



International Summer School on

Basic Concepts and First-Principles Computations for Surface Science:

Applications in Chemical Energy Conversion and Storage

Norderney, Germany, July 21-26, 2013

Let's start

Electronic-Structure Theory

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
5	PRB (1996)	13731	Efficient Iterative Schemes for Ab Initio Total-Energy ...	Kresse and Furthmüller
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
10	PR (1964)	9789	Inhomogeneous Electron Gas	Hohenberg and Kohn
11	PRB (1981)	9787	Self-Interaction Correction to Density-Functional Approx. ...	Perdew and Zunger
12	PRB (1992)	9786	Atoms, Molecules, Solids, and Surfaces - Applications of the ...	Perdew, Chevary, ...
13	PRB (1986)	9313	Density-Functional Approx. for the Correlation-Energy ...	Perdew
14	PR (1934)	9271	Note on an Approximation Treatment for Many-Electron Systems	Møller and Plesset
15	PRB (1994)	9100	Projector Augmented-Wave Method	Bloch
16	PRL (1980)	7751	Ground-State of the Electron-Gas by a Stochastic Method	Ceperley and Alder
17	PRL (1987)	7663	Inhibited Spontaneous Emission in Solid-State Physics ...	Yablonovitch
18	PRL (1986)	7589	Atomic Force Microscope	Binnig, Quate, Gerber
19	PRB (1991)	7425	Efficient Pseudopotentials for Plane-Wave Calculations	Troullier and Martins
20	PRB (1993)	6925	Ab initio Molecular Dynamics for Liquid Metals	Kresse and Hafner
21	PR (1961)	6467	Effects of Configuration Interaction on Intensities and Phase Shifts	Fano
22	PR (1957)	6260	Theory of Superconductivity	Bardeen, Cooper, Schrieffer

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

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

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

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

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

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

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

No open question here!

Born-Oppenheimer Approximation

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N; \mathbf{R}_1, \dots, \mathbf{R}_M) = \sum_{\nu} \Lambda_{\nu}(\{\mathbf{R}_I\}) \Phi_{\nu}(\{\mathbf{r}_k\})$$

Where Φ_{ν} are solutions of the “electronic Hamiltonian”:

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

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

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

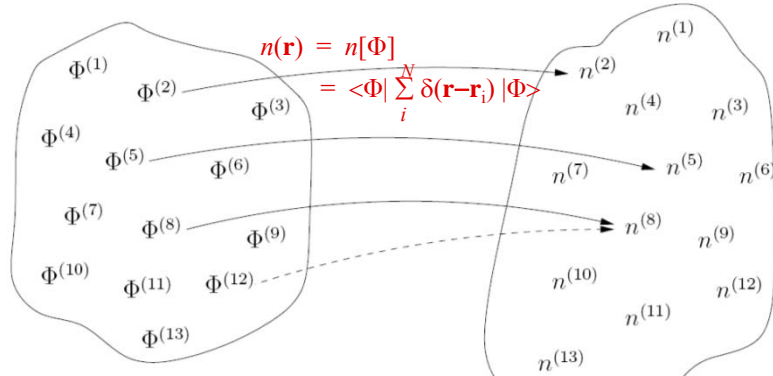
It does not account for correlated dynamics of ions and electrons. For example:

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

How can we solve:

$$H_{\{\mathbf{R}_I\}}^e \Phi_{v,\{\mathbf{R}_I\}}(\mathbf{r}_k) = E_{v,\{\mathbf{R}_I\}}^e \Phi_{v,\{\mathbf{R}_I\}}(\mathbf{r}_k) \quad (i)$$
$$H^e = T^e + V^{e-e} + V^{e-ion}$$

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 $n(\mathbf{r})$.

