sum_n \iint dk_x dk_y \delta[E - E_n - \frac{\hbar^2}{2m^*}(k_x^2 + k_y^2)] =$$

$$= \frac{L_x L_y}{2\pi^2}\sum_n \int_0^\infty 2\pi k_\parallel dk_\parallel \delta(E - E_n - \frac{\hbar^2}{2m^*}k_\parallel^2) =$$

$$= \frac{L_x L_y}{\pi}\frac{2m^*}{\hbar^2}\sum_n \int_0^\infty k_\parallel dk_\parallel \delta(E - E_n - k_\parallel^2)$$

$k_\parallel^2 = \varepsilon_\parallel$

$$\boxed{G(E) = \frac{Sm^*}{\pi\hbar^2}\sum_n \int_0^\infty d\varepsilon_\parallel \delta(E - E_n - \varepsilon_\parallel) = \frac{Sm^*}{\pi\hbar^2}\sum_n \Theta(E - E_n)}$$

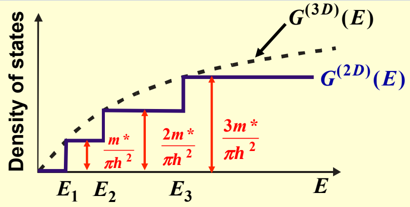
$\Theta(x)$ - Heaviside step function $\Theta(x) = 1$ for $x > 0$ and $\Theta(x) = 0$ for $x < 0$

Density of States of a Two-Dimensional Electron Gas

$$G(E)=\frac{Sm^*}{\pi h^2}\sum_n \Theta(E-E_n)$$

Often the density of states per unit area, $G(E)/S$, is used to eliminate the size of the sample

- Each term in the sum corresponds to the contribution from one subband.
- The contributions of all subbands are equal and independent of energy.
- **The DOS of 2DEG exhibits a staircase-shaped energy dependence, with each step being associated with one of the energy states.**



Density of states for 2DEG in an infinitely deep potential well

$$G^{(3D)}(E)=\left(\frac{m^*}{h^2}\right)^{3/2}\frac{\sqrt{2}}{\pi^2}\sqrt{E}$$

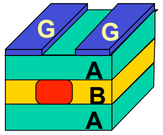
$$\varepsilon(\vec{k})=\frac{\hbar^2}{2m^*}\vec{k}^2$$

For large n, the staircase function lies very close to the bulk curve $G^{(3D)}(E)$

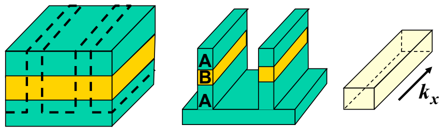
Electron States in Quantum Wires

- **To make the transition from a two-dimensional electron gas to a one-dimensional electron gas, the electrons should be confined in two directions and only 1 degree of freedom should remain, that is, one should design a two-dimensional confining potential $U(y,z)$.**

Two of the simplest examples of structures providing electron confinement in two dimensions

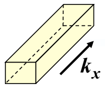


(a) Based on the split-gate technique



(b) Uses an etching technique

Electron States in Quantum Wires



- **Free movement in the x-direction,**
- **Confinement in the y, z directions**
- **Confinement potential $U(y,z)$**

$$F(x,y,z)=e^{ik_xx}F_n(y,z)$$

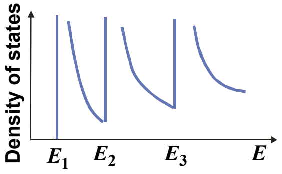
$$-\frac{h^2}{2m^*}\left(\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)F_n(y,z)+U(y,z)F_n(y,z)=E_nF_n(y,z)$$

$$E_n(k_x)=E_n+\frac{h^2}{2m^*}k_x^2$$

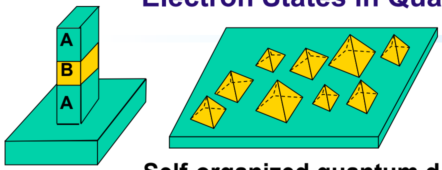
Density of states for one-dimensional electrons

$$G^{(1D)}(E)=2\sum_{n,k_x}\delta(E-E_n-\frac{h^2k_x^2}{2m^*})$$

$$G^{(1D)}(E)=\frac{L_x}{\pi}\sqrt{\frac{2m^*}{h^2}}\sum_n\frac{1}{\sqrt{E-E_n}}\Theta(E-E_n)$$



Electron States in Quantum Dots



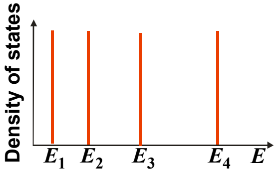
Self-organized quantum dots

Electrons confined in all directions
$U(x,y,z)$

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

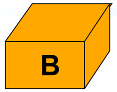
Density of states for zero dimensional (0D) electrons (artificial atoms)

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



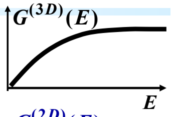
Density of States of Electrons in Semiconductor Quantum Structures

