Chair of Condensed Matter Physics
Institute of Theoretical Physics
Faculty of Physics, Universityof Warsaw

Semester Zimowy 2011/2012

Wykład

Modelowanie Nanostruktur

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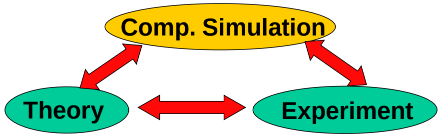
Computational Sciences

- Computational Physics
- Computational Astrophysics and Cosmology
- Computational Geophysics
- Computational Chemistry
- Computational Biology
- Computational Engineering
- Computational Materials Science
- Computational Nanoscience (Modeling of Nanostructures)



Modelowanie Nanostruktur, *2011/2012*
Jacek A. Majewski

Wykład 2 – *11 X 2011*

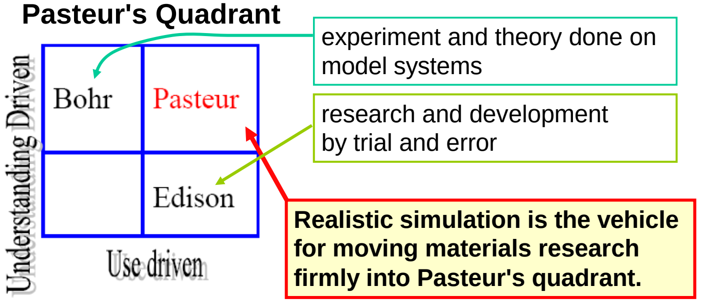
Density Functional Theory – the key to the Computational (Nano)Materials Science & *ab initio* Modeling of Nanostructures

The Basics

Computational Materials Science: A Scientific Revolution about to Materialize

- Due to the complexity of materials systems, progress has necessarily proceeded either within the Bohr quadrant or Edison's quadrant

Pasteur's Quadrant



experiment and theory done on model systems

research and development by trial and error

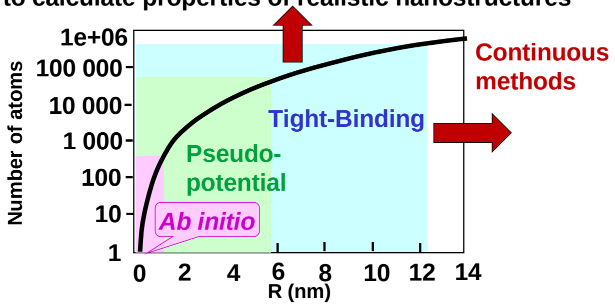
Realistic simulation is the vehicle for moving materials research firmly into Pasteur's quadrant.

Recent technological developments
cause increasing demands
for (nano)materials with specific properties

→ Modeling of nanostructures

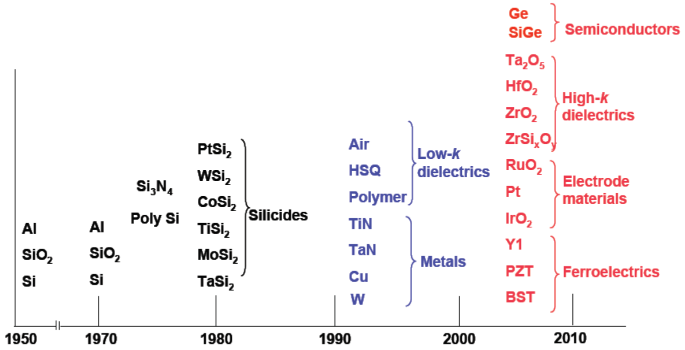
Atomistic vs. Continuous Methods

- **Microscopic approaches can be applied to calculate properties of realistic nanostructures**



Number of atoms in a spherical Si nanocrystal as a function of its radius R.
Current limits of the main techniques for calculating electronic structure.
Nanostructures commonly studied experimentally
lie in the size range 2-15 nm.

New Materials for Si- Technology



- **Moore's Law increasingly relies on material innovations !**

Recent technological developments cause increasing demands for materials with specific properties

- **Experiments are without doubt the most important approach in studying nanomaterials**
- **However, Kohn and co-workers opened a new avenue to *study properties of nanomaterials from first-principles* with the formulation of *density functional theory (DFT)*.**

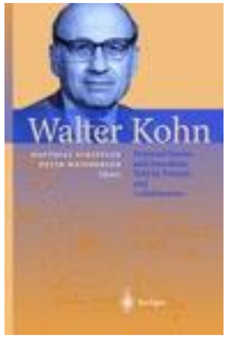
P. Hohenberg, W. Kohn, *Phys. Rev.* **136**, B864 (1964).

Usage of Density Functional Theory (DFT)

- Using DFT many practical problems of materials science (nano science) have been solved successfully.
- DFT is now employed not only by physicists, but also by chemists, geophysicists, biophysicists, metallurgist, and in other scientific fields.
- The computational implementations of DFT together with modern solid state theory allow it to obtain reliable results for ***thermodynamic, mechanical, electrical and magnetic properties*** of
  - metals,
  - semiconductors, or
  - insulators

  without any adjustable parameters fitted to the experiment.

80th birthday of Walter Kohn



“Walter Kohn –
Personal Stories and Anecdotes
Told by Friends and Collaborators”

eds. Matthias Scheffler &
Peter Weinberger

Springer Verlag

DFT – Nobel Prize in Chemistry, 1998

The big impact of DFT has been clearly high lightened by awarding the Nobel Prize in Chemistry in 1998 for the **development** and **application** of DFT.

Walter Kohn

Born in 1923

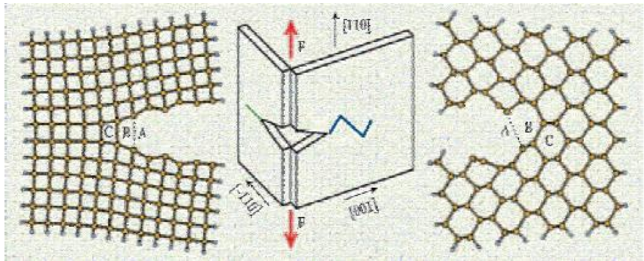
John A. Pople

1925 - 2004

DFT – Applied to real materials

- There are numerous applications of DFT in chemistry and physics (> 10 000 papers a year)
- The use of DFT based methods is still very new in the field of engineering
- The simulation of cracks in materials belongs to the most challenging problems in materials science.
- While the crack itself is a macroscopic property, the physical processes at the crack tip itself involve **the breaking of bonds governed by quantum mechanics**.

Anisotropic crack propagation in Silicon

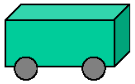


The DFT simulations give different energies for bond breaking along different crack directions =
crack in Si propagates differently depending on crystal plane and direction.

J. Kortus, *Microstructure Analysis in Materials Science*, 2005

Materials Science:
Why *ab-initio* approach is needed?

- A model
  as simple as possible



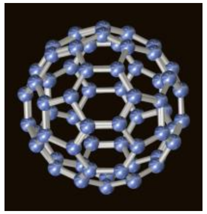
- A model
  non-empirical and realistic

- **Explanation and extrapolation of experimental results**
- **Physical insight**
- **Qualitative physics**

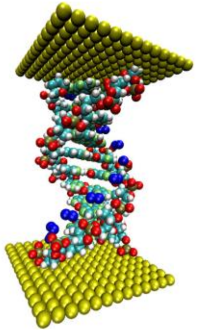
- **Reliable predictions of matter's properties**
- **Design of new materials**
- **Unexpected phenomena and unusual conditions (e.g., extreme pressures)**

Fundamental problem in nano science

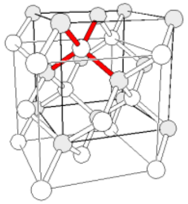
A fundamental problem in nanomaterials science is the prediction of condensed matter's electronic structure



C_{60} - molecule



DNA - molecule



Crystal - diamond

Materials Science:
Examples of Schrödinger Equation?

