Basics of density-functional theory and fast guide to actual calculations

Matthias Scheffler
http://www.fhi-berlin.mpg.de/th/th.html

I. From the many-particle problem to the Kohn-Sham functional

II. From the total energy to materials science and bio-physics

"the ab initio line of computational sciences and engineering"

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

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

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

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

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

w3.rz-berlin.mpg.de/
~michaeli/member/
MaterialsScienceLectures/
k3-2005.pdf

Born-Oppenheimer Approximation

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

Where Φ_v are solutions of the “electronic Hamiltonian”:

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

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

frequently (commonly) applied approximations:

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

⇨ electronic and nuclear degrees of freedom decouple

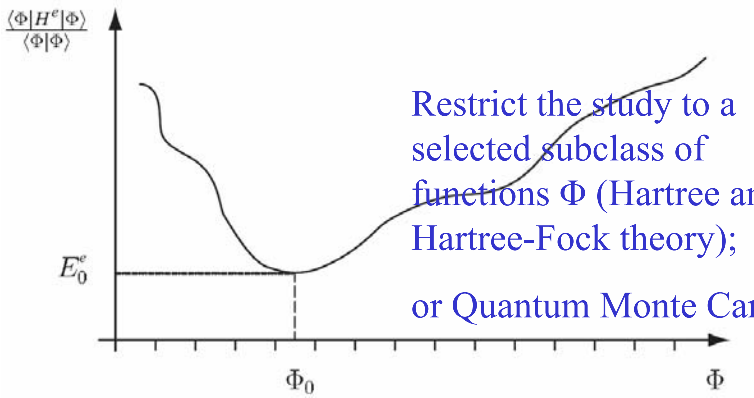
Some Limits of the Born-Oppenheimer Approximation

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

- polaron-induced superconductivity
- dynamical Jahn-Teller effect
- some phenomena of diffusion in solids
- non-adiabaticity in molecule-surface scattering
- etc.

Wave-Function Theories

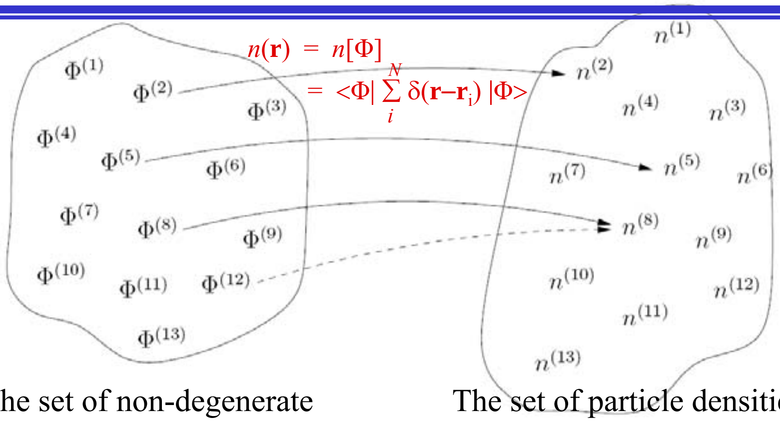
$$H^e = \sum_{k=1}^{N} -\frac{\hbar^2}{2m}\nabla^2_{\mathbf{r}_k} + \sum_{k=1}^{N} v(\mathbf{r}_k) + \frac{1}{2}\frac{1}{4\pi\varepsilon_0}\sum_{\substack{k,k'\\ k\neq k'}}^{N,N}\frac{e^2}{|\mathbf{r}_k-\mathbf{r}_{k'}|}$$



Restrict the study to a selected subclass of functions Φ (Hartree and Hartree-Fock theory);

or Quantum Monte Carlo.

The Hohenberg-Kohn Theorem (1964)



$$n(\mathbf{r}) = n[\Phi] = \langle\Phi|\sum_{i}^{N}\delta(\mathbf{r}-\mathbf{r}_i)|\Phi\rangle$$

The set of non-degenerate ground state wave functions Φ of arbitrary *N*-particle Hamiltonians.

The set of particle densities *n*(**r**) belonging to non-degenerate ground states of the *N*-particle problem.