3D
Bulk

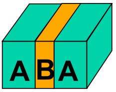


$$\varepsilon_c(\vec{k}) = \varepsilon_{c0} + \frac{\hbar^2}{2m^*}\vec{k}^2$$

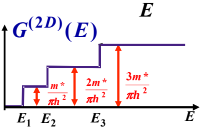
$$G^{(3D)}(E) = \left(\frac{m^*}{\hbar^2}\right)^{3/2}\frac{\sqrt{2}}{\pi^2}\sqrt{E}$$



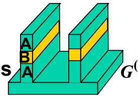
2D
Quantum Wells



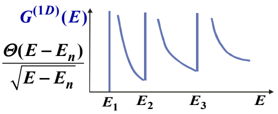
$$G^{(2D)}(E) = \frac{m^*}{\pi\hbar^2}\sum_n \Theta(E-E_n)$$



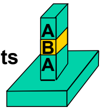
1D
Quantum Wires



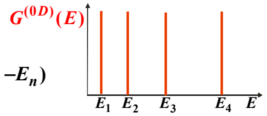
$$G^{(1D)}(E) = \sqrt{\frac{2m^*}{\pi^2\hbar^2}}\sum_n \frac{\Theta(E-E_n)}{\sqrt{E-E_n}}$$



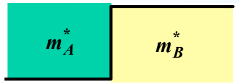
0D
Quantum Dots



$$G^{(0D)}(E) = \sum_n \delta(E-E_n)$$

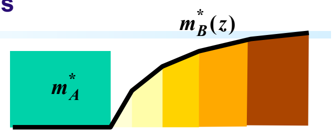


Effective Mass Theory with Position Dependent Electron Effective Mass



$z = 0$

$m_A^* \neq m_B^*$



$z = 0$

"Graded structures"

$$-\frac{\hbar^2}{2m^*(z)}\frac{d^2}{dz^2}$$ **IS NOT HERMITIAN !!**

→ Symetrization of the kinetic energy operator

$$-\frac{\hbar^2}{2}\underbrace{\frac{d}{dz}\frac{1}{m^*(z)}\frac{d}{dz}}$$

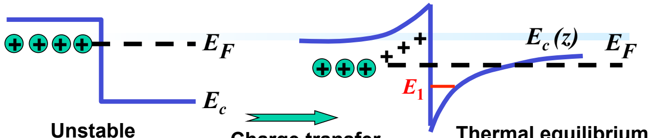
IS HERMITIAN !

$$-\frac{\hbar^2}{2}\frac{d}{dz}\left[\frac{1}{m^*(z)}\frac{d}{dz}\right]F(z) + U(z)F(z) = EF(z)$$

$F(z)$ and $\frac{1}{m^*(z)}\frac{dF(z)}{dz}$ **ARE CONTINOUOS !**

General form of the kinetic energy operator
$T = [m^*(z)]^{\alpha}\hat{p}_z[m^*(z)]^{\beta}\hat{p}_z[m^*(z)]^{\alpha}$ with $2\alpha + \beta = -1$

Effects of Doping on Electron States in Heterostructures



Unstable

Charge transfer

Thermal equilibrium

Resulting electrostatic potential

Fermi distribution function

$$\nabla^2\Phi(\vec{r}) = \frac{4\pi e}{\varepsilon}\left[\sum_{(acc)}\delta(\vec{r}-\vec{R}_A) - \sum_{(don)}\delta(\vec{r}-\vec{R}_D) - \sum_{\nu} f_\nu|\psi_\nu(\vec{r})|^2\right]$$

should be taken into account in the Effective Mass Equation

$$\left[-\frac{\hbar^2}{2m^*}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right) + U(x,y,z) - e\Phi(\vec{r})\right]\psi_\nu(\vec{r}) = E_\nu\psi_\nu(\vec{r})$$

Electrostatic potential can be obtained from the averaged acceptor and donor concentrations

$$\nabla^2\Phi(\vec{r}) = \frac{4\pi e}{\varepsilon}\left[N_A(\vec{r}) - N_D(\vec{r}) - \sum_{\nu} f_\nu|\psi_\nu(\vec{r})|^2\right]$$

- The self-consistent problem, so-called "Schrödinger-Poisson" problem

3D nano-device simulator - nextnano^3

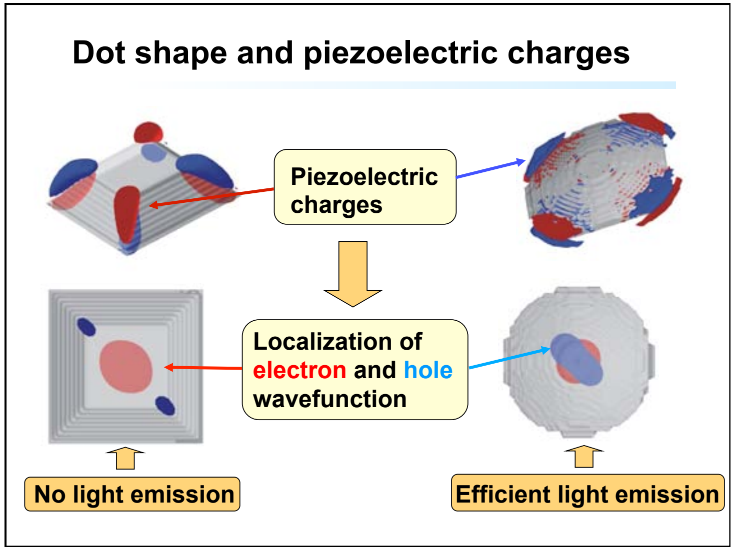
Simulator for 3D semiconductor nano-structures:

