

From Quantum Mechanics to Materials Design

The Basics of Density Functional Theory

Volker Eyert

Center for Electronic Correlations and Magnetism
Institute of Physics, University of Augsburg

December 03, 2010



Outline

- 1 Formalism
 - Definitions and Theorems
 - Approximations
- 2 Applications



Outline

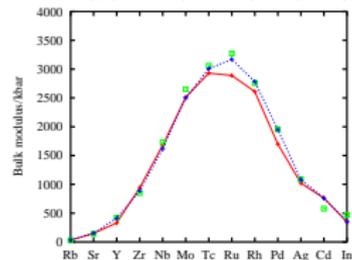
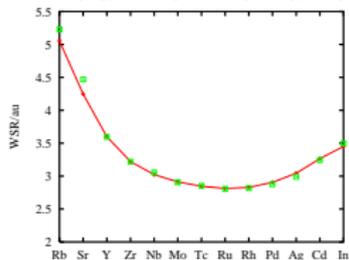
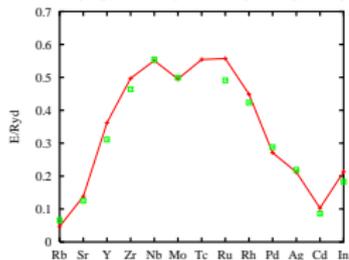
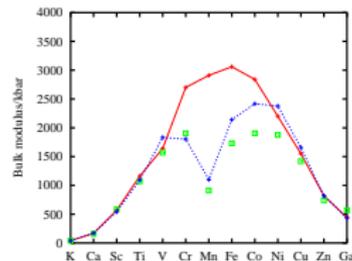
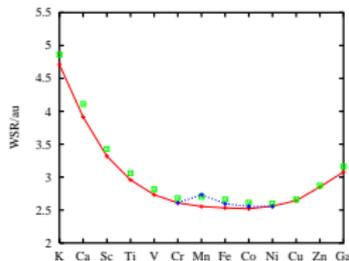
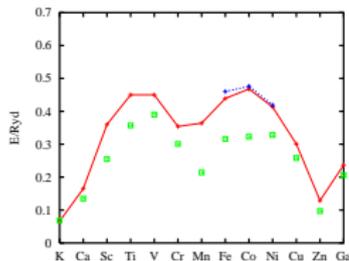
- 1 Formalism
 - Definitions and Theorems
 - Approximations

- 2 Applications



Calculated Electronic Properties

Moruzzi, Janak, Williams (IBM, 1978)



Cohesive Energies
 $\hat{=}$ Stability

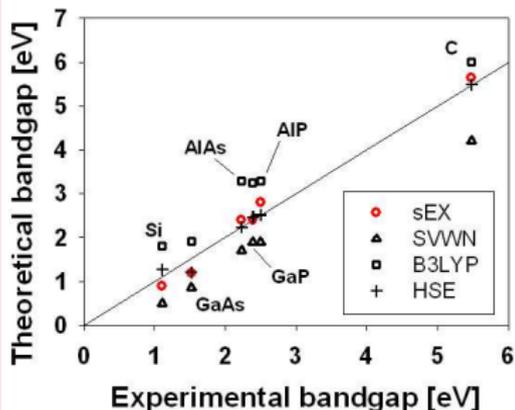
Wigner-Seitz-Rad.
 $\hat{=}$ Volume

Compressibility
 $\hat{=}$ Hardness



Energy band structures from screened HF exchange

Si, AlP, AlAs, GaP, and GaAs



Experimental and
theoretical bandgap
properties

Shimazaki, Asai,
JCP **132**, 224105 (2010)



Outline

- 1 **Formalism**
 - Definitions and Theorems
 - Approximations
- 2 Applications



Key Players

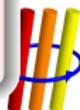
Hamiltonian (within Born-Oppenheimer approximation)

$$\begin{aligned} H &= H_{el,kin} + H_{el-el} + H_{ext} \\ &= \sum_i \left[-\frac{\hbar^2}{2m} \nabla_i^2 \right] + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\substack{i,j \\ j \neq i}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_i v_{ext}(\mathbf{r}_i) \end{aligned}$$

where

$$\sum_i v_{ext}(\mathbf{r}_i) = \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\substack{\mu\nu \\ \mu \neq \nu}} \frac{Z_\mu Z_\nu}{|\mathbf{R}_\mu - \mathbf{R}_\nu|} - \frac{e^2}{4\pi\epsilon_0} \sum_\mu \sum_i \frac{Z_\mu}{|\mathbf{R}_\mu - \mathbf{r}_i|}$$