- **Materials are composed of nuclei** $\{Z_\alpha, M_\alpha, \vec{R}_\alpha\}$ **and electrons** $\{\vec{r}_i\}$

→ **the interactions are known**

$$H = -\sum_\alpha \frac{\hbar^2 \nabla_\alpha^2}{2M_\alpha} - \sum_i \frac{\hbar^2 \nabla_i^2}{2m} + \frac{1}{2}\sum_{\alpha,\beta} \frac{Z_\alpha Z_\beta e^2}{|\vec{R}_\alpha - \vec{R}_\beta|} - \sum_{i,\alpha} \frac{Z_\alpha e^2}{|\vec{R}_\alpha - \vec{r}_i|} + \frac{1}{2}\sum_{i,j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

Kinetic energy of nuclei
Kinetic energy of electrons
Nucleus-Nucleus interaction
Electron-Nucleus interaction
Electron-Electron interaction

$$H\Psi = E\Psi$$

***Ab-initio* (first principles) Method –**
ONLY Atomic Numbers $\{Z_i\}$ as input parameters

Quantum Mechanics of Molecules and Crystals

Molecule or Crystal = a system of ***nuclei (Ions)*** and ***electrons***

Nuclei – mass M, coordinates X, and momenta P, $X \equiv \{\vec{R}_1, \vec{R}_2, \ldots, \vec{R}_{N_{nucl}}\}$
(M, X, P)

Electrons – (m,x,p) $x \equiv \{\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N\}$

$$\boxed{H = \hat{T}_{el} + U(x,X) + \hat{T}_{Nucl}}$$

Kinetic energy of electrons

$$\hat{T}_{el} = \sum_{i=1}^{N} \frac{1}{2m} \vec{p}_i^{\,2} = -\sum_{i=1}^{N} \frac{\hbar^2}{2m} \vec{\nabla}_i^2$$

Kinetic energy of the nuclei

$$\hat{T}_{Nucl} = \sum_{\alpha=1}^{N_{nucl}} \frac{1}{2m} \vec{P}_i^{\,2} = -\sum_{\alpha=1}^{N_{nucl}} \frac{\hbar^2}{2M_\alpha} \vec{\nabla}_\alpha^2$$

Potential energy = The total Coulomb energy of nuclei and electrons

$$U(x,X) = \hat{V}_{en}(x,X) + \hat{V}_{ee}(x) + \hat{V}_{NN}(X)$$

Electron-nucleus

$$\hat{V}_{en}(x,X) = \sum_{i\alpha} \frac{-Z_\alpha e^2}{|\vec{r}_i - \vec{R}_\alpha|}$$

Electron-Electron

$$\hat{V}_{ee}(x) = \sum_{i<j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

Nucleus-Nucleus

$$\hat{V}_{NN}(X) = \sum_{\alpha<\beta} \frac{e^2}{|\vec{R}_\alpha - \vec{R}_\beta|}$$

The Adiabatic Approximation (Born-Oppenheimer)

- **The Schrödinger equation for the electrons in the presence of fixed ions**

➡ $$\boxed{\hat{H}_{el} \Psi_n(X,x) = E_n(X) \Psi_n(X,x)}$$

Parametric dependence on ionic positions

- **The energy levels of the system of ions are determined by solving**

$$\boxed{[\hat{H}_N + E(K',X)]\,\chi(Q,K',X) = \varepsilon(Q)\,\chi(Q,K',X)}$$

The electronic energy contributes to the potential energy of the ion system.
This implies that the potential energy depends on the state of the electrons.

The Adiabatic Approximation (Born-Oppenheimer)

M. Born & J. R. Oppenheimer, Ann. Phys. 84, 457 (1927)

- It is natural to consider the full Hamiltonian of the system to be the sum of an *ionic* and an *electronic* part

$$\boxed{\hat{H} = \hat{H}_N + \hat{H}_{el}}$$

$$\boxed{\hat{H}_N = \hat{T}_{Nucl} + \hat{V}_{NN}(X)}$$

$$\boxed{\hat{H}_{el} = \hat{T}_{el} + \hat{V}_{en}(x,X) + \hat{V}_{ee}(x)}$$

Quantum Mechanics:
System of N electrons in an external potential

- Adiabatic approximation – interacting electrons move in the 'external' potential of nuclei (ions) at fixed positions $\{\vec{R}_1, \vec{R}_2, \ldots\}$

$$\hat{T} = \sum_{i=1}^{N} -\frac{\hbar^2}{2m} \vec{\nabla}_i^2 \qquad \boxed{\hat{H} = \hat{T} + \hat{V}_{en} + \hat{V}_{e-e}} \qquad \hat{V}_{e-e} = \sum_{i<j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

$$\hat{V}_{en} = \sum_{i\alpha} \frac{-Z_\alpha e^2}{|\vec{r}_i - \vec{R}_\alpha|} = \hat{V}_{ext} = \sum_i \upsilon_{ext}(\vec{r}_i) \qquad \left(E_{nn} = \sum_{\alpha<\beta} \frac{Z_\alpha Z_\beta e^2}{|\vec{R}_\beta - \vec{R}_\alpha|} \right)$$

Schrödinger equation

$$H\Psi = E\Psi$$

$$\Psi(\{\vec{R}_\alpha\}, \vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) \equiv \Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$$

Many particle wave function $N \approx 10^{23}$

Ritz Variational Principle → Ground State Energy of the system

$$E_0 = \min_{\Psi \to N} \langle \Psi | \hat{H} | \Psi \rangle = \min_{\Psi \to N} \langle \Psi | \hat{T} + \hat{V}_{e-e} + \hat{V}_{ext} | \Psi \rangle$$

$\Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$ Many-particle wavefunction

$$E[\Psi] = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

$$E[\Psi] \geq E_0$$

Full minimization of the functional $E[\Psi]$ with respect to all allowed N-electron wave functions

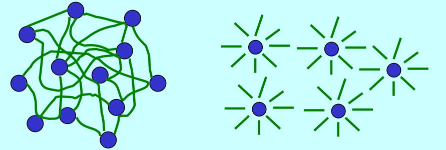
Quantum Mechanics:
System of N electrons in an external potential

Schrödinger equation

$$H\Psi = E\Psi$$

Exact analytical solutions are not known even for two electrons !