- 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



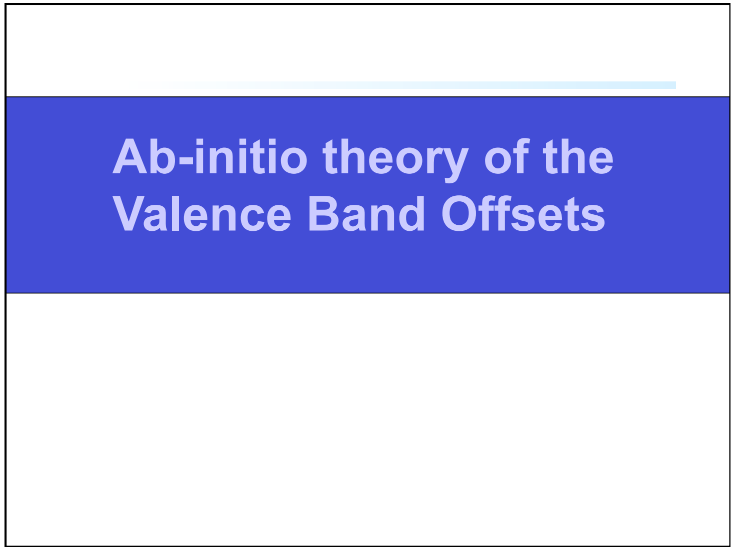
Dot shape and piezoelectric charges

Piezoelectric charges

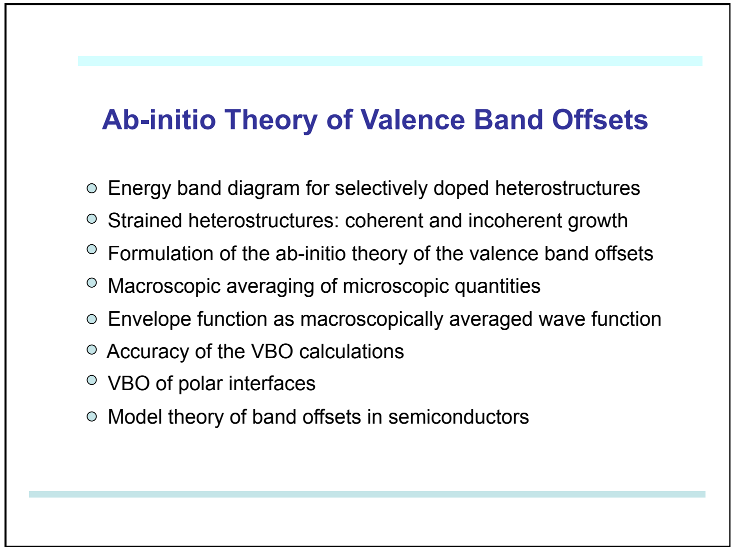
Localization of electron and hole wavefunction

No light emission

Efficient light emission

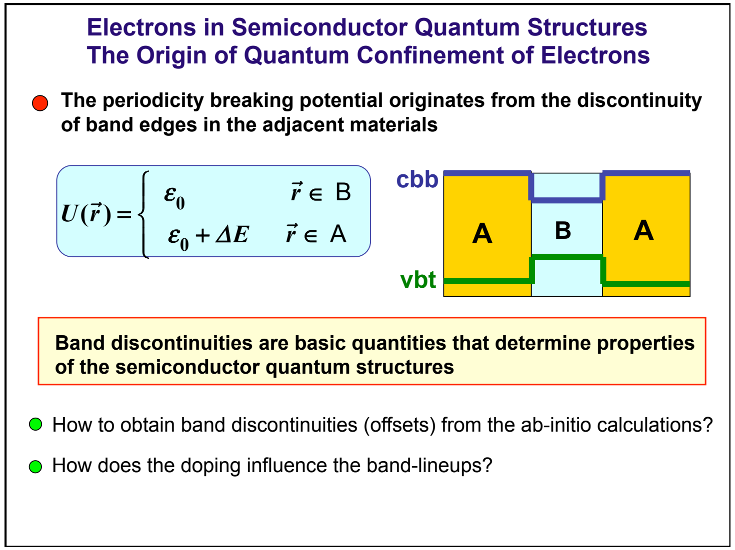


Ab-initio theory of the Valence Band Offsets



Ab-initio Theory of Valence Band Offsets

- Energy band diagram for selectively doped heterostructures
- Strained heterostructures: coherent and incoherent growth
- Formulation of the ab-initio theory of the valence band offsets
- Macroscopic averaging of microscopic quantities
- Envelope function as macroscopically averaged wave function
- Accuracy of the VBO calculations
- VBO of polar interfaces
- Model theory of band offsets in semiconductors



Electrons in Semiconductor Quantum Structures
The Origin of Quantum Confinement of Electrons