The dashed arrow is not possible

Density Functional Theory

The energy of the ground state of a many-electron system : $E_0\,(\{\mathbf{R}_I\}) = \mathrm{Min}_\Phi <\Phi|H^e|\Phi>$

Hohenberg and Kohn (1964): The functional

$$n(\mathbf{r}) \;=\; n[\Phi] \;=\; <\Phi|\sum_i \delta(\mathbf{r}-\mathbf{r}_i)\,|\Phi>$$

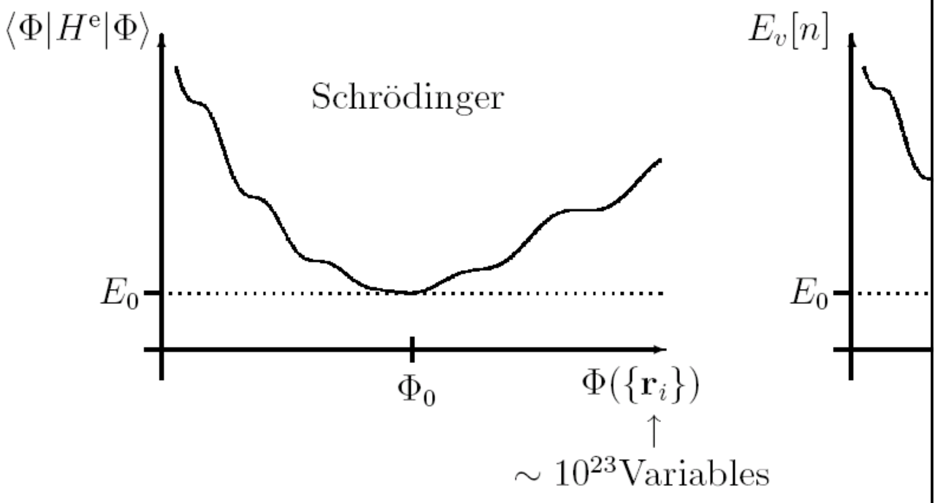
can be inverted, *i.e.,*

$$\Phi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_{N,}) = \Phi[n(\mathbf{r})] \;\; .$$

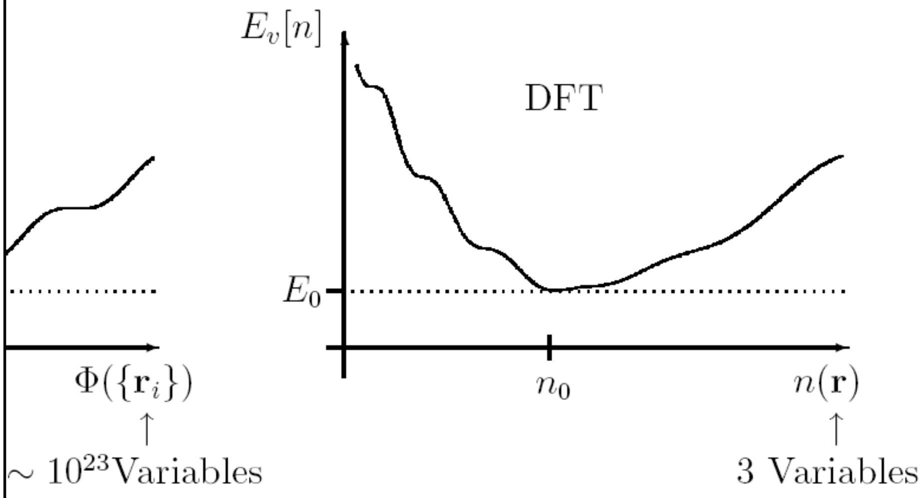
This implies:

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

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

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

-- The many-body Hamiltonian determines everything.

-- There is a one-to-one correspondence between the ground-state electron-density and the ground-state wave function.

Summary of Hohenberg-Kohn Density-Functional Theory (DFT) -- 1964

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

-- The many-body Hamiltonian determines everything.

-- There is a one-to-one correspondence between the ground-state electron-density and the ground-state wave function.

