DFT AND BEYOND
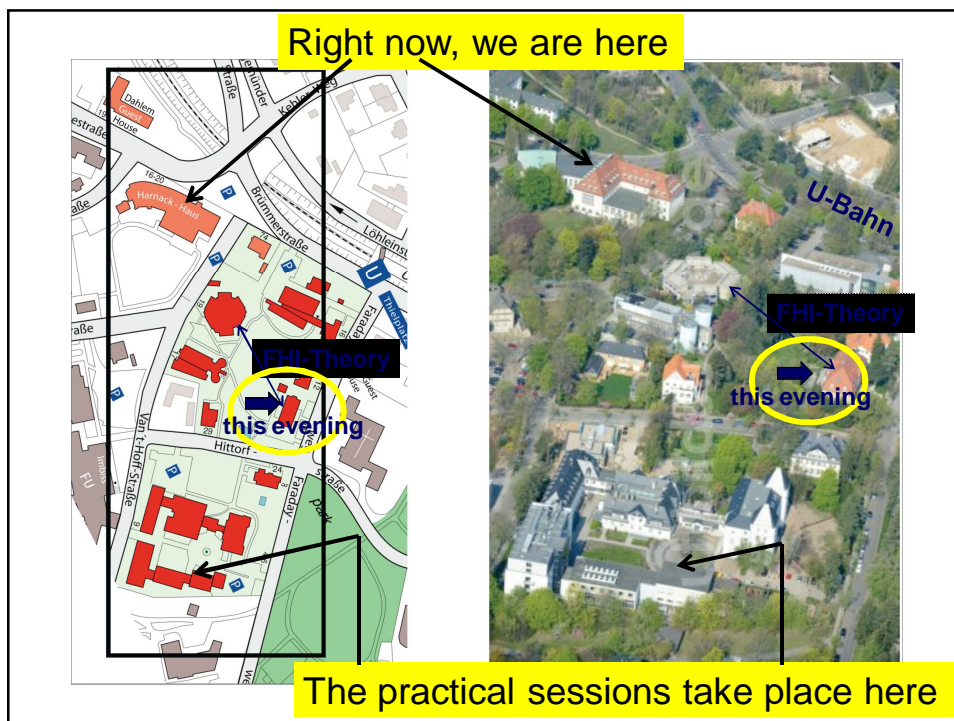**Hands-on Tutorial Workshop**
2011 BERLIN

on *Ab Initio* Molecular Simulations:
Towards a First-Principles Understanding of
Materials Properties and Functions
Berlin, July 12 - 21, 2011

Welcome to Berlin and welcome to the Fritz Haber Institute of the Max Planck Society

KAISER WILHELM
INSTITUT FÜR
PHYSIKALISCHE CHEMIE
UND ELEKTROCHEMIE

Right now, we are here

The practical sessions take place here

on *Ab Initio* Molecular Simulations:
Towards a First-Principles Understanding of
Materials Properties and Functions
Berlin, July 12 - 21, 2011

Let's start!

**Computational Materials Sciences
from First Principles:
Status, Achievements, Challenges**

Modeling Materials and Bio-Molecular 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: $\Psi(\mathbf{r_1}, \cdots \mathbf{r_N}; \mathbf{R_1}, \cdots \mathbf{R_M})$

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

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

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

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

???

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

$\Longrightarrow$ 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 some transport issues 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:

- [hidden by red box]
- [hidden by red box] ystals
- [hidden by red box]
- [hidden by red box] ing
- [hidden by red box] ge
- etc.

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

How can we solve:

