Density functional theory

The energy of the ground state of a many-electron system:

$E_0 (\{ R_i \}) = \text{Min}_\Psi \langle \Psi | H | \Psi \rangle$

Hohenberg and Kohn (1964): The functional

$n(r) = n[\Psi] = \langle \Psi | \sum_i \delta (r - r_i) | \Psi \rangle$

can be inverted, i.e.,

$\Psi (r_1, r_2, \ldots, r_N) = \Psi [n(r)]$

This implies:

$E_0 (\{ R_i \}) = \text{Min}_{n_\Psi} E_{R_i} [n]$
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Kohn and Sham (1965):

\[ E_{\{R_i\}}[n] = T[n] + \int d^3r \ \nu^{\text{nuc}}_{\{R_i\}}(r)n(r) \]

\[ + \frac{1}{2} \int \int d^3r d^3r' \ \frac{n(r)n(r')}{|r-r'|} + E^{\text{xc}}[n] \]

with local-density approximation or generalized gradient approximation

Accuracy of geometries is better than 0.1 Å. Accuracy of calculated energies (relative) is better than 0.2 eV [for special cases better than 0.01 eV].

Methods

- **Density functional theory**
  - *ab initio* pseudopotentials
    (the thi98md - code --- www.fhi-berlin.mpg.de/th/th.html)
  - FP-LAPW (the WIEN – code by P. Blaha, K. Schwarz, et al.; M. Petersen et al., CPC 126 (2000))
  - All-electron, numerical basis set
    (the DMol3 - code by B. Delley, et al.)

- **ab initio** Molecular Dynamics
- **ab initio** Lattice Gas Hamiltonian
- **ab initio** kinetic Monte Carlo
- **ab initio** Quantum Dynamics
The first (convincing) DFT calculations: Stability of crystals and crystal phase transitions

M. T. Yin and M. L. Cohen
PRB 26 (1982)

see also:
V. L. Moruzzi, J. F. Janak, and A. R. Williams
Calculated Electronic Properties of Metals
Pergamon Press (1978)

Ab initio melting curve of Fe as function of pressure

D. Alfe, M. J. Gillan, and G. D. Price
NATURE 401 (1999)

Microscopic processes controlling the growth -- Example: III-V semiconductors

1) deposition of Ga and As
2) adsorption of Ga
3) diffusion of Ga
4) desorption of Ga
5) adsorption of As$_2$
6) dissociation of As$_2$
7) diffusion of As
8) desorption of As
9) island nucleation
10) growth
**STM Imaging of GaAs(001)**

Measured filled state image at $V_{tip} = -2.1$ eV

Simulated image: local density of states integrated to 0.3 eV below the valence band maximum

LaBella, Yang, Bullock, Thibado, Kratzer & Scheffler, PRL 83, 2989 (1999).

**Voltage Dependence of the STM Current**

STM Simulation

Data

Theory

LaBella, Yang, Bullock, Thibado, Kratzer & Scheffler, PRL 83, 2989 (1999).
Unusually stable site for Ga adatom inside the trench-site As-dimer


P. Kratzer & M. S., to be published

Transition State Theory

\[
\Gamma = \frac{k_B T}{h} \exp \left( \frac{-\Delta F}{k_B T} \right)
\]

\[
\Delta F = -k_B T \ln Z_{TS} + k_B T \ln Z_A
\]

\[
\Gamma = \Gamma_0 \exp \left( \frac{-\Delta E}{k_B T} \right)
\]

\[
\Gamma_0 = \frac{k_B T}{h} \exp \left( \frac{\Delta S^{(vib)}}{k_B} - \frac{\Delta I^{(vib)}}{k_B T} \right)
\]
Theory of the kinetics of growth

1) Analysis of all possibly relevant processes
2) Calculate the rates of all important processes
   \[ \Gamma^{(i)} = \Gamma_0^{(i)} \exp \left( -\frac{\Delta E^{(i)}}{k_B T} \right) \]
3) Statistical approach to describe
   - deposition
   - diffusion
   - nucleation
   - growth
   \[ \text{kinetic Monte Carlo method} \]

Flowchart of kinetic Monte Carlo Simulation

- Go over all atoms and determine all processes which are possible. Get:
  \[ \Gamma^{(i)} = \Gamma_0^{(i)} \exp \left( -\frac{\Delta E^{(i)}}{k_B T} \right) \]
  [If a novel configuration occurs: interrupt and do DFT.]
- Get two random numbers \( r_1, r_2 \) from \([0,1]\)
- Calculate \( R = \sum \Gamma^{(i)} \) and find process \( \tilde{k} \):
  \[ \sum_{i=1}^{\tilde{k}-1} \Gamma^{(i)} \geq r_1 R \geq \sum_{i=1}^{\tilde{k}} \Gamma^{(i)} \]
- Do process \( \tilde{k} \), i.e., move one atom
- Adjust the clock: \( t \rightarrow t - \ln(r_2) / R \)
- Unsuccessful processes are avoided

Sketch of the kMC Approach

Graphical sketch of the statistics of the process that will be chosen in the kMC approach. Each bar corresponds to a certain atom. The color refers to the type of process, and the thickness to the rate.

