institute for pure & applied mathematics

Hands-on Summer School: Electronic Structure Theory for Materials and (Bio)molecules

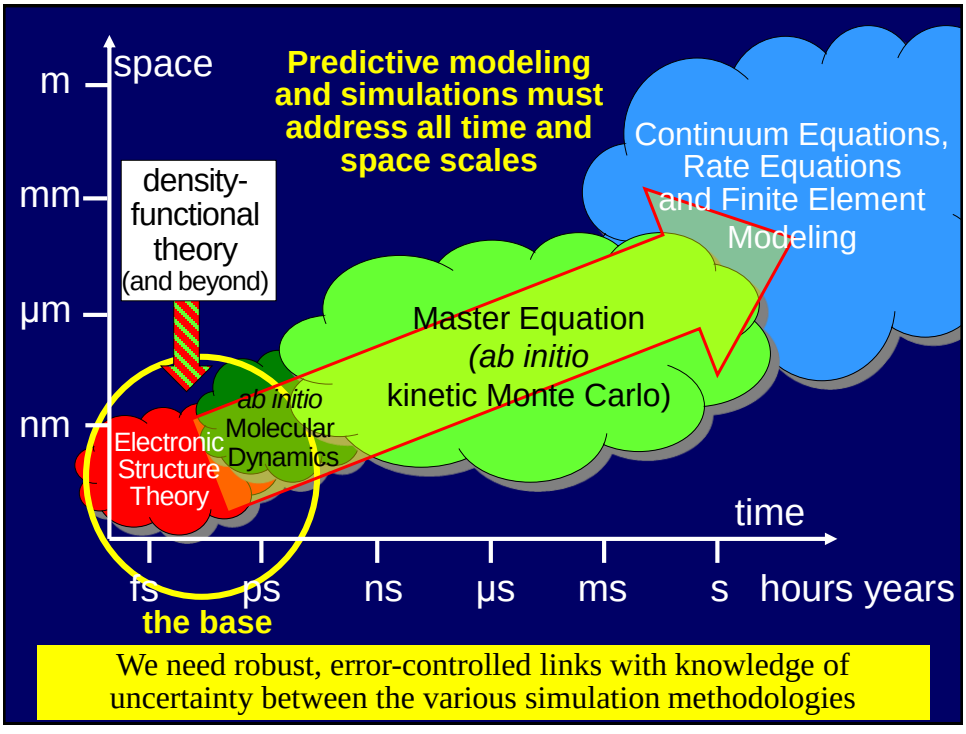
July 21 - August 1, 2014

Monday, July 21, 2014

Morning Session

First Principles - Overview

8:00 - 9:00	Breakfast
9:00 - 9:30	Welcome and Opening Remarks
9:30 - 10:30	**Matthias Scheffler (Fritz-Haber-Institut der Max-Planck-Gesellschaft)** "Overview: Electronic Structure Theory for the Ground State"
11:00 - 12:00	**Kieron Burke (University of California, Irvine (UCI))** "Electronic Structure Beyond the Ground State"



Theoretical Concepts and Some Examples (Results)

1. Electronic-Structure Theory
2. *Ab initio* Atomistic Thermodynamics
3. Molecular Dynamics
4. Kinetic Monte Carlo Approach

Modeling Materials Properties and Functions: The Many-Body Schrödinger Equation

$$(\hat{T}^{e} + \hat{T}^{ion} + \hat{V}^{e-e} + \hat{V}^{e-ion} + \hat{V}^{ion-ion})\Psi = E\Psi$$

With: $\Psi(\mathbf{r_1}, \cdots \mathbf{r_N}; \mathbf{R}_1, \cdots \mathbf{R_M})$

$$\hat{T}^{e} = \sum_{k=1}^{N} \frac{\mathbf{p}_k^2}{2m} \qquad \hat{T}^{ion} = \sum_{I=1}^{M} \frac{\mathbf{P}_I^2}{2M_I}$$

$$\hat{V}^{e-e} = \frac{1}{2}\frac{1}{4\pi\epsilon_0}\sum_{k\neq k'}^{N,N} \frac{e^2}{|\mathbf{r_k} - \mathbf{r_{k'}}|}$$

$$\hat{V}^{ion-ion} = \frac{1}{2}\frac{1}{4\pi\epsilon_0}\sum_{I\neq I'}^{M,M} \frac{Z_I Z_{I'}}{|\mathbf{R_I} - \mathbf{R_{I'}}|}$$

$$\hat{V}^{e-ion}(\mathbf{r_k}, \mathbf{R_I}) = \sum_{\mathbf{k=1}}^{\mathbf{N}}\sum_{\mathbf{I=1}}^{\mathbf{M}} \mathbf{v_I^{ion}}(|\mathbf{R_I} - \mathbf{r_k}|)$$

Modeling Materials Properties and Functions: The Many-Body Schrödinger Equation

$$(\hat{T}^e + \hat{T}^{ion} + \hat{V}^{e-e} + \hat{V}^{e-ion} + \hat{V}^{ion-ion})\Psi = E\Psi$$

With: $\Psi(\mathbf{r_1}, \cdots \mathbf{r_N}; \mathbf{R}_1, \cdots \mathbf{R_M})$

$$\hat{T}^e = \sum_{k=1}^{N} \frac{\mathbf{p}_k^2}{2m} \qquad \hat{T}^{ion} = \sum_{I=1}^{M} \frac{\mathbf{P}_I^2}{2M_I}$$

$$\hat{V}^{e-e} = \frac{1}{2}\frac{1}{4\pi\epsilon_0}\sum_{k\neq k'}^{N,N} \frac{e^2}{|\mathbf{r_k} - \mathbf{r_{k'}}|}$$

???

$$\hat{V}^{ion-ion} = \frac{1}{2}\frac{1}{4\pi\epsilon_0}\sum_{I\neq I'}^{M,M} \frac{Z_I Z_{I'}}{|\mathbf{R_I} - \mathbf{R_{I'}}|}$$

$$\hat{V}^{e-ion}(\mathbf{r_k}, \mathbf{R_I}) = \sum_{k=1}^{N}\sum_{I=1}^{M} v_I^{ion}(|\mathbf{R_I} - \mathbf{r_k}|)$$

We know the operators and the interactions. We can write them down.

No open question here!

Born-Oppenheimer Approximation

$$\Psi(\mathbf{r_1}, \cdots \mathbf{r_N}; \mathbf{R_1}, \cdots \mathbf{R_M}) = \sum_{\nu} \Lambda_\nu(\{\mathbf{R_I}\})\Phi_{\nu\,\{\mathbf{R_I}\}}(\{\mathbf{r_k}\})$$

Where Φ_ν are solutions of the "electronic Hamiltonian":

$$H^e_{\{\mathbf{R_I}\}}\Phi_{\nu,\{\mathbf{R_I}\}}(\{\mathbf{r_k}\}) = E^e_{\nu,\{\mathbf{R_I}\}}\Phi_{\nu,\{\mathbf{R_I}\}}(\{\mathbf{r_k}\})$$

$$H^e = T^e + V^{e-e} + V^{e-ion}$$

frequently (commonly) applied approximations:

- neglect non-adiabatic coupling (terms of order m/M_I)
- keep only Λ_0

⇒ the dynamics of electrons and nuclei decouple

Some Limits of the Born-Oppenheimer Approximation

It does not account for correlated dynamics of ions and electrons. For example:

- polaron-induced superconductivity
- dynamical Jahn-Teller effect at defects in crystals
- some phenomena of diffusion in solids
- non-adiabaticity in molecule-surface scattering and chemical reactions
- relaxation and transport of charge carriers (e^- or h)
- etc.

