



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

Summer Semester 2013

Lecture

Modeling of Nanostructures and Materials

Jacek A. Majewski

E-mail: Jacek.Majewski@fuw.edu.pl



Modeling of Nanostructures and Materials

Jacek A. Majewski

Lecture 3 – March 7, 2013

- Kohn-Sham realization of DFT
 - Functionals
 - Generalizations of K-S equations
 - Examples of calculations

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

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

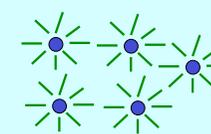
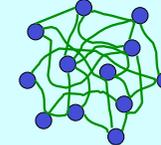
Kinetic energy of nuclei Nucleus-Nucleus interaction Electron-Electron interaction
 Kinetic energy of electrons Electron-Nucleus interaction

$$H\Psi = E\Psi$$

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

Density Functional Theory (DFT) in Kohn-Sham realization

Interacting particles Independent particles



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

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

$$\phi_1(\vec{x}_1) \phi_2(\vec{x}_2) \dots \phi_3(\vec{x}_{10^{23}})$$

This reduction is rigorously possible !

DFT- The Kohn- Sham Method

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

System of **interacting** electrons with density $\rho(\vec{r})$

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

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

"Fictitious" or Kohn-Sham reference system
 $T_s[\rho]$ $\rho_s(\vec{r}) = \rho(\vec{r})$

$$E[\rho] = \int d\vec{r} v_{\text{ext}}(\vec{r})\rho(\vec{r}) + T_s[\rho] + U[\rho] + E_x[\rho] + E_c[\rho]$$

- $\rho(\vec{r}) = \sum_{i=1}^N \varphi_i^*(\vec{r})\varphi_i(\vec{r})$ unknown!!!
- $T_s[\rho] = -\frac{\hbar^2}{2m} \sum_{i=1}^N \int d\vec{r} \varphi_i^*(\vec{r}) \nabla^2 \varphi_i(\vec{r})$
- $E_x[\rho] = -\frac{1}{2} \sum_i \iint d\vec{r} d\vec{r}' \varphi_i^*(\vec{r}) \left(\sum_j \frac{\varphi_j(\vec{r})\varphi_j^*(\vec{r}')}{|\vec{r}-\vec{r}'|} \right) \varphi_i(\vec{r}')$

The Kohn- Sham Method – The Kohn-Sham Equations

- Schrödinger-like equations with local potential

$$v_H(\vec{r}) = \frac{\delta U}{\delta \rho} = \int d\vec{r}' \frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}$$

$$\frac{\delta E_x[\rho]}{\delta \rho}$$

$$\frac{\delta E_c[\rho]}{\delta \rho}$$

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + v_{\text{ext}}(\vec{r}) + v_H(\vec{r}) + v_x(\vec{r}) + v_c(\vec{r}) \right] \varphi_i(\vec{r}) = \varepsilon_i \varphi_i(\vec{r})$$

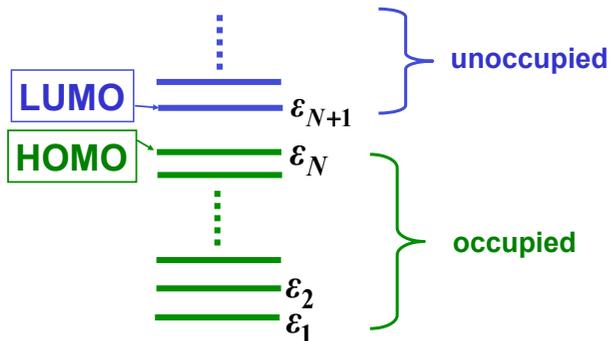
$$v_{\text{ext}}(\vec{r}) = -e^2 \sum_{s,n} \frac{Z_s}{|\vec{r}-\vec{r}_s - \vec{R}_n|}$$

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

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

The Kohn- Sham Method – 'Aufbau' principle

How to calculate one particle density?



