Large-scale numerical calculations for understanding the physics of materials

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DFT: Methodology & numerics

Molecular self-assembly and recognition

Transport & optical properties of nanowires

Magnetic properties

Summary & outlook
Density functional theory (DFT) calculations

Hohenberg Kohn theorem:

\[ E_e[n] = T_0[n] + \frac{1}{2} \int \frac{n(r)n(r')}{|r-r'|} dr dr' + \int n(r)V(r) dr + E_{XC}[n] \]

approximate exchange-correlation energy locally using values for the homogenous electron gas

\[ E_{XC}[n] \approx E_{LDA}^{XC}[n] = \int n(r)\epsilon_{hom}^{XC}(n(r)) dr \]

solution: effective single-particle Schrödinger (Kohn-Sham) equation

\[ \left\{ -\frac{\nabla^2}{2} + \int \frac{n(r')}{|r-r'|} dr' + V(r) + \frac{\delta E_{LDA}^{XC}}{\delta n(r)} \right\} \psi_j(r) = \varepsilon \psi_j(r) \quad n(r) = \sum_{j=occ} |\psi_j(r)|^2 \]

energy dependent on atomic positions → optimise geometry

[Walter Kohn, Nobel Prize for chemistry in 1998]
provide: number of atoms (or chemical potential of species)

Computational scheme

external potential

inter-atomic forces

self-consistent electron structure

\[ \psi_j^{(i+1)} = \hat{O} \psi_j^{(i)} \]

structurally relaxed ground state

vibrational and thermal properties

spectroscopic and transport properties
Numerical implementation in real space:
Mehrstellen discretisation

- Kohn-Sham equation in reciprocal (k) space

\[-\frac{1}{2} \nabla^2 \psi_{nk} + i \vec{k} \times \nabla \psi_{nk} + \frac{1}{2} k^2 \psi_{nk} + V_{\text{eff}} \psi_{nk} = \varepsilon_{nk} \psi_{nk}\]

- Compact discretisation with Mehrstellen operators A and B

\[-\frac{1}{2} A_{\text{Mehr}} \left[ \psi_{nk} \right] + B_{\text{Mehr}} \left[ i \vec{k} \times \nabla \psi_{nk} + \frac{1}{2} k^2 \psi_{nk} + V_{\text{eff}} \psi_{nk} \right] = \varepsilon_{nk} B_{\text{Mehr}} \psi_{nk}\]

\[A_{\text{Mehr}} [f(\vec{r})] = a f(\vec{r}) + \sum_{i=1}^{3} b_i f(\vec{r} \pm h_i \hat{r}_i) + \sum_{i,j} c_{i,j} f(\vec{r} \pm h_i \hat{r} + h_j \hat{r}_j)\]

\[B_{\text{Mehr}} [f(\vec{r})] = a' f(\vec{r}) + \sum_{i=1}^{3} b'_i f(\vec{r} \pm h_i \hat{r}_i)\]

[E. L. Briggs, D. J. Sullivan, J. Bernholc, PRB 54, 14362 (1996)]
Wave functions, as well as the charge density and potentials are distributed by regions over the processors.

Communication between neighbouring processors only

Convergence acceleration using multigrid for simultaneously relaxing high- and low-frequency solutions.

![Diagram](image)
Numerical: efficient parallelisation

Numerical implementation in reciprocal space: plane-wave expansion (VASP)

\[ \psi_j = \frac{1}{\sqrt{V}} \sum_G e^{i(k+G)\cdot r} c_j(G) \]

- parallelization over bands
- parallelization over plane waves
- low communication
- reduced memory usage
- high memory usage
- high communication

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typical system sizes

- 500 - 1300 atoms $\rightarrow$ 5000 - 13000 electr. $\rightarrow$ 16 - 120 GB mem. usage
- system requirements: 32 - 80 CPUs $\Rightarrow$ 24h - 2w

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Top down or bottom up?

Lithography has led to atomistic dimensions!

Introducing Moore's Law into the future:

- 90nm Node 2003
- 65nm Node 2005
- 45nm Node 2007
- 32nm Node 2009
- 22nm Node 2011
- 16nm Node 2013
- 11nm Node 2015
- 8nm Node 2017

Future: molecular self-assembly?

[JV Barth et al., Nature 437, 671 (2005)]
methionine superlattice @ Ag(111) → 1D electron gas

row of Fe monomers in molecular resonator @ Ag(111) → 0D confinement

In order to exploit molecular self-organization, it needs to be understood!
How to control/understand/predict molecular self-assembly?