- Yellow: Ga diffusion in the trench;
- Light blue: Ga diffusion perpendicular to trench;
- Green: Ga enters an As dimer;
- Dark blue: Ga diffusion parallel to steps;
- Red: \( \text{As}_2 \) adsorption into the intermediate.
Adsorption, diffusion, island nucleation, and growth of GaAs

1/60 of the full simulation cell
As$_2$ pressure $= 1.33 \times 10^{-8}$ bar
Ga deposition rate $= 0.1$ ML/s
$T = 700$ K

P. Kratzer & M. S., PRL 88, 036102 (2002)

Island density

Log$_{10}$ of island density does not increase linearly with $1/T$; Unusual increase of island density with increasing $T$ (for $T > 800$ K).

Self-Assembly of Nano-Scale Structures at Semiconductor Surfaces

Motivation:
Single-electron transistor
LEDs and laser diodes
For InAs/GaAs the SK model describes only a part of the full picture.

Equilibrium shape of quantum dots

Stoichiometry and structure of the surface depend on the environment

(surface energy: $\gamma_0 A_0 = E_{\text{total}} - N_{\text{Ga}} \mu_{\text{Ga}} - N_{\text{In}} \mu_{\text{In}} - N_{\text{As}} \mu_{\text{As}}$

(surface stress: $\tau_0 = \gamma_0 + (\frac{\partial \gamma}{\partial \varepsilon})_{\varepsilon=0}$)
As poor As rich

Surface energies of clean GaAs (001)

As chemical potential (eV)

Surfene energy (eV/Å²)

Sung-Hoon Lee, W. Moritz, & M.S., PRL 85, 3890 (2000)

S. Moll, M.S., and E. Pehlke, PRB 58, 4566 (1998)


InP islands on GaP(001)


InP islands on GaInP grown by MOVPE
Samuelson et al. (1996)
Oxidation catalysis, e.g.:

\[
\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2
\]

A "simple", prototypical surface chemical reaction

CO\textsubscript{2} formation at Ru supported catalysts and Ru single crystals.

At UHV conditions Ru is least active for CO oxidation. At high-pressure conditions it is best.

Oxygen adsorption on Ru(0001)

Temperature programmed desorption (TPD)

1) Prepare the adsorbate layer, coverage $\Theta_{\text{init}}$ at temperature $T_{\text{init}}$
2) Change $T$ with time, e.g. $T = T_{\text{init}} + \alpha \cdot t$
   and measure $\Delta \Theta (t)$
   typically $\alpha = 0.1 \text{ - } 10 \text{ K/s}$

Problem: Often important adatom-adatom distances are too big to be tractable directly by DFT (this also refers to disorder)

Lattice-Gas Hamiltonian

$\Delta E = \frac{1}{2} \sum_{i} \sum_{j} V^{(2)}(d_{ij})\sigma_{i}\sigma_{j} + \frac{1}{6} \sum_{i} \sum_{j} \sum_{k} V^{(3)}(d_{ij},d_{ik},d_{jk})\sigma_{i}\sigma_{j}\sigma_{k} + ...$

$\Delta E$ Total Interaction Energy
$s_{n,\alpha}(i=j,k)$ Site Occupancy
$d_{n,\alpha}(i=\alpha,j,k)$ Distance
$V^{(2)}$ Pair Interaction
$V^{(3)}$ Trio Interaction

Distances up to 30-th nearest neighbor

Temperature programmed desorption spectra: O/Ru(0001)

Theory | Experiment
--- | ---

Heating rate: 6 K/s

Stampfl et al., PRL 83 (1999)
Transition-Metal Oxides as Oxidation Catalysts

Catalytic activity of Ru(0001) is due to RuO$_2$(110) domains, that form in the reactive environment.

