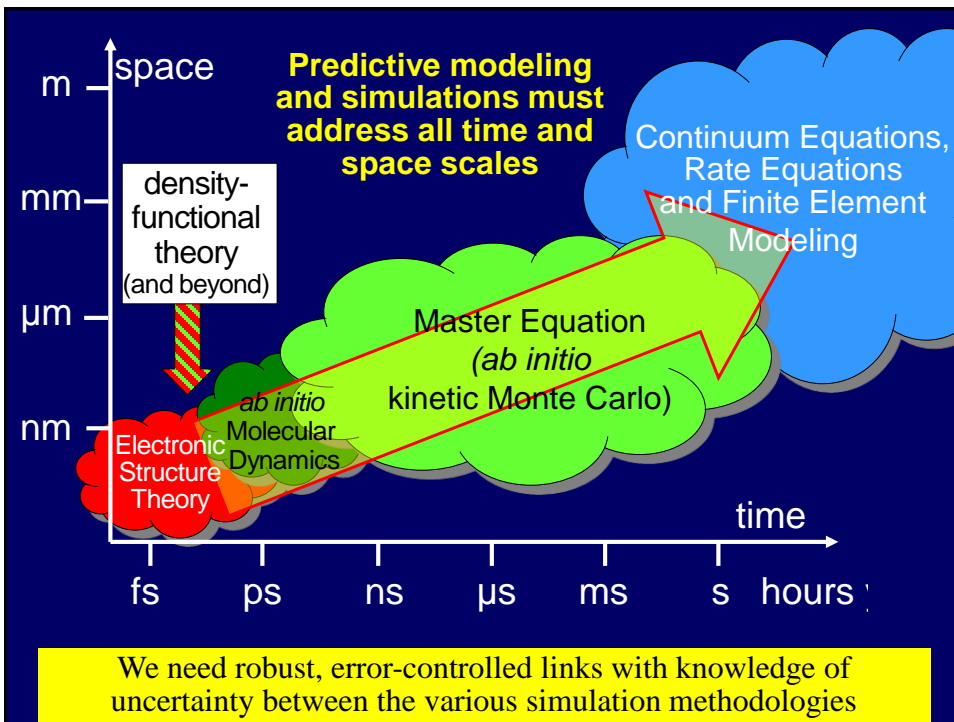


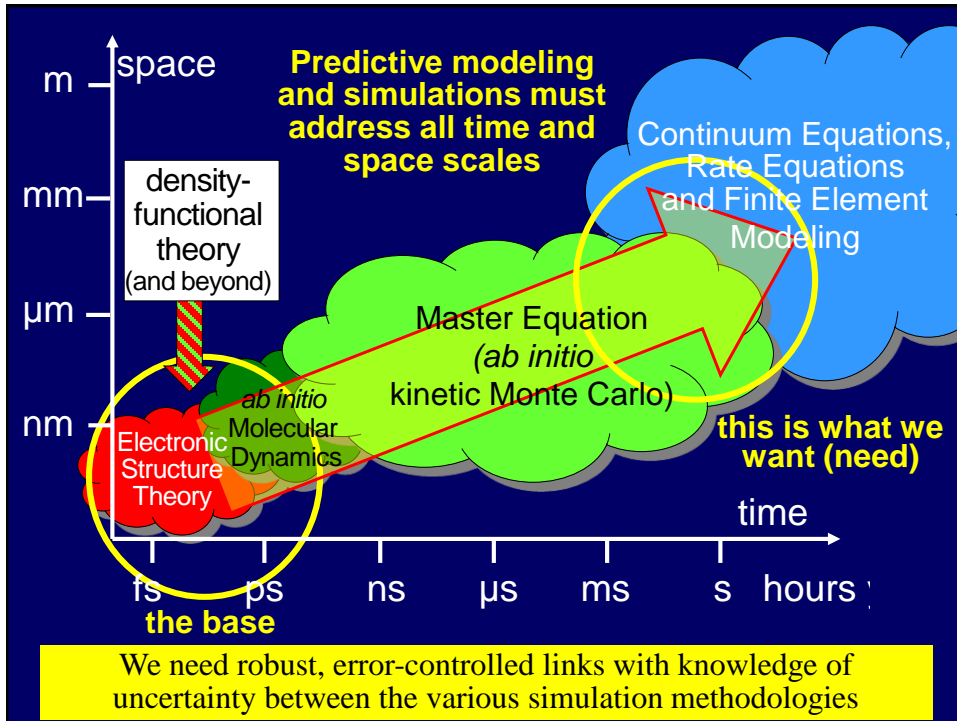


Summer School of the Max-Planck-EPFL Center for Molecular Nanoscience & Technology

July 27 - 31, 2015 in Schloss Ringberg, Germany

	Monday	Tuesday	Wednesday	Thursday	Friday
WE 8:45 - 9:55 Prog Invit		Silke Biermann - <i>Electronic structure calculations using dynamical mean field theory</i>	Ivano Tavernelli - <i>Trajectory- based nonadiabatic dynamics using time-dependent density functional theory</i>	Cecile Hebert - <i>Investigation of molecules at surfaces and chemical reactions by transmission electron microscopy: is a dream becoming true ?</i>	
AR 9:55 - 11:05 Ven Trav		Matthieu Verstraete - <i>Ab initio approaches to electron transport</i>	Ole Hellman - <i>Phonons and anharmonics</i>	Andrea Cepellotti - <i>Thermal Transport in 2D Materials</i>	Alec Wodtke - <i>The dynamics of molecular interactions and chemical reactions at metal surfaces: Testing the foundations of theory</i>
	11:05	Coffee break	Coffee break	Coffee break	Coffee break
AR 11:25 - 12:35		Carsten Baldauf - <i>Molecular dynamics of peptides in isolation and computation on physical observables</i>	Matthias Scheffler - <i>Big-Data Analytics for Materials Science: Concepts, Challenges, and Hype</i>	Markus Eistner - <i>Multiscale simulations of biological structures and processes</i>	Examinations
	12:35	Lunch	Lunch	Lunch	Lunch
	14:15 - 15:25	Tom Rizzo - <i>Biomolecules in isolation - challenges and benchmarks for theory</i>	Christian Carbogno - <i>Thermal Conductivities from First Principles Molecular Dynamics</i>		
	15:25	Coffee break	Coffee break	Coffee break	
	15:50 - 17:00	Matthias Scheffler - <i>Electronic Structure Theory: Introduction and Overview</i>	Michele Cerlotti - <i>Representing and understanding patterns in materials and molecules</i>	Sergey Levchenko - <i>Defects in Solids at realistic conditions</i>	Group discussion
	17:00 - 18:10	Claudia Draxl - <i>Beyond density-functional theory: GW and the Bethe- Salpeter equation</i>	Klaus Kern - <i>Molecular nanostructures at surfaces</i>	Karsten Jacobsen - <i>Computational Screening of Light-Absorbing Materials</i>	
	18:30	Dinner break	Dinner break	Dinner break	Conference Dinner
	20:00 - 21:10	Hardy Gross - <i>Time-dependent density functional theory</i>	poster parade+session	Anatole von Lilienfeld - <i>Machine Learning in Chemical Space</i>	





