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

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

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Continuous methods

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.

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Electron in an external field

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

\( \psi(\vec{r}) = \varepsilon \psi(\vec{r}) \)

Periodic potential of crystal

Non-periodic external potential

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

Band Structure

Band structure of Germanium

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

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k.P method for the band structure calculations

Valence (6) and conduction bands (2) computed for k-points closed to \( k_0 \)

Band structure known in \( k_0 \)

14x14 k.p
Envelope Function Theory- Degenerate Bands

- Matrices obtained from k.p method, (e.g., 8 band k.p method)
  \[ \hat{H}_{ab} = D^{(0)}_{ab} + \sum_{\mu=1}^{3} D^{(1)}_{ab} \mu \mu + \sum_{\mu=1}^{3} \sum_{\nu=1}^{3} D^{(2)}_{ab} \mu \nu \mu \nu \]

  - 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

  - One author – one notation
    e.g., Luttinger parameters
    \[ \gamma_1 = \frac{2m}{3\hbar^2}(L + 2M) - 1 \]
    \[ \gamma_2 = \frac{m}{3\hbar^2}(L - M) \]
    \[ \gamma_3 = \frac{m}{3\hbar^2}N \]

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

Electron in an external field

- \( \frac{p^2}{2m} + V(r) + U(r) \)
- \( \psi (\vec{r}) = e \psi (\vec{r}) \)

  - Periodic potential of crystal
  - Non-periodic external potential

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

Which external fields?
- Shallow impurities, e.g., donors
- Magnetic field \( B, \vec{B} = \text{curl} \vec{A} = \vec{V} \times \vec{A} \)
- Heterostructures, Quantum Wells, Quantum wires, Q. Dots

Does equation that involves the effective mass and a slowly varying function exist?

\[ \frac{p^2}{2m} + U(r) \psi (\vec{r}) = eF(\vec{r}) \]

Envelope Function Theory – Effective Mass Equation
Envelope Function Theory – Degenerate Bands

- Matrices obtained from k.p method, (e.g., 8 band k.p method)
  \[ \hat{H}_{ab} = D^{(0)}_{ab} + \sum_{\mu=1}^{3} D^{(1)\mu}_{ab} k_{\mu} + \sum_{\mu=1}^{3} \sum_{\nu=1}^{3} D^{(2)\mu\nu}_{ab} k_{\mu} k_{\nu} \]

- The effect of non-periodic external potential can be described by a system of differential equations for the envelope functions
  \[ \sum_{b=1}^{3} \sum_{\mu=1}^{3} D^{(2)\mu}_{ab} (-i \nabla_{\mu}) (-i \nabla_{\nu}) + \sum_{\mu=1}^{3} D^{(1)\mu}_{ab} (-i \nabla_{\mu}) + D^{(0)}_{ab} + U(\vec{r}) \delta_{ab} F_{n}(\vec{r}) = \varepsilon F_{n}(\vec{r}) \]

- Wave function \( \psi(\vec{r}) = \sum_{n=1}^{x} F_{n}(\vec{r}) u_{n}(\vec{r}) \)
- Basis theory for studies of low dimensional systems

Envelope Function Theory - Applications

a) Magnetic field
- Minimal coupling principle for full Hamiltonian \( \hat{\mathcal{H}} \rightarrow \hat{\mathcal{H}} + \frac{e}{c} \mathcal{A}(\vec{r}) \)
- In effective Hamiltonian \( \hat{\mathcal{H}}_{\text{eff}} \rightarrow \frac{e}{c} A_{\mu} \hat{\mathcal{A}}_{\mu} \)
- Non-degenerate case - conduction band electrons
  \[ \frac{e}{c} \mathcal{A}(\vec{r}) \rightarrow \frac{e}{c} \mathcal{A}(\vec{r}) \]
- Degenerate case of valence band
  \[ \sum_{b=1}^{3} [D^{(2)\mu}_{ab} (-i \nabla_{\mu} - \frac{e}{c} A_{\mu}(\vec{r})) (-i \nabla_{\nu} - \frac{e}{c} A_{\nu}(\vec{r}))] F_{n}(\vec{r}) = \varepsilon F_{n}(\vec{r}) \]

b) Donors in semiconductors
c) Low dimensional semiconductor structures

Envelope Function Theory – Effective Mass Equation


EME does not couple different bands

Special case of constant (or zero) external potential
\( U(\vec{r}) = 0 \Rightarrow F_{n}(\vec{r}) = \exp(\mathcal{A} \cdot \vec{r}) \Rightarrow \psi(\vec{r}) \) Bloch function

\[ \psi(\vec{r}) = F_{n}(\vec{r}) u_{n}(\vec{r}) \]