Some Limits of the Born-Oppenheimer Approximation

It does not account for correlated dynamics of ions and electrons. For example:

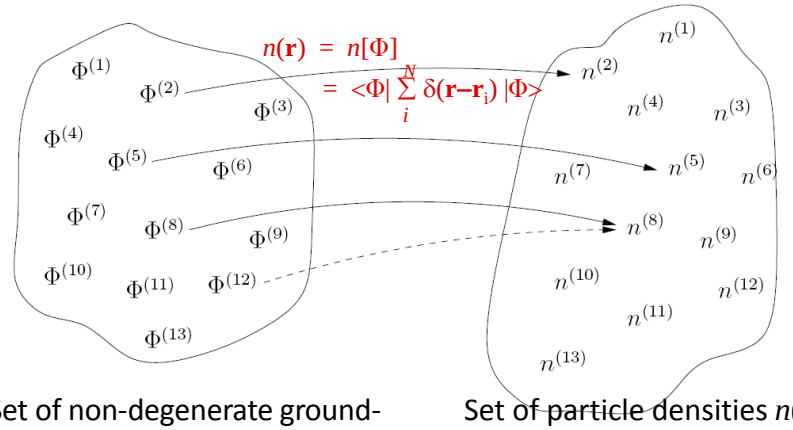
These limits can be severe. Nevertheless, we will use the BO approximation in the following.

How can we solve:

$$H^e_{\{\mathbf{R_I}\}}\Phi_{\nu,\{\mathbf{R_I}\}}(\mathbf{r_k}) = E^e_{\nu,\{\mathbf{R_I}\}}\Phi_{\nu,\{\mathbf{R_I}\}}(\mathbf{r_k})$$

$$H^e = T^e + V^{e-e} + V^{e-ion}$$

The Hohenberg-Kohn Theorem (1964)

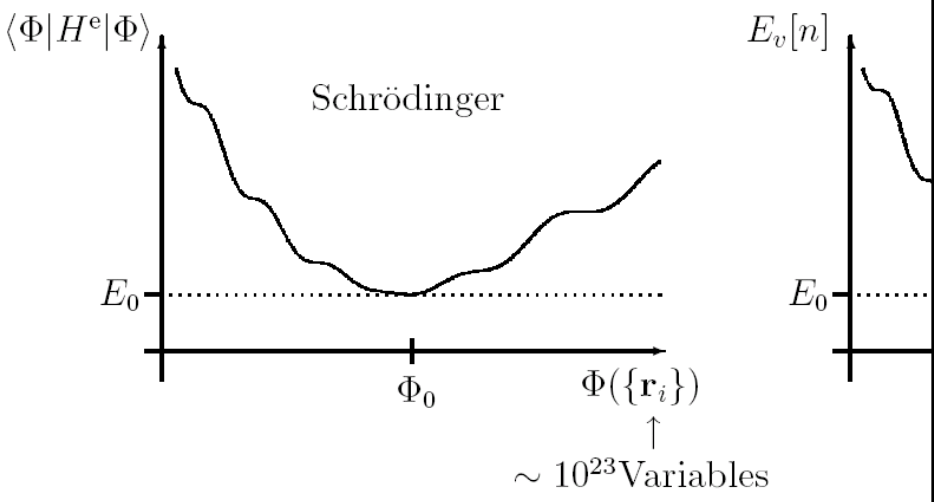


Set of non-degenerate ground-state wave functions Φ of arbitrary N-electron Hamiltonians.

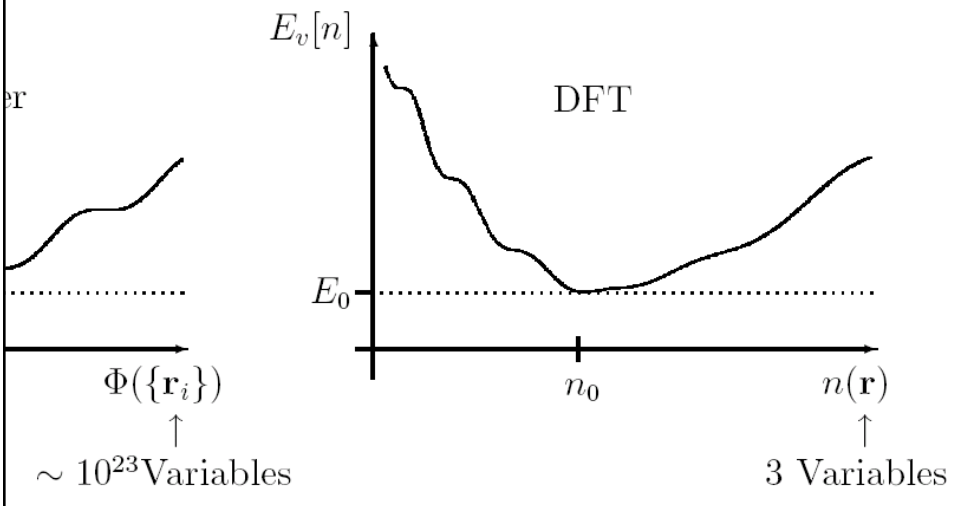
Set of particle densities $n(\mathbf{r})$ belonging to non-degenerate N-electron ground states.

The dashed arrow is not possible. Thus, here is a one-to-one correspondence between Φ and $n(r)$.

Comparison of Wave-Function and Density-Functional Theory



Comparison of Wave-Function and Density-Functional Theory

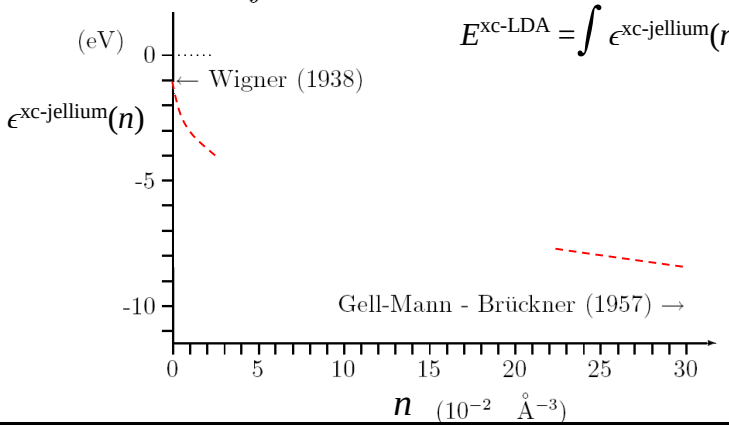


The xc Functional

T_s, E^{Hartree}, and E^{xc} are all ***universal*** functionals in $n(\mathbf{r})$, i.e., they are independent of the special system studied. (general theory: see the work by Levy and Lieb)

$$E^{\text{xc}}[n] = \int \epsilon^{\text{xc}}[n] n(\mathbf{r}) d^3\mathbf{r} = E^{\text{xc-LDA}}[n] + O(\nabla n)$$

$$E^{\text{xc-LDA}} = \int \epsilon^{\text{xc-jellium}}(n)\ n(\mathbf{r})\ d^3\mathbf{r}$$