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: $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N; \mathbf{R}_1, \dots, \mathbf{R}_M)$

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

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

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

$$\hat{V}^{e-ion}(\mathbf{r}_k, \mathbf{R}_I) = \sum_{k=1}^N \sum_{I=1}^M v_I^{ion}(|\mathbf{R}_I - \mathbf{r}_k|)$$

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: $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N; \mathbf{R}_1, \dots, \mathbf{R}_M)$

Dirac: “The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and **the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.** It therefore becomes desirable that **approximate practical methods of applying quantum mechanics should be developed**, which can lead to an explanation of the main features of complex atomic systems without too much computation.”

Proceedings of the Royal Society of London. Ser. A, Vol. 123, No. 792 (6 April 1929)

Born-Oppenheimer Approximation

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N; \mathbf{R}_1, \dots, \mathbf{R}_M) = \sum_v \Lambda_v(\{\mathbf{R}_I\}) \Phi_{v, \{\mathbf{R}_I\}}(\{\mathbf{r}_k\})$$

Where Φ_v are solutions of the “electronic Hamiltonian”:

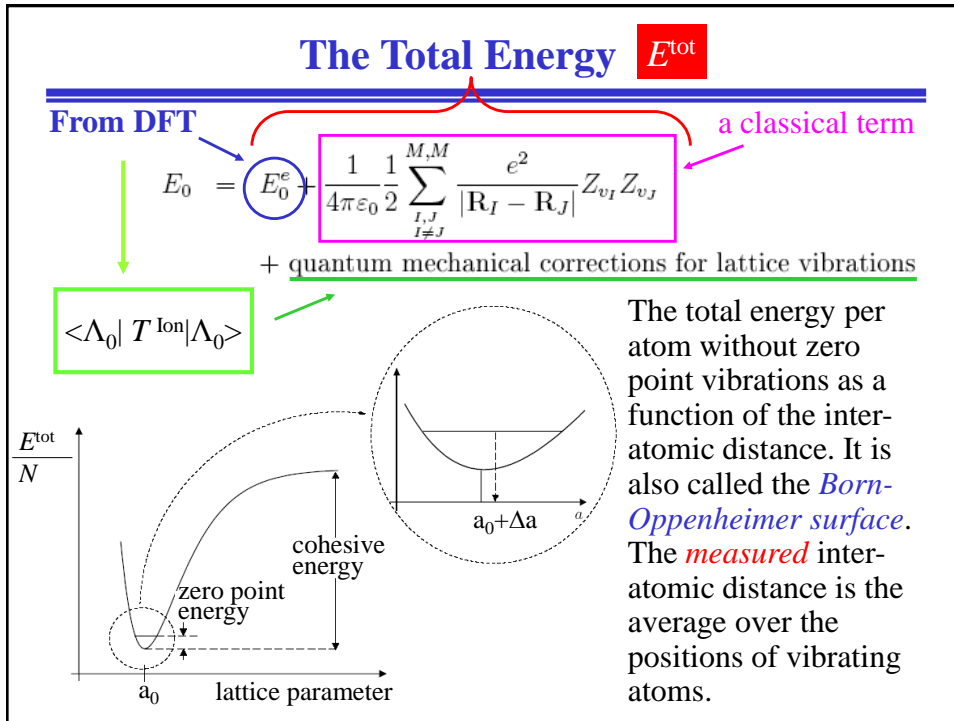
$$H_{\{\mathbf{R}_I\}}^e \Phi_{v, \{\mathbf{R}_I\}}(\{\mathbf{r}_k\}) = E_{v, \{\mathbf{R}_I\}}^e \Phi_{v, \{\mathbf{R}_I\}}(\{\mathbf{r}_k\})$$

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

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:

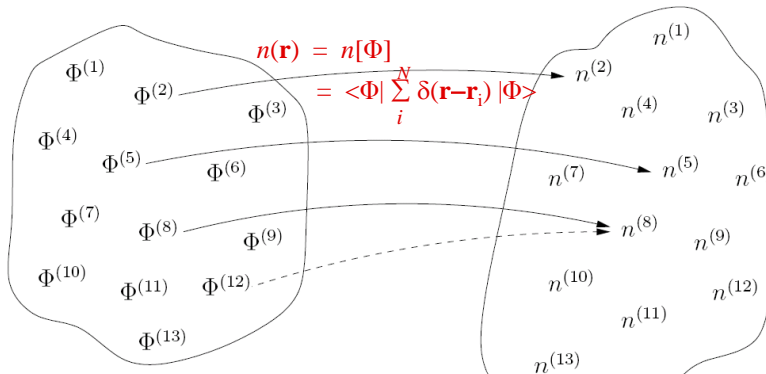
These limits can be severe.
Nevertheless, we will use the BO approximation in the following.

How can we solve:

$$H_{\{\mathbf{R}_I\}}^e \Phi_{V,\{\mathbf{R}_I\}}(\mathbf{r}_k) = E_{V,\{\mathbf{R}_I\}}^e \Phi_{V,\{\mathbf{R}_I\}}(\mathbf{r}_k) \quad (1)$$

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

The Hohenberg-Kohn Theorem (1964)

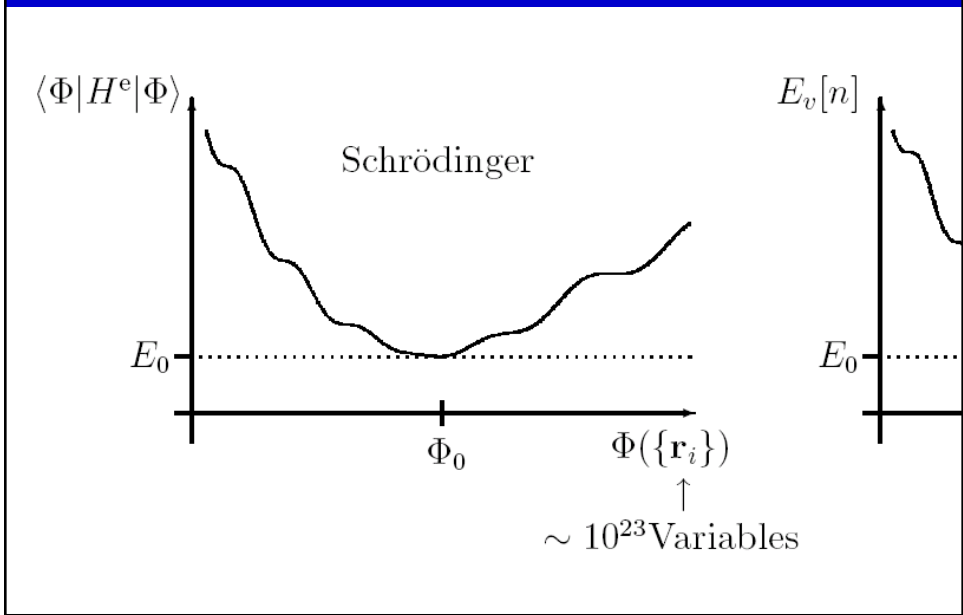


Set of non-degenerate ground-state wave functions Φ of arbitrary N -electron Hamiltonians.