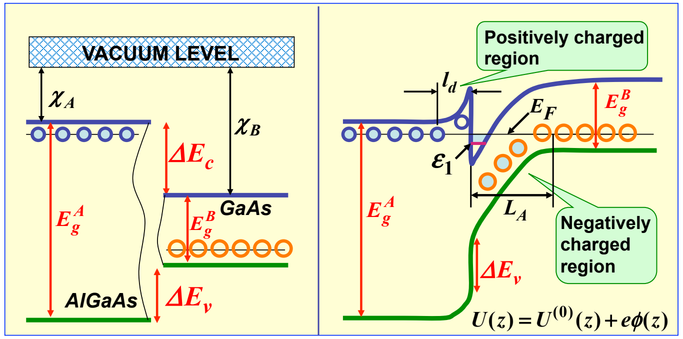
- **The periodicity breaking potential originates from the discontinuity of band edges in the adjacent materials**

$$U(\vec r)=\begin{cases}\varepsilon_0 & \vec r\in \mathrm{B}\\ \varepsilon_0+\Delta E & \vec r\in \mathrm{A}\end{cases}$$

Band discontinuities are basic quantities that determine properties of the semiconductor quantum structures

- How to obtain band discontinuities (offsets) from the ab-initio calculations?
- How does the doping influence the band-lineups?

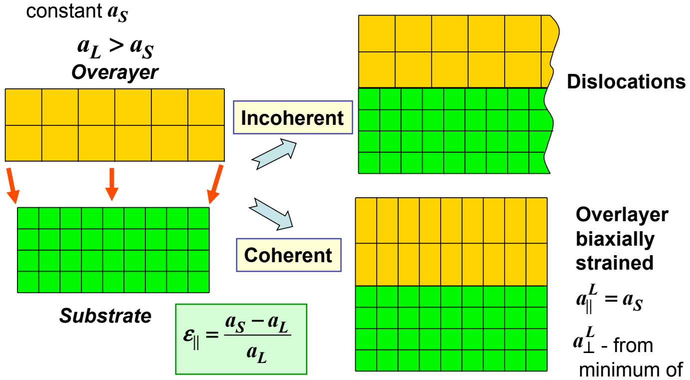
Energy band diagram of a selectively doped AlGAAs/GaAs Heterostructure before (left) and after (right) charge transfer



- χ_A and χ_B - The electron affinities of material A & B
- The Fermi level in the ***GaAlAs*** material is supposed to be pinned on the donor level.
- The narrow bandgap material GaAs is slightly p doped.

Strained Heterostructures: Coherent and Incoherent Structures

An overlayer with lattice constant a_L is grown on a substrate with lattice constant a_S



Overlayer biaxially strained

$a_\parallel^L = a_S$

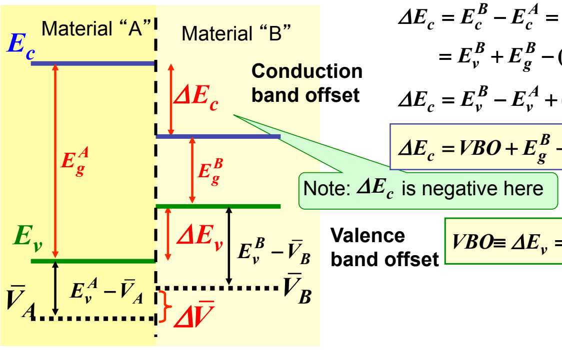
$a_\perp^L$ - from minimum of elastic energy

$$\varepsilon_\parallel = \frac{a_S - a_L}{a_L}$$

The coherent growth is possible only up to ***critical thickness*** of the overlayer

---

Ab-initio Theory of the Band Offsets Formulation of the problem



$$\Delta E_c = E_c^B - E_c^A =$$

$$= E_v^B + E_g^B - (E_v^A + E_g^A)$$

$$\Delta E_c = E_v^B - E_v^A + (E_g^B - E_g^A)$$

$$\boxed{\Delta E_c = VBO + E_g^B - E_g^A}$$

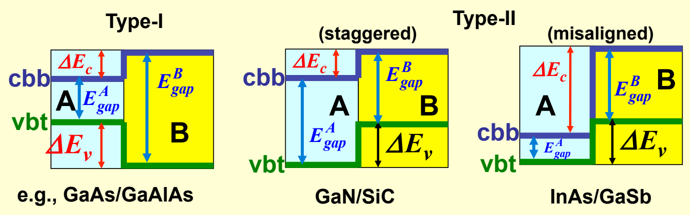
Note: ΔE_c is negative here

$$\boxed{VBO \equiv \Delta E_v = E_v^B - E_v^A}$$

$\bar{V}_A$ and $\bar{V}_B$ are averaged potentials in material A and B, respectively

PROBLEM: Averaged potential in bulk crystal is unknown !!!

Various possible band-edge lineups in heterostructures



ΔE_v - Valence Band Offset (VBO) ΔE_c - Conduction band offset

Type-I: ΔE_v and ΔE_c **have opposite signs**

Type-II: ΔE_v and ΔE_c **have the same signs**

Ab-initio Theory of the Band Offsets

Why the position of the averaged potential is unknown in bulk crystal ?