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

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

Comparison of Wave-Function and Density-Functional theory

$\langle \Phi | H^e | \Phi \rangle$

$F_v[n]$

Schrödinger

E_0

E_0

Φ_0

$\Phi(\{r_i\})$
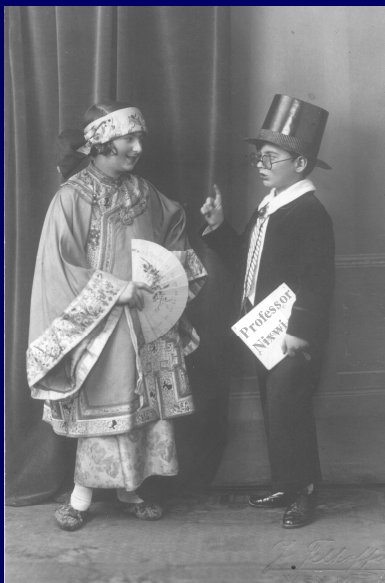
$\uparrow$

$\sim 10^{23}$ Variables
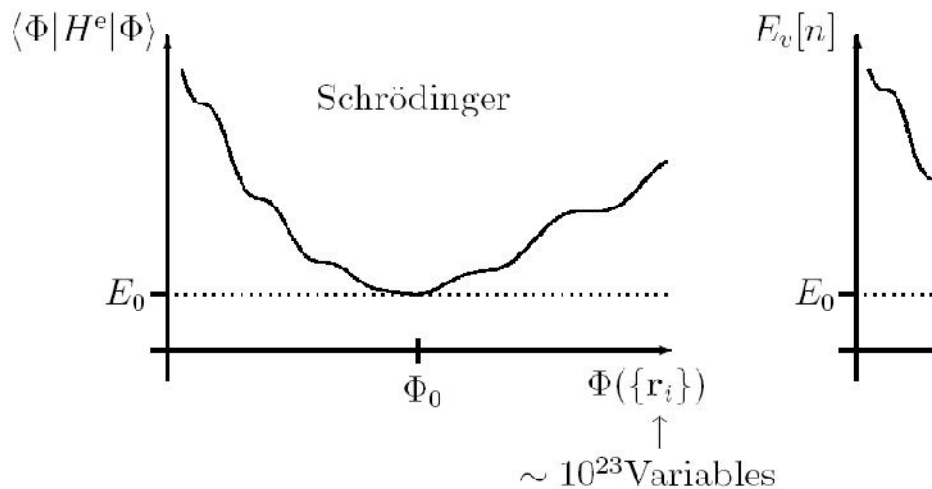
Comparison of Wave-Function and Density-Functional theory
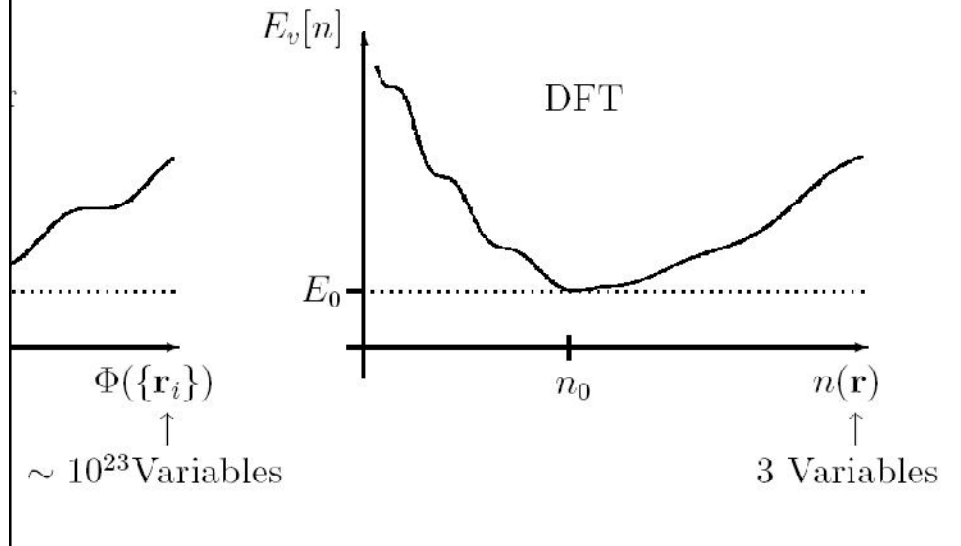
Summary of Hohenberg-Kohn Density-Functional Theory (DFT) -- 1964

-- The many-body Hamiltonian determines everything. (standard quantum mechanics)

-- There is a one-to-one correspondence between the ground-state wave function and the many-body Hamiltonian [or the nuclear (or ionic) potential, $v(\mathbf{r})$]. (standard quantum mechanics)

-- There is a one-to-one correspondence between the ground-state electron-density and the ground-state wave function. (Hohenberg and Kohn)
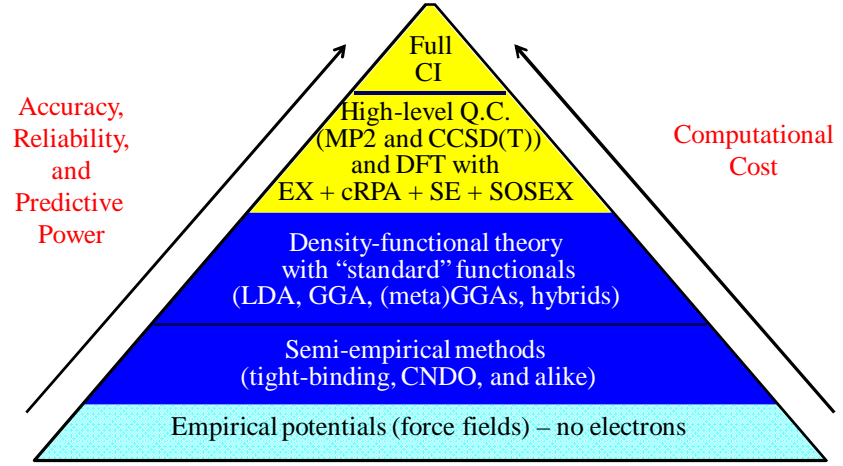
34 years before DFT invention