- Approximations are needed !
- Concept of independent particles moving in an effective potential



Idea: consider electrons as independent particles moving in an effective potential

$\Psi(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_{10^{23}})$ $\qquad$ $\varphi(\vec{x}_1)\varphi(\vec{x}_2)\ldots\varphi(\vec{x}_{10^{23}})$

Hartree-Fock Approximation

$$\Phi_{H-F} \Rightarrow E[\Phi_{H-F}] = \frac{<\Phi_{H-F}\,|\,\hat{H}\,|\,\Phi_{H-F}>}{<\Phi_{H-F}\,|\,\Phi_{H-F}>}$$

$$H = H_0 + \frac{1}{2}\sum_{i,j} U(\vec{x}_i, \vec{x}_j)$$

$$H_0 = \sum_i H_0(i) = \sum_i -\frac{1}{2}\nabla_i^2 + V_{ext}(\vec{r}_i) \qquad U(\vec{x}_i, \vec{x}_j) = \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

Variational Principle

$$\Rightarrow \quad H_0\psi_i(\vec{x}_i) + \left[\sum_{j=1}^{N}\int \psi^*{}_j(\vec{x}_j) U(\vec{x}_i, \vec{x}_j)\psi_j(\vec{x}_j)d\vec{x}_j\right]\psi_i(\vec{x}_i)$$

$$-\left[\sum_{j=1}^{N}\int \psi^*{}_j(\vec{x}_j) U(\vec{x}_i, \vec{x}_j)\psi_i(\vec{x}_j)d\vec{x}_j\right]\psi_j(\vec{x}_i) = \varepsilon_i\psi_i(\vec{x}_i)$$

Hartree and Hartree-Fock Approximation

Ansatz for the wave-function

Hartree Method

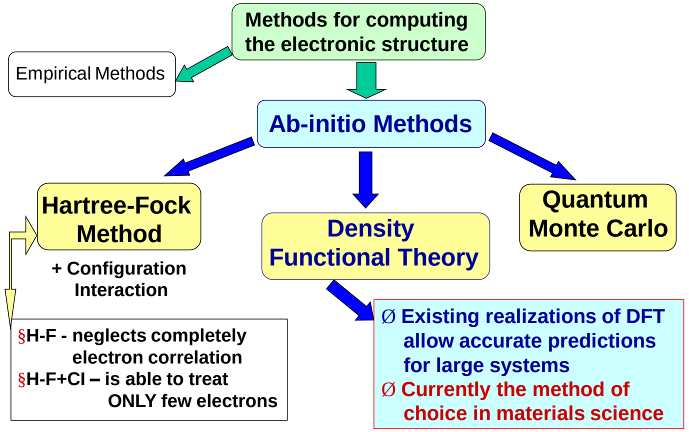
$$\Psi_{Hartree}(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_N) = \psi_1(\vec{x}_1)\psi_2(\vec{x}_2)\ldots\psi_N(\vec{x}_N)$$

Hartree-Fock Method

$$\Psi_{H-F}(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \psi_1(\vec{x}_1) & \psi_2(\vec{x}_1) & \cdots & \psi_N(\vec{x}_1) \\ \psi_1(\vec{x}_2) & \psi_2(\vec{x}_2) & \cdots & \psi_N(\vec{x}_2) \\ \vdots & \vdots & & \vdots \\ \psi_1(\vec{x}_N) & \psi_2(\vec{x}_N) & \cdots & \psi_N(\vec{x}_N) \end{vmatrix}$$

ψ_i - one-electron wavefunction of the *ith* level

Spectrum of Electronic Hamiltonian:
What *ab initio* methods do we have?



Methods for computing the electronic structure

Empirical Methods

Ab-initio Methods

Hartree-Fock Method

+ Configuration Interaction

Density Functional Theory

Quantum Monte Carlo

§H-F - neglects completely electron correlation
§H-F+CI – is able to treat ONLY few electrons

Ø Existing realizations of DFT allow accurate predictions for large systems
Ø Currently the method of choice in materials science

Density Functional Theory (DFT)

P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964)

- **One particle density – Basic quantity of DFT**

$$\rho(\vec r)=\left\langle \Psi(\vec r_1,\vec r_2,\dots,\vec r_N)\,\middle|\,\sum_i \delta(\hat{\vec r}_i-\vec r)\,\middle|\,\Psi(\vec r_1,\vec r_2,\dots,\vec r_N)\right\rangle$$

$$= N\int d\vec r_2,\dots,d\vec r_N\,\Psi^*(\vec r,\vec r_2,\dots,\vec r_N)\Psi(\vec r,\vec r_2,\dots,\vec r_N)$$

- The DFT is based on two fundamental theorems for a functional of the one particle density.
- **One particle density determines the ground state energy of the system**
- Modern formulation – constrained-search method of Mel Levy

Mel Levy, Proc. Natl. Acad. Sci. USA, vol. 76, No. 12, p.606 (1979).

Density Functional Theory – constrained search formulation

Mel Levy, Proc. Natl. Acad. Sci. USA, vol. 76, No. 12, p.606 (1979).

Functional of the one particle density $F[\rho] \doteq \min_{\Psi\to\rho}\left\langle \Psi_\rho \middle| \hat T+\hat V_{e-e} \middle| \Psi_\rho\right\rangle$

The functional $F[\rho]$ searches all many particle functions Ψ that yield the input density $\rho(\vec r)$ and then delivers the minimum of $\left\langle \hat T+\hat V_{e-e}\right\rangle$

Theorem I $\int d\vec r v_{ext}(\vec r)\rho(\vec r)+F[\rho]\ge E_0$

Theorem II $\int d\vec r v_{ext}(\vec r)\rho_0(\vec r)+F[\rho_0]=E_0$

ρ_0 - ground state density
E_0 - ground state energy

Let us define function Ψ^{ρ}_{min} that minimizes $\left\langle \Psi_\rho \middle| \hat T+\hat V_{e-e} \middle| \Psi_\rho\right\rangle$

$$F[\rho]=\left\langle \Psi^{\rho}_{min} \middle| \hat T+\hat V_{e-e} \middle| \Psi^{\rho}_{min}\right\rangle \qquad F[\rho_0]=\left\langle \Psi^{\rho_0}_{min} \middle| \hat T+\hat V_{e-e} \middle| \Psi^{\rho_0}_{min}\right\rangle$$

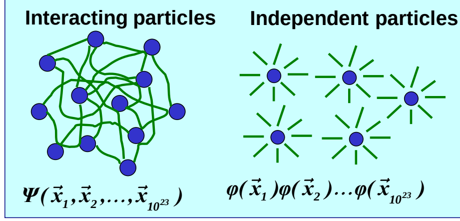
Proof of Theorem I:

$$\int d\vec r v_{ext}(\vec r)\rho(\vec r)+F[\rho]=\int d\vec r v_{ext}(\vec r)\rho(\vec r)+\left\langle \Psi^{\rho}_{min} \middle| \hat T+\hat V_{e-e} \middle| \Psi^{\rho}_{min}\right\rangle=$$

$$=\left\langle \Psi^{\rho}_{min} \middle| \hat V_{ext}+\hat T+\hat V_{e-e} \middle| \Psi^{\rho}_{min}\right\rangle\ge E_0$$

Ritz variational principle

Density Functional Theory (DFT) in Kohn-Sham realization



$\Psi(\vec x_1,\vec x_2,\dots,\vec x_{10^{23}})$ $\qquad$ $\varphi(\vec x_1)\varphi(\vec x_2)\dots\varphi(\vec x_{10^{23}})$

Idea: consider electrons as independent particles moving in an effective potential

This reduction is rigorously possible !