- NO ABSOLUTE ENERGY SCALE IN INFINITE CRYSTAL !!

Coulomb interaction: $\frac{1}{r}$

Crystal potential $\boxed{V = V_{SR} + V_{LR}}$

Short range potential V_{xc}^{LDA}

Electrostatic potential $V_{LR} = V_H^{el} + V^{el-ion}$

Averaged crystal potential $\bar{V} = \langle V_{SR} \rangle + \langle V_{LR} \rangle$

$$\langle V_{LR} \rangle = \underset{\infty}{V_H^{el}(\vec{G}=0)} + \underset{-\infty}{V^{el-ion}(\vec{G}=0)}$$

$$V_H^{el}(\vec{G}) \sim \frac{1}{\vec{G}^2}$$

exists but unknown!

Ab-initio Theory of the Band Offsets

$$VBO = E_v^B - E_v^A = (E_v^B - \bar{V}_B) - (E_v^A - \bar{V}_A) + (\bar{V}_B - \bar{V}_A) =$$

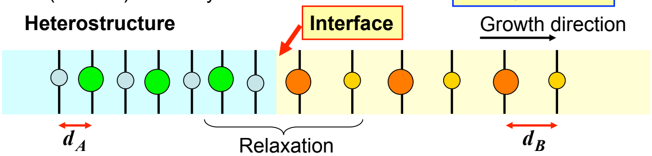
$$= \underbrace{(E_v^B - \bar{V}_B)} - \underbrace{(E_v^A - \bar{V}_A)} + \underbrace{\Delta\bar{V}} = \Delta E_{BS} + \Delta\bar{V}$$

From calculations for two separate bulks

From calculation for superlattice

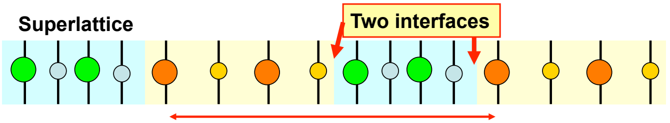
One (or both) bulk may be strained

Heterostructure



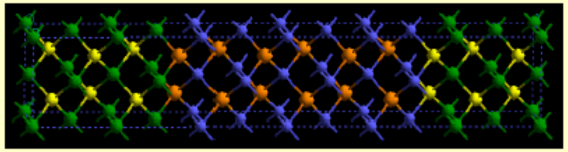
Bulk values of distances between atomic planes far from interface

Superlattice



Superlattice period

Ab-initio calculations for superlattice



- **Full relaxation of atomic positions in the unit cell**

  Atoms at the interfaces relax stronger than atoms in the middle of the structure (so-called bulk region)

- **Relaxation of the unit cell length along the growth direction**

  Takes into account the strain effects

Ab-initio Theory of the Band Offsets

- **Output** of the ab-initio calculations – the microscopic charge density

  $\rho(\vec{r}) = \rho_{el}(\vec{r}) + \rho_{ion}(\vec{r})$ $\qquad \rho_{ion}(\vec{r}) = \sum_{l,\alpha} Z_{l,\alpha}\delta(\vec{r} - \vec{R}_l - \vec{\tau}_\alpha)$

  changes strongly on the atomic scale

- Correspondingly, the electrostatic potential is also strongly oscillating on atomic scale

  $V_{elst}(\vec{r}) = V_H(\vec{r}) + V_{ion}^{LR}(\vec{r})$ $\qquad \nabla^2 V_{elst}(\vec{r}) = -4\pi e^2 \rho(\vec{r})$

- How to obtain changes of the potential on the macroscopic scale ?
- How to obtain the change in the averaged potential ?

Ab-initio Theory of the Band Offsets
Macroscopic averaging of microscopic quantities

A. Baldareschi, S. Baroni, and R. Resta, *Phys. Rev. Lett.* **61**, 734 (1988).

- $\bar{f}(z'')=\frac{1}{S}\int_S dxdy f(x,y,z'')$

Lateral averaging
Over the area of the lateral unit cell

Macroscopic averaging

- $\bar{\bar{f}}(z)=\int dz'\int dz'' w_A(z-z')w_B(z'-z'')\bar{f}(z'')$

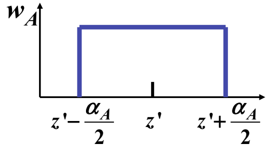
With suitable weighting functions

$\alpha_A=2d_A$

$\alpha_B=2d_B$

(for heterostructures grown along [001] directions)

$$w_A(z-z')=\frac{1}{\alpha_A}\Theta(\alpha_A/2-|z-z'|)$$

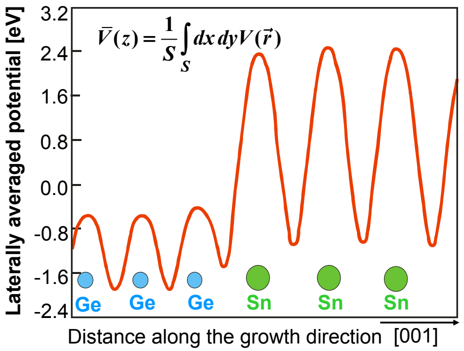


$S\alpha_A$ - Unit cell volume of bulk material A

- Analogous to electrodynamics, transition from microscopic to macroscopic fields