→ use density functional theory to quantify and rationalize long-range interactions (and thus self-organization phenomena)

→ prototypical model systems: DNA bases and amino acids on metal substrates
Model system: adenine & phenylglycine @ Cu(110)

[Chen and Richardson, Nature Materials 2, 324 (2003)]
Adsorption of single molecules

adenine@Cu(110): corrugated PES

- mutual polarization and substrate-adsorbate charge transfer attract adenine to Cu(110)
- corrugated PES: energy barriers of up to 0.5 eV hinder lateral movement

[Preuss, WGS, Bechstedt, PRL 94, 236102 (2005)]
Adsorption of single molecules

phenylglycine@Cu(110): corrugated PES

covalent bonds between amino and carboxyl groups to the substrate....

...lock the admolecule to specific substrate positions

[Blankenburg, WGS, PRB 74, 155419 (2006)]
Experiment: adenine@Cu(110)

adenine adsorbed on Cu(110) forms dimers that arrange in chains oriented along [±1,2]

[Q Chen, NV Richardson, Nature Materials 2, 324 (2003)]
Co-adsorption of S-(R-)phenylglycine shows chiral recognition!

S-phenylglycine decorates adenine chains running along [1,2] only

R-phenylglycine decorates [-1,2] chains only

What drives the enantio-discrimination? Direct molecule-molecule interactions like in the **three-point contact model** for chiral recognition?
Three-point contact model seems not applicable...

...due to large distances between molecules

Chen & Richardson
second guess: template effect due to chain direction

S-phenylglycine along [1,2]  

R-phenylglycine along [1,2]  

$\Delta E_{S-R} = E_S - E_R = 0.01 \text{ eV (DFT-GGA)}; \ ... = 0.03 \text{ eV (DFT-GGA+vdW)}$

effect does exist, but is very small and favors the wrong direction  
(compared to experiment)
Do need to include the adenine - study model system
encouraging results

adenine and S-phenylglycine along [1,2]

adenine and R-phenylglycine along [1,2]

\[ \Delta E_{S-R} = E_S - E_R = -0.1 \text{ eV (DFT-GGA)} \]

total-energy results suitable to explain experiment mechanism of enantiospecific recognition?

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energy analysis

- stronger substrate-molecule bonding for S-Pgl
  \[ \Delta E_{s-r, bond} = -0.05 \text{ eV} \]

- nearly offset higher strain for S-Pgl
  \[ \Delta E_{s-r, strain} = 0.03 \text{ eV} \]

- more attractive Pgl-adenine interaction for S-Pgl
  \[ \Delta E_{s-r, inter} = -0.08 \text{ eV} \]

Hydrogen bond responsible?
Bader analysis of hydrogen bond...

...finds no difference within numerical accuracy!

Which functional group is causing the chiral recognition? $\rightarrow$ split amino acid!
Ammonia in R or S position yields same energy difference as amino acid!

\[ \Delta E_{s-r,NH_3} = -0.12 \text{eV} \]

reason? electrostatics:

electron transfer from substrate to molecule for both adenine and the amino group

\[ \rightarrow 0.08 \text{eV Madelung energy difference} \]
Chiral recognition explained by

substrate locking (corrugated PES!)
+ substrate-adsorbate charge transfer

→ “three-point contact model” for chiral recognition may include longe-range Coulomb interaction!
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Atomic scale interconnects?

- Traditional VLSI copper interconnect: Increasing resistance with shrinking structure size
- New type of interconnect required for future nanoelectronics → ballistic transport
- Intel currently experimenting with carbon nanotubes as interconnects
- Need to understand electron transport at nanometer scale
Model system: In/Si(111)-(4×1) surface

- Easily accessible for both experiment and theory
- No contribution to nanowire conduction by Si-substrate
- => Ideal testbed for study of transport properties at nanometer scale

By now established structural model for room temperature (RT) phase
- 2-atom In „zig-zag“ chains separated by single-atom insulating Si-chain
- => atomic size In nanowires

[S. J. Park, H. W. Yeom, PRL 93 106402 (2004)]
In/Si(111)-(4×1) surface: Open questions

Transport properties

- What happens upon adsorption of additional In/foreign atoms on top of the wires?
- Experiment: Conductance of room temperature In chains ~ halved by additional 0.1ML of In
- Conductance quenching mechanism & influence of other adatom species unknown

Structure

- Cooling nanowires below 120K leads to period doubling phase transition
- Structural properties of low temperature (LT) phase & nature of phase transition unclear

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[Tanikawa, et al., PRL 93 016801 (2004)]

[S. J. Park, H. W. Yeom, PRL 93 106402 (2004)]
Electron transport - Methodology

- Ohm's law
  \[ I = \frac{1}{R} U = GU \]

- Macroscopic vs. mesoscopic (Landauer) conductivity
  \[ G = \frac{\sigma W}{L} \quad G = \frac{2e^2}{\hbar} \mathcal{T}(E) \]

