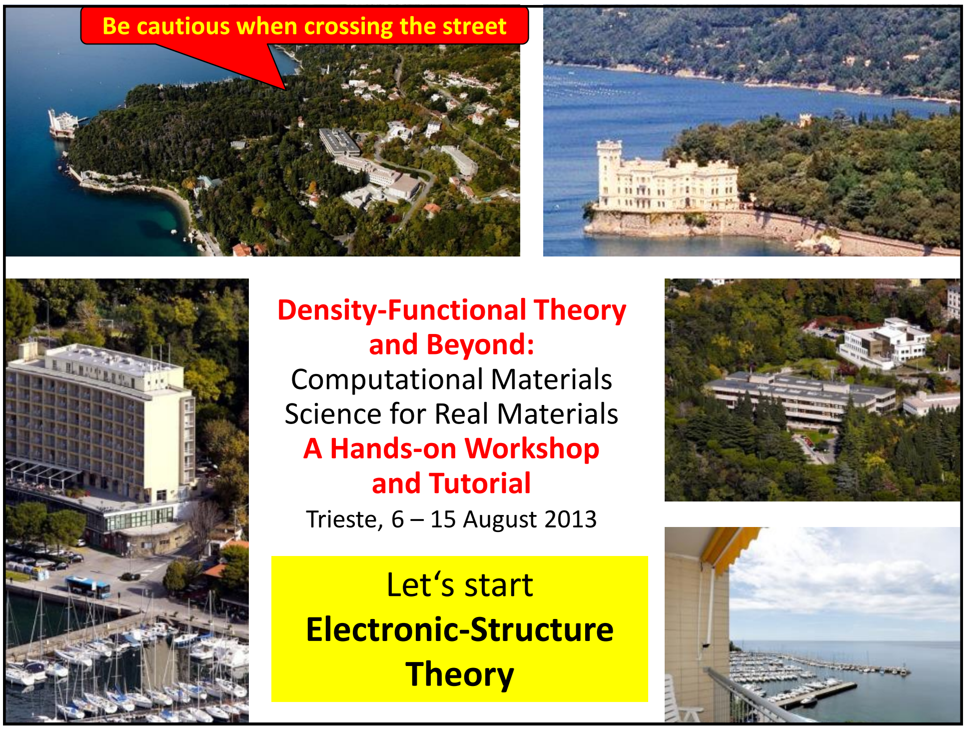
Density-Functional Theory and Beyond:
Computational Materials Science for Real Materials
A Hands-on Workshop and Tutorial
Trieste, 6 – 15 August 2013



Be cautious when crossing the street

Density-Functional Theory and Beyond:
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Let‘s start
Electronic-Structure Theory

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

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

???

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

No open question here!

Born-Oppenheimer Approximation

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

Where Φ_v are solutions of the "electronic Hamiltonian":

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

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

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:

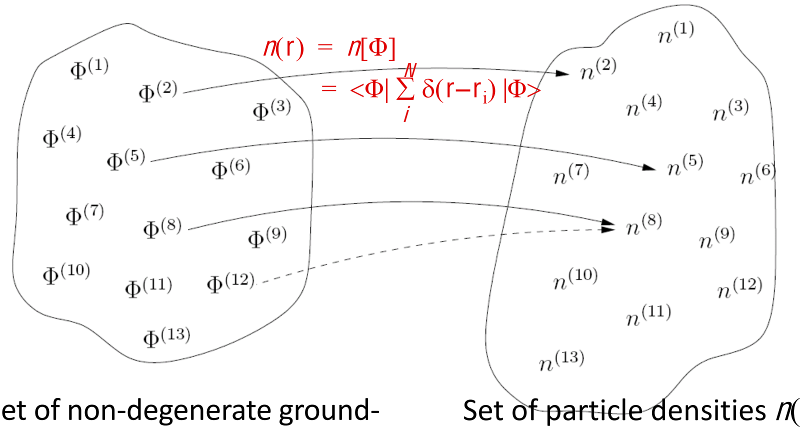
These limits can be severe. Nevertheless, we will use the BO approximation in the following.

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 $n(\mathrm{r})$ 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 $n(r)$.

Density Functional Theory

The energy of the ground state of a many-electron system : $E_0(\{R_I\}) = \mathrm{Min}_\Phi \langle\Phi| H^e |\Phi\rangle$

Hohenberg and Kohn (1964): The functional

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

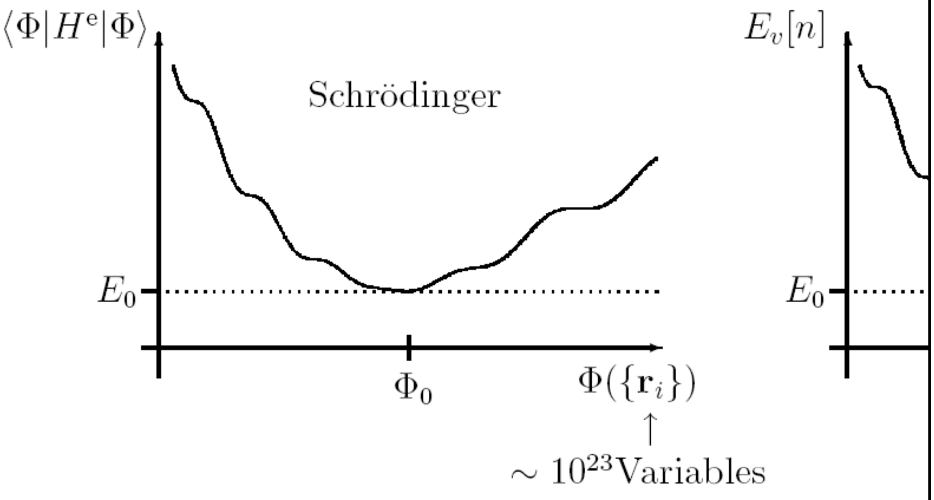
can be inverted, *i.e.*,

$$\Phi(\mathrm{r}_1, \mathrm{r}_2, \ldots, \mathrm{r}_N) = \Phi[n(\mathrm{r})] \; .$$