Ab-initio calculations of VBO
Laterally averaged potential

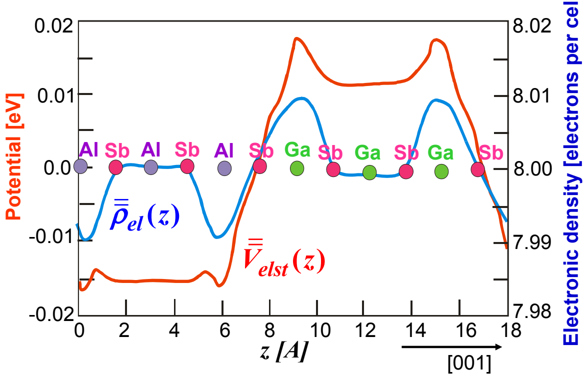
Ge/Sn [001] heterostructure



- Very similar shape of the laterally averaged density

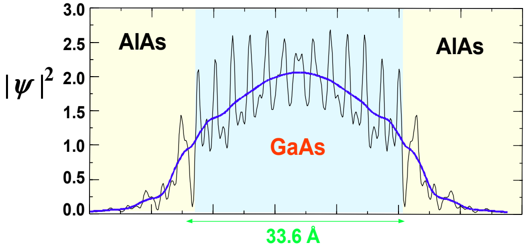
Ab-initio calculations of VBO
Macroscopic averaged density and potential

AlSb/GaSb (001) heterostructure



Ab-initio calculations for superlattices
Laterally and macroscopically averaged wave function of the conduction band bottom

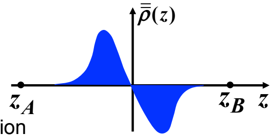
[001] $(AlAs)_{12}(GaAs)_{12}$



- Macroscopically averaged wave function resembles envelope function
- Envelope Function Theory = Continuum theory (on macroscopic scale)

Ab-initio Theory of the Band Offsets

Relation between macroscopically averaged density $\bar{\bar{\rho}}(z)$ and macroscopically averaged electrostatic potential $\bar{\bar{V}}_{elst}(z)$



Bulk region
of material “A”

Interface

$$\boxed{\frac{d^2\bar{\bar{V}}_{elst}(z)}{dz^2} = -4\pi e^2\bar{\bar{\rho}}(z)}$$

$$\Delta\bar{V} = \bar{\bar{V}}_{elst}(z_B) - \bar{\bar{V}}_{elst}(z_A)$$

$$\Delta\bar{V} = \underbrace{4\pi e^2\int_{z_A}^{z_B} z\bar{\bar{\rho}}(z)dz}_{\text{Dipole}} + 4\pi e^2[z_A E(z_A) - z_B E(z_B)]$$

Electric field

$$q_{AB} = \int_{z_A}^{z_B}\bar{\bar{\rho}}(z)dz \quad \text{or} \quad q_{AB} = E(z_A) - E(z_B)$$

Monopole charge
at the interface

$\Delta\bar{V}$ - Dipole at the interface (provided monopole charge vanishes)

Accuracy of the VBO calculations

Better than	Experiment for GaN/GaP : 1.8 +/- 0.6 eV
Worse than	Theory for InP/$Ga_{0.47}In_{0.53}As$: 0.31 +/- 0.01 eV

Comparison with experiment

1) **Simple systems – isovalent heterostructures**

	Theory	Experiment
(001) Si/Ge	0.79 eV, 0.76 eV	0.74 +/- 0.13 eV
(001) AlAs/GaAs	0.45 - 0.55 eV	0.37 - 0.53 eV
AlSb/GaSb	0.37 eV	0.40 – 0.45 eV

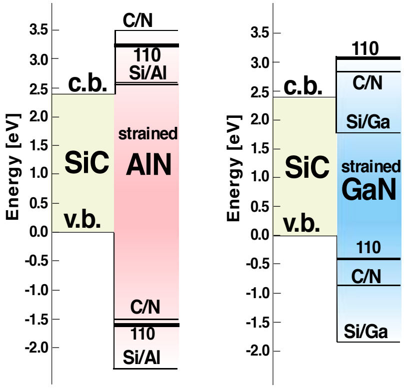
2) **Complicated heterostructures (heterovalent, polar)**

GaAs/ZnSe Ge/ZnSe SiC/GaN

Strong dependence of the offsets on the chemical composition of the interface

Ab-initio calculations of VBOs

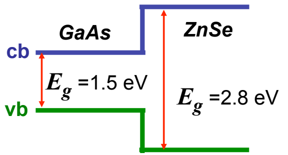
Band Offsets for SiC/AlN and SiC/GaN heterostructure



- [001] SiC/AlN – always Type-I heterostructure
- [001] SiC/GaN – Type-I or Type-II heterostructure depending on the interface composition
- **VBOs of [001] interfaces are determined by interface dipole = chemistry**

“110” indicates nonpolar interfaces of the [110] SiC/AlN or SiC/GaN heterostructures