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

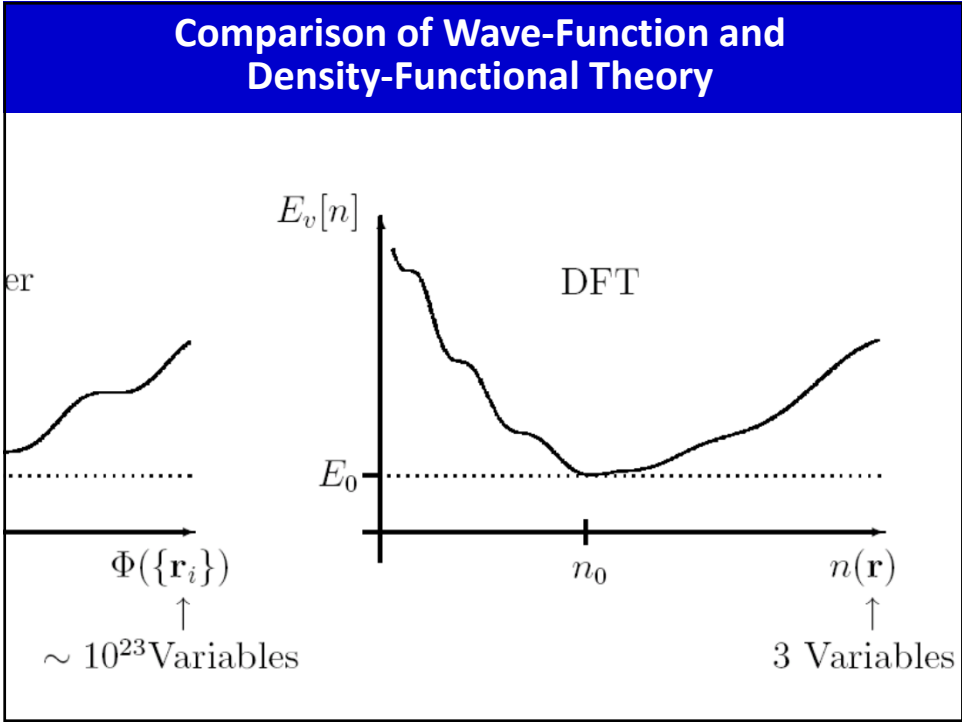
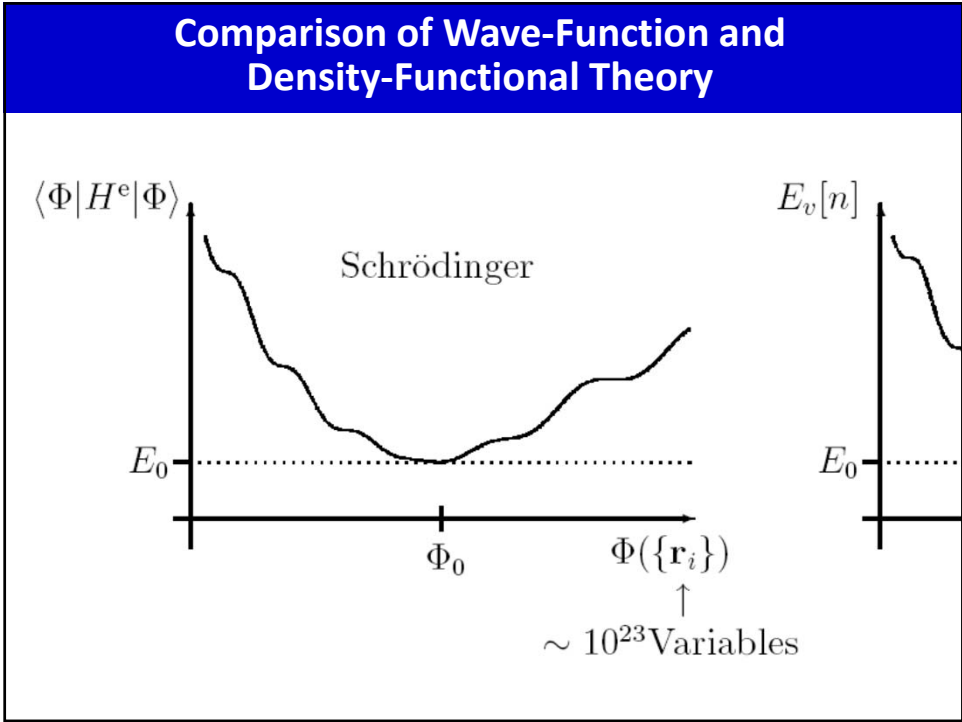
$$n(\mathbf{r}) = n[\Phi] = \langle \Phi | \sum_i \delta(\mathbf{r}-\mathbf{r}_i) | \Phi \rangle$$

can be inverted, *i.e.*,

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

This implies:

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



34 years before
DFT invention



34 years after
DFT invention



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)

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

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

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 $n(r)$

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



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.