34 years after DFT invention

State-of-The-Art of (Electronic) Structure Theory

$$H \Psi = E \Psi$$

Full CI

High-level Q.C. (MP2 and CCSD(T)) and DFT with EX + cRPA + SE + SOSEX

Density-functional theory with "standard" functionals (LDA, GGA, (meta)GGAs, hybrids)

Semi-empirical methods (tight-binding, CNDO, and alike)

Empirical potentials (force fields) – no electrons

Accuracy, Reliability, and Predictive Power

Computational Cost

State-of-The-Art of (Electronic) Structure Theory

$$H\,\Psi = E\,\Psi$$

Full CI

High-level Q.C. (MP2 and CCSD(T)) and DFT with EX + cRPA + SE + SOSEX

Accuracy, Reliability, and Predictive Power

Computational Cost

no long-range van der Waals interactions

Empirical potentials (force fields) – no electrons

Kohn and Sham (1965):

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

with
$$E^{\mathrm{Hartree}}[n] = \frac{1}{2}\frac{e^2}{4\pi\varepsilon_0}\iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3\mathbf{r}\,d^3\mathbf{r}'$$

And $T_s[n]$ the functional of the kinetic energy of **non-interacting** electrons. $E^{\mathrm{xc}}[n]$ contains all the unknowns.

At fixed electron number N the variational principle gives

$$\delta\left\{ E_v[n] - \mu\left(\int n(\mathbf{r})d^3\mathbf{r} - N\right)\right\} = 0$$

or
$$\frac{\delta E_v^{[n]}}{\delta_n} = \boxed{\mu = \frac{\delta T_s[n]}{\delta n(\mathbf{r})} + v^{\mathrm{eff}}(\mathbf{r})}$$
Kohn-Sham equation

Kohn and Sham (1965):

$$v^{\text{eff}}(\mathbf{r}) \;=\; v(\mathbf{r}) + \frac{e^2}{4\pi\varepsilon_0} \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d^3 r' + \frac{\delta E^{\text{xc}}[n]}{\delta n(\mathbf{r})}$$

Because $T_s[n]$ is the functional of non-interacting particles we effectively "restrict" the allowed densities to those that can be written as
This implies:

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\varphi_i(\mathbf{r})|^2$$

Kohn-Sham equation

$$\left\{ -\frac{\hbar^2}{2m}\nabla^2 + v^{\text{eff}}(\mathbf{r}) \right\} \varphi_i(\mathbf{r}) = \epsilon_i\, \varphi_i(\mathbf{r})$$

$v^{\text{eff}}(\mathbf{r})$ depends on the density that we are seeking.

$$
\begin{aligned}
T_s[n] \quad &= \sum_{k=1}^{N} \langle \varphi_k \left| -\tfrac{\hbar^2}{2m}\nabla^2 \right| \varphi_k \rangle \quad, \\
&= \sum_{k=1}^{N} \epsilon_k - \int v^{\text{eff}}[n^{\text{in}}](\mathbf{r}) n(\mathbf{r}) d^3 r \quad.
\end{aligned}
$$

The Kohn-Sham Ansatz

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

- Only the ground state density and the ground state energy are required to be the same as in the original many-body problem.

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

- Maybe the exact $E^{\text{xc}}[n]$ functional cannot be written as a closed mathematical expression. Maybe we need to take a detour similar to that taken for $T_s[n]$? The challenge: Find useful, approximate xc functionals.

Perdew's Dream: Jacob's Ladder in DFT

accuracy ↑

6	our favorite	
5	unoccupied $\psi_i(\mathbf{r})$,	e.g., ACFD-RPA
4	occupied $\psi_i(\mathbf{r})$,	hybrid functional (B3LYP, PBE0, HSE, …)
3	$\tau(\mathbf{r})$,	meta-GGA (e.g., TPSS)
2	$\nabla n(\mathbf{r})$,	GGA (e.g., PBE)
1	$n(\mathbf{r})$,	LDA

past and presence

$\tau(\mathbf{r})$:	Kohn-Sham kinetic energy density
ACFD :	adiabatic connection fluctuation dissipation theorem (Bohm, Pines (1953); Gell-Mann, Brueckner (1957); Langreth, Perdew (1977); Gunnarsson, Lundqvist (1975, 1976)
RPA :	random phase approximation

## Challenges for the Near Future
Quantum-Mechanics Based Technology

Create new materials and systems by design, e.g. better catalysts, quantum dots, quantum wires, inorganic/organic hybrids, etc.