Density Functional Theory – constrained search formulation

Proof of Theorem II: $E_0\le\left\langle \Psi^{\rho_0}_{min} \middle| \hat V_{ext}+\hat T+\hat V_{e-e} \middle| \Psi^{\rho_0}_{min}\right\rangle$

From variational principle

$$\left\langle \Psi_0 \middle| \hat V_{ext}+\hat T+\hat V_{e-e} \middle| \Psi_0\right\rangle\le\left\langle \Psi^{\rho_0}_{min} \middle| \hat V_{ext}+\hat T+\hat V_{e-e} \middle| \Psi^{\rho_0}_{min}\right\rangle$$

$$\int d\vec r v_{ext}(\vec r)\rho_0(\vec r)+\left\langle \Psi_0 \middle| \hat T+\hat V_{e-e} \middle| \Psi_0\right\rangle\le\int d\vec r v_{ext}(\vec r)\rho_0(\vec r)+\left\langle \Psi^{\rho_0}_{min} \middle| \hat T+\hat V_{e-e} \middle| \Psi^{\rho_0}_{min}\right\rangle$$

(A) $\left\langle \Psi_0 \middle| \hat T+\hat V_{e-e} \middle| \Psi_0\right\rangle\le\left\langle \Psi^{\rho_0}_{min} \middle| \hat T+\hat V_{e-e} \middle| \Psi^{\rho_0}_{min}\right\rangle$

But, on the other hand, from the definition of $\Psi^{\rho_0}_{min}$

(B) $\left\langle \Psi_0 \middle| \hat T+\hat V_{e-e} \middle| \Psi_0\right\rangle\ge\left\langle \Psi^{\rho_0}_{min} \middle| \hat T+\hat V_{e-e} \middle| \Psi^{\rho_0}_{min}\right\rangle$

[(A) & (B) true] $\Rightarrow\left\langle \Psi_0 \middle| \hat T+\hat V_{e-e} \middle| \Psi_0\right\rangle=\left\langle \Psi^{\rho_0}_{min} \middle| \hat T+\hat V_{e-e} \middle| \Psi^{\rho_0}_{min}\right\rangle$

$$\boxed{F[\rho_0]=\left\langle \Psi^{\rho_0}_{min} \middle| \hat T+\hat V_{e-e} \middle| \Psi^{\rho_0}_{min}\right\rangle}$$

$$\int d\vec r v_{ext}(\vec r)\rho_0(\vec r)+\left\langle \Psi_0 \middle| \hat T+\hat V_{e-e} \middle| \Psi_0\right\rangle=F[\rho_0]+\int d\vec r v_{ext}(\vec r)\rho_0(\vec r)$$

$$\left\langle \Psi_0 \middle| \hat V_{ext}+\hat T+\hat V_{e-e} \middle| \Psi_0\right\rangle=F[\rho_0]+\int d\vec r v_{ext}(\vec r)\rho_0(\vec r)$$

$$\boxed{E_0=F[\rho_0]+\int d\vec r v_{ext}(\vec r)\rho_0(\vec r)}$$

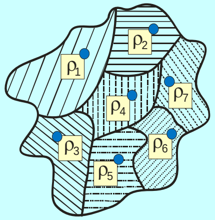
Density Functional Theory – Constrained Search Formulation
Relation to Ritz Variational Principle

The ground-state energy minimization procedure of $E[\Psi] = \frac{<\Psi|\hat{H}|\Psi>}{<\Psi|\Psi>}$ can be divided into two steps

$$E_0[\Psi] = \min_{\Psi\to N}\left\langle\Psi\,|\,\hat{T}+\hat{V}_{e-e}+\hat{V}_{ext}\,|\,\Psi\right\rangle = \min_{\rho\to N}\left[\min_{\Psi\to\rho}\left\langle\Psi^{\rho}\,|\,\hat{T}+\hat{V}_{e-e}+\hat{V}_{ext}\,|\,\Psi^{\rho}\right\rangle\right]$$

- ● The inner minimization is constrained to all wave functions that give $\rho(\vec{r})$,
- ● while the outer minimization releases this constrain by searching all $\rho(\vec{r})$

Percus-Levy partition of the N-electron Hilbert space



- Each shaded area is the set of Ψ that integrate to a particular $\rho(\vec{r})$
- The minimization $\Psi\to\rho$ for a particular ρ is constrained to the shaded area associated with this ρ, and is realized by one point (denoted by ●) in this shaded area.
- The minimization $\rho\to N$ is over all such points.

Density Functional Theory

PROBLEM: exact functional $F[\rho]$ is unknown !

One needs a good approximation to $F[\rho]$

$$F[\rho] = \min_{\Psi\to\rho}\left\langle\Psi_{\rho}\,|\,\hat{T}+\hat{V}_{e-e}\,|\,\Psi_{\rho}\right\rangle = \left\langle\Psi^{\rho}_{min}\,|\,\hat{T}+\hat{V}_{e-e}\,|\,\Psi^{\rho}_{min}\right\rangle$$

$$= T[\rho] + U[\rho] + \underbrace{\left\{\left\langle\Psi^{\rho}_{min}\,|\,\hat{V}_{e-e}\,|\,\Psi^{\rho}_{min}\right\rangle - U[\rho]\right\}}_{\text{Exchange \& Correlation } E_{xc}[\rho]}$$

Kinetic energy

Classical Coulomb energy

$$U[\rho] = \frac{1}{2}\iint d\vec{r}d\vec{r}\,'\frac{\rho(\vec{r})\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}$$

Exchange & Correlation $E_{xc}[\rho]$

$$\boxed{F[\rho] = T[\rho] + U[\rho] + E_{xc}[\rho]}$$

- ● The functional $F[\rho]$ is universal in the sense that it is independent of the external potential (field) $\upsilon_{ext}(\vec{r})$.

Thomas-Fermi-Method (probably the oldest approximation to DFT)

$$T^{T-F}[\rho] \cong \frac{3}{5}(3\pi^2)^{2/3}\frac{\hbar^2}{2m}\int d\vec{r}\,[\rho(\vec{r})]^{5/3} \qquad V^{T-F}_{ee}[\rho] \cong U[\rho]$$

and extensions

- § Thomas-Fermi-Dirac
- § Thomas-Fermi-Weizsacker

PROBLEM: $T^{T-F}[\rho]$

Very often these models give even qualitatively wrong results.

Density Functional Theory – Constrained Search Formulation
Relation to Ritz Variational Principle

■ $$E_0[\Psi] = \min_{\Psi\to N}\left\langle\Psi\,|\,\hat{T}+\hat{V}_{e-e}+\hat{V}_{ext}\,|\,\Psi\right\rangle =$$

$$= \min_{\rho\to N}\left[\min_{\Psi\to\rho}\left\langle\Psi^{\rho}\,|\,\hat{T}+\hat{V}_{e-e}+\hat{V}_{ext}\,|\,\Psi^{\rho}\right\rangle\right] =$$

$$= \min_{\rho\to N}\left[\min_{\Psi\to\rho}\left\langle\Psi^{\rho}\,|\,\hat{T}+\hat{V}_{e-e}\,|\,\Psi^{\rho}\right\rangle + \int d\vec{r}\upsilon_{ext}(\vec{r})\rho(\vec{r})\right] =$$

$$= \min_{\rho\to N}\left[F[\rho] + \int d\vec{r}\upsilon_{ext}(\vec{r})\rho(\vec{r})\right] =$$

● $$= \min_{\rho\to N} E[\rho]$$

$$E[\rho] = F[\rho] + \int d\vec{r}\upsilon_{ext}(\vec{r})\rho(\vec{r})$$

In ■ 2^N wave functions of 3N variables ☹

In ● O N E function of 3 variables !!! ☺

DFT- The Kohn- Sham Method

*W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965)*

W. Kohn & L. Sham (1965) invented an ingenious indirect approach to the kinetic- energy functional.

They turned density functional theory into a practical tool for rigorous calculations

The main idea:

System of interacting electrons with density $\rho(\vec{r})$ ⟷ **System of non-interacting electrons with the same density $\rho(\vec{r})$**

“Real” system

$\rho(\vec{r})$ $T[\rho]$

“Fictitious” or Kohn-Sham reference system

$T_S[\rho]$ $\rho_S(\vec{r}) = \rho(\vec{r})$

$$E[\rho] = \int d\vec{r}\upsilon_{ext}(\vec{r})\rho(\vec{r}) + T_S[\rho] + U[\rho] + E_{xc}[\rho]$$

- $E_{xc}[\rho] = V_{ee}[\rho] - U[\rho] + T[\rho] - T_S[\rho]$
- ***Exchange-correlation functional*** contains now the difference between kinetic energy functional of interacting and non-interacting electrons.