Walter Kohn



Certainties about Density Functional Theory

1. **DFT in principle:** It is exact; a universal $E^{xc}[n]$ functional “exists”.
2. **DFT in practice:** It is probably not possible to write down $E^{xc}[n]$ 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 shows that “simple” approximations to the exchange-correlation functional can provide good results – if you know what one is doing.

The search (research) for new xc functionals goes on...

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



The exchange-correlation functional

5	our favorite	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 Berlin, July 2013
 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

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
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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.

“Level 5 plus” Viewed in the Many-Body Framework

Perturbation theory:

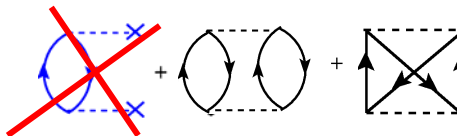
$H = H^0 + H'$ with $H^0|\phi_n\rangle = E_n^{(0)}|\phi_n\rangle$ and $|\phi_n\rangle =$ Slater det.
 $|\phi_0\rangle =$ ground state, $|\phi_{i,a}\rangle =$ single excitations, $|\phi_{ij,ab}\rangle =$ double exci.

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

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

single excitations double excitations

**Using HF input, this is
Møller-Plesset pertur-
bation 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)

“Level 5 plus” Viewed in the Many-Body Framework

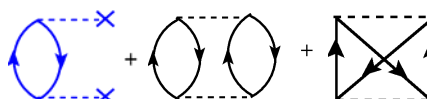
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single excitations double excitations

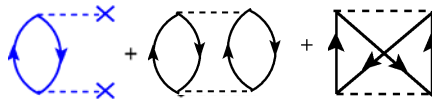


Adding all ring diagrams from higher order perturbations:

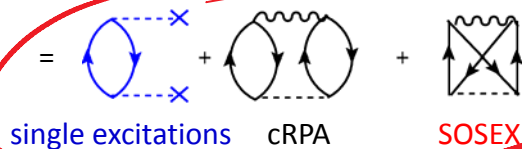
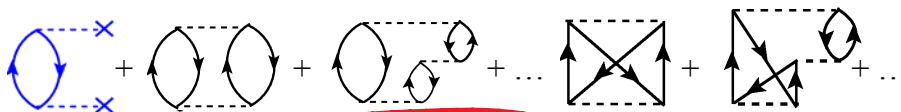
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“Level 5 plus” Viewed in the Many-Body Framework

single excitations double excitations



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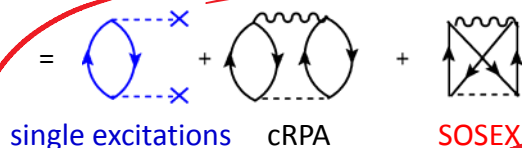
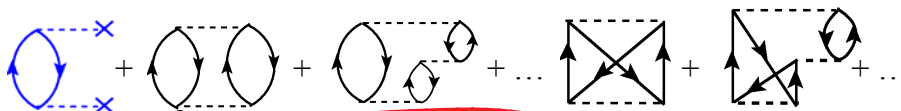


X. Ren, A. Tkatchenko, P. Rinke, and M.S., *PRL* **106**, (2011).
J. Paier, X. Ren, P. Rinke, A. Grüneis, G. Kresse, G. E. Scuseria, M.S., *NJP* (2012).

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Renormalized second order perturbation theory
sets the reference for materials.