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):

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

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:

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

Kohn-Sham equation

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

$$T_s[n] = \sum_{k=1}^{N} \langle \varphi_k | -\frac{\hbar^2}{2m}\nabla^2 | \varphi_k \rangle \quad ,$$

$$= \sum_{k=1}^{N} \epsilon_k - \int v^{\rm eff}[n^{\rm in}](\mathbf{r})\, n(\mathbf{r})\, d^3\mathbf{r} \quad .$$

The Kohn-Sham Ansatz

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

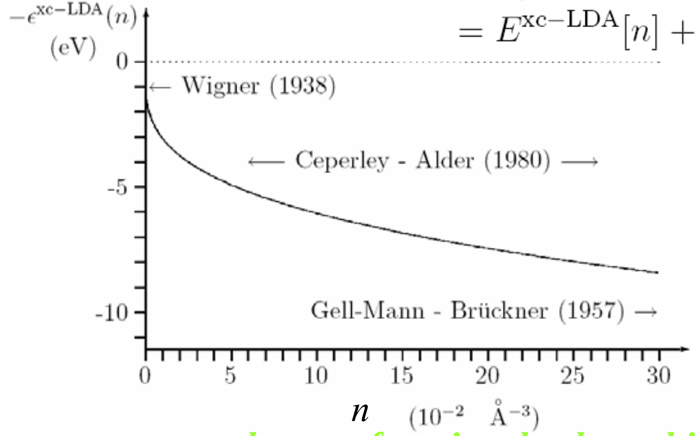
-- Only the ground state density and the ground state energy are required to be the same as in the original many-body problem.

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

-- Maybe the exact $E^{\rm xc}[n]$ functional cannot be written as a closed mathematical expression. Maybe there is a detour similar to that taken for $T_s[n]$? The challenge is to find useful, approximate xc functionals.

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)

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

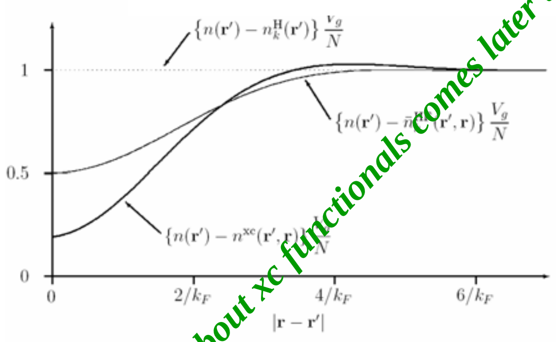


neglecting $O(\nabla n)$ is the local-density approximation

more about xc functionals: later this week

The Exchange-Correlation Hole

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



Comparison of Hartree, Hartree-Fock, and density-functional theories for jellium

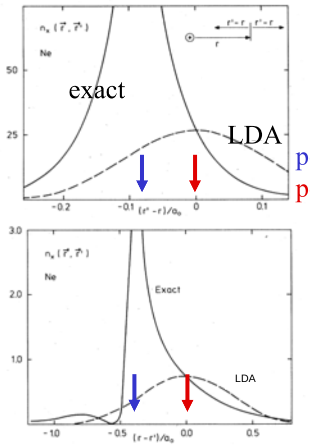
more about xc functionals comes later this week

For non-jellium systems and the LDA (or the GGA) the shape of $n^{\text{xc}}(\mathbf{r},\mathbf{r}')$ is incorrect. However, only its spherical average enters:

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

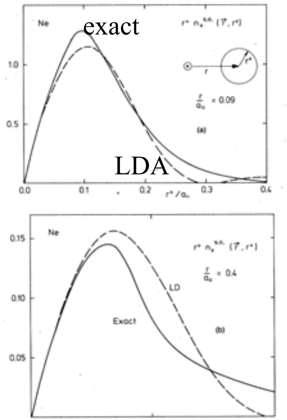
The Exchange Hole in Ne Atom

O. Gunnarsson, M. Jonson, and B. I. Lundqvist, Phys. Rev. B ***20****, 3136 (1979)*



position of nucleus
position of electron

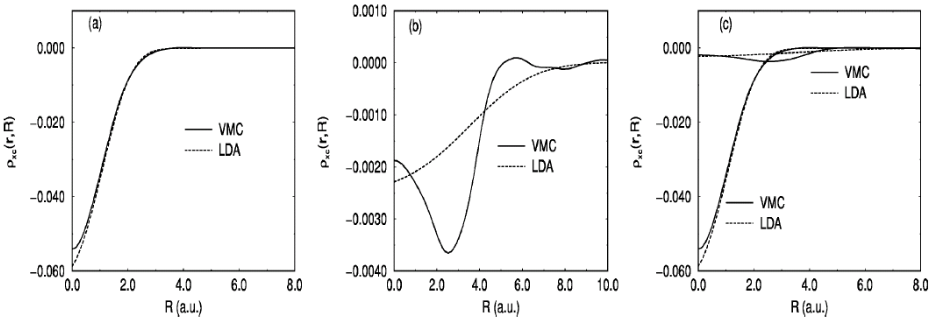
Exchange hole $n^x(\mathbf{r},\mathbf{r'})$