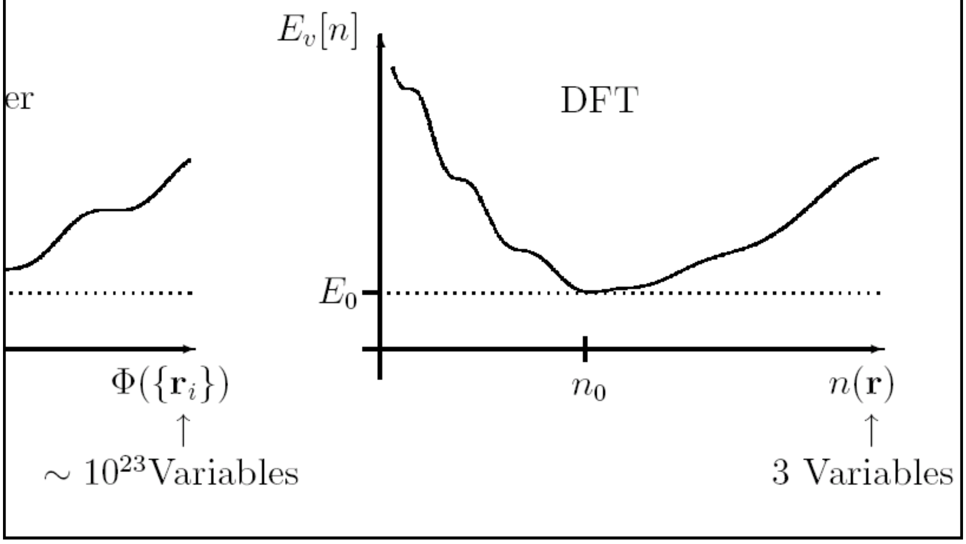
This implies:

$$E_0(\{R_I\}) = \mathrm{Min}_{n(\mathrm{r})} E_{\{R\}}[n]$$

Comparison of Wave-Function and Density-Functional Theory



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, *$v(r)$*].
(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):

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

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):

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

Because $T_s[n]$ is the functional of non-interacting particles we effectively restrict the allowed densities to those that can be written as $\boxed{n(\mathbf{r}) = \sum_{i=1}^{N}|\varphi_i(\mathbf{r})|^2}$

This implies:

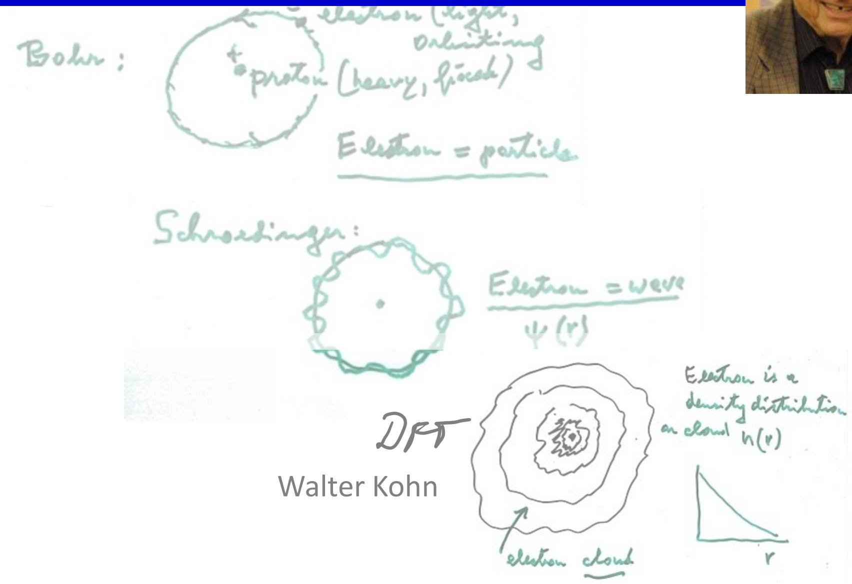
$$\boxed{\left\{-\frac{\hbar^2}{2m}\nabla^2 + v^{\mathrm{eff}}(\mathbf{r})\right\}\varphi_i(\mathbf{r}) = \epsilon_i\,\varphi_i(\mathbf{r})}$$

Kohn-Sham equation

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

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

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!**

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

- 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.

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.

Certainties about Density Functional ry

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

1. DFT in principle: It is exact; a uni
   $E^{xc}[n]$ functional "exists".
2. DFT in practice: It is prob ot possible to write down $E^{xc}[n]$ as a close hematical expression. We need approxim .

The success of D oves that "simple" approximations to the exchan relation functional can provide good results – if nows what one is doing.