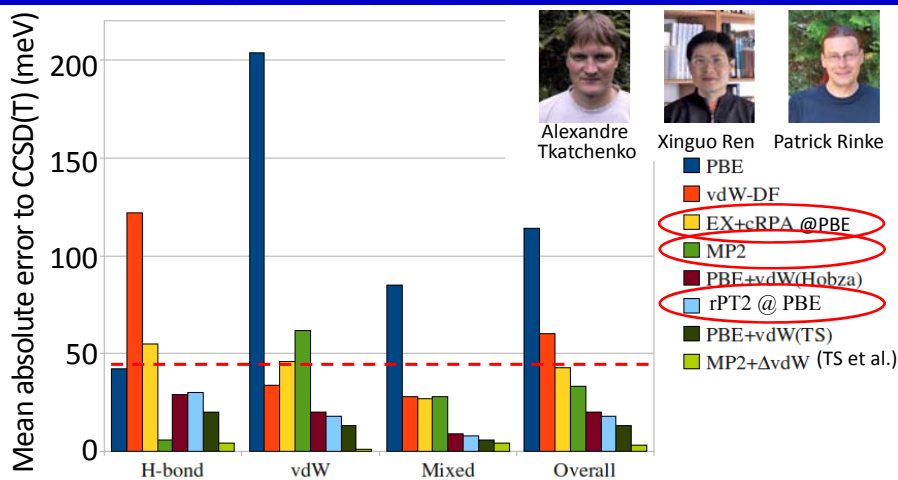
- better than LDA, PBE, MP2
- comparable to CCSD
- not as accurate as CCSD(T)



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

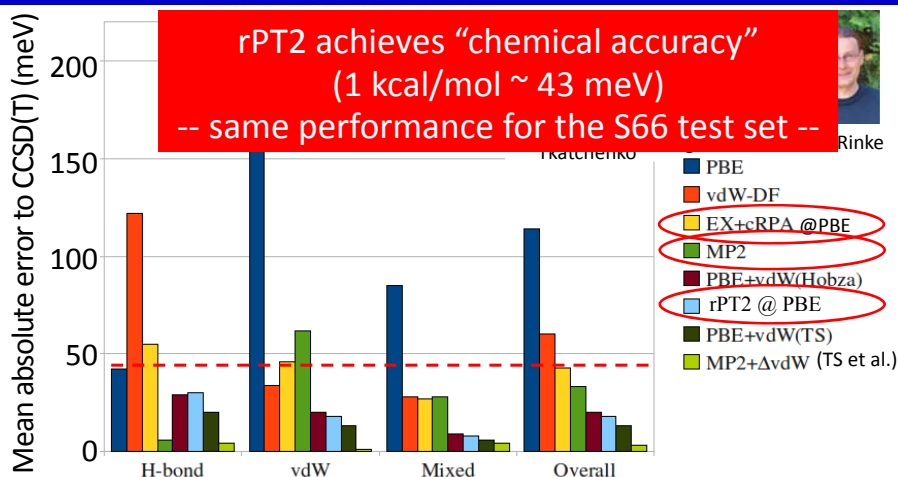
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Performance of rPT2 for Weak Intermolecular Interactions: S22 Test Set



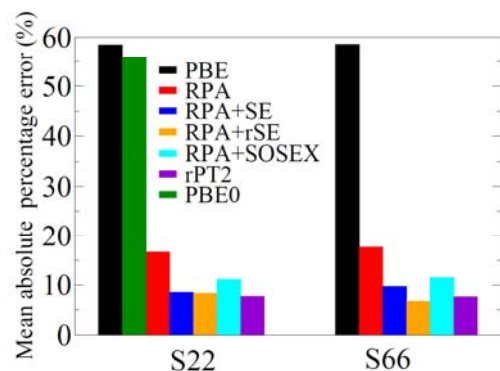
CCSD(T): Jurecka, Sponer, Cerny, Hobza, *PCCP* (2006). **Langreth-Lundqvist:** Gulans, Puska, Nieminen, *PRB* (2009); **rPT2:** X. Ren et al. *PRL* (2011) and to be published.
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Performance of rPT2 for Weak Intermolecular Interactions: S22 and S66 Test Sets