The Kohn- Sham Method – Kinetic energy functional

How the $T_S[\rho]$ looks like ?

Hamiltonian of the non-interacting reference system

$$H_S = \sum_i^N -\frac{\hbar^2}{2m}\vec{\nabla}_i^2 + \sum_i^N \upsilon_S(\vec{r}_i) \qquad \upsilon_S(\vec{r}) \text{ - local potential}$$

For this system there will be an

exact determinantal ground-state wave function

$$\Phi = \frac{1}{\sqrt{N!}} det[\varphi_1, \varphi_2, \dots, \varphi_N]$$

, where φ_i are the N lowest eigenstates of the one-electron Hamiltonian

$$\hat{h}_S\varphi_i = \left[-\frac{\hbar^2}{2m}\vec{\nabla}^2 + \upsilon_S(\vec{r})\right]\varphi_i(\vec{r}) = \varepsilon_i\varphi_i(\vec{r})$$

The density

$$\rho(\vec{r}) = \sum_{i=1}^N \varphi^*_i(\vec{r})\varphi_i(\vec{r})$$

The Kohn-Sham Method: Variational Procedure

We cast the Hohenberg-Kohn variational problem in terms of the one-particle (Kohn-Sham) orbitals

$$E_0 = \min_{\rho\to N} E[\rho] =$$

$$= \min_{\rho\to N}\left\{T_S[\rho] + U[\rho] + E_{xc}[\rho] + \int d\vec{r}\upsilon_{ext}(\vec{r})\rho(\vec{r})\right\}$$

$$= \min_{\rho\to N}\left\{[\underset{\Phi\to\rho}{Min}\langle\Phi|\hat{T}|\Phi\rangle] + U[\rho] + E_{xc}[\rho] + \int d\vec{r}\upsilon_{ext}(\vec{r})\rho(\vec{r})\right\}$$

$$= \min_{\Phi\to\rho}\left\{T_S[\Phi] + U[\rho[\Phi]] + E_{xc}[\rho[\Phi]] + \int d\vec{r}\upsilon_{ext}(\vec{r})\rho(\vec{r})\right\}$$

$$= \min_{\{\varphi_i\}\to N}\left\{T_S[\{\varphi_i\}] + U[\rho[\{\varphi_i\}]] + E_{xc}[\rho[\{\varphi_i\}]] + \sum_{i=1}^N\int d\vec{r}\varphi_i^*(\vec{r})\upsilon_{ext}(\vec{r})\varphi_i(\vec{r})\right\}$$

The dependence of the density ρ on the orbitals $\{\varphi_i\}$ is known

$$\rho(\vec{r}) = \sum_{i=1}^N \varphi^*_i(\vec{r})\varphi_i(\vec{r})$$

Variational search for the minimum of $E[\rho]$ can be equivalently performed in the space of the orbitals $\{\varphi_i\}$.

The Kohn- Sham Method – Kinetic energy functional

$T_S[\rho]$ - *can be defined by the constrained-search formula*

$$T_S[\rho] = \underset{\Phi\to\rho}{Min}\langle\Phi|\hat{T}|\Phi\rangle = \underset{\Phi\to\rho}{Min}\sum_{i=1}^N\left\langle\varphi_i\left|-\frac{\hbar^2}{2m}\vec{\nabla}^2\right|\varphi_i\right\rangle$$

The search is over all single-determinantal functions Φ that yield the given density ρ .

- The existence of the minimum has been proved by Lieb (1982).
- $T_S[\rho]$ is uniquely defined for any density.
- $T_S[\rho] \neq T[\rho]$

Crucial characteristics of the Kohn-Sham Method

Φ NOT Ψ

Derivation of the Kohn-Sham Equations

Performing variational search for the minimum of $E[\rho]$ one must actually constrain orbitals to be orthonormal $\int d\vec{r}\varphi_i^*(\vec{r})\varphi_j(\vec{r}) = \delta_{ij}$ (●)

Conservation of the number of particles

Let us define the constrained functional of the N orbitals

$$\Omega[\{\varphi_i\}] = E[\rho] - \sum_{i=1}^N\sum_{j=1}^N\varepsilon_{ij}\int d\vec{r}\varphi_i^*(\vec{r})\varphi_j(\vec{r})$$

where ε_{ij} are Lagrange multipliers for the constrain (●).

For $E[\rho]$ to be minimum, it is necessary that $\delta\Omega[\{\varphi_i\}] = 0$

$$\frac{\delta}{\delta\varphi_i^*(\vec{r})}\left\{E[\rho] - \sum_{i=1}^N\sum_{j=1}^N\varepsilon_{ij}\int d\vec{r}'\varphi_i^*(\vec{r}')\varphi_j(\vec{r}')\right\} = 0$$

Note: $\frac{\delta}{\delta\varphi_i^*(\vec{r})} = \frac{\delta\rho}{\delta\varphi_i^*(\vec{r})}\frac{\delta}{\delta\rho}$

The variational procedure leads to equations:

$$\left[-\frac{\hbar^2}{2m}\vec{\nabla}^2 + \upsilon_{ext}(\vec{r}) + \upsilon_H(\vec{r}) + \upsilon_{xc}(\vec{r})\right]\varphi_i(\vec{r}) = \sum_{j=1}^N\varepsilon_{ij}\varphi_j(\vec{r})$$

$$\upsilon_H(\vec{r}) = \frac{\delta U}{\delta\rho} = \int d\vec{r}'\frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} \qquad \upsilon_{xc}(\vec{r}) = \frac{\delta E_{xc}[\rho]}{\delta\rho}$$

Derivation of the Kohn-Sham Equations

In Kohn-Sham method exchange-correlation functional can be split into separate exchange and correlation functional $E_{xc}[\rho] = E_x[\rho] + E_c[\rho]$

$$E_x[\rho] = -\frac{1}{2}\sum_i \iint d\vec{r}d\vec{r}\,'\varphi_i^*(\vec{r})\left(\sum_j \frac{\varphi_j(\vec{r})\varphi_j^*(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\right)\varphi_i(\vec{r}\,')$$

Exchange energy functional

Correlation energy functional

Exchange potential

Correlation potential

$$\upsilon_{xc}(\vec{r}) = \frac{\delta E_x[\rho]}{\delta\rho} + \frac{\delta E_c[\rho]}{\delta\rho} \quad = \quad \upsilon_x(\vec{r}) \quad + \quad \upsilon_c(\vec{r})$$

Kohn-Sham potential (**local potential !**)

$$\upsilon_{KS}(\vec{r}) = \upsilon_{ext}(\vec{r}) + \upsilon_H(\vec{r}) + \upsilon_x(\vec{r}) + \upsilon_c(\vec{r}) \quad (= \upsilon_S(\vec{r})\ )$$

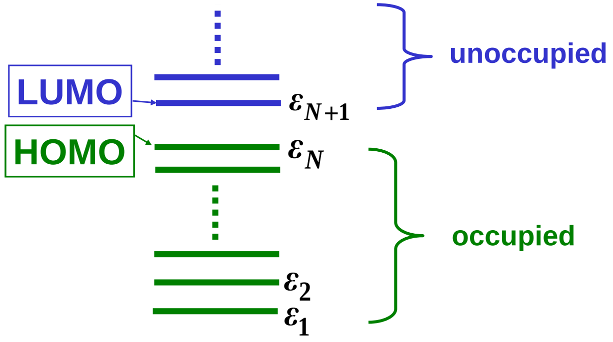
$\hat{H}_{KS} = -\frac{\hbar^2}{2m}\vec{\nabla}^2 + \upsilon_{KS}(\vec{r})$ **is hermitian** $\Rightarrow$ ε_{ij} **is also hermitian**

$(\varepsilon_{ij} = \langle\varphi_i | \hat{H}_{KS} | \varphi_j\rangle)$

Unitary transformation of $\{\varphi_i\}$ diagonalizes ε_{ij}, but the density and $\hat{H}_{KS}$ remain invariant.