μ : ions with charge Z_μ , i : electrons



Key Players

Electron Density Operator

$$\hat{\rho}(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) = \sum_{\alpha\beta} \chi_{\alpha}^*(\mathbf{r}) \chi_{\beta}(\mathbf{r}) \mathbf{a}_{\alpha}^{\dagger} \mathbf{a}_{\beta}$$

χ_{α} : single particle state



Key Players

Electron Density Operator

$$\hat{\rho}(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) = \sum_{\alpha\beta} \chi_{\alpha}^*(\mathbf{r}) \chi_{\beta}(\mathbf{r}) \mathbf{a}_{\alpha}^{\dagger} \mathbf{a}_{\beta}$$

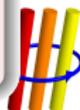
χ_{α} : single particle state

Electron Density

$$\rho(\mathbf{r}) = \langle \Psi | \hat{\rho}(\mathbf{r}) | \Psi \rangle = \sum_{\alpha} |\chi_{\alpha}(\mathbf{r})|^2 n_{\alpha}$$

$|\Psi\rangle$: many-body wave function, n_{α} : occupation number

$$\text{Normalization: } N = \int d^3\mathbf{r} \rho(\mathbf{r})$$



Key Players

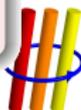
Functionals

Universal Functional (**independent of ionic positions!**)

$$F = \langle \Psi | H_{el,kin} + H_{el-el} | \Psi \rangle$$

Functional due to External Potential:

$$\begin{aligned} \langle \Psi | H_{ext} | \Psi \rangle &= \langle \Psi | \sum_i v_{ext}(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}_i) | \Psi \rangle \\ &= \int d^3\mathbf{r} v_{ext}(\mathbf{r}) \rho(\mathbf{r}) \end{aligned}$$



Authors

Pierre C. Hohenberg



Walter Kohn



Lu Jeu Sham



Hohenberg and Kohn, 1964: Theorems

1st Theorem

The external potential $v_{ext}(\mathbf{r})$ is determined, apart from a trivial constant, by the electronic ground state density $\rho(\mathbf{r})$.

2nd Theorem

The total energy functional $E[\rho]$ has a minimum equal to the ground state energy at the ground state density.



Hohenberg and Kohn, 1964: Theorems

1st Theorem

The external potential $v_{ext}(\mathbf{r})$ is determined, apart from a trivial constant, by the electronic ground state density $\rho(\mathbf{r})$.

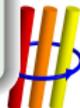
2nd Theorem

The total energy functional $E[\rho]$ has a minimum equal to the ground state energy at the ground state density.

Nota bene

Both theorems are formulated for the ground state!

- Zero temperature!
- No excitations!



Hohenberg and Kohn, 1964: Theorems

Maps

Ground state $|\Psi_0\rangle$ (from minimizing $\langle\Psi_0|H|\Psi_0\rangle$):

$$v_{\text{ext}}(\mathbf{r}) \xrightarrow{(1)} |\Psi_0\rangle \xrightarrow{(2)} \rho_0(\mathbf{r})$$



Hohenberg and Kohn, 1964: Theorems

Maps

Ground state $|\Psi_0\rangle$ (from minimizing $\langle\Psi_0|H|\Psi_0\rangle$):

$$v_{\text{ext}}(\mathbf{r}) \xrightarrow{(1)} |\Psi_0\rangle \xrightarrow{(2)} \rho_0(\mathbf{r})$$