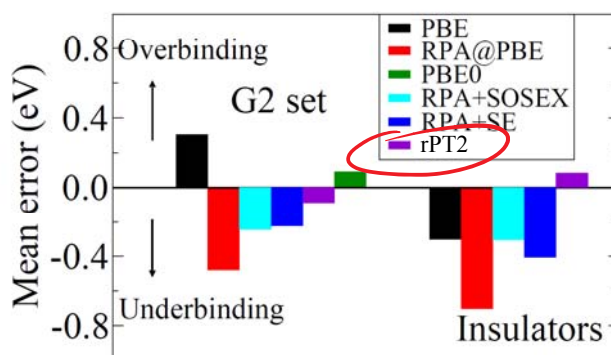
X. Ren, P. Rinke,
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PEB, July 19 (2013)

Bonding type	hydrogen	dispersion	mixed
S22 [1]	7	8	7
S66 [2]	23	23	20

[1] Jurečka, Šponer, Černý, and Hobza, PCCP **8**, 1985 (2006).

[2] Rezac, Riley, and Hobza, J. Chem. Theo. Comp. **7** 2427 (2011).

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).

Get Real! Consider Temperature, Pressure, and Doping; *Ab Initio* Atomistic Thermodynamics

$$\mu_{\text{O}_2}(T, p)$$