The Kohn- Sham Method – ‚Aufbau' principle

How to calculate one particle density?



The Kohn- Sham Method – The Kohn-Sham Equations

- **Schrödinger-like equations with local potential**

$$\upsilon_H(\vec{r}) = \frac{\delta U}{\delta\rho} = \int d\vec{r}\,'\frac{\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} \qquad \frac{\delta E_x[\rho]}{\delta\rho} \qquad \frac{\delta E_c[\rho]}{\delta\rho}$$

$$\left[-\frac{\hbar^2}{2m}\vec{\nabla}^2 + \upsilon_{ext}(\vec{r}) + \upsilon_H(\vec{r}) + \upsilon_x(\vec{r}) + \upsilon_c(\vec{r})\right]\varphi_i(\vec{r}) = \varepsilon_i\varphi_i(\vec{r})$$

$$\upsilon_{ext}(\vec{r}) = -e^2\sum_{s,n}\frac{Z_s}{|\vec{r}-\vec{\tau}_s-\vec{R}_n|}$$

$$\rho(\vec{r}) = \sum_{i=1}^{N}\varphi^*_i(\vec{r})\varphi_i(\vec{r})$$

- **These equation are nonlinear and must be solved iteratively (self-consistently)**

The Kohn- Sham Method – The Total Energy

$$E[\rho] = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\int d\vec{r}\varphi_i^*(\vec{r})\vec{\nabla}^2\varphi_i(\vec{r}) + U[\rho] + E_x[\rho] + E_c[\rho] + \int d\vec{r}\upsilon_{ext}(\vec{r})\rho(\vec{r})$$

$$E = \sum_{i=1}^{N}\varepsilon_i \underbrace{-\frac{1}{2}\iint d\vec{r}d\vec{r}\,'\frac{\rho(\vec{r})\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} + E_x[\rho] + E_c[\rho] - \int d\vec{r}(\upsilon_x(\vec{r}) + \upsilon_c(\vec{r}))\rho(\vec{r})}_{\text{so-called double counting correction}}$$

Sum of the one-particle Kohn-Sham energies

$$\sum_{i=1}^{N}\varepsilon_i = \sum_{i=1}^{N}\left\langle\varphi_i \left| -\frac{\hbar^2}{2m}\vec{\nabla}^2 + \upsilon_{KS}(\vec{r}) \right| \varphi_i\right\rangle = T_S[\rho] + \int d\vec{r}\upsilon_{KS}(\vec{r})\rho(\vec{r})$$

Energy of the reference system

differs from the energy of 'real' system

The Kohn- Sham Method – Problems

- **Physical meaning of the Kohn-Sham orbital energies ε_i ?**
  (Note, these energies were introduced as Lagrange multipliers)
  - Strictly speaking there is none ☹
  - The Kohn-Sham orbital energy of the highest occupied level is equal to the minus of the ionization energy, $\varepsilon_{max} = \mu = -I$ ☺
  - Extension to non-integer occupation numbers $0 \le f_i \le 1$
    $\rho(\vec{r}) = \sum_i f_i \varphi_i^*(\vec{r})\varphi_i(\vec{r})$ $\quad \boxed{\frac{\partial E}{\partial f_i} = \varepsilon_i}$ Janak theorem (1978) ☺
  - Kohn-Sham energies may be considered as the zero order approximation to the energies of quasi-particles in the many-particle theory. ☺
- **Correlation energy functional $E_c[\rho]$ (also $\upsilon_c(\vec{r})$) is *unknown* for *non-homogeneous* systems**
  - $E_c[\rho]$ - ***is known*** for ***homogeneous*** electron gas (constant density) ☺

Exchange and Correlation Energy of Homogeneous Electron Gas

- **Homogeneous electron gas** (free electron gas or “jellium”)

Wave functions: $\psi(\vec{k},\vec{r}) = \frac{1}{\sqrt{\Omega}} e^{i\vec{k}\cdot\vec{r}}$ Constant electron density: $\rho = N/\Omega$

Exchange energy per unit volume

$$E_x = -\frac{3}{2}\left(\frac{3}{\pi}\right)^{1/3} e^2 \rho^{4/3} = \varepsilon_x^{\text{hom}} \rho$$

Exchange energy per particle

$$\varepsilon_x^{\text{hom}} = -\frac{3}{2}\left(\frac{3}{\pi}\right)^{1/3} e^2 \rho^{1/3}$$

$$\varepsilon_x^{\text{hom}} = -\frac{3}{2}\left(\frac{9}{4\pi^2}\right)^{1/3} \frac{1}{r_s} \quad \text{in } [Ry]$$

$$\varepsilon_x^{\text{hom}}(r_s) = -0.91633/r_s \ [Ry]$$

- Dimensionless parameter characterizing density:

$$r_s = \frac{1}{a_B}\left(\frac{3}{4\pi\rho}\right)^{1/3} \qquad \rho \text{ in } (a_B)^{-3} \Longrightarrow$$

- **Quantum Monte-Carlo simulations for homogeneous electron gas**
  D. M. Ceperly & B. J. Alder, Phys. Rev. Lett. ***45****, 566 (1980)*

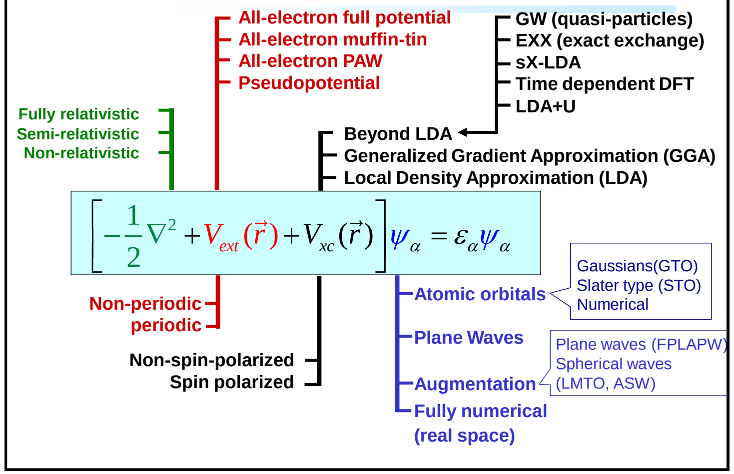
Parametrization: *J. P. Perdew & A. Zunger, Phys. Rev. B* ***23****, 5048 (1981)*

Correlation energy per particle

$$\varepsilon_c^{\text{hom}}(r_s) = \begin{cases} A\ln r_s + B + Cr_s \ln r_s + Dr_s & \text{for } r_s < 1 \\ \gamma/(1+\beta_1\sqrt{r_s} + \beta_2 r_s) & \text{for } r_s \ge 1 \end{cases} \quad [Ry]$$