GaAs/ZnSe (001) heterostructure- Valence Band Offsets



Type I **-** heterostructure

Theory

● One mixed layer [As/Se]	-0.62 eV
One mixed layer [Ga/Zn]	-1.59 eV
○ Two mixed layers	-1.05 eV, -1.17 eV

Experiment

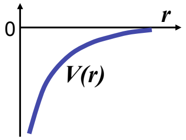
● Interface grown in the Se-rich case	-0.58 eV
○ Interface grown in the Zn-rich case	-1.2 eV

Model Theory of Band Offsets in Semiconductors

Chris G. Van de Walle, *Physical Review B* **39**, 1871 (1989)

- **Semiconductor = Superposition of neutral spherical atoms**

  There exists absolute zero of energy in an atom!



$$\rho_{solid} = \sum_{\alpha} \rho_{at}^{\alpha}(\vec{r} - \vec{R}_{\alpha})$$

$$V_{elst}^{\alpha} = \frac{-Z_{\alpha}e^2}{|\vec{r}|} + V_H^{\alpha}$$

$$\langle V_{elst} \rangle = \sum_{\alpha} \frac{1}{\Omega_0} \int \left(\frac{-Z_{\alpha}e^2}{|\vec{r} - \vec{R}_{\alpha}|} + V_H^{\alpha}(\vec{r}) \right) d^3\vec{r}$$

$$\boxed{\Delta\bar{V} = \bar{V}_B - \bar{V}_A = \langle V_{elst} \rangle_A - \langle V_{elst} \rangle_B}$$

Runs over atoms in the unit cell

- **Pretty good approximation for homopolar interfaces**

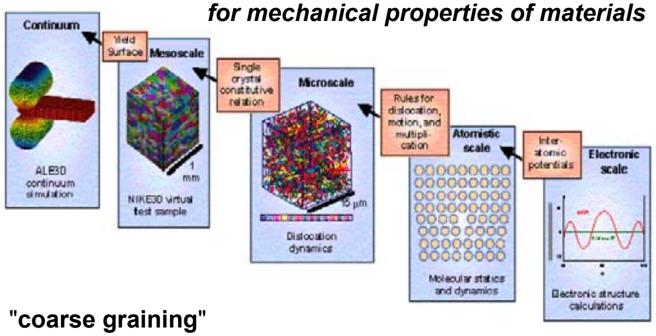
Main points of the lecture:

MODELING of NANOSTRUCTURES & MATERIALS

Lengths & time scales
Multiscale simulations

Computational Materials Science – Multi-scale Simulations

A schematic of the multi-scale challenge for mechanical properties of materials



"**coarse graining**"
the forces among the aggregated pieces can be accurately described by a new model with "renormalized" interactions.

Computational Materials Science: A Scientific Revolution about to Materialize

- The materials science community is on the verge of a paradigm shift in the way it does science with the promise of building a sturdy bridge across the "valley of death" between basic science and technological impact.

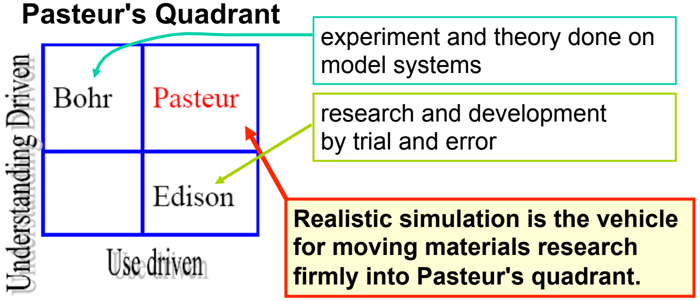
- A useful construct for thinking about this potential paradigm is "**Pasteur's Quadrant**."

D. E. Stokes, *"Pasteur's Quadrant, Basic Science and Technological Innovation,,*
The Brookings Institution, Washington D.C., 1997

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

Pasteur's Quadrant

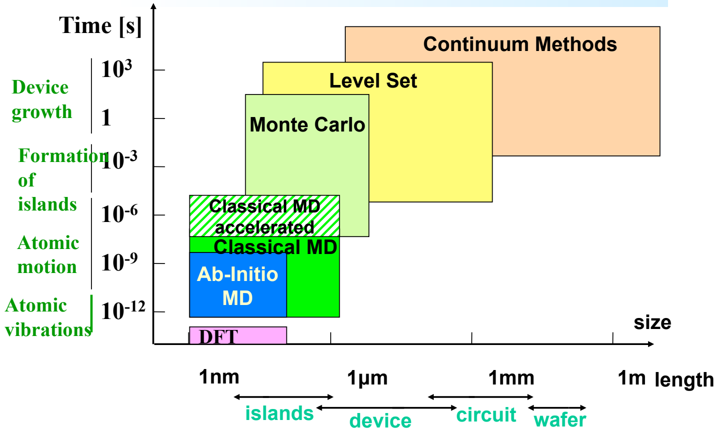


experiment and theory done on model systems

research and development by trial and error

Realistic simulation is the vehicle for moving materials research firmly into Pasteur's quadrant.