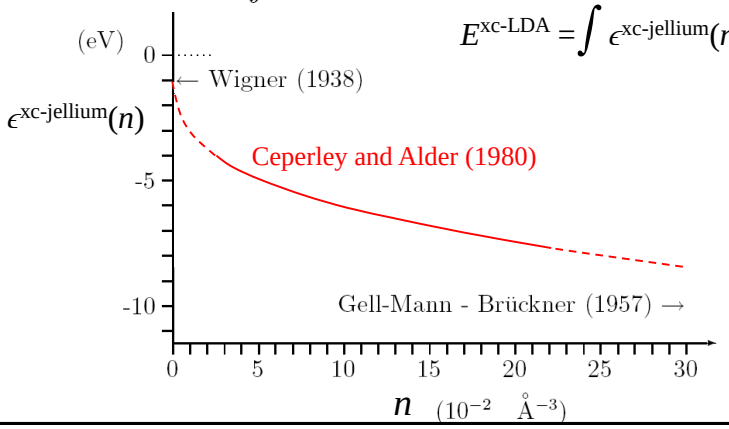
neglecting $O(\nabla n)$ is the local-density approximation

The xc Functional

T_s, E^{Hartree}, and E^{xc} are all ***universal*** functionals in $n(\mathbf{r})$, i.e., they are independent of the special system studied. (general theory: see the work by Levy and Lieb)

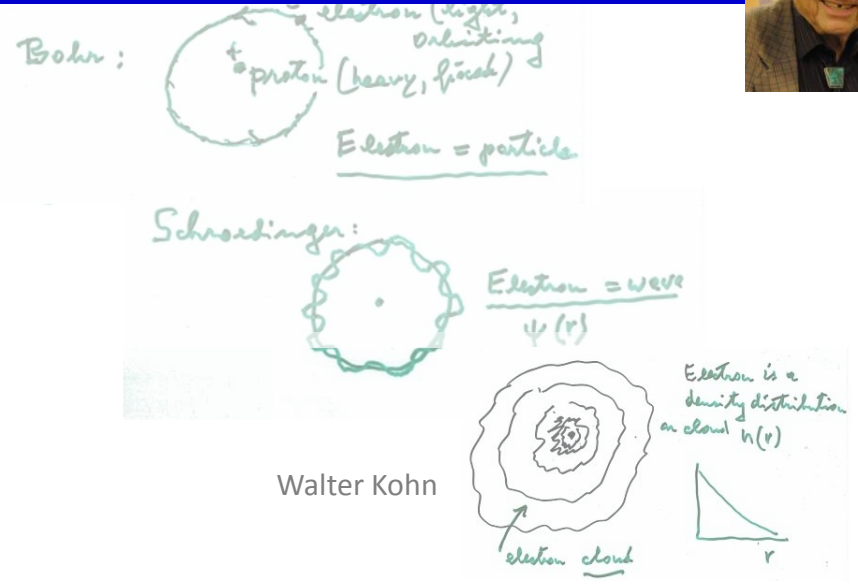
$$E^{\text{xc}}[n] = \int \epsilon^{\text{xc}}[n] n(\mathbf{r}) d^3\mathbf{r} = E^{\text{xc-LDA}}[n] + O(\nabla n)$$

$$E^{\text{xc-LDA}} = \int \epsilon^{\text{xc-jellium}}(n)\ n(\mathbf{r})\ d^3\mathbf{r}$$



neglecting $O(\nabla n)$ is the local-density approximation

The Kohn-Sham Ansatz of Density-Functional Theory



Walter Kohn

The Kohn-Sham Ansatz of Density-Functional Theory

- Kohn-Sham (1965): Replace the original many-body problem by an independent electron problem **that can be solved!**

$$E_v[n] = T_s[n] + \int v(\mathbf{r})\, n(\mathbf{r})\, d^3\mathbf{r} + E^{\text{Hartree}}[n] + E^{xc}[n]$$

- With $T_s[n]$ the kinetic energy functional of independent electrons, and $E^{xc}[n]$ the unknown functional.
- The challenge is to find useful, approximate xc functionals.

The Kohn-Sham Ansatz of Density-Functional Theory

Approximate xc functionals have been very successful but there are problems

- for certain bonding situations (vdW, hydrogen bonding, certain covalent bonds)
- for highly correlated situations, and
- for excited states.

- The challenge is to find useful, approximate xc functionals.

Perdew's Dream: Jacob's Ladder in Density-Functional Theory

The exchange-correlation functional

our favorite

accuracy

5	unoccupied $\psi_i(\mathbf{r})$,	EX + cRPA, as given by ACFD
4	occupied $\psi_i(\mathbf{r})$,	hybrids (B3LYP, PBE0, HSE, …)
3	$\tau\,(\mathbf{r})$,	meta-GGA (e.g., TPSS)
2	$\nabla n(\mathbf{r})$,	Generalized Gradient Approximation
1	$n(\mathbf{r})$,	Local-Density Approximation

$\tau(\mathbf{r})$: Kohn-Sham kinetic-energy density

EX: exact exchange: $E_x = -\frac{1}{2}\sum_{occ}\iint d\mathbf{r}\,d\mathbf{r}'\frac{\psi_n^*(\mathbf{r})\psi_m(\mathbf{r})\psi_m^*(\mathbf{r}')\psi_n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$

cRPA : random-phase approximation for correlation

ACFD : adiabatic connection fluctuation dissipation theorem

Bohm, Pines (1953); Gell-Mann, Brueckner (1957);
Gunnarsson, Lundqvist (1975, 1976); Langreth, Perdew (1977);
X. Ren, P. Rinke, C. Joas, and M. S., Invited Review, Mater. Sci. 47, 21 (2012)

Perdew's Dream: Jacob's Ladder in Density-Functional Theory

The exchange-correlation functional

our favorite

accuracy

5	unoccupied $\psi_i(\mathbf{r})$,	EX + cRPA, as given by ACFD
4	occupied $\psi_i(\mathbf{r})$,	hybrids (B3LYP, PBE0,
3	$\tau\,(\mathbf{r})$,	meta-GGA (e.g.
2	$\nabla n(\mathbf{r})$,	Generaliz
1	$n(\mathbf{r})$,	Loca

$\tau(\mathbf{r})$: Kohn-Sham

EX: exact

cRPA

ation dis

(19 ueckner (1957);
arsson, Lun , 1976); Langreth, Perde
X. Ren, P. Rinke, C. and M. S., Invited Review, Ma

Functionals of level 1 and 2 suffer from severe self-interaction errors.

Functionals of level 1, 2, 3, & 4 are lacking the long-range vdW tails.

With "Level 5 plus" validation (error estimation) is becoming possible.

hn, July 2013

ew Becke Kohn Gross

"Level 5 plus" Viewed in the Many-Body Framework

Perturbation theory:

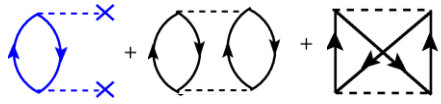
$H = H^0 + H'$ with $H^0|\phi_n\rangle = E_n^{(0)}|\phi_n\rangle$ and $|\phi_n\rangle$ = Slater det.