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

The exchange-correlation functional

accuracy

our favorite

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

Berlin, July 2013

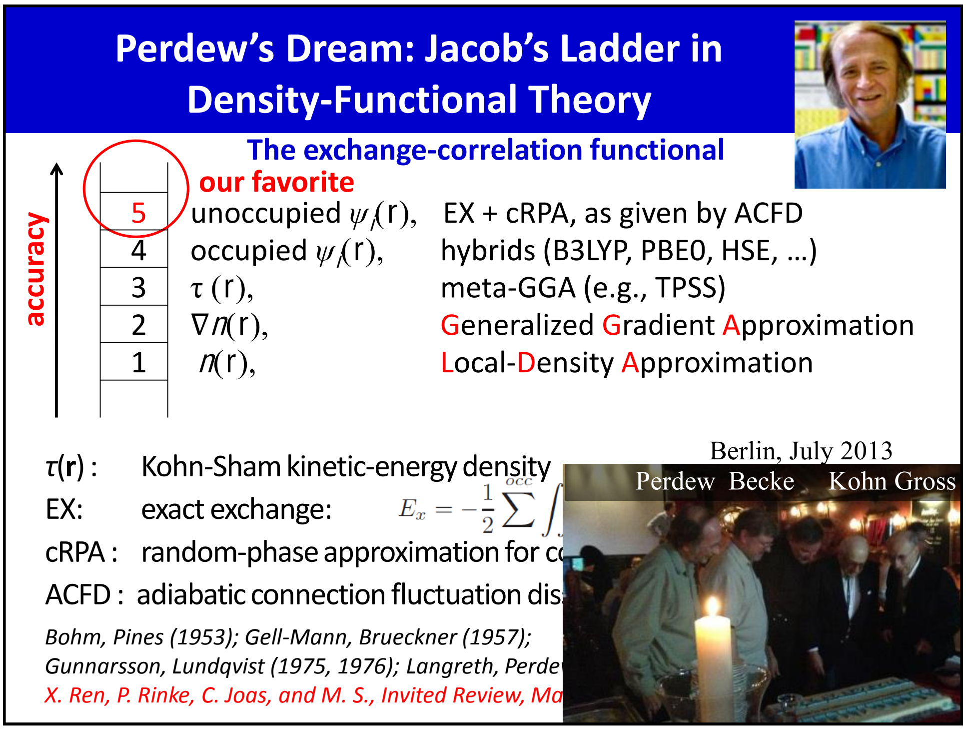
$\tau(\mathbf{r})$: Kohn-Sham kinetic-energy density

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

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

EX: exact exchange: $E_x = -\frac{1}{2}\sum^{occ}\int$

cRPA : random-phase approximation for c

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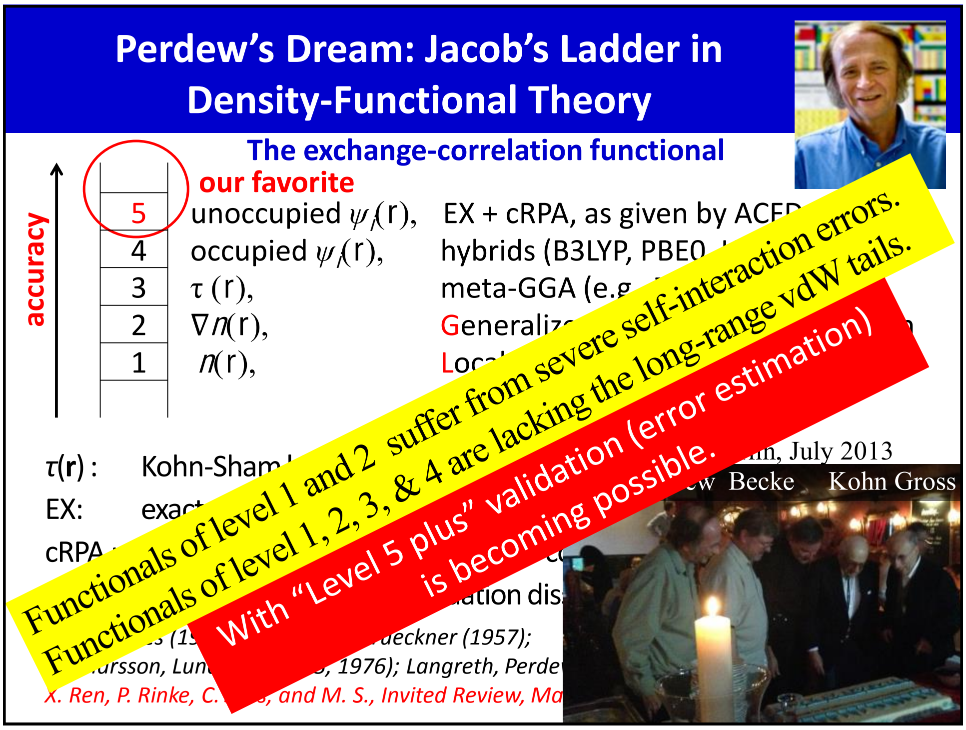
X. Ren, P. Rinke, C. Joas, and M. S., Invited Review, Ma