The Kohn- Sham Method – The Total Energy

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

$$E = \sum_{i=1}^N \varepsilon_i - \frac{1}{2} \iint d\vec{r} d\vec{r}' \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} + E_x[\rho] + E_c[\rho] - \int d\vec{r} (v_x(\vec{r}) + v_c(\vec{r}))\rho(\vec{r})$$

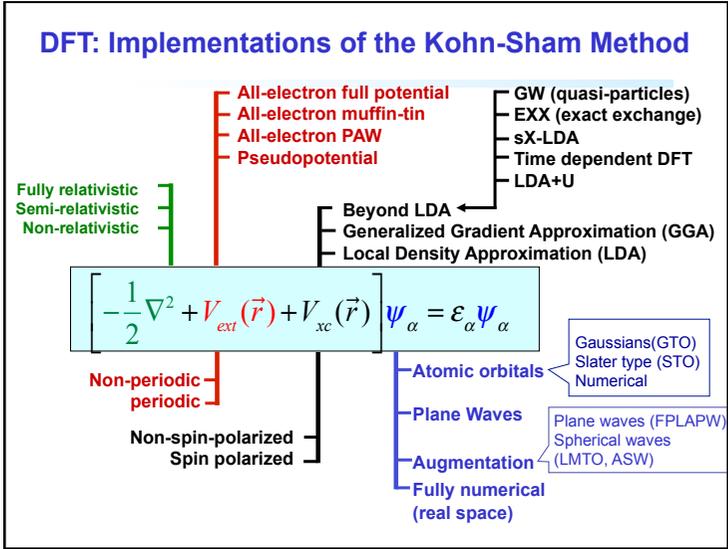
so-called double counting correction

Sum of the one-particle Kohn-Sham energies

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

Energy of the reference system

differs from the energy of 'real' system



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

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

Exchange energy per particle

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

- Dimensionless parameter characterizing density:

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

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

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

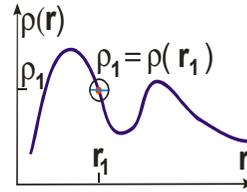
Correlation energy per particle

$$\epsilon_c^{\text{hom}}(r_s) = \begin{cases} A \ln r_s + B + C r_s \ln r_s + D r_s & \text{for } r_s < 1 \\ \gamma / (1 + \beta_1 \sqrt{r_s} + \beta_2 r_s) & \text{for } r_s \geq 1 \end{cases} \text{ [Ry]}$$

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

Local Density Approximation (LDA)

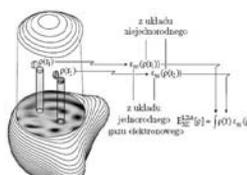
In atoms, molecules, and solids the electron density is not homogeneous



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

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

$$\epsilon_{xc}^{\text{hom}} = \epsilon_x^{\text{hom}} + \epsilon_c^{\text{hom}}$$



GGA - Gradient Corrections to LDA

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

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

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

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

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 is known.

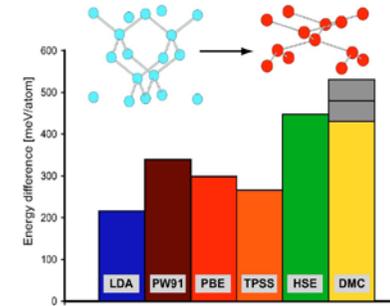
$$v_{xc} = \frac{\delta E_{xc}}{\delta \rho}$$

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 Scuseria

and also many correlation functionals

Accuracy Benchmarks of the different DFT Functionals



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

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

Exact Exchange Method (EXX)

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

Main difficulty:

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

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

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

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

Exact Exchange Method (EXX)

Solution: v_x is the first functional derivative of E_x

→ First order perturbation theory determines exactly $\frac{\delta E_x}{\delta \rho}$

→ Apply chain rule $v_x = \frac{\delta E_x}{\delta \rho} = \sum_i \frac{\delta E_x}{\delta \varphi_i} \times \frac{\delta \varphi_i}{\delta v_{KS}} \times \frac{\delta v_{KS}}{\delta \rho}$