$|\phi_0\rangle$ = ground state, $|\phi_{i,a}\rangle$ = single excitations, $|\phi_{ij,ab}\rangle$ = double exci.

$$E_0^{(0)} = \langle\phi_0|\, H^0\, |\phi_0\rangle, \quad E_0^{(1)} = \langle\phi_0|\, H'\, |\phi_0\rangle$$

$$E_0^{(2)} = \sum_{n\neq 0} \frac{|\langle\phi_0|\, H'\, |\phi_n\rangle|^2}{E_0^{(0)} - E_n^{(0)}} = \sum_{i,a} \frac{|\langle\phi_0|\, H'\, |\phi_{i,a}\rangle|^2}{E_0^{(0)} - E_{i,a}^{(0)}} + \sum_{ij,ab} \frac{|\langle\phi_0|\, H'\, |\phi_{ij,ab}\rangle|^2}{E_0^{(0)} - E_{ij,ab}^{(0)}}$$

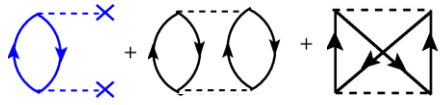
single excitations double excitations



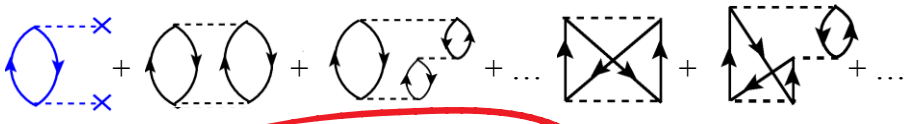
X. Ren, P. Rinke, C. Joas, and M. S., Invited Review, Mater. Sci. 47, 21 (2012)
X. Ren, P. Rinke, G.E. Scuseria, and M. Scheffler, Phys. Rev. B, in print (2013)

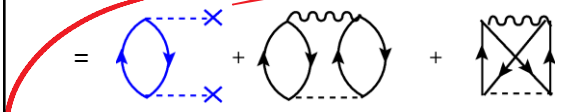
$$E_0^{(2)} = \sum_{n\neq 0} \frac{|\langle\phi_0|\, H'\, |\phi_n\rangle|^2}{E_0^{(0)} - E_n^{(0)}} = \sum_{i,a} \frac{|\langle\phi_0|\, H'\, |\phi_{i,a}\rangle|^2}{E_0^{(0)} - E_{i,a}^{(0)}} + \sum_{ij,ab} \frac{|\langle\phi_0|\, H'\, |\phi_{ij,ab}\rangle|^2}{E_0^{(0)} - E_{ij,ab}^{(0)}}$$

single excitations double excitations



Adding all ring diagrams from higher order perturbations:





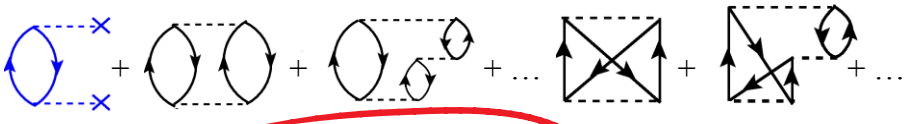
single excitations cRPA SOSEX

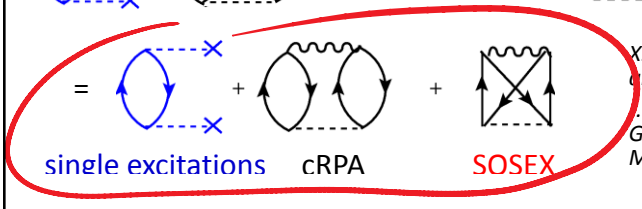
*X. Ren, A. Tkatchenko, P. Rinke, and M.S., PRL **106**, (2011).*
. Paier, X. Ren, P. Rinke, A. Grüneis, G. Kresse, G. E. Scuseria, M.S., NJP (2012).

X. Ren, P. Rinke, C. Joas, and M. S., Invited Review, Mater. Sci. 47, 21 (2012)
X. Ren, P. Rinke, G.E. Scuseria, and M. Scheffler, Phys. Rev. B, in print (2013)

Renormalized second order perturbation theory sets the reference for materials.

-- better than LDA, PBE, MP2
-- comparable to CCSD
-- not as accurate as CCSD(T)



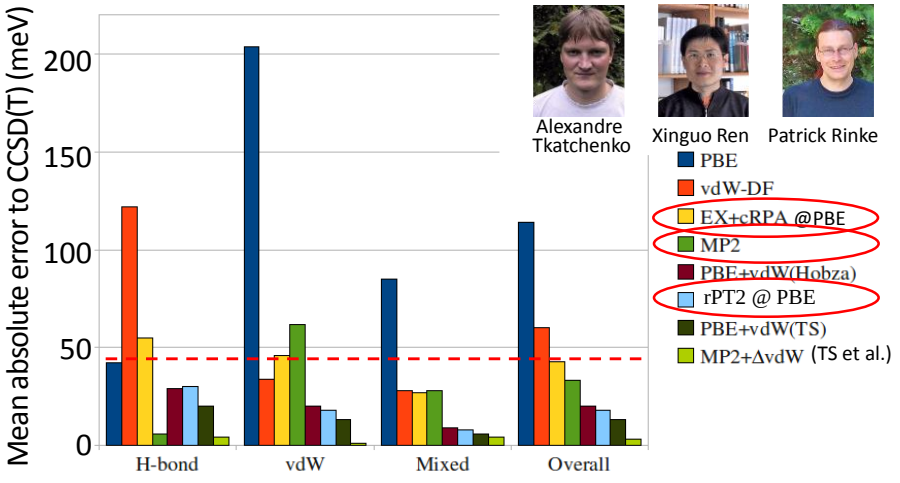


*X. Ren, A. Tkatchenko, P. Rinke, and M.S., PRL **106**, (2011).*

. Paier, X. Ren, P. Rinke, A. Grüneis, G. Kresse, G. E. Scuseria, M.S., NJP (2012).

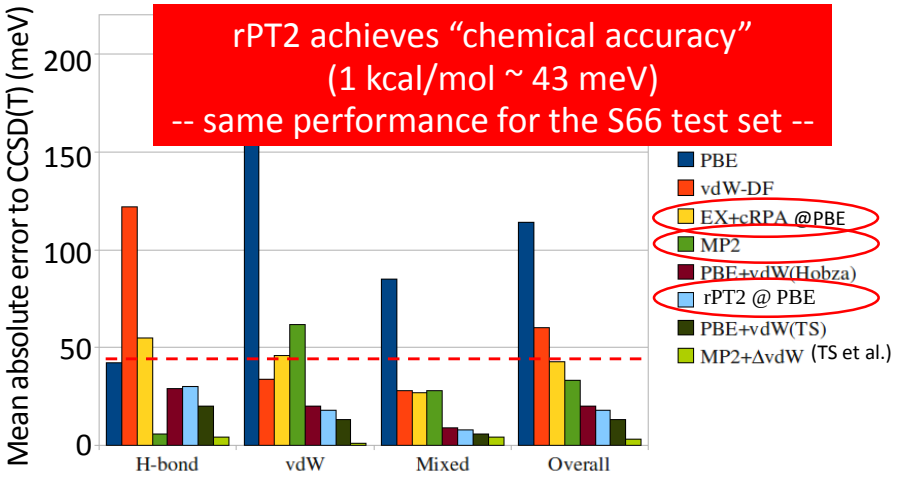
X. Ren, P. Rinke, C. Joas, and M. S., Invited Review, Mater. Sci. 47, 21 (2012)
X. Ren, P. Rinke, G.E. Scuseria, and M. Scheffler, Phys. Rev. B, in print (2013)

Performance of rPT2 for Weak Intermolecular Interactions: S22 Test Set



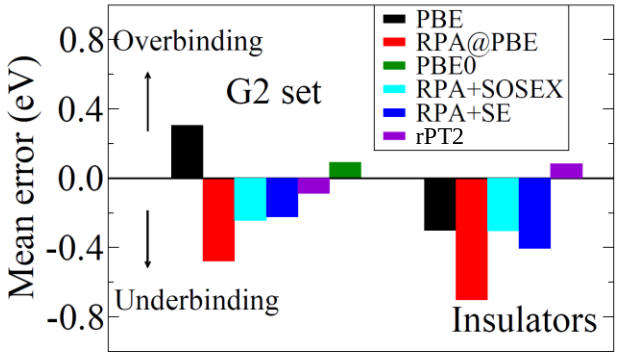
CCSD(T): *Jurecka, Sponer, Cerny, Hobza, **PCCP** (2006).* ***Langreth-Lundqvist :*** *Gulans, Puska, Nieminen, **PRB** (2009);* ***rPT2:*** *X. Ren et al. **PRL** (2011) and to be published.*
TS: *A. Tkatchenko and M.S., **PRL** (2009); A. Tkatchenko et al., **JCP** (2009).*

Performance of rPT2 for Weak Intermolecular Interactions: S22 Test Set



CCSD(T): *Jurecka, Sponer, Cerny, Hobza,* ***PCCP*** *(2006).* ***Langreth-Lundqvist :*** *Gulans, Puska, Nieminen,* ***PRB*** *(2009);* ***rPT2:*** *X. Ren et al.* ***PRL*** *(2011) and to be published.* ***TS****: A. Tkatchenko and M.S.,* ***PRL*** *(2009); A. Tkatchenko et al.,* ***JCP*** *(2009).*

Atomization Energies with rPT2



solids:
C, Si, SiC,
BN, BP,
AlN, AlP,
LiH, LiF,
LiC, MgO.