Berlin, July 2013



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

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cRPA
ation dis
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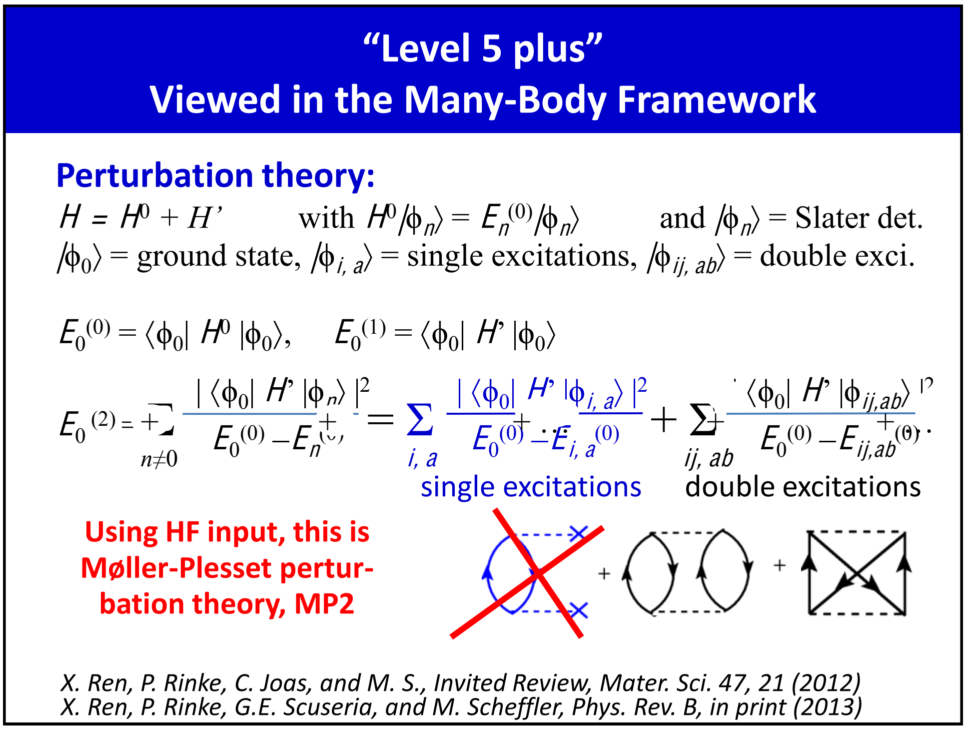
rsson, Lun, 1976); Langreth, Perde
X. Ren, P. Rinke, C., and M. S., Invited Review, Ma

n, July 2013

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.

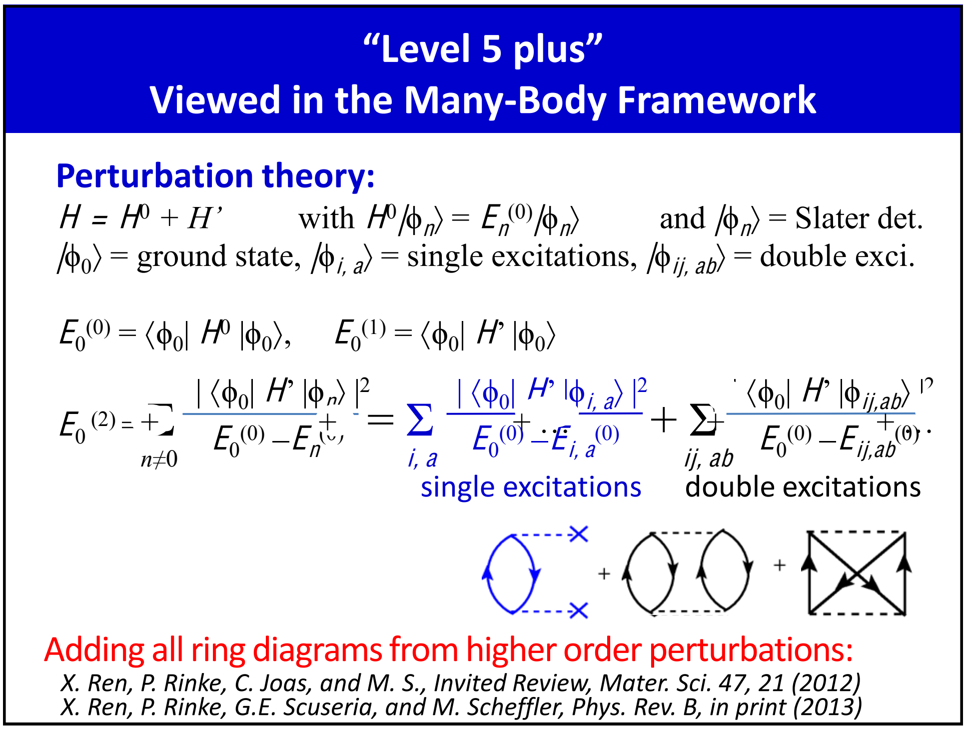
$|\phi_0\rangle$ = ground state, $|\phi_{i,a}\rangle$ = single excitations, $|\phi_{ij,ab}\rangle$ = double exci.

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

$$E_0^{(2)} = \sum_{n\neq0} \frac{|\langle\phi_0| H' |\phi_n\rangle|^2}{E_0^{(0)} - E_n^{(0)}} = \underbrace{\sum_{i,a} \frac{|\langle\phi_0| H' |\phi_{i,a}\rangle|^2}{E_0^{(0)} - E_{i,a}^{(0)}}}_{\text{single excitations}} + \underbrace{\sum_{ij,ab} \frac{|\langle\phi_0| H' |\phi_{ij,ab}\rangle|^2}{E_0^{(0)} - E_{ij,ab}^{(0)}}}_{\text{double excitations}}.$$

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)



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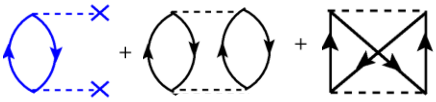
$$E_0^{(2)} = \sum_{n\neq0} \frac{|\langle\phi_0| H' |\phi_n\rangle|^2}{E_0^{(0)} - E_n^{(0)}} = \underbrace{\sum_{i,a} \frac{|\langle\phi_0| H' |\phi_{i,a}\rangle|^2}{E_0^{(0)} - E_{i,a}^{(0)}}}_{\text{single excitations}} + \underbrace{\sum_{ij,ab} \frac{|\langle\phi_0| H' |\phi_{ij,ab}\rangle|^2}{E_0^{(0)} - E_{ij,ab}^{(0)}}}_{\text{double excitations}}.$$