Modeling of Nanostructures with EMT (EFT)
Envelope Function Theory - Shallow impurities

- Shallow impurities (donors and acceptors) can be described by the Coulombic potential $U(r)$:
  $$
  \hat{H} = \frac{\hat{p}^2}{2m} + V_{\text{crystal}}(\vec{r}) + U(\vec{r})
  $$

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

  $$
  \sum_{n=1}^{6} |D_{2n-1}^{(2)}| \psi_\alpha(\vec{r}) F_j(\vec{r}) = EF_j(\vec{r})
  $$

  **Elliptically deformed hydrogen problem**

- 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 $\Delta$ axis

- Effective mass theory (+ EFT) predicts that

- 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)

**Effective mass theory**

$$
E_2(1s) = m\frac{\hbar^2}{m^* c^2} = a_B m^* c^2 = a_B E_m^* m^*
$$

- Effective Rydberg
- The wavefunction of the ground state is
  $$
  F_0(\vec{r}) = \frac{1}{\sqrt{\pi a_B}} e^{-r/a_B^*}
  $$

- The chemical potential $\mu$ is the energy difference between the ground and excited states

- 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
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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: SiO₂/Si, GaAs/AlGaAs, GaInAs/InP, GaSb/AlSb, GaN/AlN, GaN/NaN, 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 - e.g., GaAs/GaAlAs, InAs/GaSb, GaN/SiC.

Band lineup in GaAs / GaAlAs

Quantum Well with Al mole fraction equal 20%

Various possible band-edge lineups in heterostructures - e.g., GaAs/GaAlAs, InAs/GaSb.

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

Effective Mass Equation of an Electron in a Quantum Well

\[ -\frac{\hbar^2}{2m^*} \left( \frac{\partial^2 F_x}{\partial x^2} + \frac{\partial^2 F_y}{\partial y^2} + \frac{\partial^2 F_z}{\partial z^2} \right) + U(z) = \frac{\hbar^2}{2m^*} \frac{\partial^2 F_x}{\partial x^2} + \frac{\hbar^2}{2m^*} \frac{\partial^2 F_y}{\partial y^2} + \frac{\hbar^2}{2m^*} \frac{\partial^2 F_z}{\partial z^2} \]

\[ \Rightarrow F_x = e^{-\alpha x}, \quad F_y = e^{-\alpha y}, \quad F_z = e^{-\alpha z} \]

\[ \Rightarrow E_x = \frac{\hbar^2}{2m^*} \alpha^2, \quad E_y = \frac{\hbar^2}{2m^*} \alpha^2, \quad E_z = \frac{\hbar^2}{2m^*} \alpha^2 \]

\[ \Rightarrow E_{\text{eff}} = \frac{\hbar^2}{2m^*} \alpha^2 \]
Conduction band states of a Quantum Well

\[ E_n(k) = \frac{\hbar^2}{2m^*} k^2 + E_{in} \]

\[ F(z) = \frac{1}{A} \exp\left(ik_x x + k_y y\right) \]

Energy associated with the quantum state \( V \)

Spin quantum number

Continuous two-dimensional vector

A quantum number characterizing the transverse quantization of the electron states

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

\[ S = L_x L_y \]

Density of States of a Two-Dimensional Electron Gas

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

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

\[ S = L_x L_y \] - is the surface of the system

\[ \Theta(x) \] - 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

\[ G(E) = \frac{S}{\pi \hbar^2} \sum_n \Theta(E - E_n) \]

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.

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.