J. Paier, X. Ren, P. Rinke, G. Scuseria, A. Grueneis, G. Kresse, and M.S., New J. Phys. ***14****, 043001 (2012).*

Theoretical Concepts and Some Examples (Results)

1. Electronic-Structure Theory
2. *Ab initio* Atomistic Thermodynamics
3. Molecular Dynamics
4. Kinetic Monte Carlo Approach

Ab initio Atomistic Thermodynamics

Assumption of thermodynamic equilibrium

This means that any information about time-scales is lost. We look at the system after infinite time.

Note that in reality the kinetics *can* be very slow; an extreme example is C-diamond ↔ graphite.

Sometimes it is important (and possible) to define a *constrained equilibrium*.

Thermodynamics (A Brief Reminder)

Thermodynamic potentials:

Internal energy	$U(S, V) = E^{tot} + U^{vib}$
Enthalpy	$H(S, p) = U + pV$
(Helmholtz) free energy	$F(T, V) = U - TS$
Gibbs free energy	$G(T, p) = U - TS + pV$

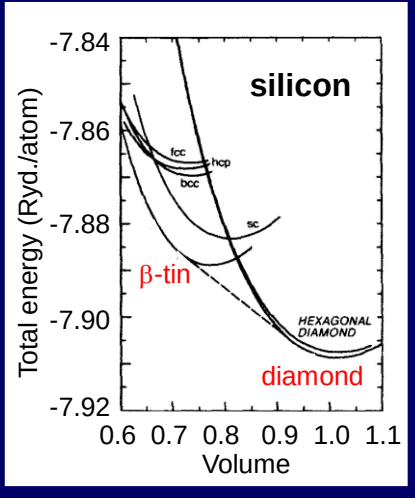
E^{tot} contains energy contributions from chemical binding (structure) as well as electronic excitations, if present. U^{vib} is the energy of vibrations. For poly-atomic systems E^{tot} and U^{vib} are best calculated by DFT.

At thermodynamic equilibrium the corresponding thermodynamic potential assumes its minumum.

Chemical potential $\mu = (\partial G/ \partial N)_{T, p}$ =
= the cost to remove a particle from the system.

The first (convincing) DFT calculations:

Stability of crystals and crystal phase transitions



M. T. Yin and M. L. Cohen PRB 26 (1982) < and PRL 1980 >

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

Ab Initio Atomistic Thermodynamics
Effect of a Surrounding Gas Phase on Surface Structure and Composition

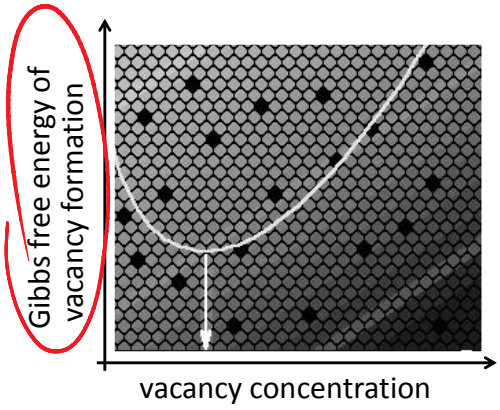
C. M. Weinert and M. Scheffler, Mat. Sci. Forum 10-12, 25 (1986).
E. Kaxiras et al., Phys. Rev. B 35, 9625 (1987)
X.-G. Wang et al., Phys. Rev. Lett. 81, 1038 (1998)
K. Reuter and M. Scheffler, Phys. Rev. B 65, 035406 (2002)

Get Real!
Consider Temperature, Pressure, and Doping

Example questions:

What controls the equilibrium concentration of vacancies at a surface?

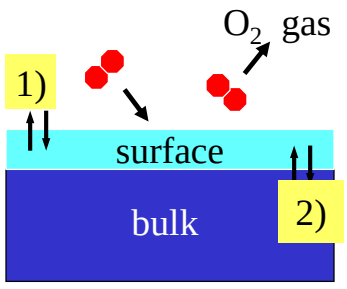
What controls the number of adsorbed atoms and the order of their ensemble?



Surface in Contact with a One-Component Gas Phase – Example: O_2 @ Pd

$$\gamma_{surf.} = 1/A\,[\,G(N_O, N_{Pd}) - N_O\,\mu_O - N_{Pd}\,\mu_{Pd}\,]$$

N_O = # of O atoms in the system
N_{Pd} = # of Pd atoms (substrate) in the system



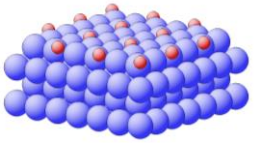
Concept of thermodynamic reservoirs:

1) The environment can give and take O atoms at an energy $\mu_O = 1/2\,\mu_{O_2}$

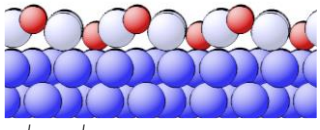
$$\mu_O(T, p) = \tfrac{1}{2}\,\mu_{O_2}(T, p^0) + \tfrac{1}{2}\,k_B T \ln(p/p^0)$$

2) Also the bulk of the substrate is practically of infinite size and acts as a reservoir for the Pd atoms: $\mu_{Pd} = g_{Pd}^{bulk}$

Oxide Formation on Pd(100)