Spherical average around the electron

Exchange-Correlation Hole in Silicon

R. Q. Hood, M. Y. Chou, A. J. Williamson, G. Rajagopal, and R. J. Needs, PRB ***57****, 8972 (1998)*

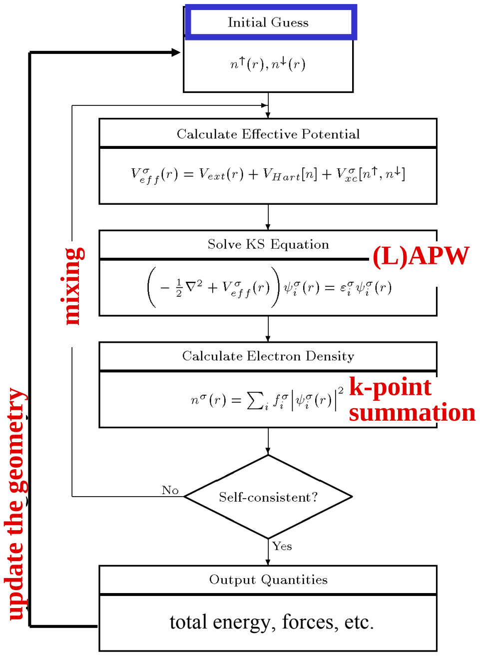


The spherically averaged exchange-correlation hole in variational Monte Carlo (VMC) and DFT-LDA with (a) one electron fixed at the bond center, (b) one electron fixed at the tetrahedral interstitial site, and (c) plots (a) and (b) superimposed with the same scale.

Solving the Kohn-Sham Equations

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

The self-consistent field method



Initial Guess

$n^{\uparrow}(r), n^{\downarrow}(r)$

Calculate Effective Potential

$V^{\sigma}_{eff}(r) = V_{ext}(r) + V_{Hart}[n] + V^{\sigma}_{xc}[n^{\uparrow}, n^{\downarrow}]$

Solve KS Equation

$\left(-\frac{1}{2}\nabla^2 + V^{\sigma}_{eff}(r)\right)\psi^{\sigma}_i(r) = \varepsilon^{\sigma}_i \psi^{\sigma}_i(r)$

(L)APW

Calculate Electron Density

$n^{\sigma}(r) = \sum_i f^{\sigma}_i \left|\psi^{\sigma}_i(r)\right|^2$

k-point summation

Self-consistent?

No

Yes

Output Quantities

total energy, forces, etc.

mixing

update the geometry

The Total Energy

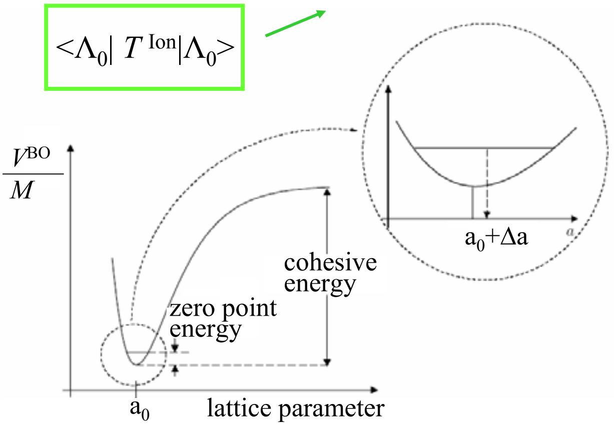
From DFT

a classical term

$$E_0 = \boxed{E^e_0} + \boxed{\frac{1}{4\pi\varepsilon_0}\frac{1}{2}\sum_{\substack{I,J\\I\neq J}}^{M,M}\frac{e^2}{|\mathbf{R}_I - \mathbf{R}_J|}Z_{v_I}Z_{v_J}}$$

$$+ \underline{\text{quantum mechanical corrections for lattice vibrations}}$$

$\boxed{<\Lambda_0|\, T^{\text{Ion}}|\Lambda_0>}$



The total energy per atom without zero point vibrations as a function of the inter-atomic distance. The measured interatomic distance is the average over the positions of vibrating atoms.