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 Dots

Self-organized quantum dots

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

Density of states for one-dimensional electrons

\[ G^{(1D)}(E) = 2 \sum_{n,k_x} \Theta(E - E_{n,k_x}) \]

\[ E_{n,k_x} = E_n + \frac{\hbar^2 k_x^2}{2m} \]

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

\[ G^{(0D)}(E) = \sum_{\nu} \Theta(E - E_{\nu}) \]
The self-consistent problem, so-called "Schrödinger-Poisson" problem

**Effective Mass Theory with Position Dependent Electron Effective Mass**

\[ m_\text{eff}(z) = m_A + m_B z \]

"Graded structures"

- IS NOT HERMITIAN !!
- IS HERMITIAN!
- ARE CONTINUOUS!

**General form of the kinetic energy operator**

\[ E = \left[ m^*(z) \right] \cdot p \cdot p \cdot m^*(z) \]

with \( 2\alpha + \beta = -1 \)

**3D nano-device simulator - nextnano³**

- 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

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

\[ U(\mathbf{\vec{r}}) = \begin{cases} \epsilon_0 & \mathbf{\vec{r}} \in B \\ \epsilon_0 + \Delta E & \mathbf{\vec{r}} \in A \end{cases} \]

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

- \( V_A \) and \( V_B \) - 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.

**Ab-initio Theory of the Band Offsets**

**Formulation of the problem**

\[
\Delta E_c = E_{c_A} - E_{c_B} = (E_{c_A} - E_{c_B}) = (E_{cf_A} + E_{c_A} + E_{cf_B} + E_{c_B}) - (E_{cf_A} + E_{c_A} + E_{cf_B} + E_{c_B}) = E_{c_A} - E_{c_B}
\]

\[
\Delta E_v = E_{v_A} - E_{v_B} = (E_{v_A} - E_{v_B}) = (E_{v_A} + E_{v_B}) - (E_{v_A} + E_{v_B}) = E_{v_A} - E_{v_B}
\]

Note: \( \Delta E_c \) is negative here

\( \bar{E_c} \) and \( \bar{E_v} \) are averaged potentials in material A and B, respectively

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

**Various possible band-edge lineups in heterostructures**

Type-I: \( \Delta E_c \) and \( \Delta E_v \) have opposite signs

Type-II: \( \Delta E_c \) and \( \Delta E_v \) have the same signs

**Strained Heterostructures:**

**Coherent and Incoherent Structures**

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

\( a_L > a_S \)

**Overlap**

- **Dislocations**
- **Coherent**
- **Incoherent**

**Critical Thickness**

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

**Overlayer**

- Biaxially strained

\( a_L^* = a_S \)

- From minimum of elastic energy

**GaN/SiC**

- Valence Band Offset (VBO)

\( \Delta E_v \) - Conduction band offset

\( \Delta E_c \) - Valence Band Offset (VBO)

- Type-I: \( \Delta E_v \) and \( \Delta E_c \) have opposite signs

- Type-II: \( \Delta E_v \) and \( \Delta E_c \) have the same signs

**Various materials**

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

**Type-I:**

- \( \Delta E_v \) and \( \Delta E_c \) have opposite signs

**Type-II:**

- \( \Delta E_v \) and \( \Delta E_c \) 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 \( V = V_{SR} + V_{LR} \)

Short range potential \( V_{LDA} \)

Electrostatic potential \( V_{el} \)

Averaged potential \( \langle V \rangle = \langle V_{SR} \rangle + \langle V_{LR} \rangle \)

\[ V_{LR}(G) \approx \frac{1}{G^2} \]

exists but unknown!

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

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

\[ \rho(\vec{r}) = \rho_{el}(\vec{r}) + \rho_{ion}(\vec{r}) \]

changes strongly on the atomic scale

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

\[ V_{el}(\vec{r}) = V_{el}^{LR}(\vec{r}) \]

\[ \nabla^2 V_{el}(\vec{r}) = -4\pi\varepsilon^2 \rho(\vec{r}) \]

- 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

\[ \bar{f}(z') = \frac{1}{S} \int dxdyf(x,y,z') \]
Lateral averaging
Over the area of the lateral unit cell

\[ \bar{f}(z) = \int dz' \int dz'' w_A(z-z')w_B(z'-z'') \bar{f}(z'') \]
Macroscopic averaging
With suitable weighting functions
\[ \alpha_A = 2d_A \]
\[ \alpha_B = 2d_B \]
(for heterostructures grown along [001] directions)

\[ w_A(z-z') = \frac{1}{\alpha_A} \phi \left( \frac{a_A}{2} - |z-z'| \right) \]

\[ S \alpha_A \text{ - Unit cell volume of bulk material } A \]