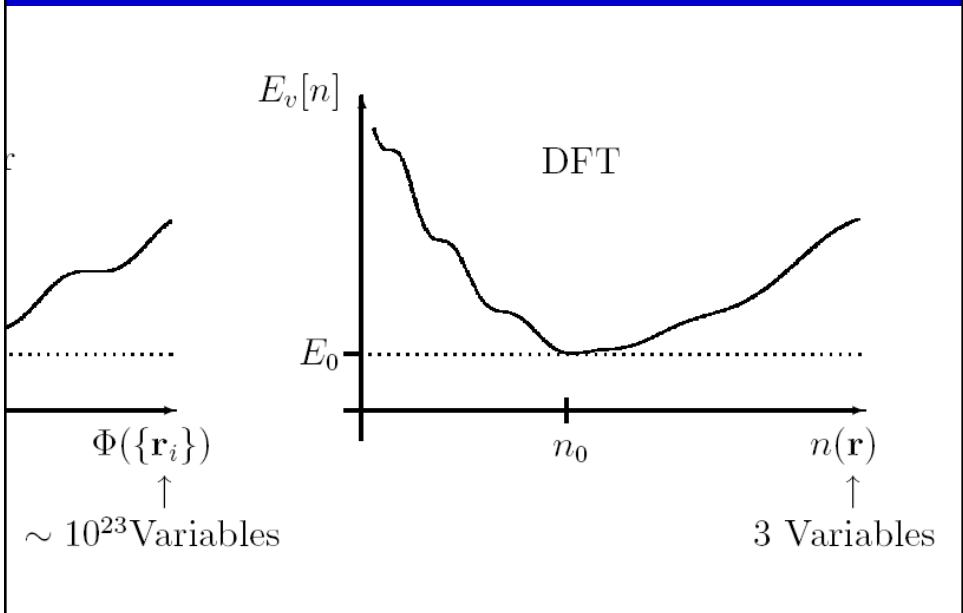
Set of particle densities $n(\mathbf{r})$ belonging to non-degenerate N -electron ground states.

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

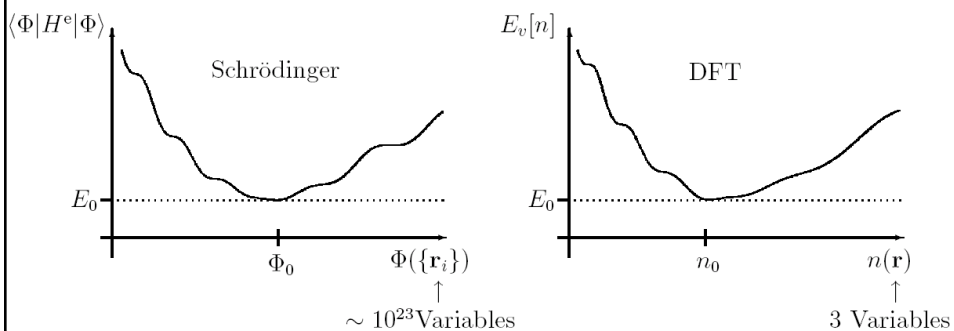
Comparison of Wave-Function and Density-Functional Theory



Comparison of Wave-Function and Density-Functional Theory



Comparison of Wave-Function and Density-Functional Theory



Density Functional Theory

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

$$E_0(\{\mathbf{R}_I\}) = \text{Min}_{\Phi} \langle \Phi | H^e | \Phi \rangle$$

Hohenberg and Kohn (1964): The functional

$$n(\mathbf{r}) = n[\Phi] = \langle \Phi | \sum_i \delta(\mathbf{r} - \mathbf{r}_i) | \Phi \rangle$$

can be inverted, *i.e.*,


$$\Phi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \Phi[n(\mathbf{r})] .$$


This implies:



$$E_0(\{\mathbf{R}_I\}) = \text{Min}_{n(\mathbf{r})} E_{\{\mathbf{R}\}}[n]$$

The Kohn-Sham Ansatz of Density-Functional Theory



Bohr:  electron (light, orbiting)
 + proton (heavy, fixed)
 Electron = particle

Schrodinger:  Electron = wave
 $\psi(r)$

DFT
 Walter Kohn  Electron is a density distribution on cloud $n(r)$
 electron cloud 

The Kohn-Sham Ansatz of Density-Functional Theory

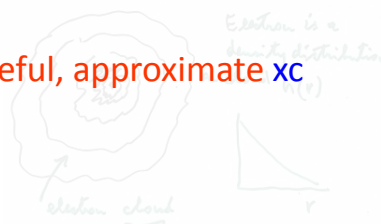


- Kohn-Sham (1965): Replace the original many-body problem by an independent electron problem that can be solved!

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

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

Walter Kohn



Kohn and Sham (1965):

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

with
$$E^{\text{Hartree}}[n] = \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}d^3\mathbf{r}'$$

And $T_s[n]$ the functional of the kinetic energy of **non-interacting** electrons. $E^{\text{xc}}[n]$ 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
$$\frac{\delta E_v^{[n]}}{\delta n} = \mu = \frac{\delta T_s[n]}{\delta n(\mathbf{r})} + v^{\text{eff}}(\mathbf{r})$$
 Kohn-Sham equation

Kohn and Sham (1965):

$$v^{\text{eff}}(\mathbf{r}) = v(\mathbf{r}) + \frac{e^2}{4\pi\epsilon_0} \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' + \frac{\delta E^{\text{xc}}[n]}{\delta n(\mathbf{r})}$$

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:

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

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

Kohn-Sham equation

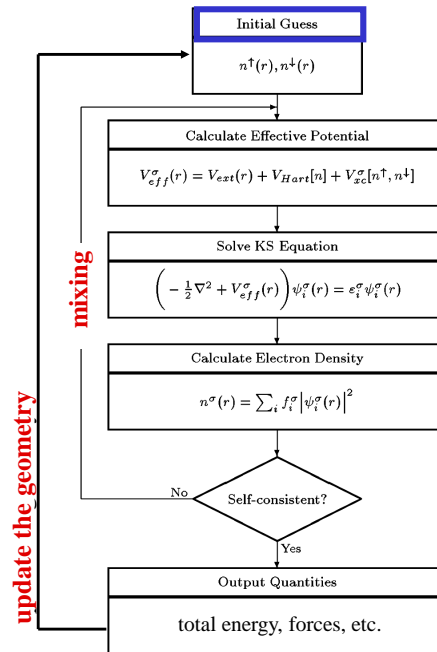
$v^{\text{eff}}(\mathbf{r})$ depends on the density that we are seeking.