Most-Cited Papers in APS Journals

11 papers published in APS journals since 1893 with >1000 citations in APS journals (~5 times as many references in all science journals)

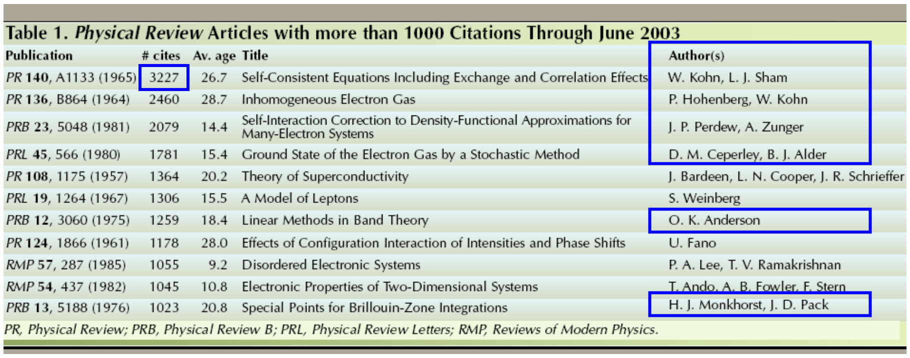


Table 1. *Physical Review* Articles with more than 1000 Citations Through June 2003

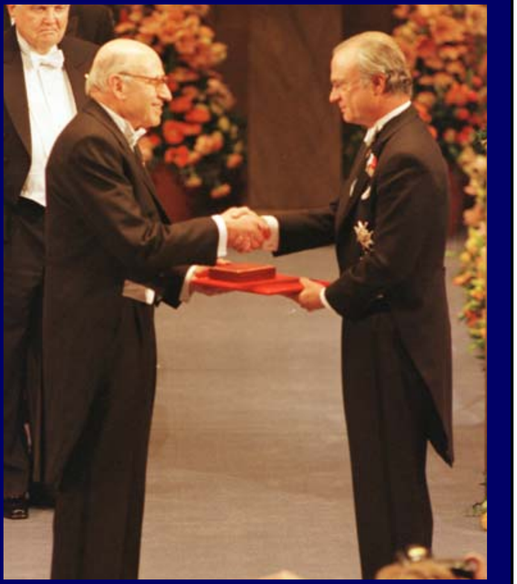
Publication	# cites	Av. age	Title	Author(s)
PR **140**, A1133 (1965)	3227	26.7	Self-Consistent Equations Including Exchange and Correlation Effects	W. Kohn, L. J. Sham
PR **136**, B864 (1964)	2460	28.7	Inhomogeneous Electron Gas	P. Hohenberg, W. Kohn
PRB **23**, 5048 (1981)	2079	14.4	Self-Interaction Correction to Density-Functional Approximations for Many-Electron Systems	J. P. Perdew, A. Zunger
PRL **45**, 566 (1980)	1781	15.4	Ground State of the Electron Gas by a Stochastic Method	D. M. Ceperley, B. J. Alder
PR **108**, 1175 (1957)	1364	20.2	Theory of Superconductivity	J. Bardeen, L. N. Cooper, J. R. Schrieffer
PRL **19**, 1264 (1967)	1306	15.5	A Model of Leptons	S. Weinberg
PRB **12**, 3060 (1975)	1259	18.4	Linear Methods in Band Theory	O. K. Anderson
PR **124**, 1866 (1961)	1178	28.0	Effects of Configuration Interaction of Intensities and Phase Shifts	U. Fano
RMP **57**, 287 (1985)	1055	9.2	Disordered Electronic Systems	P. A. Lee, T. V. Ramakrishnan
RMP **54**, 437 (1982)	1045	10.8	Electronic Properties of Two-Dimensional Systems	T. Ando, A. B. Fowler, F. Stern
PRB **13**, 5188 (1976)	1023	20.8	Special Points for Brillouin-Zone Integrations	H. J. Monkhorst, J. D. Pack

PR, Physical Review; PRB, Physical Review B; PRL, Physical Review Letters; RMP, Reviews of Modern Physics.