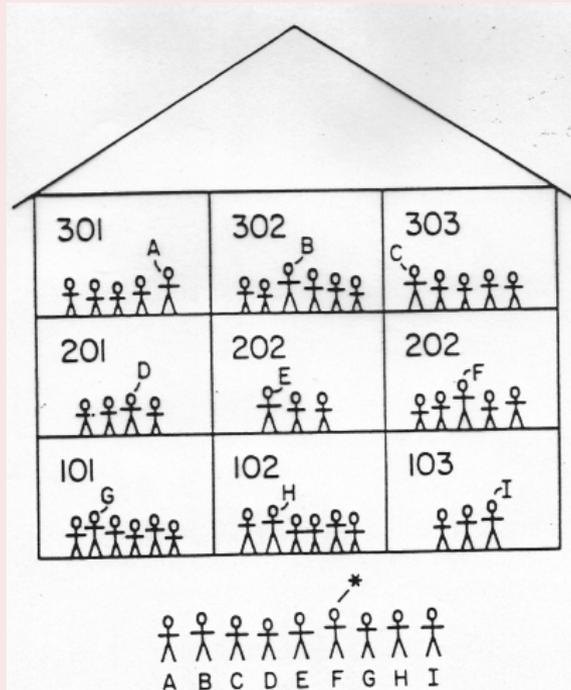
1st Theorem

$$v_{\text{ext}}(\mathbf{r}) \xleftrightarrow{(1)} |\Psi_0\rangle \xleftrightarrow{(2)} \rho_0(\mathbf{r})$$



Levy, Lieb, 1979-1983: Constrained Search

Percus-Levy partition



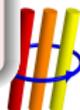
Levy, Lieb, 1979-1983: Constrained Search

Variational principle

$$\begin{aligned} E_0 &= \inf_{|\Psi\rangle} \langle \Psi | H | \Psi \rangle \\ &= \inf_{|\Psi\rangle} \langle \Psi | H_{el,kin} + H_{el-el} + H_{ext} | \Psi \rangle \\ &= \inf_{\rho(\mathbf{r})} \left[\inf_{|\Psi\rangle \in S(\rho)} \langle \Psi | H_{el,kin} + H_{el-el} | \Psi \rangle + \int d^3\mathbf{r} v_{ext}(\mathbf{r})\rho(\mathbf{r}) \right] \\ &=: \inf_{\rho(\mathbf{r})} \left[F_{LL}[\rho] + \int d^3\mathbf{r} v_{ext}(\mathbf{r})\rho(\mathbf{r}) \right] = \inf_{\rho(\mathbf{r})} E[\rho] \end{aligned}$$

$S(\rho)$: set of all wave functions leading to density ρ

$F_{LL}[\rho]$: Levy-Lieb functional, universal (independent of H_{ext})



Levy, Lieb, 1979-1983: Constrained Search

Levy-Lieb functional

$$\begin{aligned}
 F_{LL}[\rho] &= \inf_{|\Psi\rangle \in \mathcal{S}(\rho)} \langle \Psi | H_{el,kin} + H_{el-el} | \Psi \rangle \\
 &= \underbrace{T[\rho] + W_{xc}[\rho]} + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\
 &= G[\rho] + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}
 \end{aligned}$$

Functionals

- Kinetic energy funct.: $T[\rho]$ not known!
- Exchange-correlation energy funct.: $W_{xc}[\rho]$ not known!
- Hartree energy funct.: $\frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$ known!



Thomas, Fermi, 1927: Early Theory

Approximations

- ignore exchange-correlation energy functional:

$$W_{xc}[\rho] \stackrel{!}{=} 0$$

- approximate kinetic energy functional:

$$T[\rho] = C_F \int d^3\mathbf{r} (\rho(\mathbf{r}))^{\frac{5}{3}}, \quad C_F = \frac{3}{5} \frac{\hbar^2}{2m} (3\pi^2)^{\frac{2}{3}}$$

Failures

- 1 atomic shell structure missing
→ periodic table can not be described
- 2 no-binding theorem (Teller, 1962)



Kohn and Sham, 1965: Single-Particle Equations

Ansatz

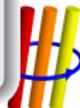
- 1 use different splitting of the functional $G[\rho]$

$$T[\rho] + W_{xc}[\rho] = G[\rho] \stackrel{!}{=} T_0[\rho] + E_{xc}[\rho]$$

- 2 reintroduce single-particle wave functions

Imagine: non-interacting electrons with same density

- Density: $\rho(\mathbf{r}) = \sum_{\alpha}^{\text{occ}} |\chi_{\alpha}(\mathbf{r})|^2$ known!
- Kinetic energy funct.:
 $T_0[\rho] = \sum_{\alpha}^{\text{occ}} \int d^3\mathbf{r} \chi_{\alpha}^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 \right] \chi_{\alpha}(\mathbf{r})$ known!
- Exchange-correlation energy funct.: $E_{xc}[\rho]$ not known!