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

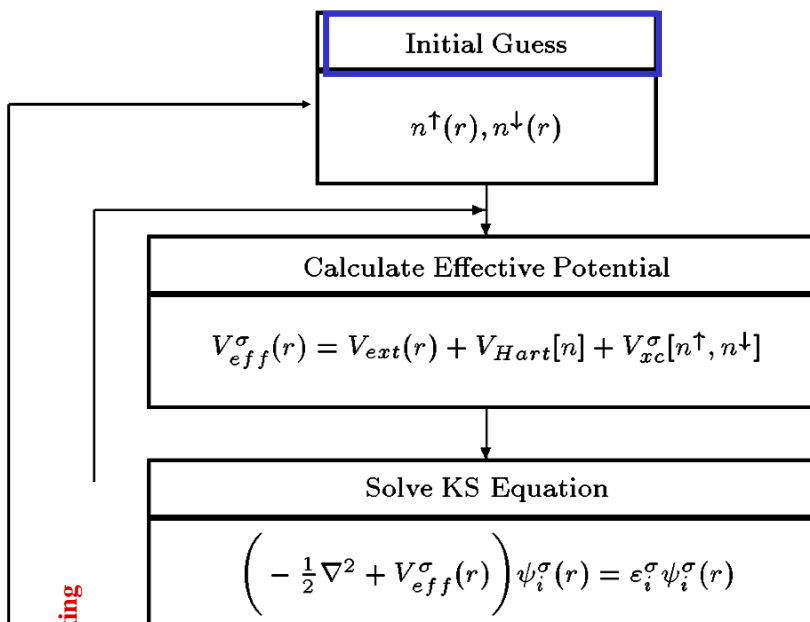
Solving the Kohn-Sham Equations

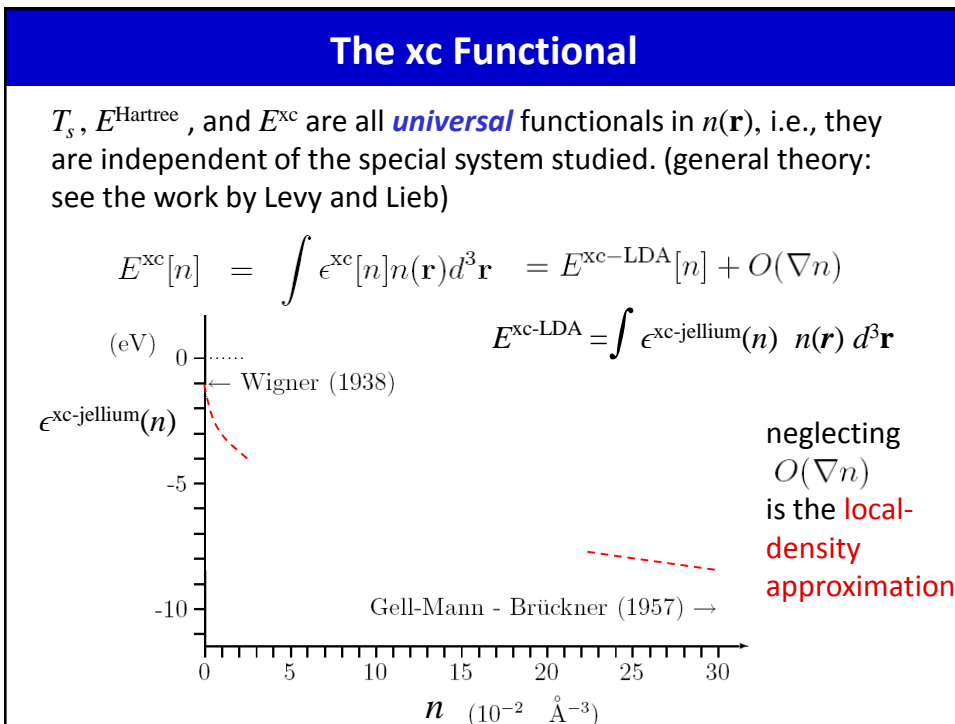
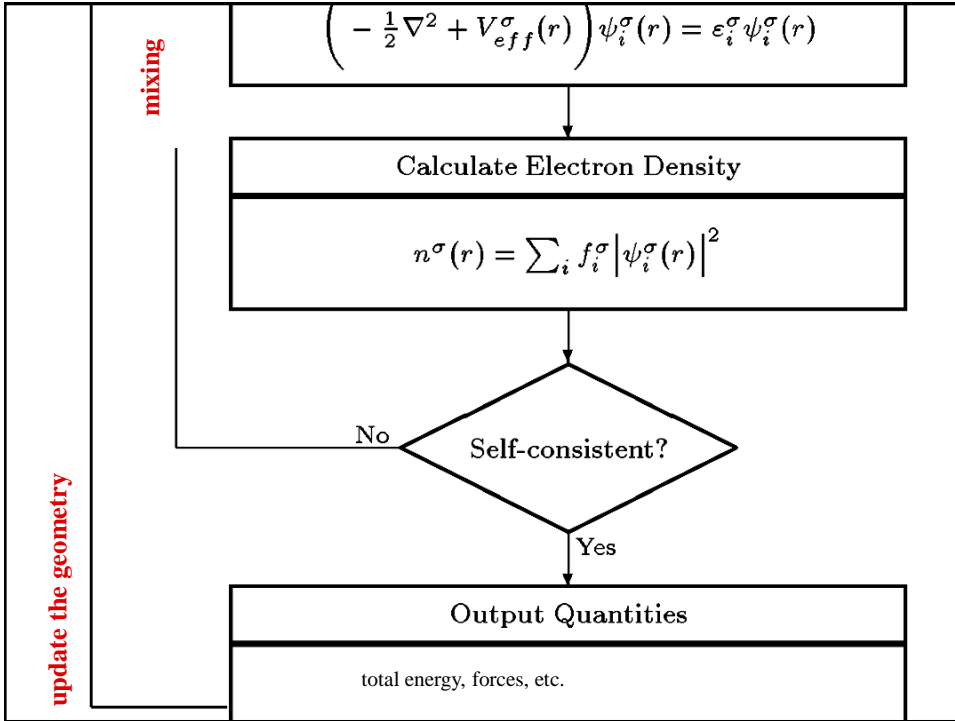
- Structure, types of atoms
- Guess for input
- Solve KS Eqs.
- New density
- Self-consistent?
- Output:
 - Total energy, force, ...
 - KS eigenvalues