For nanotechnology to become affordable, nano-structures will have to build themselves; normal manufacturing methods will be useless
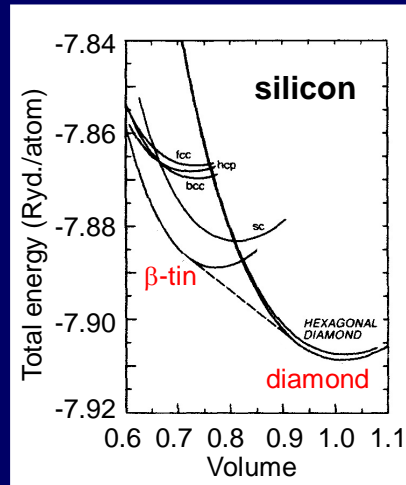⟹ self-organization and assembly.

Make progress in understanding biological systems starting from the fundamental equations of quantum mechanics.

Bridging the time and length scales; some examples:
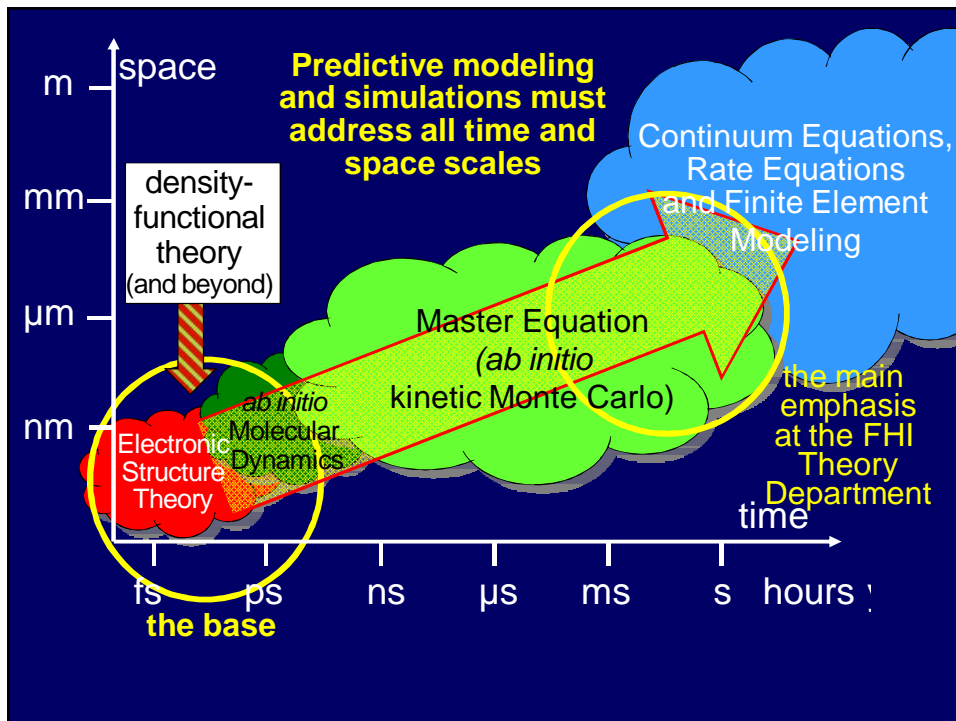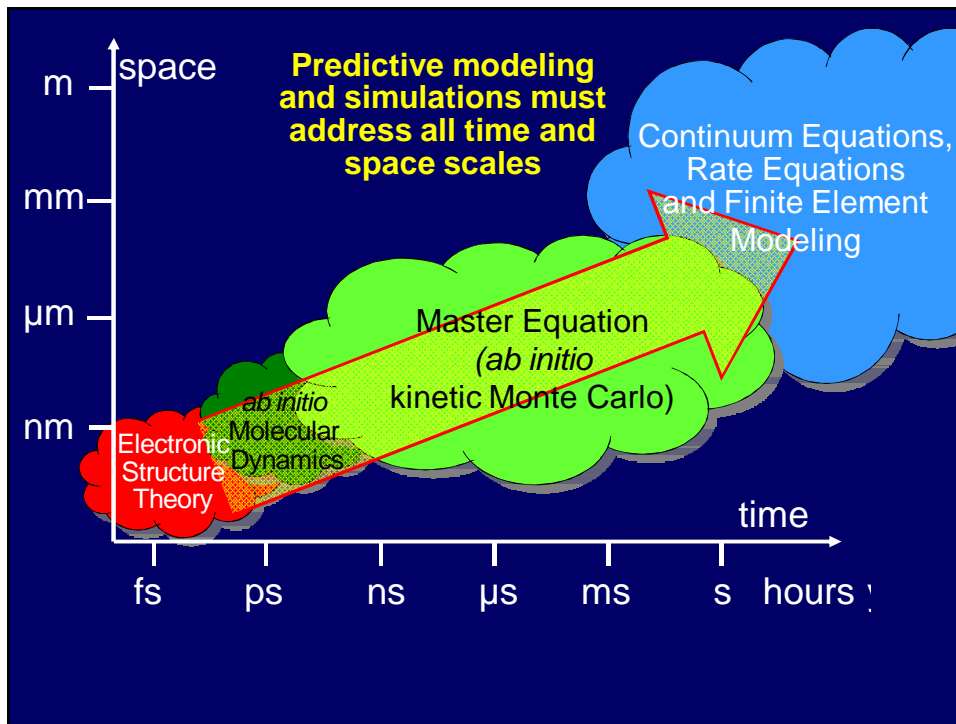
The first (convincing) DFT calculations:
Stability of crystals and crystal phase transitions
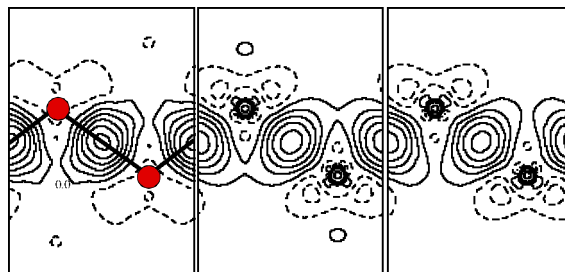