Adding all ring diagrams from higher order perturbations:

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

single excitations double excitations



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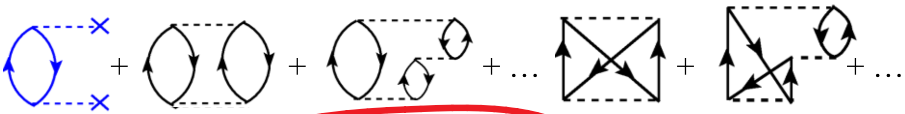
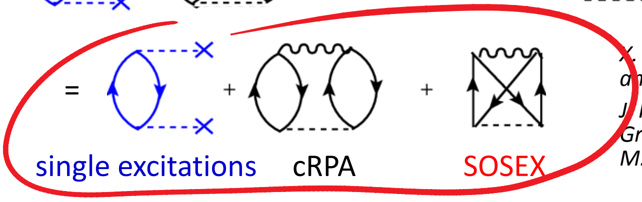




single excitations cRPA SOSEX

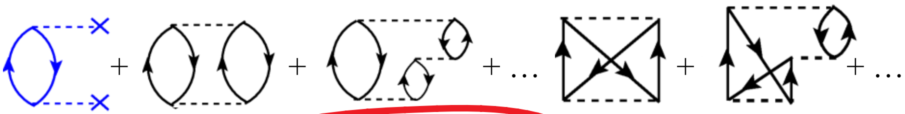
*X. Ren, A. Tkatchenko, P. Rinke, and M.S., PRL **106**, (2011).*

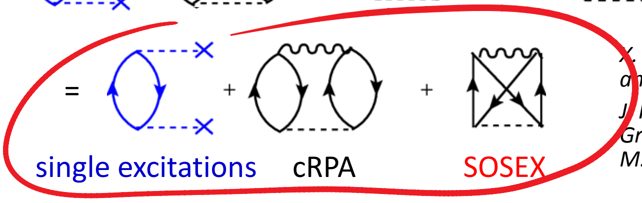
J. Paier, X. Ren, P. Rinke, A. Grüneis, G. Kresse, G. E. Scuseria, M.S., NJP (2012).

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)





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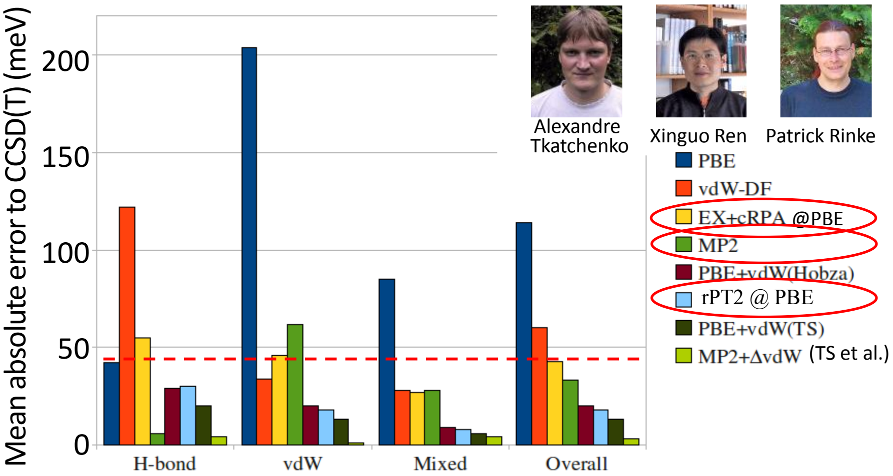
X. Ren, P. Rinke, G.E. Scuseria, and M. Scheffler, Phys. Rev. B, in print (2013)

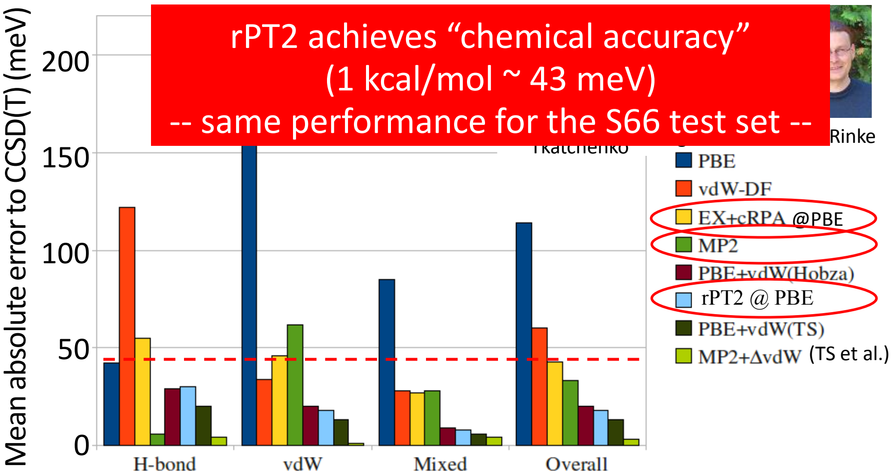
Performance of rPT2 for Weak Intermolecular Interactions: S22 Test Set



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

rPT2 achieves "chemical accuracy"
(1 kcal/mol ~ 43 meV)
-- same performance for the S66 test set --