$$G(T, p) = E^{\text{tot}} + F^{\text{vib}} - TS^{\text{conf}} + pV + N\mu_{\text{O}}(T, p) + n\epsilon_{\text{F}}$$

DFT

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

C.M. Weinert and M.S.,
Mat. Sci. Forum 10-12,
25 (1986).

K. Reuter, C. Stampfl, and
M.S., in: *Handbook of Materials Modeling, Vol. 1.* (Ed.
Sid Yip), Springer 2005.

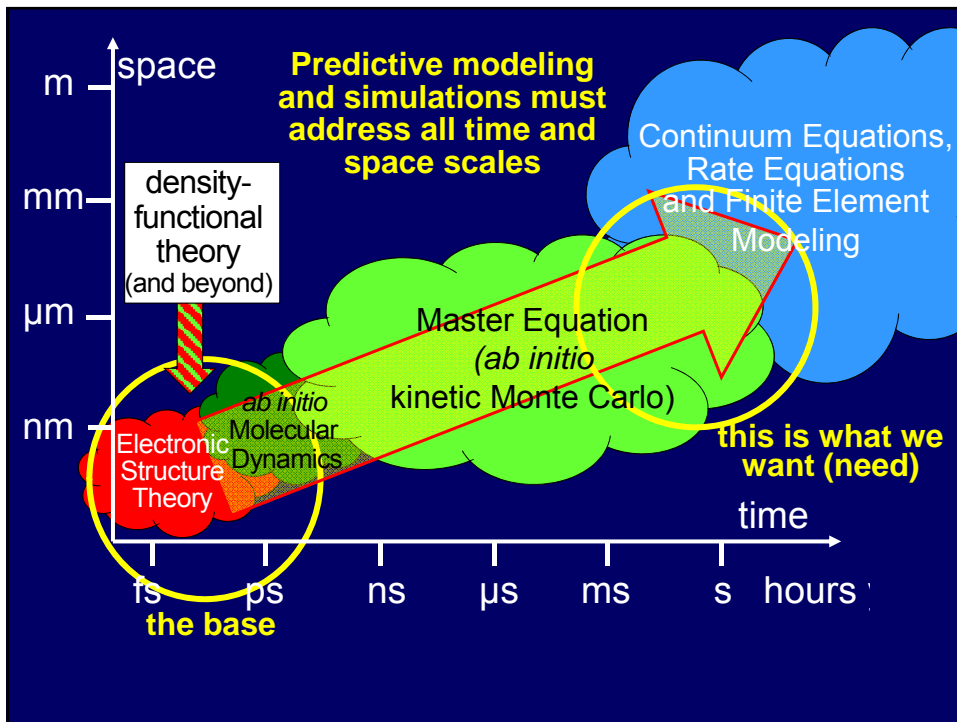
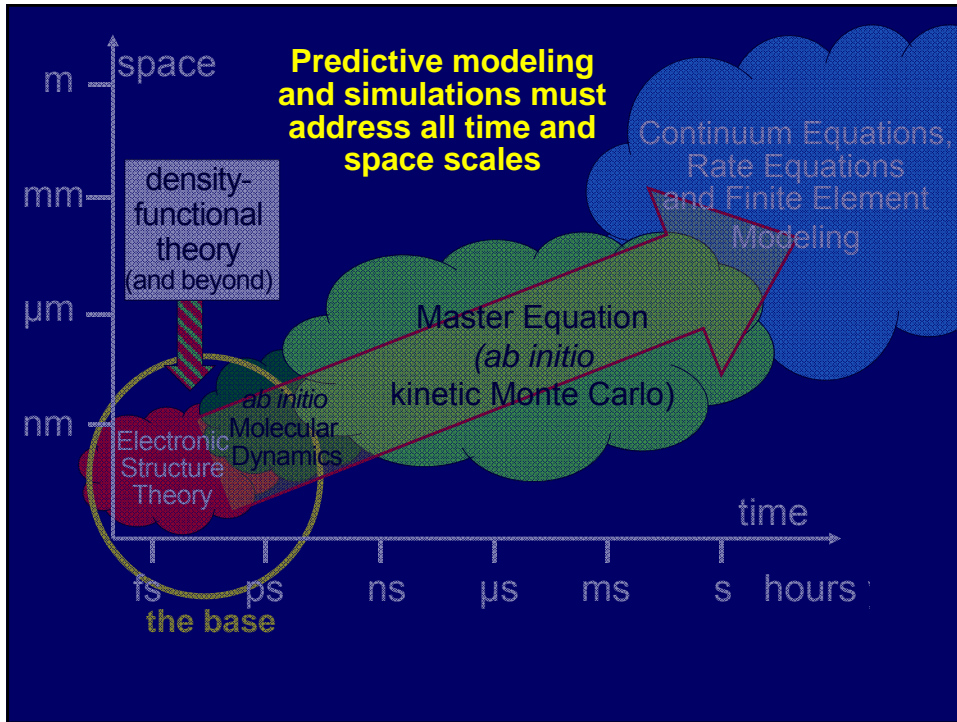
Challenges for the Near Future Quantum-Mechanics Based Technology