**M. T. Yin and
M. L. Cohen
PRB 26 (1982)
<PRL (1980)>**

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

Electron Density of Si

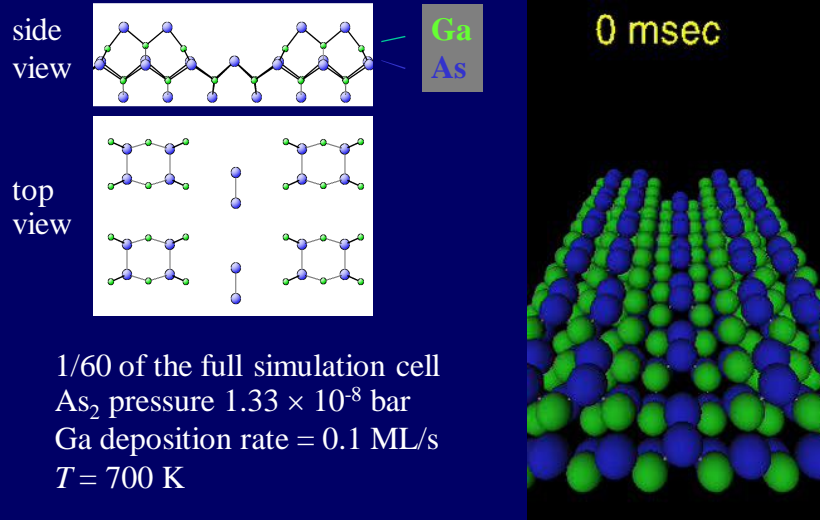Electron density *difference* from sum of atoms

experiment   DFT-LDA   DFT-GGA

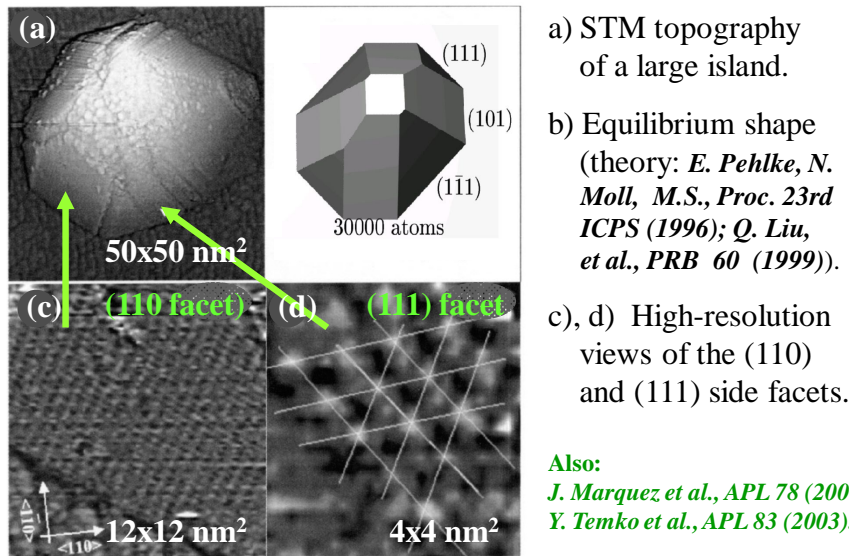*J. M. Zuo, P. Blaha, and K. Schwarz, J. Phys. Cond. Mat. 9, 7541 (1997)*