From Physics Today, June, 2005

34 years before
DFT invention

34 years after
DFT invention



From:
Walter Kohn - Personal Stories and Anecdotes Told by Friends and Collaborators.
M. Scheffler,
P. Weinberger (Eds.),
Springer-Verlag, Berlin Heidelberg New York
2003, 309 p.
ISBN 3-540-00805-5.

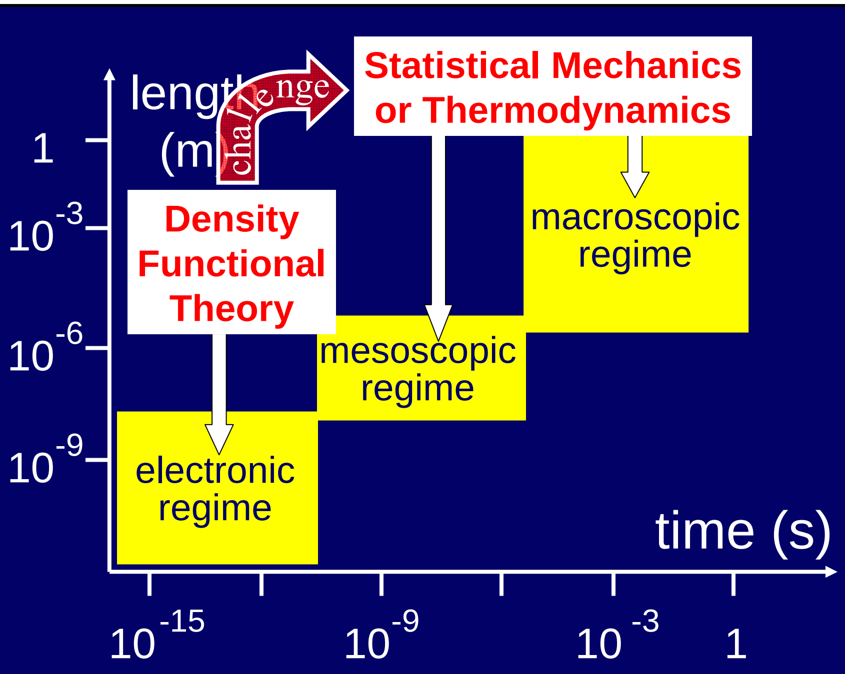
Challenges for the Near Future
Quantum-Mechanics Based Technology

Create new materials and systems by design, e.g. quantum dots, quantum wires, nano-catalysis, 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