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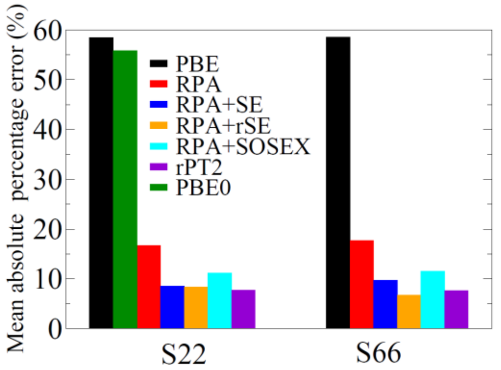
Performance of rPT2 for Weak Intermolecular Interactions: S22 and S66 Test Sets



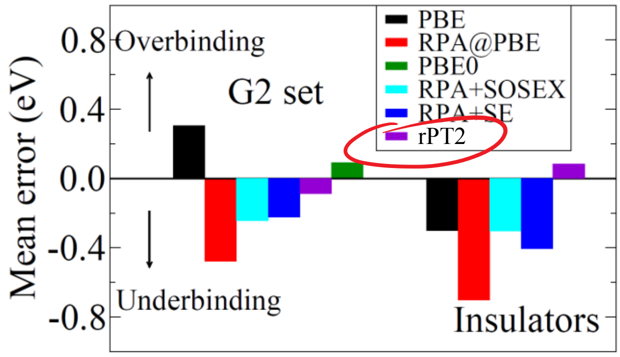
X. Ren, P. Rinke,
G. Scuseria, and M.S.
PEB, July 19 (2013)

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).

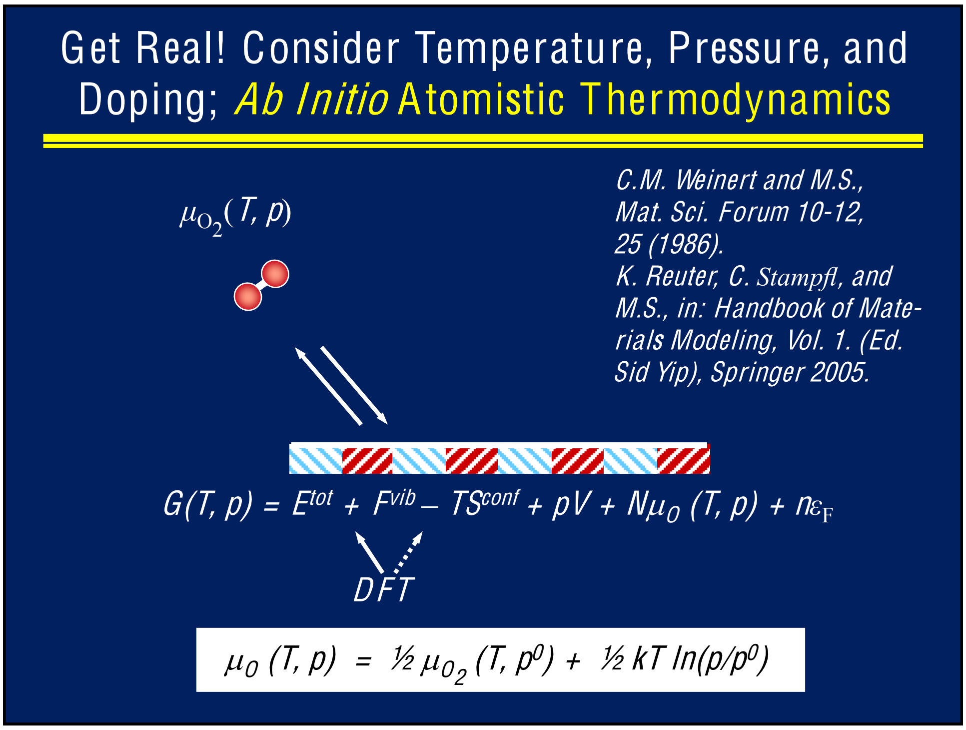
[2] Rezac, Riley, and Hobza, J. Chem. Theo. Comp. **7** 2427 (2011).