$A, B, C, D, \gamma, \beta_1, \beta_2$ - fitted parameters

DFT: Implementations of the Kohn-Sham Method



All-electron full potential
All-electron muffin-tin
All-electron PAW
Pseudopotential

GW (quasi-particles)
EXX (exact exchange)
sX-LDA
Time dependent DFT
LDA+U

Fully relativistic
Semi-relativistic
Non-relativistic

Beyond LDA ←
Generalized Gradient Approximation (GGA)
Local Density Approximation (LDA)

$$\left[-\frac{1}{2}\nabla^2 + V_{ext}(\vec{r}) + V_{xc}(\vec{r})\right]\psi_\alpha = \varepsilon_\alpha \psi_\alpha$$

Non-periodic
periodic

Non-spin-polarized
Spin polarized

Atomic orbitals
Gaussians(GTO)
Slater type (STO)
Numerical

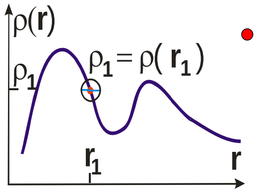
Plane Waves

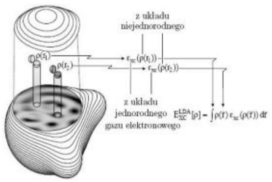
Augmentation
Plane waves (FPLAPW)
Spherical waves (LMTO, ASW)

Fully numerical (real space)

Local Density Approximation (LDA)

In atoms, molecules, and solids the electron density is not homogeneous





- **The main idea of the *Local Density Approximation*: the density is treated *locally* as constant**

$$E_{xc}^{LDA}[\rho] = \int d\vec{r}\,\rho(\vec{r})\,\varepsilon_{xc}^{\text{hom}}(\rho(\vec{r}))$$

$$\varepsilon_{xc}^{\text{hom}} = \varepsilon_x^{\text{hom}} + \varepsilon_c^{\text{hom}}$$

GGA - Gradient Corrections to LDA

Gradient Expansion Approximation

*D. C. Langreth & M. J. Mehl, Phys. Rev. B **28**, 1809 (1983)*

$$E_{xc}^{GEA}[\rho] = E_{xc}^{LDA}[\rho] + \int d\vec{r}\,\rho(\vec{r})C_{xc}[\rho]\frac{|\nabla\rho(\vec{r})|^2}{\rho(\vec{r})^{4/3}}]$$

Generalized Gradient Approximation

*J. P. Perdew & Y. Wang, Phys. Rev. B **33**, 8800 (1986)*

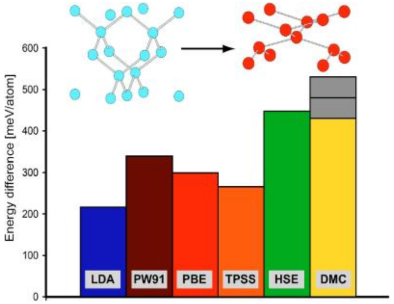
$$E_{xc}^{GGA}[\rho] = \int d\vec{r}\, f_{xc}(\rho(\vec{r}), \nabla\rho(\vec{r}))$$

f_{xc} **-constructed to fulfill maximal number of "summation rules"**

Exchange-correlation potential can be calculated very easily, since explicit dependence of E_{xc} on the density ρ is known.

$$\upsilon_{xc} = \frac{\delta E_{xc}}{\delta\rho}$$

Accuracy Benchmarks of the different DTF Functiona



Difference in energy per atom in the diamond phase and in the **β-tin phase** of Si.

Phys. Rev. B 74, 121102(R) (2006)

Examples of exchange functionals

- Becke 88: Becke's 1988 functional,
- Perdew-Wang 91
- Barone's Modified PW91
- Gill 96
- PBE: The 1996 functional of Perdew, Burke and Ernzerhof
- OPTX: Handy's OPTX modification of Becke's exchange functional
- TPSS: The exchange functional of Tao, Perdew, Staroverov, and Scuser

and also many correlation functionals

Exact Exchange Method (EXX)

Exact Exchange for non-homogeneous systems + E_c in LDA or GGA

Main difficulty:

How to calculate the exchange potential $\upsilon_x(\vec{r}) = \frac{\delta E_x[\rho]}{\delta\rho(\vec{r})}$ ***?***

*M. Städele et al., Phys. Rev. B **59**, 10031 (1999).*

$$\boxed{E_x[\rho] = -\frac{1}{2}\sum_i \iint d\vec{r}d\vec{r}\,'\varphi_i^*(\vec{r})\left(\sum_j \frac{\varphi_j(\vec{r})\varphi_j^*(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\right)\varphi_i(\vec{r}\,')}$$

Problem: Explicit dependence of $E_x[\rho]$ (i.e., $\varphi_i[\rho]$) on ρ is unknown

Hybrid functionals

Hybrid functionals include a mixture of Hartree-Fock exchange with DFT exchange-correlation

EXAMPLE:

O3LYP: A three-parameter functional similar to B3LYP:

$$\mathbf{E_{xc}} = A^*E_X^{LSD}+(1-A)^*E_X^{HF}+B^*\Delta E_X^{OPTX}+C^*\Delta E_C^{LYP}+(1-C)E_C^{VWN}$$

Lead very often to better accuracy with experiments

Extensions of the DFT – Spin-polarized systems

U. Von Barth & L. Hedin, J. Phys. C ***5****, 1629 (1972)*

- For example, systems with odd number of electrons

$$\rho_\uparrow \neq \rho_\downarrow \qquad \rho = \rho_\uparrow + \rho_\downarrow$$

- Energy functional of both spin densities $E_{xc}[\rho_\uparrow,\rho_\downarrow]$

  Alternatively $E_{xc}[\rho, m]$ where $m = \rho_\uparrow - \rho_\uparrow$

  Spin polarization (magnetization)

- Exchange-correlation potential $\upsilon_{xc\sigma} = \dfrac{\delta E_{xc}[\rho_\sigma,\rho_{-\sigma}]}{\delta\rho_\sigma}$

$$\sigma = (\uparrow,\downarrow)$$

- **Local Spin Density Approximation (LSDA)**

Important for magnetism !

Extensions of the DFT

- **Relativistic DFT**

A. K. Rajagopal and J. Callaway, Phys. Rev. B ***7****, 1912 (1973)*

- Kinetic energy operator (free Dirac field)

$$\hat{h} = c\vec{\alpha}\cdot\vec{p} + \beta mc^2$$

- The ground-state energy is a functional of the ***four-vector current density*** $j_\mu(x)$

Extensions of the DFT

- **Finite - Temperature** $(T \neq 0)$

N. D. Mermin, Phys. Rev. ***137****, A1441 (1965)*

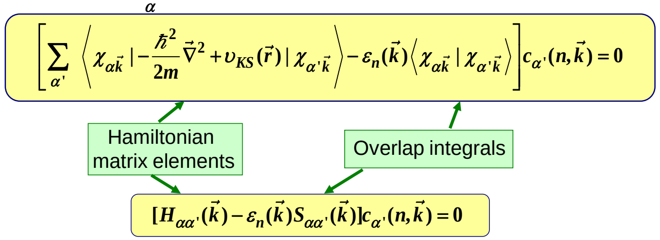
- Grand canonical ensemble, $\Omega = -k_B T \ln Tr[e^{(\mu\hat{N}-\hat{H})/k_BT}]$
- The grand potential of the a system at finite temperature is a functional of the density in the system at that temperature.