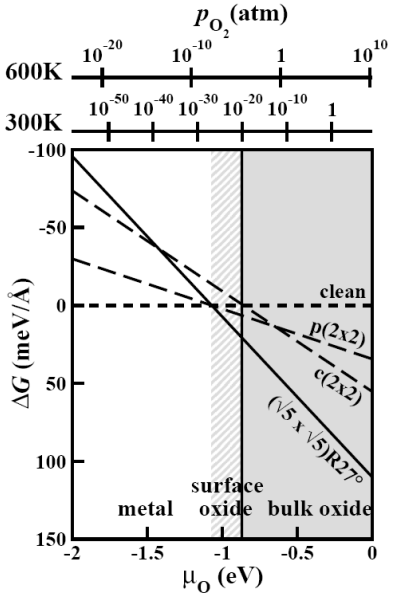


***p*(2x2) O/Pd(100)**

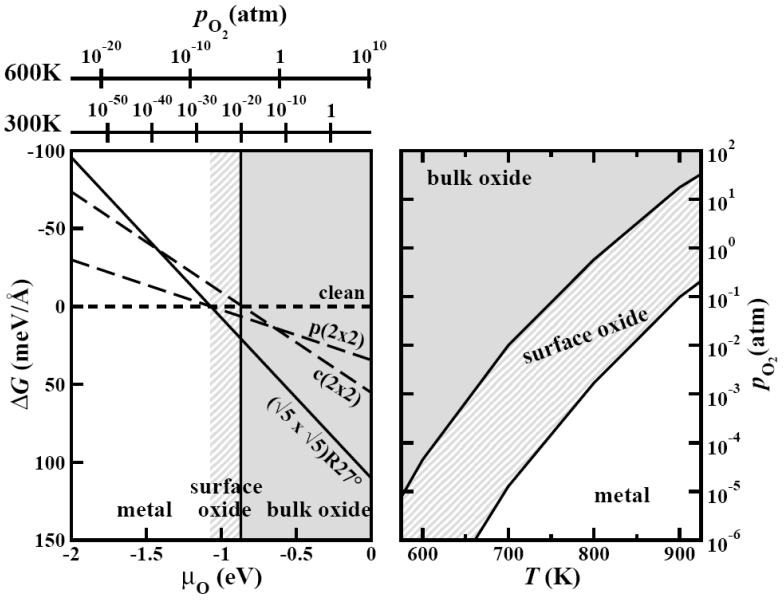


(√5 x √5)R27°

M. Todorova et al., Surf. Sci. 541, 101 (2003); K. Reuter and M. Scheffler, Appl. Phys. A 78, 793 (2004)

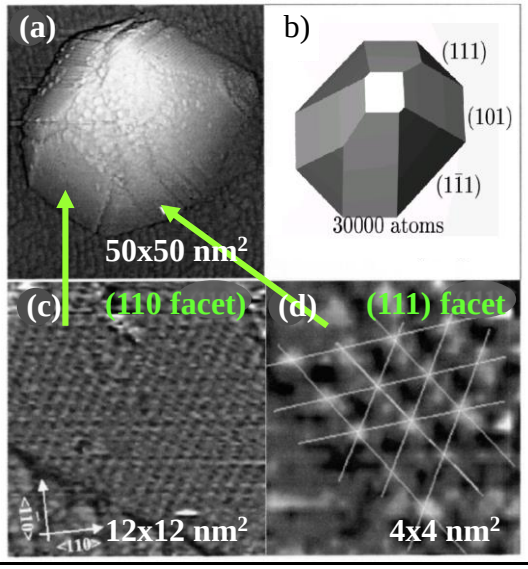


Oxide Formation on Pd(100)



InAs/GaAs(001) quantum dots close to thermodynamic equilibrium

G. Costantini et al. APL 82 (2003)



a) STM topography of a large island.

b) Equilibrium shape (theory: ***E. Pehlke, N. Moll, M.S., Proc. 23rd ICPS (1996); Q. Liu, et al., PRB 60 (1999)***).

c), d) High-resolution views of the (110) and (111) side facets.

Also:
J. Marquez et al., APL 78 (2001);
Y. Temko et al., APL 83 (2003).

Summary *Ab Initio* Atomistic Thermodynamics

Calculate *free energies* by DFT.

Exploit thermodynamic equilibria and the concept of thermal reservoirs (atomic chem. potentials).

- Concentration of point defects at finite T
- Surface structure and composition in realistic environments
- Order-order and order-disorder phase transitions

Limitations:

-- The accuracy of the xc functional (with respect to k_BT)

-- „only“ thermodynamic equilibrium

Theoretical Concepts and Some Examples (Results)

1. Electronic-Structure Theory
2. *Ab initio* Atomistic Thermodynamics
3. Molecular Dynamics
4. Kinetic Monte Carlo Approach

Brief History of MD

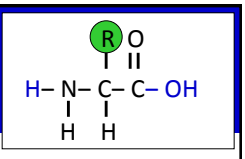
First MD simulation: B.J. Alder and T.E. Wainwright, 1956 - hard sphere liquid, phase transition

First MD simulations with a continuous potential:
G.H. Vineyard et al, 1959 -- radiation damage simulation with a pair potential
A. Rahman, 1964 - Lennard-Jones liquid

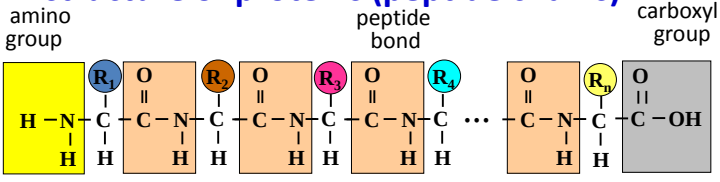
First MD with DFT energetics: R. Car and M. Parrinello, 1985 – Si crystal

Computational cost is almost always dominated by the cost of the force call (evaluating E^{tot} and $dE^{tot}/d\boldsymbol{R}$).

Stability of Secondary Structures

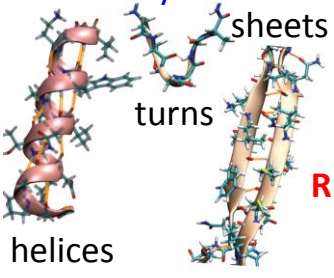


structure of proteins (peptide chains):



Mariana Rossi Carvalho

Secondary structure



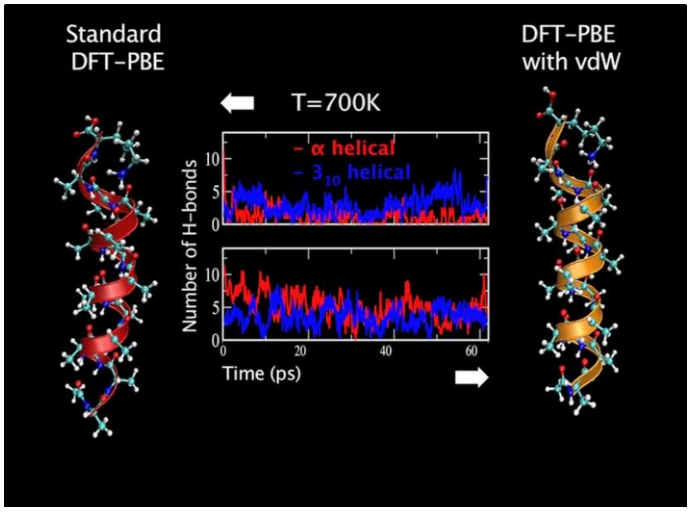
R = CH_3
= alanine

Tertiary structure

Volker Blum

Alexandre Tkatchenko

Role of vdW Interaction on (Un)folding; $Ac\text{-}Ala_{15}LysH^+$



Mariana Rossi Carvalho

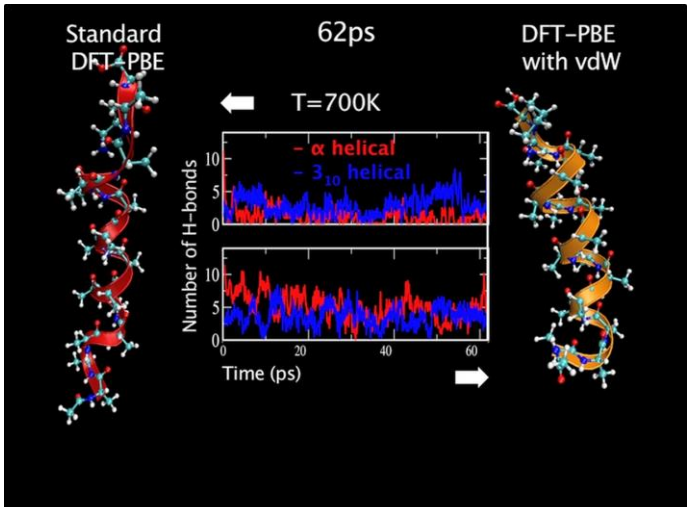
Volker Blum

Alexandre Tkatchenko

(*)H-bond = 2.5 Å between CO and NH groups

http://www.youtube.com/watch?v=Y_7G8s26zzw *PRL **106**, 118102 (2011)*

Role of vdW Interaction on (Un)folding; $Ac\text{-}Ala_{15}LysH^+$



Mariana Rossi Carvalho

Volker Blum

Alexandre Tkatchenko

(*)H-bond = 2.5 Å between CO and NH groups

http://www.youtube.com/watch?v=Y_7G8s26zzw *PRL **106**, 118102 (2011)*

What Did We Learn from Studying Polypeptides?