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

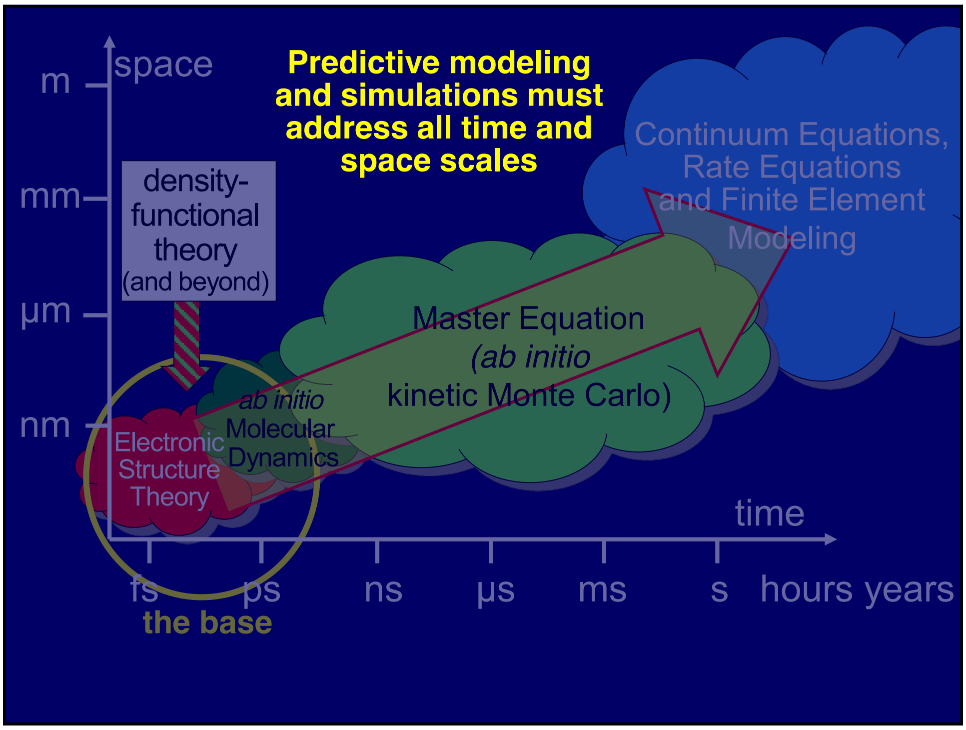
$\mu_{O_2}(T, p)$

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.

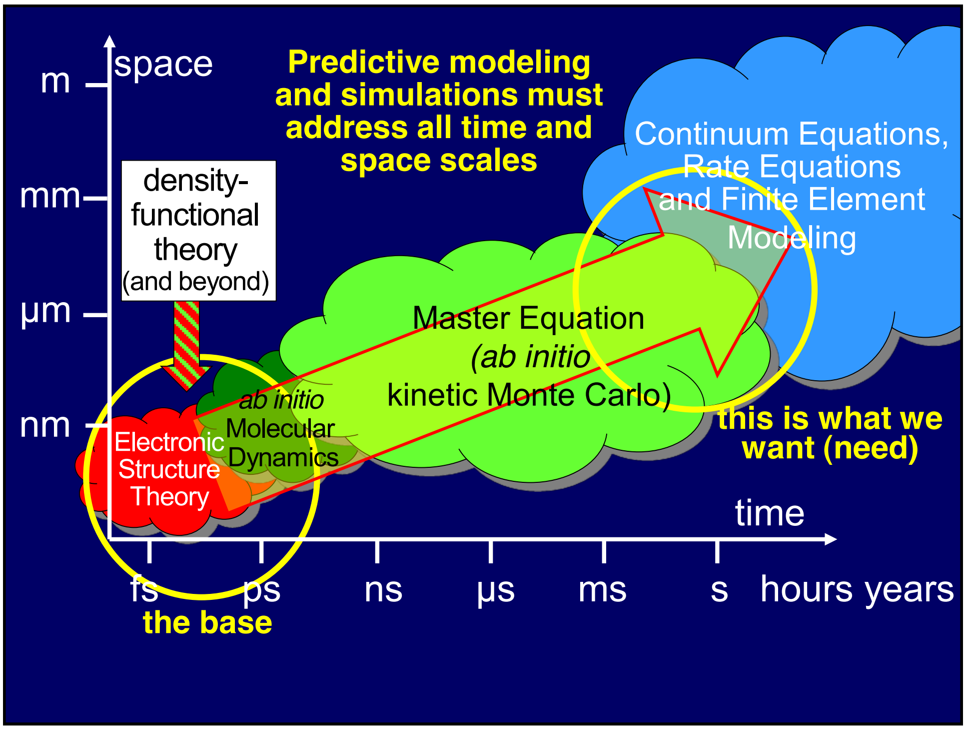
$$G(T, p) = E^{tot} + F^{vib} - TS^{conf} + pV + N\mu_O(T, p) + n\varepsilon_F$$

DFT

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



Predictive modeling and simulations must address all time and space scales



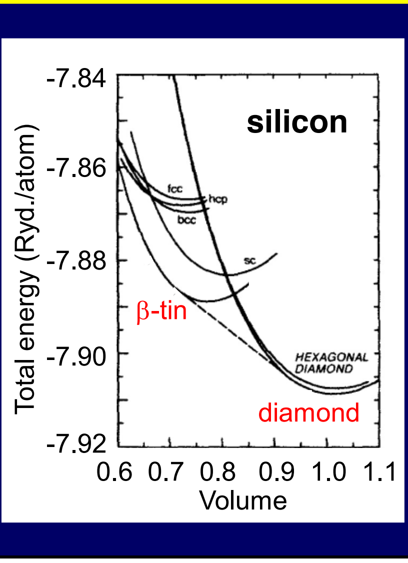
Predictive modeling and simulations must address all time and space scales

density-functional theory (and beyond)

the base

this is what we want (need)

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

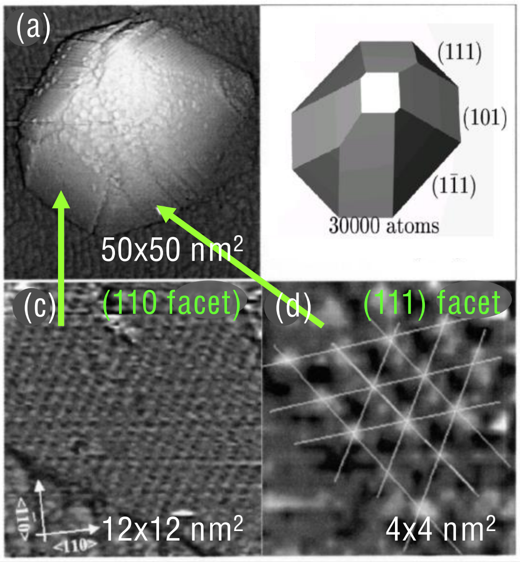


M. T. Yin and
M. L. Cohen
PRB 26 *(1982)*
< and PRL 1980 >

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

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

G. Costantini et al. APL 82 (2003)



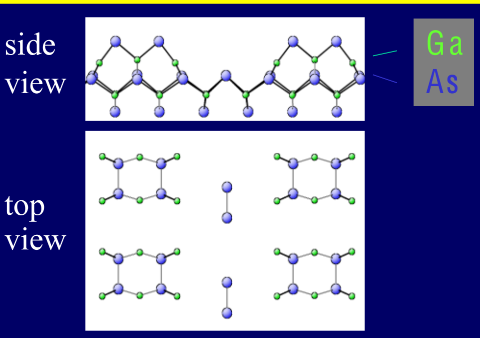
a) STM topography of a large island.