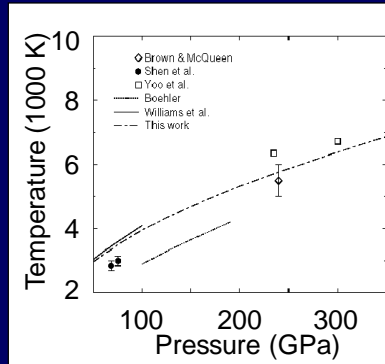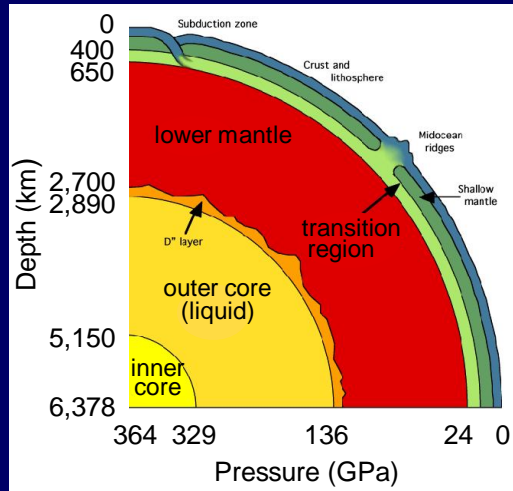## Adsorption, diffusion, island nucleation, and growth of GaAs, studied by *ab intio* kinetic Monte Carlo

side view

Ga
As

top view

0 msec

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)

InAs/GaAs(001) quantum dots close to thermodynamic equilibrium
G. Costantini et al. APL 82 (2003)

(a)

(111)

(101)

(1$\bar{1}$1)

30000 atoms

50x50 nm^2

(c) (110 facet)   (d)   (111) facet

12x12 nm^2 4x4 nm^2

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).*

13
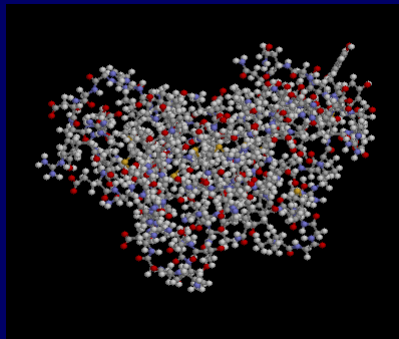
Ab initio melting curve of Fe as function of pressure

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

See also Belonoshko, Rosengren, Burakovsky, Preston, Johansson, PRB 79, 220102(R) (2009)

Stability of Short Helix Chains; towards the Understanding of Folding of Polypeptides

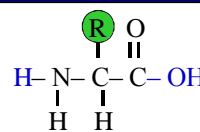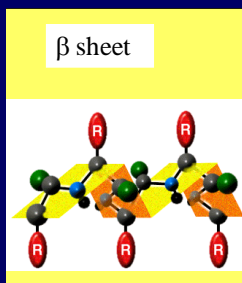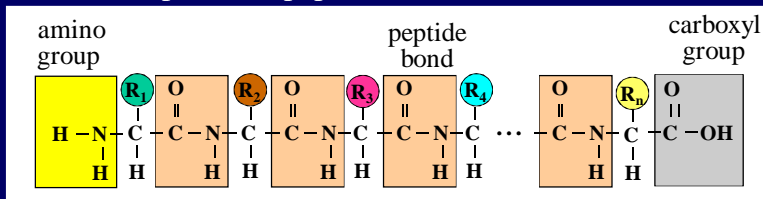peptide chain in the bovine prion protein

atomic structure

secondary and tertiary structure

http://www.rcsb.org/ -- pdb-id: 1QM0

Stability of Secondary Structures

$$H-\underset{\underset{H}{|}}{N}-\underset{\underset{H}{|}}{\overset{\overset{R}{|}}{C}}-\overset{\overset{O}{\|}}{C}-OH$$

structure of proteins (peptide chains):

amino group   peptide bond   carboxyl group

$$H-\underset{\underset{H}{|}}{N}-\underset{\underset{H}{|}}{\overset{\overset{R_1}{|}}{C}}-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-\underset{\underset{H}{|}}{\overset{\overset{R_2}{|}}{C}}-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-\underset{\underset{H}{|}}{\overset{\overset{R_3}{|}}{C}}-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-\underset{\underset{H}{|}}{\overset{\overset{R_4}{|}}{C}}\cdots\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-\underset{\underset{H}{|}}{\overset{\overset{R_n}{|}}{C}}-\overset{\overset{O}{\|}}{C}-OH$$

β sheet

α helix

Hydrogen Bond

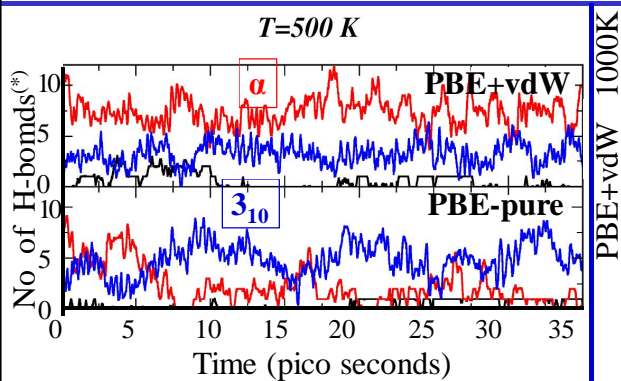secondary structure

$R = CH_3$
= alanine
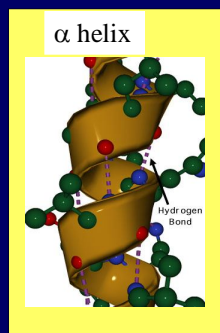
Role of vdW Interaction on (Un)folding; Comparing α, 3_{10}, and π Helices for Ac-Ala$_{15}$LysH$^+$