➡ **Applications of DFT in statistical physics**

Solution of the Kohn-Sham Equations

- Direct methods on a mesh in *r*-space
- Expansion of the Kohn-Sham orbitals in a basis $\{\chi_{\alpha\vec{k}}(\vec{r})\}$

$$\varphi_{n\vec{k}}(\vec{r}) = \mathbb{N}\sum_{\alpha} c_{\alpha}(n,\vec{k})\chi_{\alpha\vec{k}}(\vec{r})$$



$$\left[\sum_{\alpha'}\left\langle \chi_{\alpha\vec{k}} \,|\, -\frac{\hbar^2}{2m}\vec{\nabla}^2 + \upsilon_{KS}(\vec{r}) \,|\, \chi_{\alpha'\vec{k}}\right\rangle - \varepsilon_n(\vec{k})\left\langle \chi_{\alpha\vec{k}} \,|\, \chi_{\alpha'\vec{k}}\right\rangle\right] c_{\alpha'}(n,\vec{k}) = 0$$

Hamiltonian matrix elements

Overlap integrals

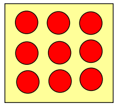
$$[H_{\alpha\alpha'}(\vec{k}) - \varepsilon_n(\vec{k})S_{\alpha\alpha'}(\vec{k})]c_{\alpha'}(n,\vec{k}) = 0$$

Eigenvalueproblem $\det[H_{\alpha\alpha'}(\vec{k}) - \varepsilon_n(\vec{k})S_{\alpha\alpha'}(\vec{k})] = 0$

➡ $\varepsilon_n(\vec{k})$ **Bandstructure**

Solution of the Kohn-Sham Equations – Survey of Methods

Multi-scattering Methods (All electron)



Muffin-tin form of the potential used to generate basis
Basis function – Numerically obtained wave function
inside the muffin-tin sphere +
augmented function outside

- **LAPW [FPLAPW] (Full Potential Linearized Augmented Plane Wave)**
  Plane waves outside muffin-tin spheres
  Considered to be the most accurate method
- **LMTO (Linearized Muffin-Tin Orbitals)**
  Hankel functions outside muffin-tin spheres
- **KKR (Kohn – Korringa – Rostoker)**
  Green's Function Method
  Very important for alloys (VCA, CPA)

Solution of the Kohn-Sham Equations – Survey of Methods involving basis

- **LCAO (Linear Combination of Atomic Orbitals)**
  All electron & pseudopotential
  Semiempirical Tight-Binding Method
- **Plane waves and pseudopotential**
  EMP – Empirical Pseudopotential Method
- **OPW (Orthogonalized Plane Waves)**
  All electron, plane waves orthogonalized to core states

Density Functional Calculations in Solids

Total energy of a solid: $E_{tot} = E_{el} + E_{ion-ion}$

$$E_{ion-ion} = \frac{e^2}{2}\sum_{nn'}\sum_{ss'}\frac{Z_s Z_{s'}}{|\vec{R}_n + \vec{\tau}_s - \vec{R}_{n'} - \vec{\tau}_{s'}|}$$

Lattice vectors $\vec{R}_n = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$ $\{\vec{a}_j\}$ - primitive translations
$\{\vec{\tau}_s\}$ - Basis vectors – positions of atoms in the unit cell

$$\boxed{E_{tot}(\{\varphi_i\},\{\vec{\tau}_s\},\{\vec{a}_j\}) = E_{el}(\{\varphi_i\},\{\vec{\tau}_s\},\{\vec{a}_j\}) + E_{ion-ion}(\{\vec{\tau}_s\},\{\vec{a}_j\})}$$

Density Functional Calculations in Solids

Equilibrium

Force on atom s:

$$\vec{F}_s = -\frac{\partial E_{tot}}{\partial \vec{\tau}_s}$$

- ● **Forces on all atoms disappear** $\vec{F}_s \equiv 0$

➡ **Equilibrium positions of atoms in the unit cell** $\{\vec{\tau}_s^{eq}\}$

- ● **Crystal is stress free** $\sigma_{\alpha\beta} = 0$

Stress tensor:

$$\sigma_{\alpha\beta} = -\frac{\partial E_{tot}}{\partial u_{\alpha\beta}}$$

$\alpha, \beta \in \{x, y, z\}$

$\vec{u}(\vec{r})$ -a vector field (deformation) that describes the displacement of every point in the solid

Before deformation: $\vec{r}$ After deformation: $\vec{r} + \vec{u}(\vec{r})$

Deformation tensor:

$$u_{\alpha\beta} = \frac{\partial u_\alpha}{\partial x_\beta}$$

➡ **Shape of the unit cell, primitive translations** $\{\vec{a}_j^{eq}\}$

DFT (LDA, GGA, EXX) for weakly correlated systems

Accuracy of Common DFT implementations

- ☐ **Accuracy of geometries is better than 0.1 A**
- ☐ **Accuracy of calculated energies (relative) is usually better than 0.2 eV**
  Very often better than 0.01 eV

☹ Band Gap problem !

☹ Unsatisfactory accuracy of discussed approximations for highly correlated systems
(mostly involving 3d – electrons)

Hellmann-Feynman Theorem

$\vec{F}_s$ **and** $\sigma_{\alpha\beta}$ **are usually calculated using Hellmann-Feynman Theorem**

H. Hellmann, "Einführung in die Quantenchemie" (Denieke, Leipzig, 1937), p.285

R. P. Feynman, Phys. Rev. 56, 340 (1939)

$$\frac{\partial E}{\partial \lambda} = \left\langle \psi(\lambda) \middle| \frac{\partial \hat{H}(\lambda)}{\partial \lambda} \middle| \psi(\lambda) \right\rangle$$

$\psi(\lambda)$ - Ground-state wavefunction of the Hamiltonian $\hat{H}(\lambda)$

Only these terms of the Hamiltonian contribute, which are explicitly dependent on the parameter λ .

DFT - further developements required

May we reach so-called chemical accuracy within DFT?

- **Exact Exchange Kohn-Sham Method – a step in this direction**
  - ➢ **Systematic improvement of existing Kohn-Sham schemes**
  - ➢ **Computationally very demanding**
    - **Bulk systems up to now**
    - **Implementations for larger systems going on**
- **Crucial - Better correlation energy functionals**

Software supporting DFT

- Abinit
- ADF
- AIMPRO
- Ascalaph Quantum
- Atomistix Toolkit
- Atompaw/PWPAW
- CADPAC
- CASTEP
- CP2K
- CPMD
- CRYSTAL06
- DACAPO
- DALTON
- deMon2K
- DFT++
- DMol3
- EXCITING
- Fireball
- FLEUR
- FSatom, dozens of free and proprietary DFT programs
- GAMESS (UK)
- GAMESS (US)
- GAUSSIAN
- GPAW
- HiLAPW
- JAGUAR
- MOLCAS
- MOLPRO
- MPQC
- NRLMOL
- NWChem
- OCTOPUS
- OpenMX
- ORCA
- ParaGauss [1]
- PARATEC [2]
- PARSEC
- PC GAMESS
- PLATO
- Parallel Quantum Solutions
- Priroda
- PWscf (Quantum-ESPRESSO)
- Q-Chem
- SIESTA
- Socorro
- Spartan
- S/PHI/nX
- SPR-KKR
- TURBOMOLE
- VASP
- WIEN

http://en.wikipedia.org

DFT - further developements required

Density functional theory has revolutionized the way scientists approach the electronic structure of atoms, molecules,and solid materials in physics, chemistry, and (nano)materials science

We are not at the end of this way!

Computational (Nano)Materials Science – The Era of Applied Quantum Mechanics

The properties of new and artificially structured materials can be predicted and explained

- *entirely by computations,*
- *using atomic numbers as the only input .*

Thank you !