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

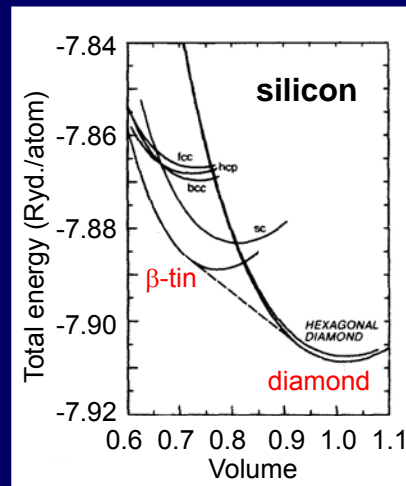
For nanotechnology to become affordable, nanostructures will have to build themselves; normal manufacturing methods will be useless

⇒ **self-organization and assembly.**

Bridging the time and length scales: some examples



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

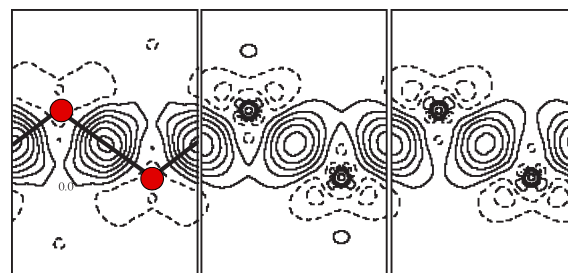


*M. T. Yin and
M. L. Cohen
PRB 26 (1982)
< and PRL 1980 >*

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

Electron Density of Si

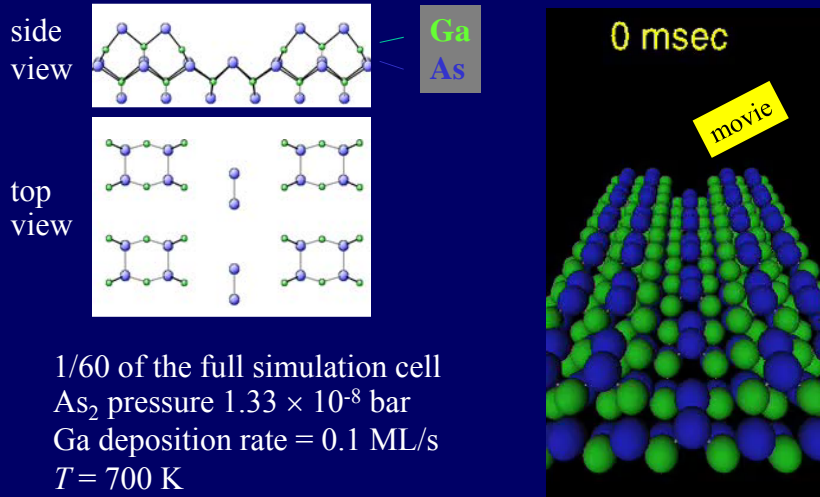
Electron density *difference* from sum of atoms



experiment DFT-LDA DFT-GGA

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

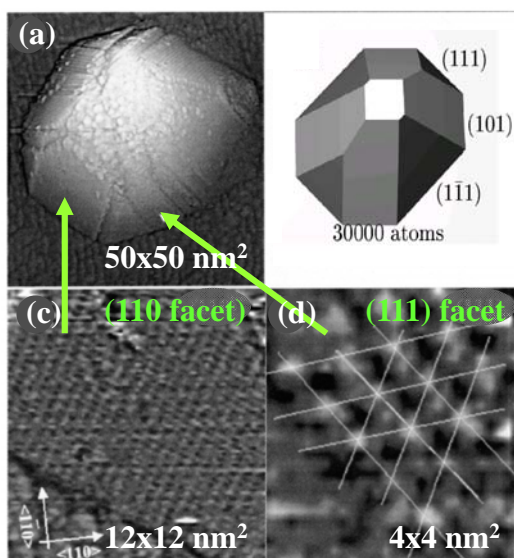
Adsorption, diffusion, island nucleation, and growth of GaAs, studied by *ab initio* kinetic Monte Carlo



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

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

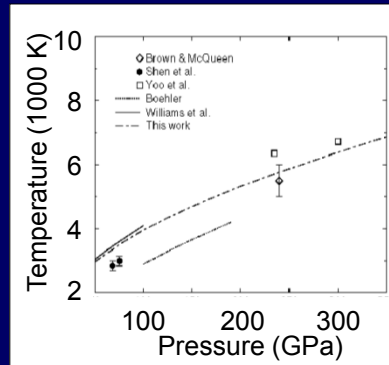
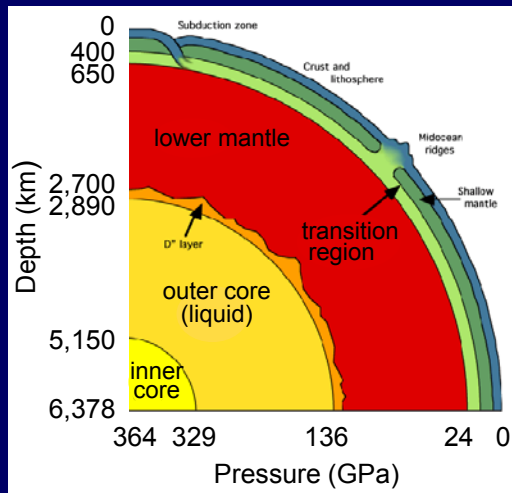
G. Costantini et al. APL 82 (2003)



- a) 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).

Ab initio melting curve of Fe as function of pressure



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

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, total energy, highest Kohn-Sham level, forces, force constants, ...**

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, a **(good) starting point** for many-body calculations.

What About Kohn-Sham Eigenvalues?