The self-consistent field method



The self-consistent field method

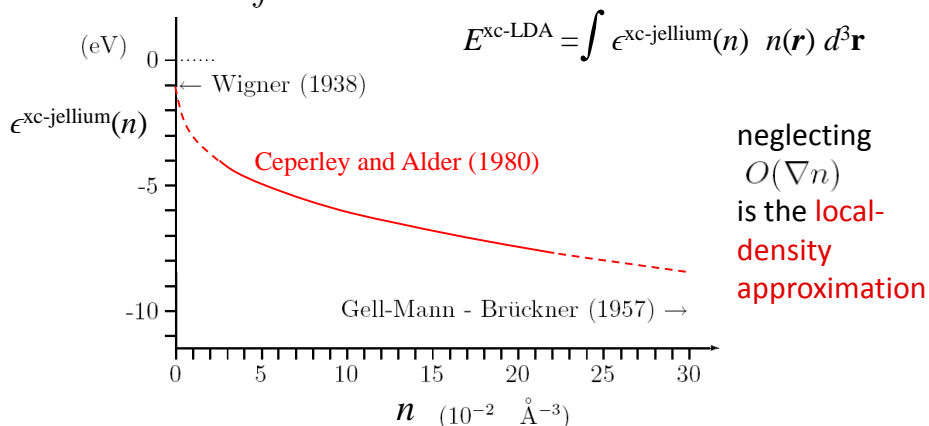




The xc Functional

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)

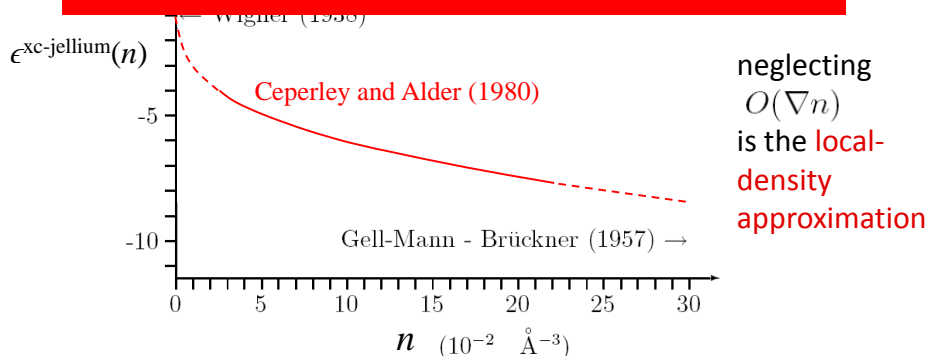
$$E^{\text{xc}}[n] = \int \epsilon^{\text{xc}}[n] n(\mathbf{r}) d^3\mathbf{r} = E^{\text{xc-LDA}}[n] + O(\nabla n)$$



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)

- 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.



Certainties about Density Functional Theory

1. **DFT in principle:** It is exact; a universal $E^{\text{xc}}[n]$ functional “exists”.
2. **DFT in practice:** It is probably not possible to write down $E^{\text{xc}}[n]$ as a closed mathematical expression. We need approximations.

The success of DFT proves that “simple” approximations to the exchange-correlation functional can provide good results – if one knows what one is doing.

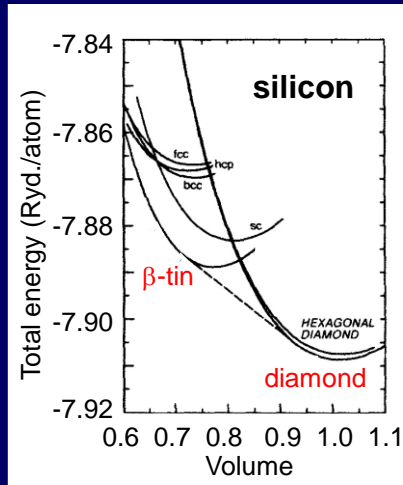
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The success of DFT proves that “simple” approximations to the exchange-correlation functional can provide good results – if one knows what one is doing.

The search (research) for new xc functionals goes on

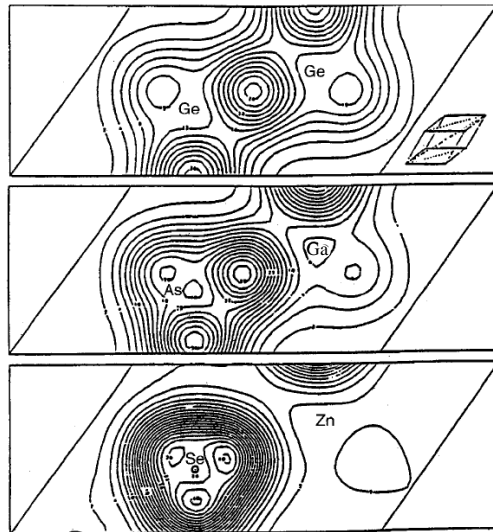
The first (convincing) DFT calculations: Stability of crystals and crystal phase transitions



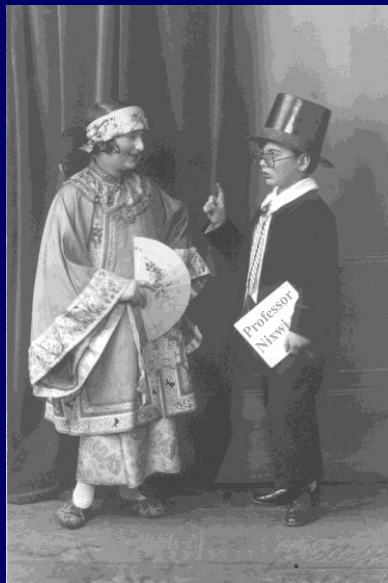
*M. T. Yin and
M. L. Cohen
PRB 26 (1982)
< and PRL 1980 >*

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

Figure 6.16: Valence electron density of Ge (top), b) GaAs (middle), and c) ZnSe (lower) in e per unit-cell volume.