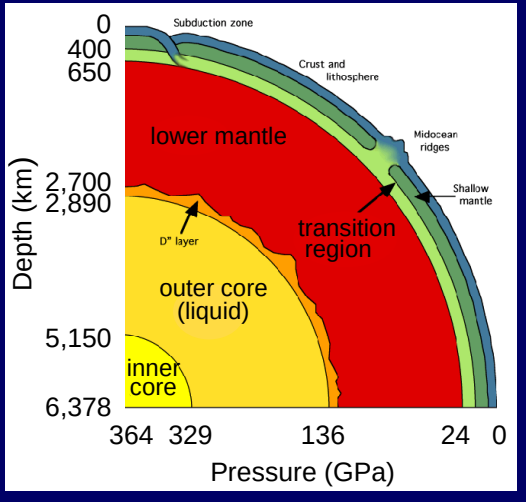
Density-functional theory (PBE+**vdW**) is able to:

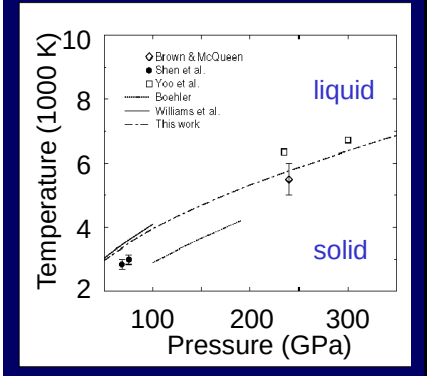
- Predict geometry and properties, analyze stability and unfolding:
  - hydrogen bonding,
  - vdW interaction, and
  - vibrational entropy.
- Verification of structure predictions against experiment (vibrational spectroscopy).

*M. Rossi, V. Blum, et al., JPCL **1** (2010).*
*A Tkatchenko, M Rossi, V Blum, J Ireta, M.S., PRL **106**, 118102 (2011)*

http://www.youtube.com/watch?v=Y_7G8s26zzw

Ab Initio Melting Curve of Fe as Function of Pressure





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

Possibilities and Limitations of MD

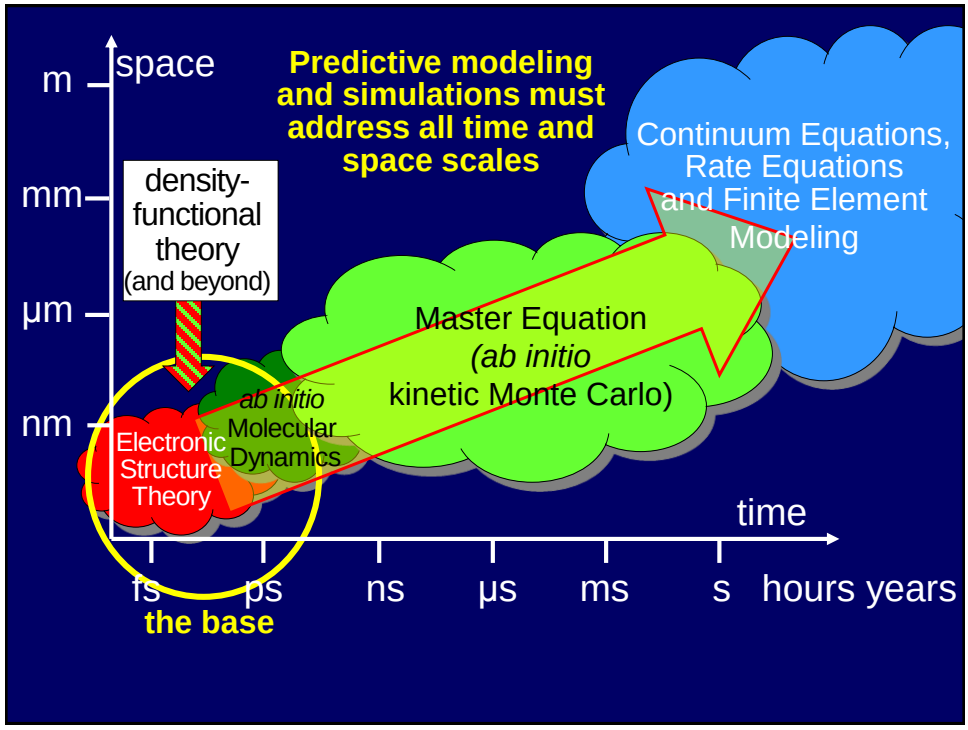
With *force fields* (no explicit quantum mechanics): 10^3 - 10^4 atoms are possible on a single processor
Much larger systems are possible via parallelization:
several million atoms are now routine; billions of atoms are possible
With DFT energies: just ~100 atoms (soon 1000)

Problems:

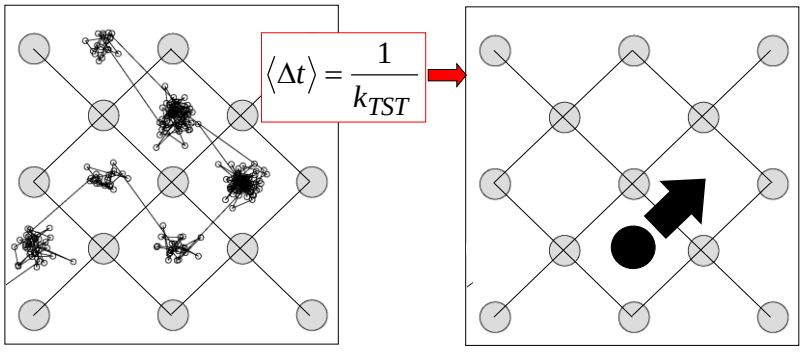
- Accuracy of the interatomic interaction
- Length scale (number of atoms)
- Time scale - limited to ~ 1 ms (with *simple* potentials) and with DFT energies up to 1 ns
- Quantum dynamical effects of the nuclei are typically ignored.
- Non adiabatic dynamics not treated properly

Theoretical Concepts and Some Examples (Results)

1. Electronic-Structure Theory
2. *Ab initio* Atomistic Thermodynamics
3. Molecular Dynamics
4. Kinetic Monte Carlo Approach



Kinetic Monte Carlo: Coarse-Graining Molecular Dynamics



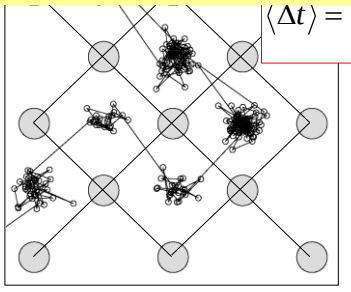
Molecular Dynamics of Co on Cu(001): The whole trajectory.

ab initio MD: up to 100 ps

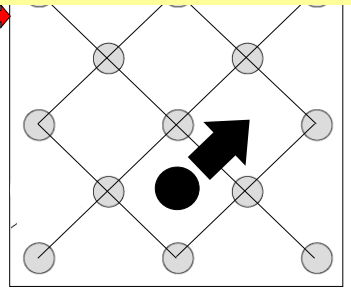
Kinetic Monte Carlo simulation: Coarse-grained hops.

ab initio kMC: up to minutes

The system vibrates in a multi-dimensional basin. Occasionally it escapes, crossing through a dividing surface to a new basin. This behavior characterizes solid-state diffusion, chemical reactions at surfaces, as well as many other systems and properties.



$$\langle \Delta t \rangle = \frac{}{k_{TST}}$$



Molecular Dynamics of Co on Cu(001): The whole trajectory.

ab initio MD: up to 50 ps

Kinetic Monte Carlo simulation: Coarse-grained hops.