The ionization energy is: $I_k = E_k^{N-1} - E^N$

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

f_i are occupation numbers

(Well defined for the highest occupied state. Otherwise, “only” in terms of constrained DFT)

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

$$= - \int_0^1 \epsilon_k(f_k) df_k$$

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:

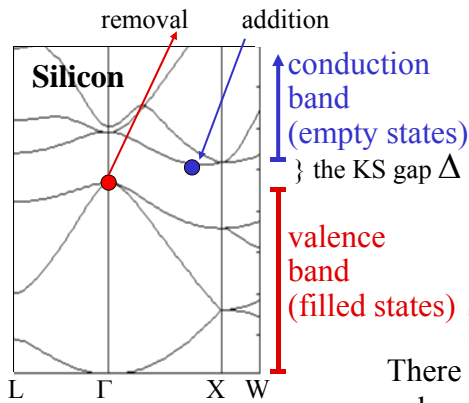
$$I_k = -\epsilon_k(0.5)$$

This is the Slater-Janak “transition state”. It is **the DFT analog of Koopmans' theorem**.

Kohn-Sham Electron Bands

Kohn-Sham band gap: $\Delta^{KS} = \epsilon_{CB} - \epsilon_{VB}$ of the N -particle system

The measured (optical) band gap is something else:



$$E_{\text{gap}} = I - A$$

$$A = E^N - E^{N+1}$$

$$I = E^{N-1} - E^N$$

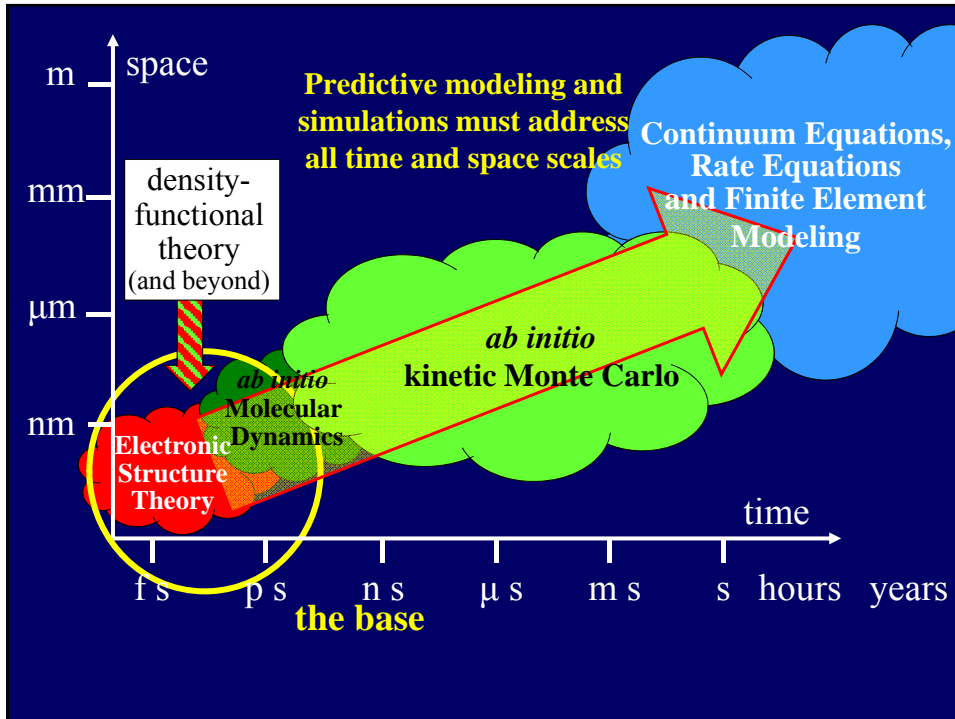
$$E_{\text{gap}} = E^{N-1} + E^{N+1} - 2E^N$$

$$= \Delta^{KS} + \Delta_{xc}$$

$$V_{xc}([n_{N+1}]; \mathbf{r}) = V_{xc}([n_N]; \mathbf{r}) + \Delta_{xc}$$

There is a discontinuity in V_{xc} at integer values of occupation numbers.

We don't know how to determine Δ_{xc} within DFT



Summary: 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.