Hierarchy of Theoretical Approaches



Materials Properties that require dynamical approach

Thermodynamic Properties

Transport Properties

- Thermal conductivity
- Viscosity
- Diffusion constants

Chemical and other properties

- Chemical reaction rates (catalytic properties, corrosion, electrochemistry)

Require dynamic treatment of ion movement

⇒ Molecular Dynamics

Molecular Dynamics

- **Classical dynamics (given by Newton equations) of atoms (ions) in the system**

$$M_I \ddot{\vec{R}}_I = \vec{F}_I$$
$$\vec{F}_I = -\nabla_I V_{eff}(\{\vec{R}_I\})$$

- **Goal – to determine classical trajectories of all atoms in the system** $\{\vec{R}_I(t)\}$

Classical & *Ab initio* Molecular Dynamics

$$\boxed{\vec{F}_I = -\nabla_I V_{eff}(\{\vec{R}_I\})}$$

Force acting on ion

Classical MD

forces calculated from the effective (empirical, predefined) potential

Ab initio MD

forces calculated from the *ab initio* calculations for electrons moving in the field ions at the instantaneous positions $\{\vec{R}_I(t)\}$

Hellmann-Feynman Theorem

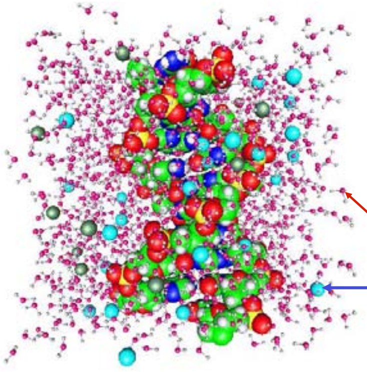
Car-Parrinello Method → **CPMD code**

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.**

Why do we need coarse-grained modeling?
An Example

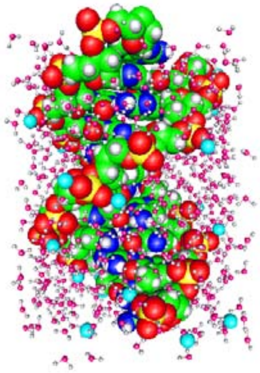
Polyelectrolyte problem: ions around DNA



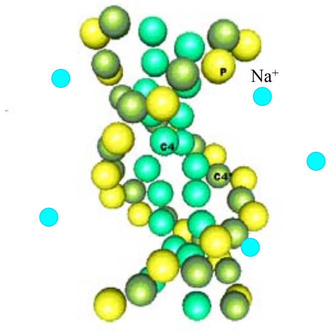
Atomistic MD
not really possible to sample distances 30 – 40 A from DNA

Coarse-grained model for ions around DNA

All-atom model



Coarse-grained model



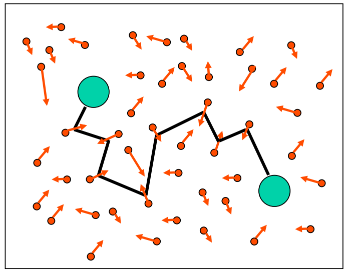
Basics of the Monte Carlo Method

- In a macroscopic system, it is difficult to treat the motions of the all (microscopic) atoms or molecules
- Macroscopic properties of a systems (i.e., how the whole system behaves) are of interest

  ⟹ **Coarse-graining necessary**
- If the time evolution of the system is coarse-grained stochastically, one achieves one class of models, so-called ***stochastic models***.
- ***Monte Carlo Method*** **–** efficient method to realize this numerically on a computer
- Monte Carlo methods provide a powerful way to solve numerically the fluctuation or relaxation in a stochastic system

Brownian Motion

A typical example of Monte Carlo method



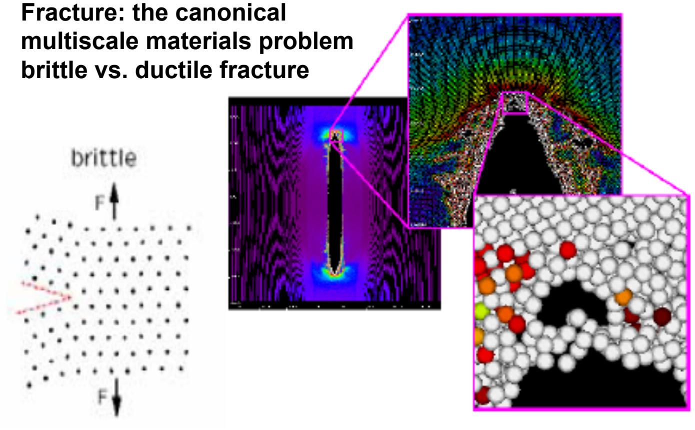
The bigger colloidal particle (Brownian particle) moves randomly, colliding with small solvent particles.

When one observes it through a microscope, one identifies the position (or velocity) of the Brownian particle only.

Applying coarse-graining procedure, the other degrees of freedom (e.g., the motion of small solvent particles) are removed and, finally they can be regarded as a **random force acting on the Brownian particle.**

Multiscale Simulations of Fracture

Fracture: the canonical multiscale materials problem brittle vs. ductile fracture



The End

Thank you !