34 years before
DFT invention



34 years after
DFT invention



MOST CITED PAPERS IN APS (FROM 1893)

	Journal	# cites	Title	Author(s)
1	PRB (1988)	39190	Development of the Colle-Salvetti Correlation-Energy ...	Lee, Yang, Parr
2	PRL (1996)	25452	Generalized Gradient Approximation Made Simple	Perdew, Burke, Ernzerhof
3	PRA (1988)	22904	Density-Functional Exchange-Energy Approximation ...	Becke
4	PR (1965)	20142	Self-Consistent Equations Including Exchange and Correlation ...	Kohn and Sham
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6	PRB (1976)	13160	Special Points for Brillouin-Zone Integrations	Monkhorst and Pack
7	PRB (1992)	10876	Accurate and Simple Analytic Representation of the Electron ...	Perdew and Wang
8	PRB (1999)	10007	From Ultrasoft Pseudopotentials to the Projector Augmented ...	Kresse and Joubert
9	PRB (1990)	9840	Soft Self-Consistent Pseudopotentials in a Generalized ...	Vanderbilt
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14	PR (1934)	9271	Note on an Approximation Treatment for Many-Electron Systems	Moller and Plesset
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21	PR (1961)	6467	Effects of Configuration Interaction on Intensities and Phase Shifts	Fano
22	PR (1957)	6260	Theory of Superconductivity	Bardeen, Cooper, Schrieffer

list was compiled ~2010

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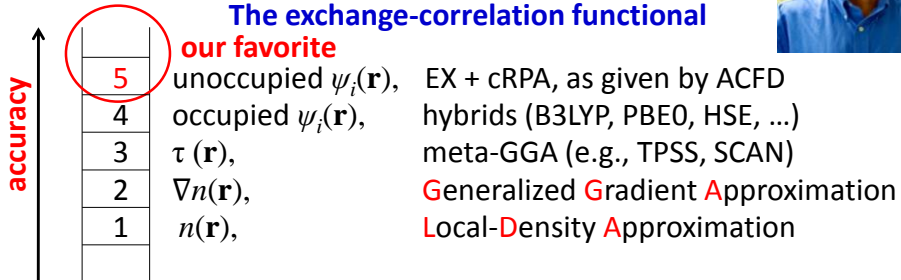
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Perdew's Dream: Jacob's Ladder in Density-Functional Theory



The exchange-correlation functional



$\tau(\mathbf{r})$: Kohn-Sham kinetic-energy density
 EX: exact exchange: $E_x = -\frac{1}{2} \sum_{occ} \int \dots$
 cRPA: random-phase approximation for c
 ACFD: adiabatic connection fluctuation dis

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

Berlin, July 2013

Perdew Becke Kohn Gross



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



↑ accuracy

5
4
3
2
1

The exchange-correlation functional

our favorite

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. TPSS)

2 $\nabla n(\mathbf{r})$, Generalized Gradient Approximation

1 $n(\mathbf{r})$, Local Density Approximation

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.

$\tau(\mathbf{r})$: Kohn-Sham
 EX: exact
 cRPA: ...
 ... Becke, Kohn Gross
 ... deckner (1957);
 ... (1976); Langreth, Perdew
 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)



"Level 5 plus"

Viewed in the Many-Body Framework

Perturbation theory:

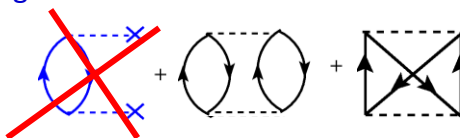
$H = H^0 + H'$ with $H^0|\phi_n\rangle = E_n^{(0)}|\phi_n\rangle$ and $|\phi_n\rangle =$ Slater det.
 $|\phi_0\rangle =$ ground state, $|\phi_{i,a}\rangle =$ single excitations, $|\phi_{ij,ab}\rangle =$ double exci.

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

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

single excitations double excitations

Using HF input, this is Møller-Plesset perturbation theory, MP2



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).*
J. 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.

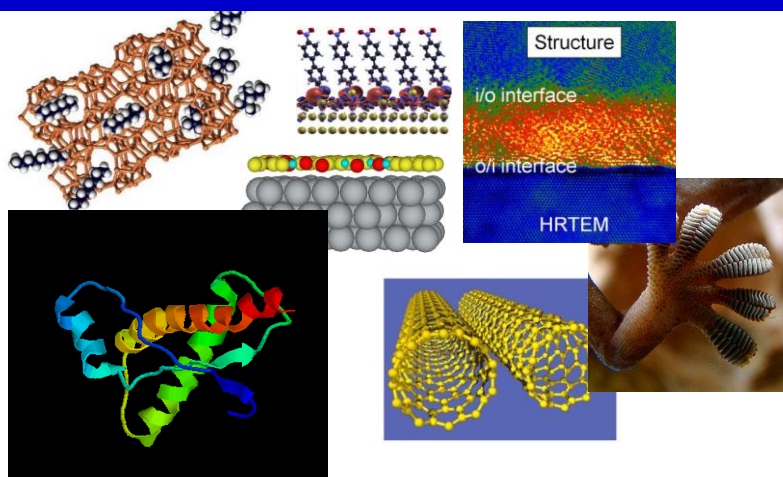
- better than LDA, PBE, MP2
- comparable to CCSD
- not as accurate as CCSD(T)

single excitations
cRPA
SOSEX

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

Role of van der Waals Interactions in Physics, Chemistry, and Biology



C_6 Coefficients in the TS Scheme (schematic)

S. Grimme: add tails $E_{\text{vdW}} = \sum_{I,J}^2 C_{6,I,J} / R_{I,J}^6$

$$C_{6AB} = \frac{3}{\pi} \int_0^\infty \alpha_A(i\omega) \alpha_B(i\omega) d\omega$$

...

$$C_{6AA}^{\text{eff}} = \underbrace{\frac{\eta_A^{\text{eff}}}{\eta_A^{\text{free}}} \left(\frac{\kappa_A^{\text{free}}}{\kappa_A^{\text{eff}}} \right)^2 \left(\frac{V_A^{\text{eff}}}{V_A^{\text{free}}} \right)^2}_{C_{6AA}^{\text{free}}}$$

Chu and
Dalgarno,
JCP **212**
(2004)



Alexandre
Tkatchenko

Calculated by DFT
– on the fly –

C_6 is a functional of the
density, $C_6 = C_6[n]$.