Very similar shape of the laterally averaged density

Ab-initio calculations of VBO
Laterally averaged potential
Ge/Sn [001] heterostructure

Distance along the growth direction [001]

Laterally averaged potential [eV]

Ab-initio calculations of VBO
Macroscopic averaged density and potential
AlSb/GaSb (001) heterostructure

Potential [eV]

Electronic density [electrons per cell]

[001]

Ab-initio calculations for superlattices
[001](AlAs)\textsubscript{12}(GaAs)\textsubscript{12}

[33.5 Å]

Macropically 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 $\tilde{\rho}(z)$ and macroscopically averaged electrostatic potential $\tilde{V}_{elst}(z)$

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

$$\Delta \tilde{V} = 4\pi e^2 \int_z^{z_B} \tilde{\rho}(z) dz + 4\pi e^2 \left( z_A E(z_A) - z_B E(z_B) \right)$$

Monopole charge at the interface

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

$\Delta \tilde{V}$ - 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/Ga0.47In0.53As : 0.31 +/- 0.01 eV

Comparison with experiment

1) Simple systems – isovalent heterostructures

<table>
<thead>
<tr>
<th>Material</th>
<th>Theory</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si/Ge (001)</td>
<td>0.79 eV, 0.76 eV</td>
<td>0.74 +/- 0.13 eV</td>
</tr>
<tr>
<td>AlAs/GaAs (001)</td>
<td>0.45 - 0.55 eV</td>
<td>0.37 - 0.53 eV</td>
</tr>
<tr>
<td>AlSb/GaSb</td>
<td>0.37 eV</td>
<td>0.40 – 0.45 eV</td>
</tr>
</tbody>
</table>

2) Complicated heterostructures (heterovalent, polar)

<table>
<thead>
<tr>
<th>Material</th>
<th>Theory</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs/ZnSe</td>
<td>0.37 eV</td>
<td>0.40 – 0.45 eV</td>
</tr>
<tr>
<td>Ge/ZnSe</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiC/GaN</td>
<td></td>
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</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Energy [eV]</th>
<th>C/N</th>
<th>Si/Ga</th>
<th>C/N</th>
<th>Si/Ga</th>
</tr>
</thead>
<tbody>
<tr>
<td>v.b.</td>
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<td></td>
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<tr>
<td>substrate</td>
<td>strained</td>
<td>strained</td>
<td>strained</td>
<td>strained</td>
</tr>
</tbody>
</table>

"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

- Semiconductor = Superposition of neutral spherical atoms
  - There exists absolute zero of energy in an atom!

\[ \rho_{\text{solid}} = \sum_{\alpha} \rho_{\alpha}(r - \mathbf{R}_{\alpha}) \]

\[ V_{\text{eff}} = -\frac{Z_{\alpha} e^2}{|\mathbf{r}|} + V_{\text{H}} \]

\[ \langle V_{\text{eff}} \rangle = \sum_{\alpha} \frac{1}{|\mathbf{r}|} \left( -\frac{Z_{\alpha} e^2}{|\mathbf{r} - \mathbf{R}_{\alpha}|} + V_{\text{H}}(\mathbf{r}) \right) d^3r \]

- 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: 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."

**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**

<table>
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<td>wafer</td>
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</table>

**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

\[
M_I \ddot{\vec{R}_I} = \vec{F}_I
\]

\[
\vec{F}_I = -\nabla_{\vec{R}_I} V_{\text{eff}}(\{\vec{R}_I\})
\]

- **Goal** – to determine classical trajectories of all atoms in the system \(\{\vec{R}_I(t)\}\)
Classical & Ab initio Molecular Dynamics

\[ \vec{F}_I = -\nabla^I V_{\text{eff}}(\{\vec{R}_i\}) \]

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 \( \to \) 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

Water molecule

Coarse-grained model for ions around DNA

All-atom model

Coarse-grained model

Na\(^+\)
**Basics of the Monte Carlo Method**

- In a macroscopic system, it is difficult to treat the motions of all (microscopic) atoms or molecules.
- Macroscopic properties of a system (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!