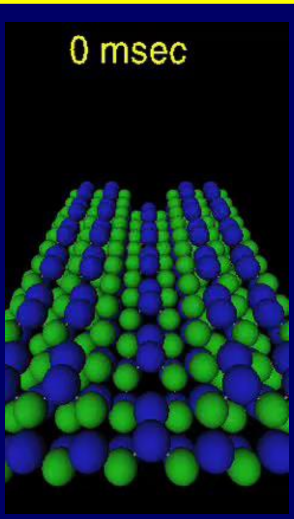
b) Equilibrium shape (theory: *E. Pehlke, N. Moll, M.S., Proc. 23rd ICPS (1996); Q. Liu, et al., PRB 60 (1999)*).

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).

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

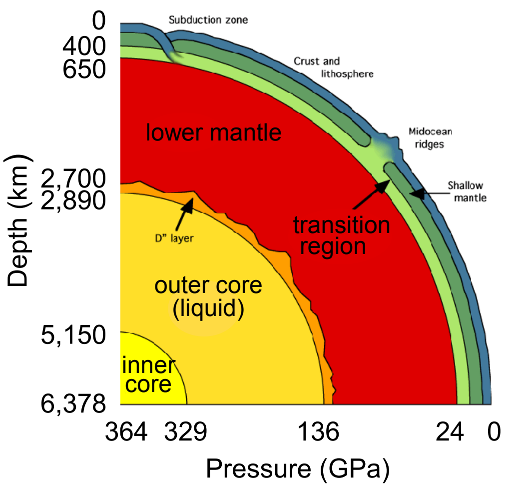


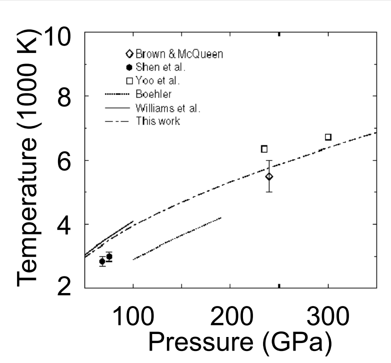


1/60 of the full simulation cell
As$_2$ pressure 1.33 × 10^{-8} bar
Ga deposition rate = 0.1 ML/s
T = 700 K

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

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 electron density, total energy, highest Kohn-Sham level, forces, **force constants, …**

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

The Kohn-Sham $\varphi_i(\mathrm{r})$ and ϵ_i give an approximate description of quasi-particles, a (good) starting point for many-body calculations.

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                          Windows

An exception  06 has occured at 0028:C11B3ADC in VxD DiskTSD(03) +
00001660.  This was called from 0028:C11B40C8 in VxD voltrack(04) +
00000000.  It may be possible to continue normally.

*  Press any key to attempt to continue.
*  Press CTRL+ALT+RESET to restart your computer.  You will
   lose any unsaved information in all applications.

                      Press any key to continue
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                         Windows

An exception  06 has occured at 0028:C11B3ADC in VxD DiskTSD(03) +
00001660.  This was called from 0028:C11B40C8 in VxD voltrack(04) +
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*  Press any key to attempt to continue.
*  Press CTRL+ALT+RESET to restart your computer.  You will
   lose any unsaved information in all applications.

                    Press any key to continue
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Kohn-Sham eigenvalues are not excitation energies.

However, $\varphi_i(r)$ 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:

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

f_i are occupation numbers

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

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

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

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

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:

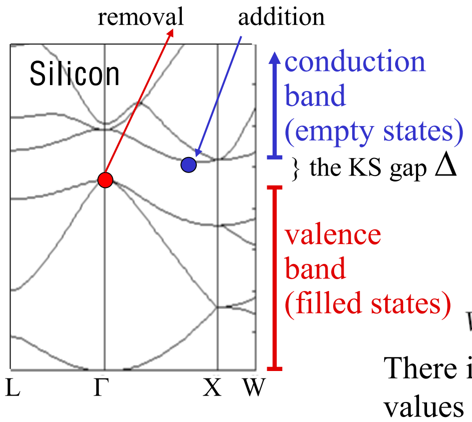
$$\boxed{I_k = -\epsilon_k(0.5)}$$

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

Kohn-Sham Electron Bands

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

The measured (optical) band gap is something else:



$$\begin{aligned} E_{\mathrm{gap}} &= I - A \quad , \\ A &= E^{N} - E^{N+1} \\ I &= E^{N-1} - E^{N} \end{aligned}$$

$$\begin{aligned} E_{\mathrm{gap}} &= E^{N-1} + E^{N+1} - 2E^{N} \\ &= \Delta^{\mathrm{KS}} + \Delta_{\mathrm{xc}} \end{aligned}$$

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

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

We don't know how to determine Δ_{xc} for crystals with DFT.

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