$(\hat{T} + v_{KS})\varphi_i = \varepsilon_i \varphi_i$ (from E_x)

$\frac{\delta \varphi_i(\vec{r})}{\delta v_{KS}(\vec{r}')} = \sum_{j \neq i} \frac{\varphi_j^*(\vec{r}') \varphi_i(\vec{r})}{\varepsilon_i - \varepsilon_j} \varphi_j(\vec{r})$ (Perturbation theory)

$\frac{\delta \rho}{\delta v_{KS}} = \frac{\delta \rho}{\delta \varphi_i} \frac{\delta \varphi_i}{\delta v_{KS}} \equiv K \Rightarrow \frac{\delta v_{KS}}{\delta \rho} = K^{-1}$

Exact Exchange Method (EXX) - CONCLUSIONS

- Systematic improvement in comparison to LDA and GGA 😊
 - Numerically very costly in comparison to LDA and GGA 😞
 - Very good basis to search for better correlation energy functionals
The work is going on ! (J. Perdew) 😊
- ➔ **New generation of the energy functionals**

Hybrid functionals

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

EXAMPLE:

O3LYP: A three-parameter functional similar to B3LYP:

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

Lead very often to better accuracy with experiments

Extensions of the DFT

• 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 – Spin-polarized systems

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

- For example, systems with odd number of electrons
 $\rho_\uparrow \neq \rho_\downarrow$ $\rho = \rho_\uparrow + \rho_\downarrow$

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

Alternatively $E_{xc}[\rho, m]$ where

$$m = \rho_\uparrow - \rho_\downarrow$$

Spin polarization (magnetization)

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

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

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

Important for magnetism !

Extensions of the DFT

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

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

- Grand canonical ensemble, $\Omega = -k_B T \ln \text{Tr}[e^{(\mu\hat{N} - \hat{H})/k_B T}]$
- 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 $\{\chi_{\alpha\vec{k}}(\vec{r})\}$

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

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

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

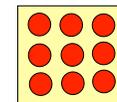
Solution of the Kohn-Sham Equations – Survey of Methods involving basis

- **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

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)

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

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

Density Functional Calculations in Solids

Equilibrium

Force on atom s :

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

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

→ 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 $\{\vec{a}_j^{eq}\}$

Hellmann-Feynman Theorem

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

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

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

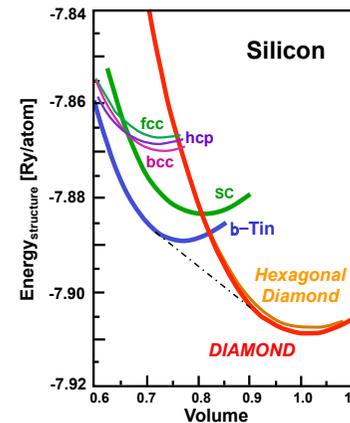
$$\frac{\partial E}{\partial \lambda} = \left\langle \psi(\lambda) \left| \frac{\partial \hat{H}(\lambda)}{\partial \lambda} \right| \psi(\lambda) \right\rangle$$

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

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

First (convincing) LDA Calculations: Stability of crystals and pressure induced phase transitions