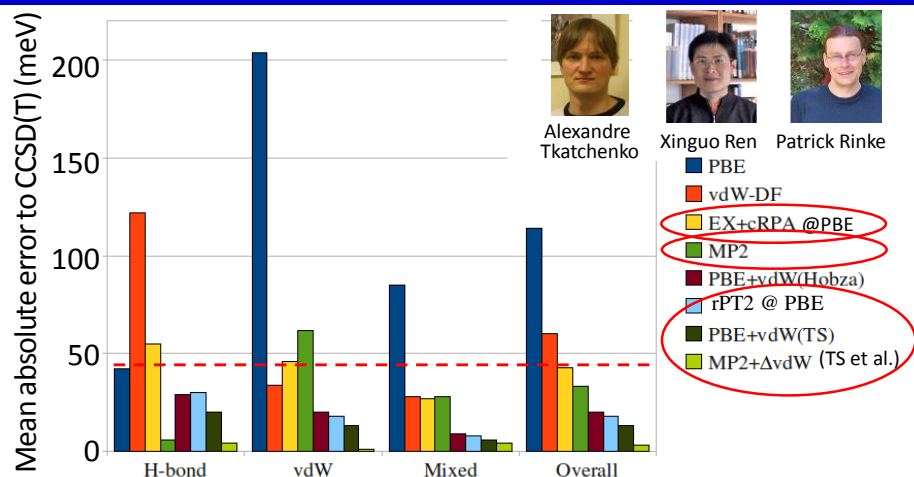
For details, see:

DFT+vdW: A. Tkatchenko and M.S., *PRL* **102** (2009).

MP2+ΔvdW: A. Tkatchenko, R. DiStasio, M. Head-Gordon, and M.S., *JCP* (2009).

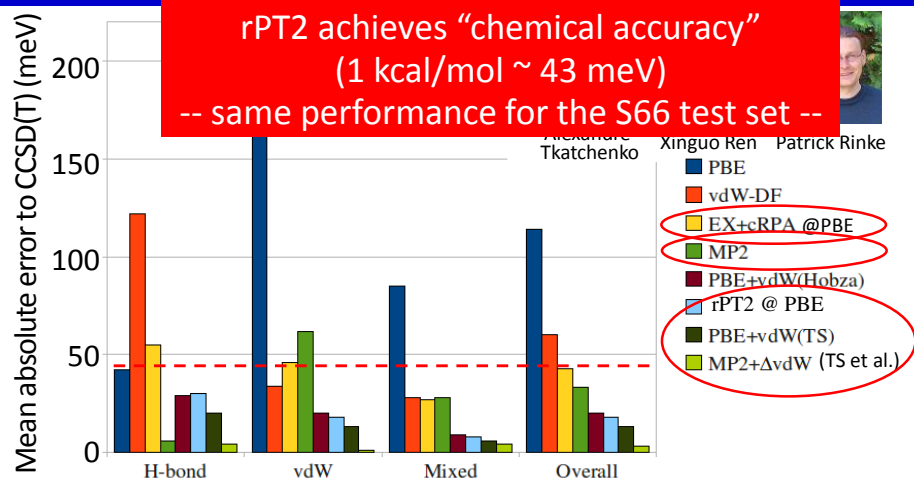
Excellent description – as long as the “pair-wise model” holds.

Performance of rPT2 for Weak Intermolecular Interactions: S22 Test Set



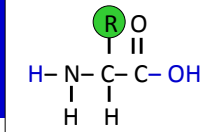
CCSD(T): Jurecka, Sponer, Cerny, Hobza, *PCCP* (2006). **Langreth-Lundqvist:** Gulans, Puska, Nieminen, *PRB* (2009); **rPT2:** X. Ren et al. *PRL* (2011) and *PRB* (2013).
TS: A. Tkatchenko and M.S., *PRL* (2009); A. Tkatchenko et al., *JCP* (2009).

Performance of rPT2 for Weak Intermolecular Interactions: S22 Test Set

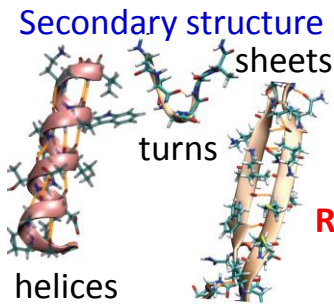
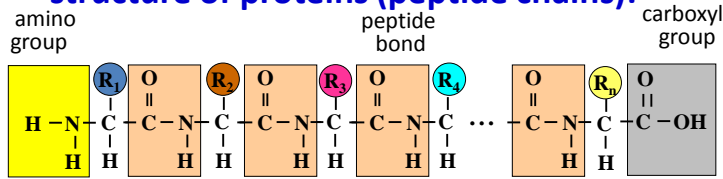


CCSD(T): Jurecka, Sponer, Cerny, Hobza, *PCCP* (2006). **Langreth-Lundqvist:** Gulans, Puska, Nieminen, *PRB* (2009); **rPT2:** X. Ren et al. *PRL* (2011) and *PRB* (2013).
TS: A. Tkatchenko and M.S., *PRL* (2009); A. Tkatchenko et al., *JCP* (2009).

Stability of Secondary Structures



structure of proteins (peptide chains):



R = CH₃
= alanine

Tertiary structure



Mariana Rossi Carvalho

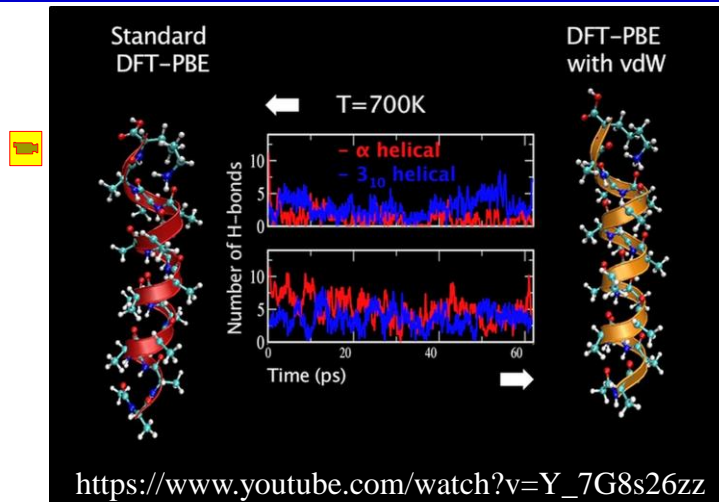


Volker Blum



Alexandre Tkatchenko

Role of vdW Interaction on (Un) folding; Ac-Ala₁₅LysH⁺



Mariana Rossi Carvalho



Volker Blum

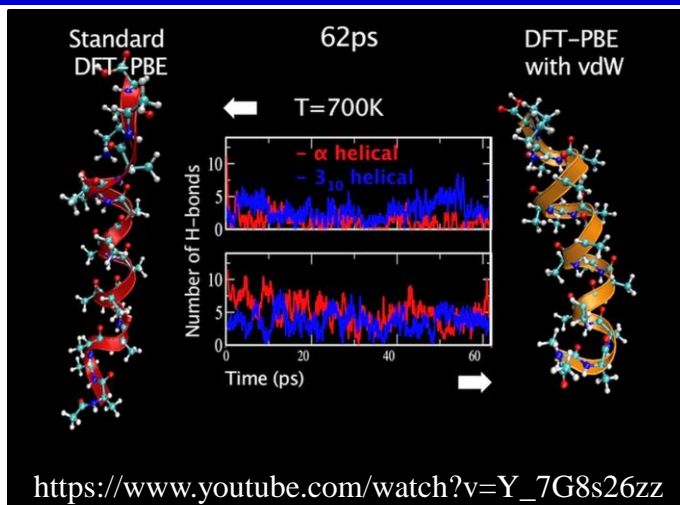


Alexandre Tkatchenko

(*)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)folded; Ac-Ala₁₅LysH⁺



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 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 \leftrightarrow graphite.