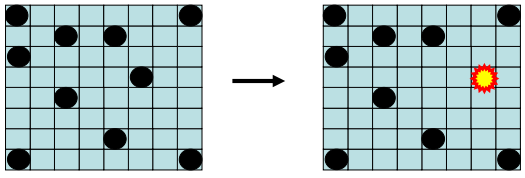
ab initio kMC: up to minutes

Master-Equation
for Molecular Simulations over Long Time Periods

$$\dot{p}_n(t) = \sum_m [w_{nm}(t)p_m(t) - w_{mn}(t)p_n(t)].$$

The probability to find at time *t* the metastable atomic configuration (conformation) *n*, follows from a gain term (transitions $m \rightarrow n$) and a loss term (transitions $n \rightarrow m$).

config. *m*

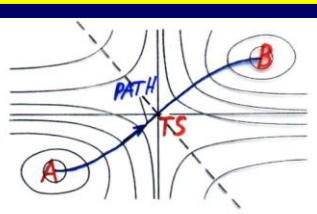


config. *n*

When the number of conformations is large, the direct solution of the master equation becomes impractical.

➡ Kinetic Monte Carlo. This is a very efficient, numerical solution of the master equation.

Transition State Theory



Transition state theory

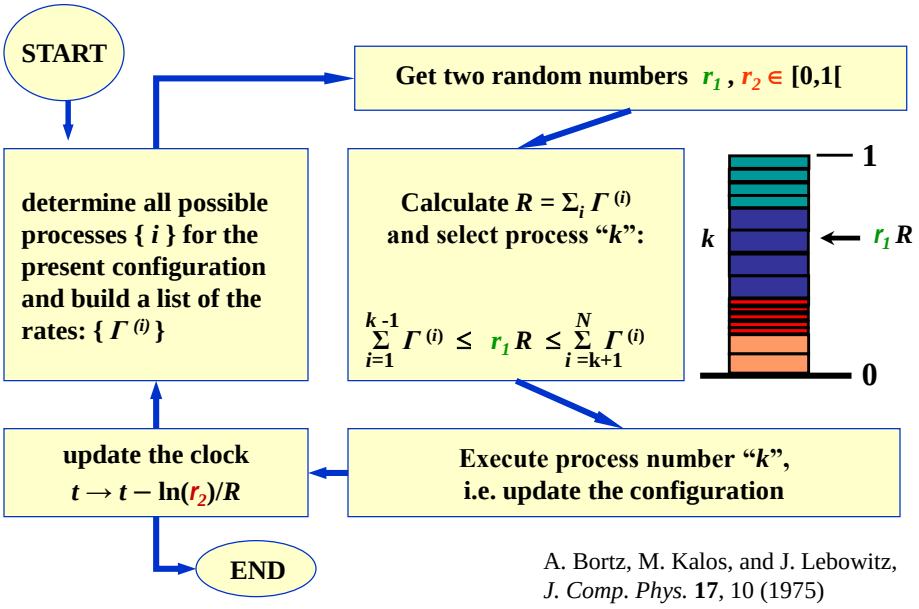
$$\Gamma = \frac{k_B T}{h} exp\left(\frac{-\Delta F}{k_B T}\right)$$

$$\Delta F = -k_B T \, ln Z_{TS} + k_B T \, ln Z_A$$

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

$$\Gamma_0 = \frac{k_B T}{h} \, exp\left(\frac{\Delta S^{vib}}{k_B} - \frac{\Delta U^{vib}}{k_B T}\right)$$

Flowchart of A Kinetic Monte-Carlo Simulation

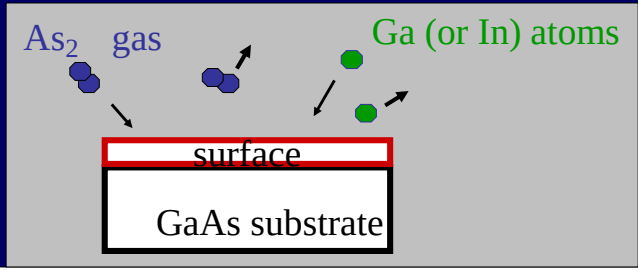


A. Bortz, M. Kalos, and J. Lebowitz, *J. Comp. Phys.* **17**, 10 (1975)

kMC Summary

- kMC is a numerical solution of the master equation.
- It gives essentially the same information as MD, but can simulate time spans $>10^{12}$ times longer.
- It can be linked to *ab initio* rate processes: free energy barriers, and their *T* dependence. Often transition state theory can be applied. Configurational entropy and resulting (kinetic) barriers are obtained by the kMC simulation. .. and more.
- The main challenge for building a reliable kMC simulation is to find all the important processes.

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

Theory of The Kinetics of Growth

1) Analysis of all possibly relevant processes using density-functional theory

2) Calculate the rates of all important processes

$$\Gamma^{(i)} = \Gamma_0^{(i)} \exp\left(-\Delta E^{(i)} / k_B T\right)$$

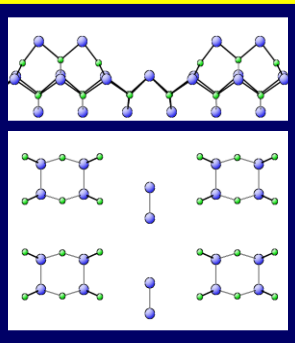
3) Statistical approach to describe
   - deposition
   - diffusion
   - nucleation
   - growth

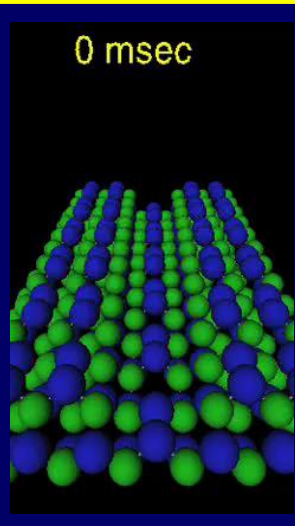
➡ **extended kinetic Monte Carlo**

Adsorption, diffusion, island nucleation, and growth of GaAs, studied by *ab intio* kinetic Monte Carlo

side view

top view





1/60 of the full simulation cell
As_2 pressure 1.33×10^{-8} bar
Ga deposition rate = 0.1 ML/s
T = 700 K

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

Summary and Outlook: Interacting Electrons Determine the Properties and Function of Real Materials

Important arenas for future theoretical work:

- Non-adiabatic effects, dissipation
- Transport (electrons, ions, heat)
- Thermodynamic phase transitions, e.g. melting
- Surfaces, nanostructures – in realistic environments
- Modeling the kinetics, e.g. of catalysts or crystal growth (self-assembly and self-organization)
- Molecules and clusters in solvents, electrochemistry, fuel cells, external fields
- Correlated systems, e.g. *f*-electron chemistry
- Biological problems

The challenges:

- ➢ Find ways to control the xc approximation
- ➢ Develop methods for bridging length and time scales
- ➢ electronic (collective) excitations