M. T. Yin & M. L. Cohen, Phys. Rev. B 26, 5668 (1982)

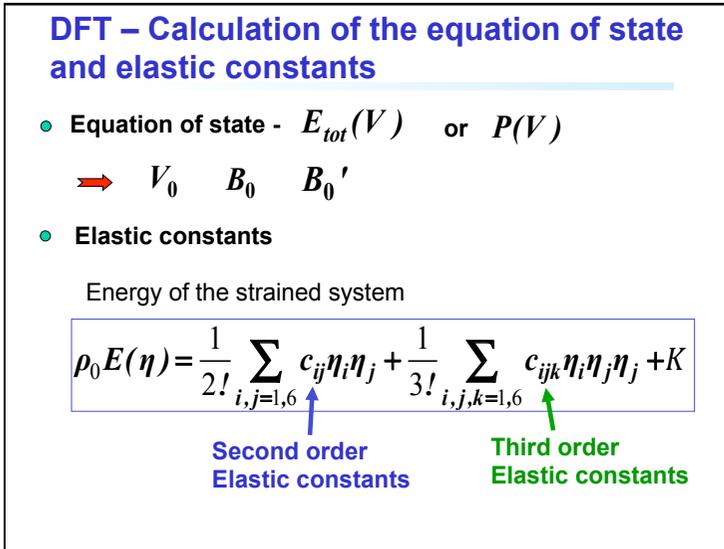
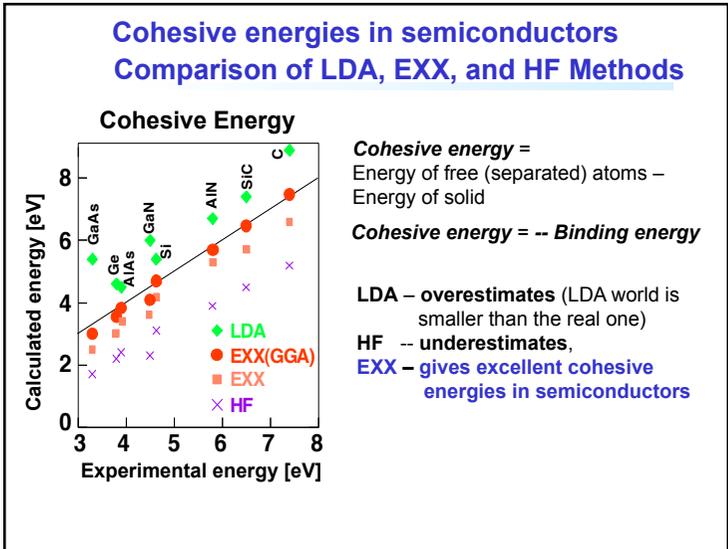
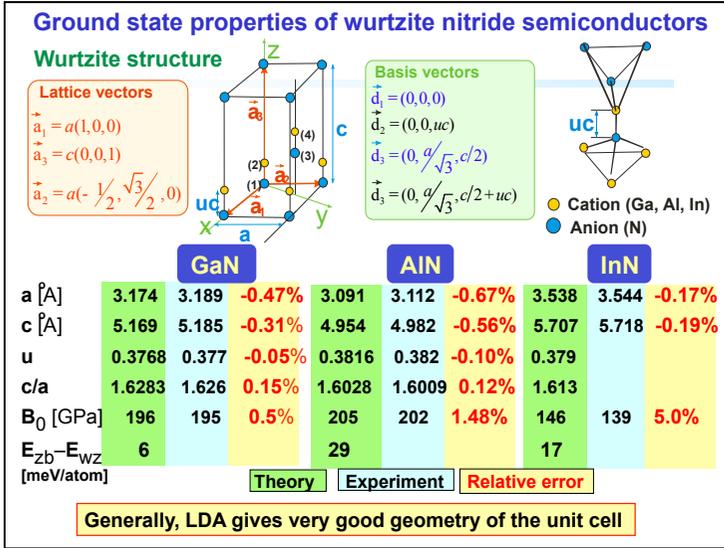
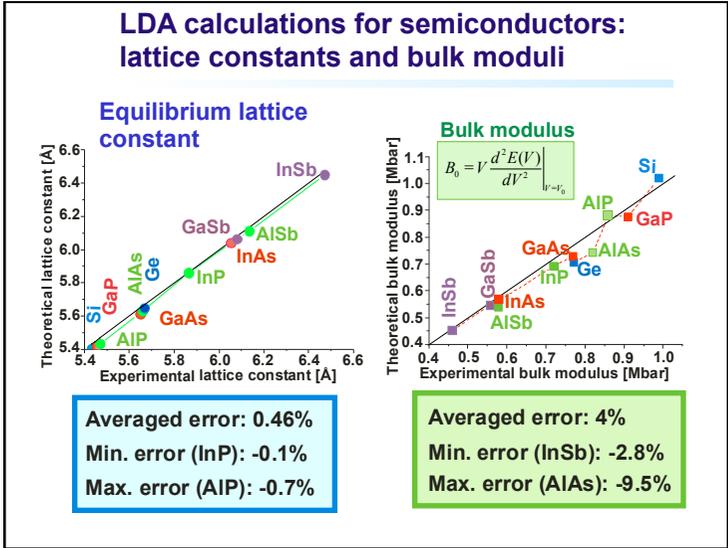