Statistical Mechanics or Thermodynamics

Density Functional Theory

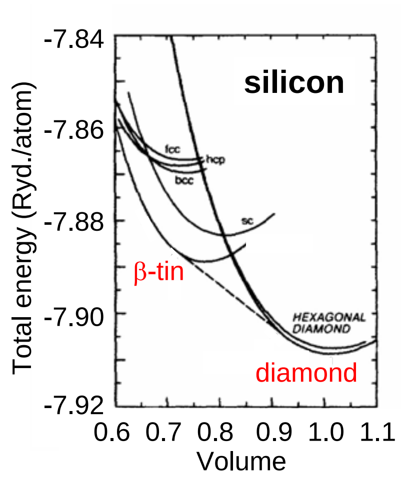
electronic regime

mesoscopic regime

macroscopic regime

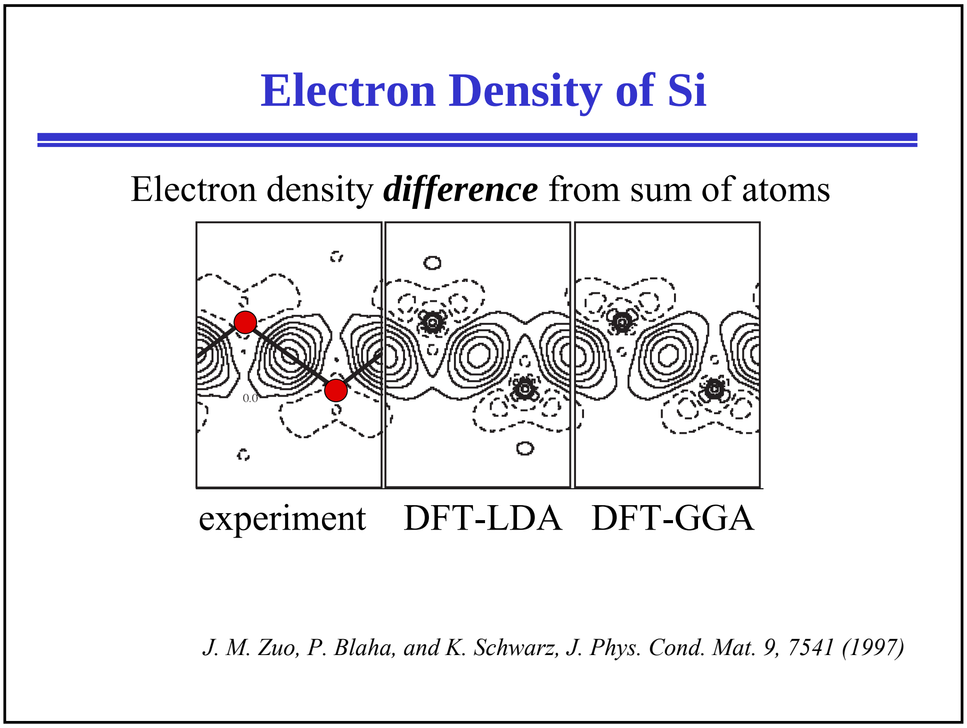
The first (convincing) DFT calculations:

Stability of crystals and crystal phase transitions



M. T. Yin and
M. L. Cohen
PRB 26 (1982)

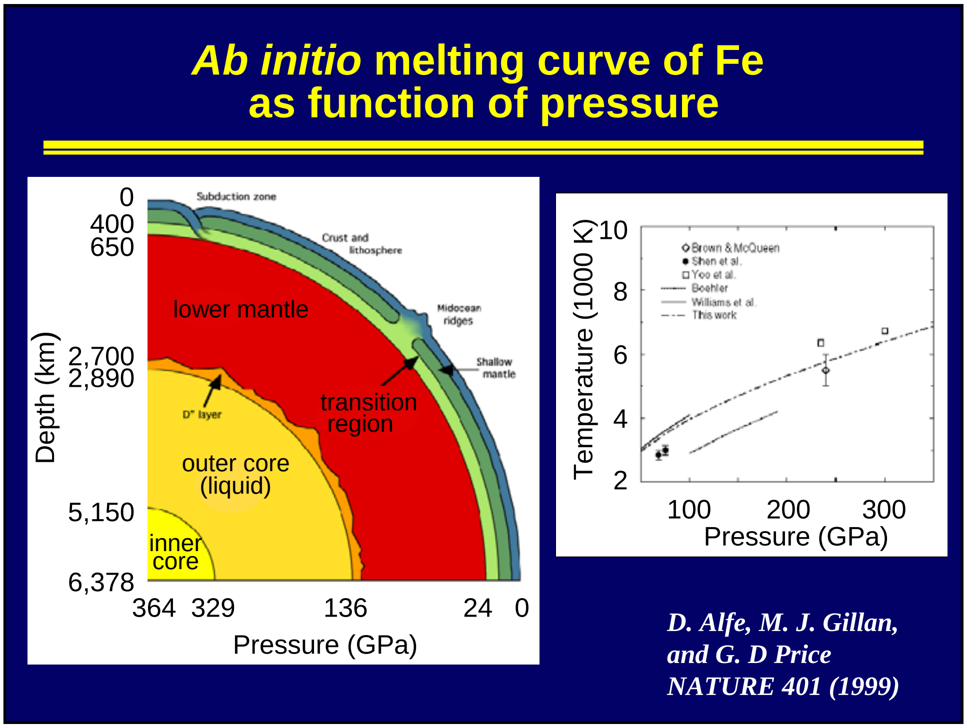
see also:
V.L. Moruzzi, J.F. Janak, and A. R. Williams
Calculated Electronic Properties of Metals
Pergamon Press (1978)