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

Thermodynamics (A Brief Reminder)

Thermodynamic potentials:

Internal energy	$U(S, V) = E^{\text{tot}} + U^{\text{vib}}$
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 minimum.

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

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)

M. Scheffler and J. Dabrowski, Phil. Mag. A 58, 107 1988).

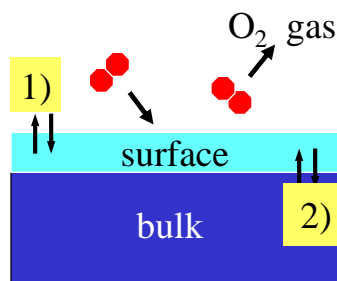
K. Reuter and M. Scheffler, Phys. Rev. B 65, 035406 (2002)

Surface in Contact with a One-Component Gas Phase – Example: O₂ @ Pd

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

N_{O} = # of O atoms in the system

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



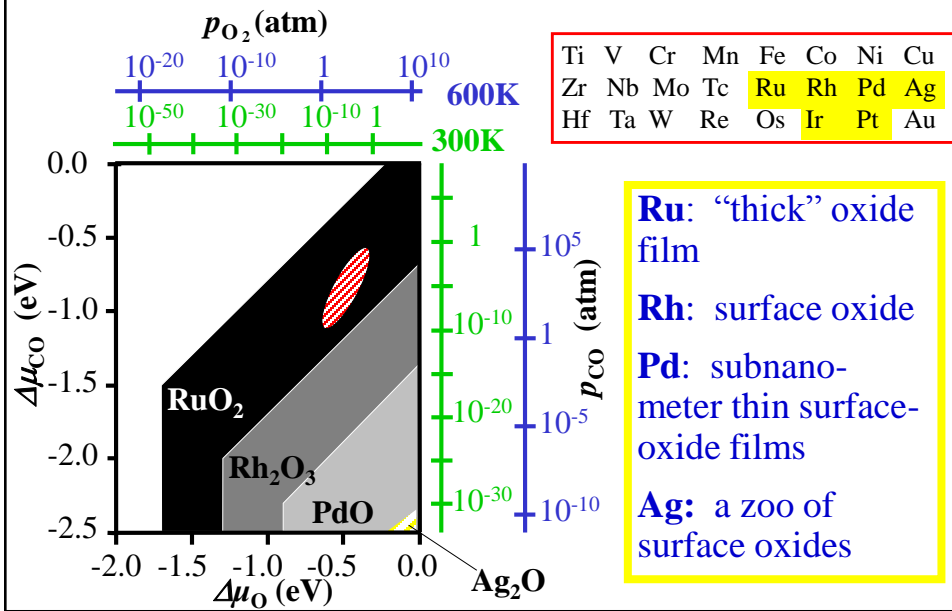
Concept of thermodynamic reservoirs:

- 1) The environment can give and take O atoms at an energy $\mu_{\text{O}} = 1/2 \mu_{\text{O}_2}$

$$\mu_{\text{O}}(T, p) = 1/2 \mu_{\text{O}_2}(T, p^0) + 1/2 k_B T \ln(p/p^0)$$

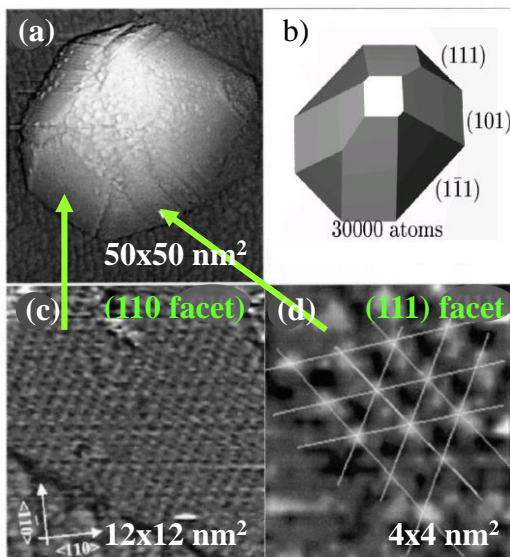
- 2) Also the bulk of the substrate is practically of infinite size and acts as a reservoir for the Pd atoms: $\mu_{\text{Pd}} = g_{\text{Pd}}^{\text{bulk}}$

Stability of Bulk Oxides in CO Oxidation Catalysis



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.

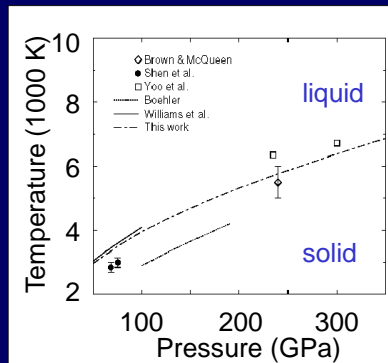
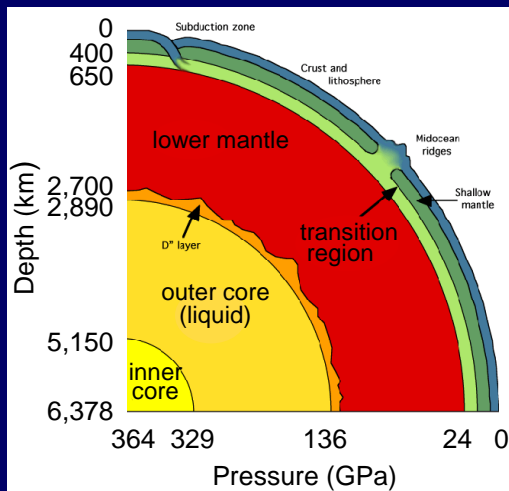
Exploit thermodynamic equilibria and the concept of thermal reservoirs (atomic chem. potentials).

- 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 $k_B T$)
- “only” thermodynamic equilibrium

Ab Initio Melting Curve of Fe as Function of Pressure



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

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
- Modeling the kinetics, e.g. of catalysts or crystal growth (self-assembly and self-organization) – in realistic environments
- Molecules and clusters (incl. bio molecules) in solvents, electrochemistry, fuel cells, external fields
- Correlated systems, e.g. *f*-electron chemistry
- Big-data analytics (statistical learning, compressed sensing, etc.)