$T=500\ K$

No of H-bomds$^{(*)}$

α   PBE+vdW

3_{10} PBE-pure

Time (pico seconds)

$^{(*)}$H-bond = 2.5 Å between CO and NH groups

PBE+vdW 1000K

PBE-pure
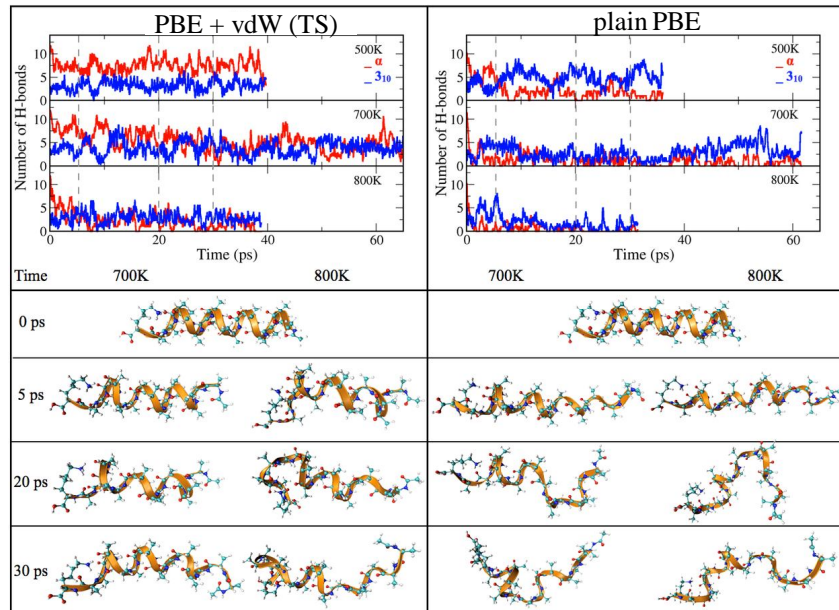

Mariana Rossi Carvalho

Volker Blum

Alexandre Tkatchenko

Ac-Ala$_{15}$-LysH$^+$: Unfolding with DFT-MD

Some remarks about excited states

What About the Kohn-Sham Eigenvalues?

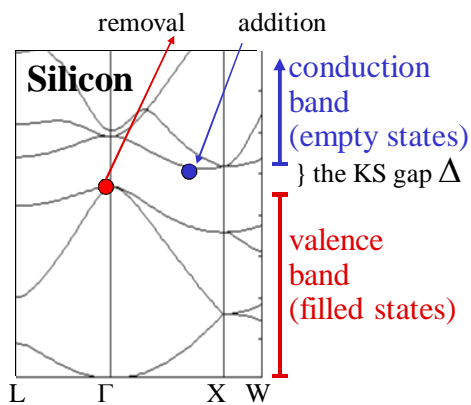The only quantities that are supposed to be correct in the Kohn-Sham approach are **density, energy, forces, …**

What about the individual $\varphi_i(\mathbf{r})$ and ϵ_i ?

The Kohn-Sham $\varphi_i(\mathbf{r})$ and ϵ_i give an approximate description of quasi-particles. Often they are a (good) starting point for many-body electronic structure theory.

Kohn-Sham Electron Bands

Kohn-Sham band gap: $\Delta = \epsilon_{\text{LB}} - \epsilon_{\text{VB}}$ of the N-particle system
The measured (optical) band gap is something else:

Silicon

removal   addition

conduction band (empty states)

} the KS gap Δ

valence band (filled states)

L   Γ   X   W

$$E_{\text{gap}} = I - A \;,$$
$$A = E^N - E^{N+1}$$
$$I = E^{N-1} - E^N$$

$$E_{\text{gap}} = E^{N-1} + E^{N+1} - 2E^N$$
$$= \Delta + \Delta\epsilon^{\text{xc}}$$

Modern calculations of E_{gap} employ the *GW* approach, starting from KS results.
Excitons, are given by the Bethe-Salpeter equation.
… and/or by time-dependent DFT
more comes *later this week*

What About the Kohn-Sham Eigenvalues?