Influence of the environment on surface structure and stoichiometry

\[ \gamma_{\text{surface}} = \gamma(T, p) = E_{\text{total}} - N_{\text{O}} \mu_{\text{O}} - N_{\text{Ru}} \mu_{\text{Ru}} \]

\[ \mu_{\text{Ru}} + 2 \mu_{\text{O}} = \mu_{\text{RuO}_2} \]

Only one independent variable:

\[ \mu_{\text{O}} (T, p) = \frac{1}{2} \mu_{\text{O}_2} (T, p^0) + \frac{1}{2} kT \ln(p/p^0) \]

K. Rester and M.S., PRB 65, 035406 (2002)
**RuO₂(110) surface terminations**

- RuO₂(110) stability regions in (T, p) space
- RuO₂ (110) surface terminations
- High pressure termination

**RuO₂ (110) stability regions in (T, p) space**

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**O on Ag(111)**

- O on Ag(111)
- O on Ag(111)
- O on Ag(111)

---

K. Reuter et al., PRB 65 (2001)

"Divide-and-conquer" strategy to determine the reaction dynamics

Three independent steps
1) Determine potential energy surface (PES) by DFT calculations (GGA for xc)
2) Analytical or numerical representation of this PES
3) Dynamics
   a) Solve time-dependent or time-independent Schrödinger equation
   b) Solve Newton's equation of motion

PES for H₂ – Pd(100)  
A. Gross and M.S., PRB 57 (1998)

Dissociative adsorption of H₂

A. Eichler et al., PRB 59 (1999)

Oscillations reflect the threshold, e.g., exit conditions of reflected beams

A. Eichler et al., PRB 59 (1999)
Molecular Dynamics Snapshots of H₂ → Pd(100)

Steering effect: aligning the incoming molecule (at low energies; here: $E_i = 0.01 $ eV)

No steering at higher energies; here: $E_i = 0.12 $ eV

Surface core level shifts (SCLS or ESCA)
Important tool for surface analysis (identification of atoms, electronic structure, nature of bonding).

Often surface core-level shifts are interpreted as an initial-state effect.
Dimerization and dimer buckling at Si(001)

- Truncated bulk geometry
- Dimer buckling
- Formation of dimers
- Alternating buckling

Buckling at the clean Si(001) surface is sensitive to electron correlation and electron-lattice coupling

- "A negative $U$ system"?
- HOMO of symmetric dimer
- HOMO of buckled dimer

Which configuration is the ground state?

- Favored by MCSCF (clusters)
- Favored by DFT (slabs)

Si $2p$ SCLS for Si(001) p(2x2)

- Experiment
- Theory (dashed: initial-state effect only; bars: including also final-state screening (by total-energy differences or transition-state theory))

For this system: screening at the surface is better than in the bulk.

Two peaks = clear proof for the buckling

**Photochemistry:** Phonon- versus electron-mediated surface reactions: Laser-induced desorption and oxidation of CO on Ru(0001)

![Diagram of CO oxidation on Ru(0001)]

Femtosecond photooxidation of CO on Ru

![Diagram showing femtosecond photooxidation of CO on Ru](image)

M. Bonn et al., SCIENCE 285 (1999)

DFT calculations at finite temperature

![Diagram showing DFT calculations](image)

M. Bonn et al., SCIENCE 285 (1999)
Stability of the $\alpha$-helix

structure of proteins (peptide chains):

amino group  |  peptide bond  |  carboxyl group

Stability of the $\alpha$-helix

$\beta$-sheet  |  $\alpha$-helix  |  secondary structure

Folding of the peptide chain

peptide chain in the bovine prion protein

atomic structure  |  secondary and tertiary structure

Enthalpy of formation of a hydrogen Bond

Enthalpy of formation: $\Delta H^\circ = E_p^N - E_{p-1}^N - \mu_{\text{peptide}}$

poly alanine ( $\boxdot$ = methyl group = CH$_3$ )

sheet (extended structure) as "reservoir"

$\alpha$-helix:  
"back bone" costs:  
$\Delta H^\circ_{\text{back}} \approx 6.5$ kcal/mol for all $N$

H-bond gain:  
$\Delta H^\circ_{\text{H-bond}} = -2.7$ kcal/mol for $N=4$
  
$\Delta H^\circ_{\text{H-bond}} = -9.5$ kcal/mol for $N=\infty$

hydrogen bond is strongly cooperative

Electronic Structure Theory
(Density Functional Theory → QMC)
⇒ Potential Energy Surface

- Dynamics of the Nuclei along this PES
- Statistical Mechanics

⇒ Thermal Equilibrium Structures
⇒ Real World