$$P_{transition} = \frac{E_{tot}^{(1)}(V_t^{(1)}) - E_{tot}^{(2)}(V_t^{(2)})}{V_t^{(2)} - V_t^{(1)}}$$

$$P = - \frac{\partial E}{\partial V}$$

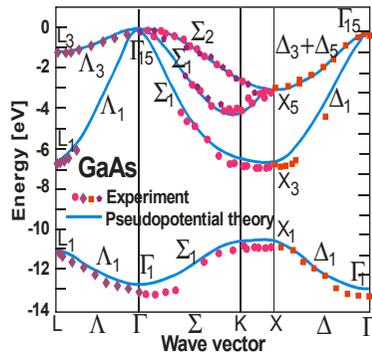
Interesting prediction:
Under high hydrostatic pressure and in low temperature silicon becomes superconducting!

Later on confirmed experimentally



LDA calculations in semiconductors

Valence bands for GaAs as determined from angle-resolved photoemission experiments and pseudopotential theory

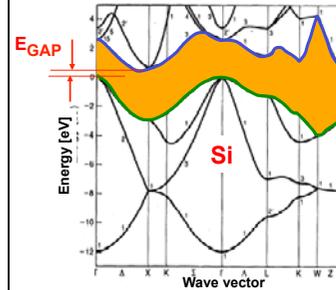


LDA gives very good description of the occupied s-p valence bands (4s & 4p) in semiconductors

Various methods of solving Kohn-Sham equations give very similar results

LDA calculations in semiconductors – Energy gap

Band structure of diamond silicon



$$E_{\text{GAP}} = E_{\text{LUMO}} - E_{\text{HOMO}}$$

Too small by factor of 2

Kohn-Sham gap

$$E_{\text{Gap}}^{\text{KS}} = \epsilon_{cbb}^{\text{KS}} - \epsilon_{vbt}^{\text{KS}}$$

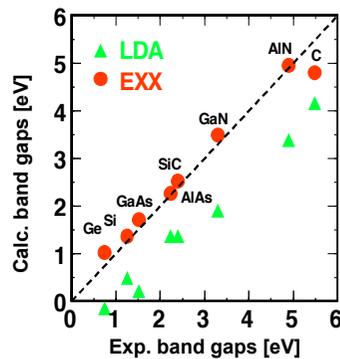
$$E_{\text{Gap}}^{\text{KS}} = \epsilon_{N+1}^{\text{KS}}(N) - \epsilon_N^{\text{KS}}(N)$$

- Relation of the Kohn-Sham gap to the *quasi-particle energy* (change of system energy caused by adding a particle) ?
 - Is the Kohn-Sham gap generally wrong, for description of one particle excitations ?
 - Does the error is caused by the approximation of the functionals ?
- “The band gap problem”

For all semiconductors and insulators, LDA (GGA) give energy gaps that are 40%-70% of experimental gaps

Fundamental band gaps in semiconductors: Local Density Approximation & Exact Exchange

Fundamental Band Gaps



EXX Method leads to Kohn-Sham gaps that agree very well with experiment

Large part of the error in the fundamental gaps is connected to the approximated functionals (LDA, GGA)

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

Accuracy of Common DFT implementations

- Accuracy of geometries is better than 0.1 Å
- 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)

DFT - further developments 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

DFT - further developments required

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

We are not at the end of this way!

Thank you!