Electron Density of Si

Electron density ***difference*** from sum of atoms

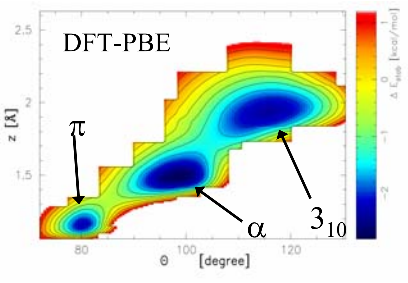
J. M. Zuo, P. Blaha, and K. Schwarz, J. Phys. Cond. Mat. 9, 7541 (1997)

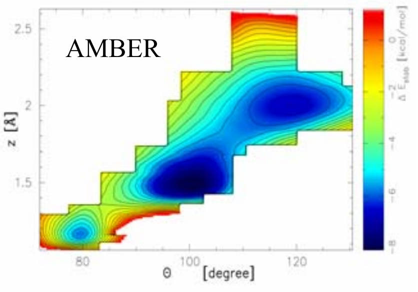


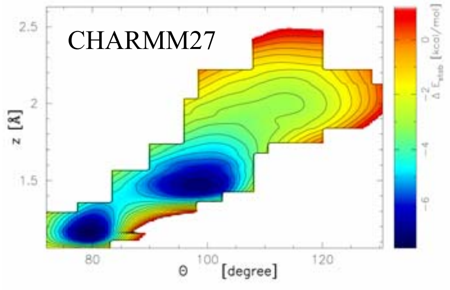
Ab initio **melting curve of Fe as function of pressure**

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

Bio-Physics: DFT vs Force Fields







both force fields predict the α-helix to be the most stable conformation

only AMBER reproduces all the helical minima

J. Ireta et al. ***more: later this week***

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

What About the Kohn-Sham Eigenvalues?

The ionization energy is:

$$\begin{aligned} I_k &= E_k^{N-1} - E^N \\ &= -\int_0^1 \frac{\partial E_v[n]}{\partial f_k} df_k \\ &= -\int_0^1 \epsilon_k(f_k)\, df_k \end{aligned}$$

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

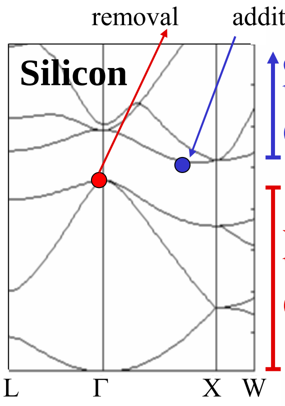
Here we assume that the positions of the atoms don’t change upon ionization, or that they change with some delay (Franck-Condon principle). Using the mean-value theorem of integral algebra gives: $\boxed{I_k = -\epsilon_k(0.5)}$

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

Kohn-Sham Electron Bands

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

The measured (optical) band gap is something else:



conduction band (empty states)

} the KS gap Δ

valence band (filled states)

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

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

Modern calculations of E_{gap} employ the *GW* approach, starting from KS energies and wave functions.

more comes *later this week*

Summary

-- *Interacting* electrons determine the properties and function of real materials and bio molecules.
-- Approximate xc functionals have been very successful, but for highly correlated situations there are problems.

Exciting arenas for theoretical work:

-- Thermodynamic phase transitions, e.g. melting.
-- Surfaces, interfaces, defects, nanostructures – in realistic environments
-- modeling kinetics, e.g. for catalysis or crystal growth (self-assembly and self-organization)
-- Molecules and clusters in solvents, electrochemistry, fuel cells, external fields, transport.
-- Biological problems

The challenges:

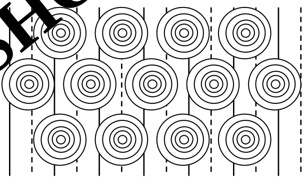
-- Find practical ways to correct the xc approximation.
-- Develop methods for bridging the length and time scales.

Three Basic Concepts for Modern Electronic Structure Calculations

Plane waves

The simplicity and speed of Fast Fourier Transforms

Requires smooth pseudopotentials



Localized orbitals

The intuitive appeal of atomic-like states; good scaling with system size.

Augmented methods

"Best of both worlds" – also most demanding.

Most general form: (L)APW

Be aware of the limitations of present xc functionals.

Use codes properly and carefully.

ENJOY THE WORKSHOP!!!