- Transmittance in Green's function formalism
  \[ \mathcal{T}(E) = \text{Tr}(\Gamma_L G_C^r \Gamma_R G_C^a) \]

- Green's function of a conductor with two semi-infinite leads
  \[ G_C(E) = (E - \mathcal{H}_C - \Sigma_L(E) - \Sigma_R(E))^{-1} \]

- Coupling-terms from self-energy operators
  \[ \Gamma_{\{L,R\}} = i \left[ \Sigma^r_{\{L,R\}}(E) - \Sigma^a_{\{L,R\}}(E) \right] \]
Electron transport - computational scheme

- **Provide:** structurally relaxed geometry
- DFT electronic structure calculation
- Ground state in plane-wave basis
- Transform into real space basis set
- Ground state in localized orbital basis
- Apply Green’s function formalism
- Landauer conductance
Adsorption of impurity atoms

- Adsorption of H, O, In, Pb on top of the nanowires
- Corrugated potential energy surfaces (PES)
Adsorption of impurity atoms

- Strong structural deformation for In & O
- Little structural deformation for H & Pb

H: $\sigma = 0.04\text{Å}$

O: $\sigma = 0.11\text{Å}$

In: $\sigma = 0.12\text{Å}$

Pb: $\sigma = 0.07\text{Å}$
Electron transport - results

- Reduction of nanowire conductance
- Explanation either by:
  - potential well scattering (Pb, O)
  - structural deformation of In nanowire (In, O)

Conductance of adatom decorated nanowires

Cond. of deformed NW without adatom itself

Potential wells at adsorption site
Electron transport - results

- Rationalization of results in terms of conduction channels (here quenched by Pb adsorption)

[Wippermann, Koch, WGS, PRL 100, 106802 (2008)]
In/Si(111)-(4×1) surface: Open questions

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Reflectance anisotropy spectra (RAS) of In/Si(111)-(4×1)

- Measure difference of reflectance parallel & perpendicular to nanowire direction (RAS) → strongly depends on surface structure
- Calculate RAS for different structural models & compare with measurement.

\[
\frac{\Delta R(\omega)}{R_0(\omega)} = \frac{16\pi d\omega}{c} \Im \left[ \frac{\alpha_{xx}(\omega) - \alpha_{yy}(\omega)}{\epsilon_b(\omega) - 1} \right]
\]

- RAS straight forwardly obtainable from dielectric function

Formation of a new RAS peak upon cooling system below 120K

[Fleischer et al., PRB 67 235318 (2003)]
Reflectance anisotropy spectra (RAS) of In/Si(111)-(4×1)

- Phase transition at 120K with period doubling: (4×1)→(8×2) reconstruction
- Semiconducting low temperature (LT) phase
- Several structural models, exact structure unclear

[S. J. Park, H. W. Yeom, PRL 93 106402 (2004)]

[Stekolnikov, Bechstedt, Wippermann, WGS, PRL 98 026105 (2007)]
Spectra nicely reproduce experiment

Two possible candidates remain:
Spectra of (8×2) trimer & hexagon models both agree with experiment!

To identify the correct structural model
investigate spectra at lower energies

Challenge for both experiment & theory
→ work in progress
Reflectance anisotropy spectra - Major transitions

Ideal (4×1)-reconstruction vs. hexagon (8×2)-reconstruction

\[ \Delta E = 1.91eV \ (\Delta \Theta \{ \bar{T} \} = 0.078) \]

\[ \Delta E = 2.16eV \ (\Delta \Theta \{ \bar{T} \} = 0.066) \]

\[ \Delta E = 1.89eV \ (\Delta \Theta \{ \bar{T} \} = 0.036) \]

\[ \Delta E = 2.17eV \ (\Delta \Theta \{ \bar{T} \} = 0.035) \]
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Ab initio g-tensor calculation for paramagnetic surface states in μc-Si:H based solar cells

\[ g = g_e 1 + \Delta g^{SO} \]

\[ g_e = 2.002 \ 319 \ 278 \ldots \ \text{(free electron value)} \]

\[ \Delta g^{SO}_{st} = \frac{\alpha}{4S} \left[ \int \frac{\partial V_{\text{eff}}}{\partial r} \times \left( j^{(1),s}_{\uparrow} - j^{(1),s}_{\downarrow} \right) d^3r \right]_t \]
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Density functional theory (+ many-body perturbation theory) + Green’s function techniques + massively parallel computing allow the quantitative prediction of a wide series of materials properties (long-range chiral recognition, electron transport, optical response, magnetic signatures....)
Thanks to
co-workers in Paderborn!

Mittwoch, 16. September 2009