The ionization energy is:

$$I_k = E_k^{N-1} - E^N$$

$$= -\int_0^1 \frac{\partial E_v[n]}{\partial f_k} df_k$$
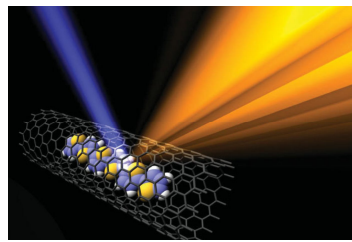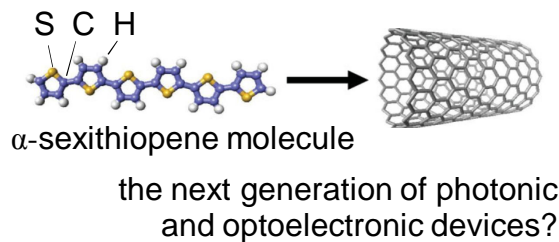
$$= -\int_0^1 \epsilon_k(f_k)\, df_k$$

(Well defined for the highest occupied state. Otherwise, this only holds approximately.)

Here we assume that the positions of the atoms don't change upon ionization, or that they change with some delay (Franck-Condon principle). Using the mean-value theorem of integral algebra gives:

$$\boxed{I_k = \epsilon_k(0.5)}$$

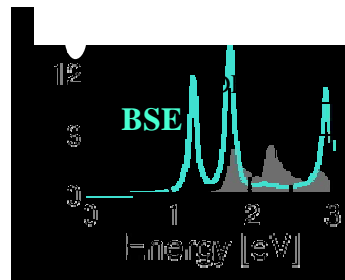This is called the Slater-Janak "transition state". It can be viewed as the DFT analog of Koopmans' theorem.

Advanced Materials: Organic-Inorganic Hybrids

M. A. Loi, et al., Adv. Mater. 22, 1635 (2010).

S C H

α-sexithiopene molecule

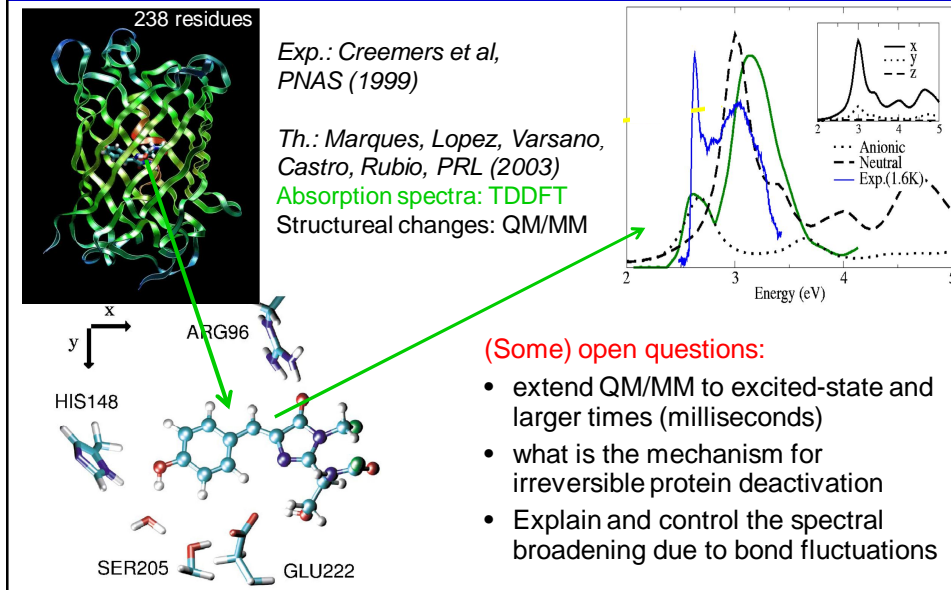the next generation of photonic and optoelectronic devices?

Combined theoretical/experimental study:
-- Which peapods are stable? (DFT)
-- What's the geometry. (DFT)
-- Light emission, light absorption (DFT plus **B**ethe-**S**alpeter **E**quation and experiment)

BSE

Energy [eV]

Biophysics: Fluorescent Proteins

238 residues

Exp.: Creemers et al, PNAS (1999)

Th.: Marques, Lopez, Varsano, Castro, Rubio, PRL (2003)
Absorption spectra: TDDFT
Structureal changes: QM/MM

x
y

ARG96

HIS148

SER205   GLU222

(Some) open questions:
- extend QM/MM to excited-state and larger times (milliseconds)
- what is the mechanism for irreversible protein deactivation
- Explain and control the spectral broadening due to bond fluctuations

---

Summary:

Interacting electrons determine the properties and function of real materials and bio molecules.

Important arenas for future theoretical work:
- -- Correlated systems, e.g. *f*-electron chemistry,
- -- 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 catalysis or crystal growth (self-assembly and self-organization),
- -- molecules and clusters in solvents, electrochemistry,
- -- biological problems, e.g. dynamics of nuclei for electronically excited states.