Kohn and Sham, 1965: Single-Particle Equations

Euler-Lagrange Equations (Kohn-Sham Equations)

$$\frac{\delta E[\rho]}{\delta \chi_{\alpha}^*(\mathbf{r})} - \varepsilon_{\alpha} \chi_{\alpha}(\mathbf{r}) = \left[-\frac{\hbar^2}{2m} \nabla^2 + v_{\text{eff}}(\mathbf{r}) - \varepsilon_{\alpha} \right] \chi_{\alpha}(\mathbf{r}) \stackrel{!}{=} 0$$

- Effective potential: $v_{\text{eff}}(\mathbf{r}) := v_{\text{ext}}(\mathbf{r}) + v_H(\mathbf{r}) + v_{\text{xc}}(\mathbf{r})$
- Exchange-correlation potential: **not known!**

$$v_{\text{xc}}(\mathbf{r}) := \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho}$$

- „Single-particle energies“:
 ε_{α} (Lagrange-parameters, orthonormalization)



Kohn and Sham, 1965: Local Density Approximation

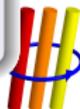
Be Specific!

- Approximate exchange-correlation energy functional

$$E_{xc}[\rho] = \int \rho(\mathbf{r}) \varepsilon_{xc}(\rho(\mathbf{r})) d^3\mathbf{r}$$

- Exchange-correlation energy density $\varepsilon_{xc}(\rho(\mathbf{r}))$
 - depends on **local** density only!
 - is calculated from **homogeneous, interacting** electron gas
- Exchange-correlation potential

$$v_{xc}(\rho(\mathbf{r})) = \left[\frac{\partial}{\partial \rho} \{ \rho \varepsilon_{xc}(\rho) \} \right]_{\rho=\rho(\mathbf{r})}$$



Kohn and Sham, 1965: Local Density Approximation

Homogeneous, Interacting Electron Gas

- Split

$$\varepsilon_{xc}(\rho) = \varepsilon_x(\rho) + \varepsilon_c(\rho)$$

- Exchange energy density $\varepsilon_x(\rho)$
(exact for homogeneous electron gas)

$$\varepsilon_x(\rho) = -\frac{3}{4\pi} \frac{e^2}{4\pi\epsilon_0} (3\pi^2\rho)^{\frac{1}{3}}$$

$$v_x(\rho) = -\frac{1}{\pi} \frac{e^2}{4\pi\epsilon_0} (3\pi^2\rho)^{\frac{1}{3}}$$

- Correlation energy density $\varepsilon_c(\rho)$
Calculate and parametrize
 - RPA (Hedin, Lundqvist; von Barth, Hedin)
 - QMC (Ceperley, Alder; Vosko, Wilk, Nusair; Perdew, Wang)



Kohn and Sham, 1965: Local Density Approximation

Limitations and Beyond

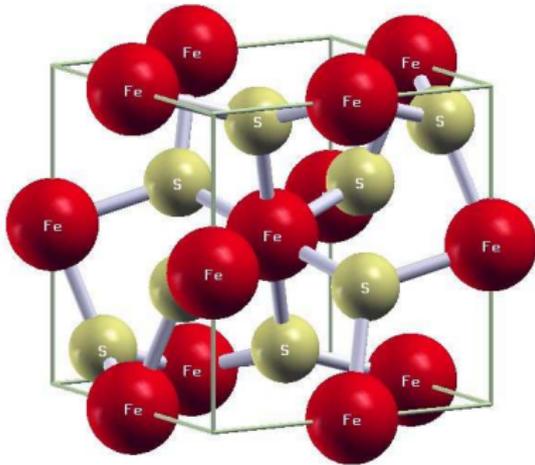
- LDA **exact** for homogeneous electron gas (within QMC)
- **Spatial variation** of ρ **ignored**
 - include $\nabla\rho(\mathbf{r}), \dots$
 - Generalized Gradient Approximation (GGA)
- Cancellation of **self-interaction** in $v_{Hartree}(\rho(\mathbf{r}))$ and $v_x(\rho(\mathbf{r}))$ **violated** for $\rho = \rho(\mathbf{r})$
 - Self-Interaction Correction (SIC)
 - Exact Exchange (EXX),
Optimized Effective Potential (OEP)
 - Screened Exchange (SX)



Outline

- 1 Formalism
 - Definitions and Theorems
 - Approximations
- 2 Applications



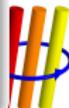
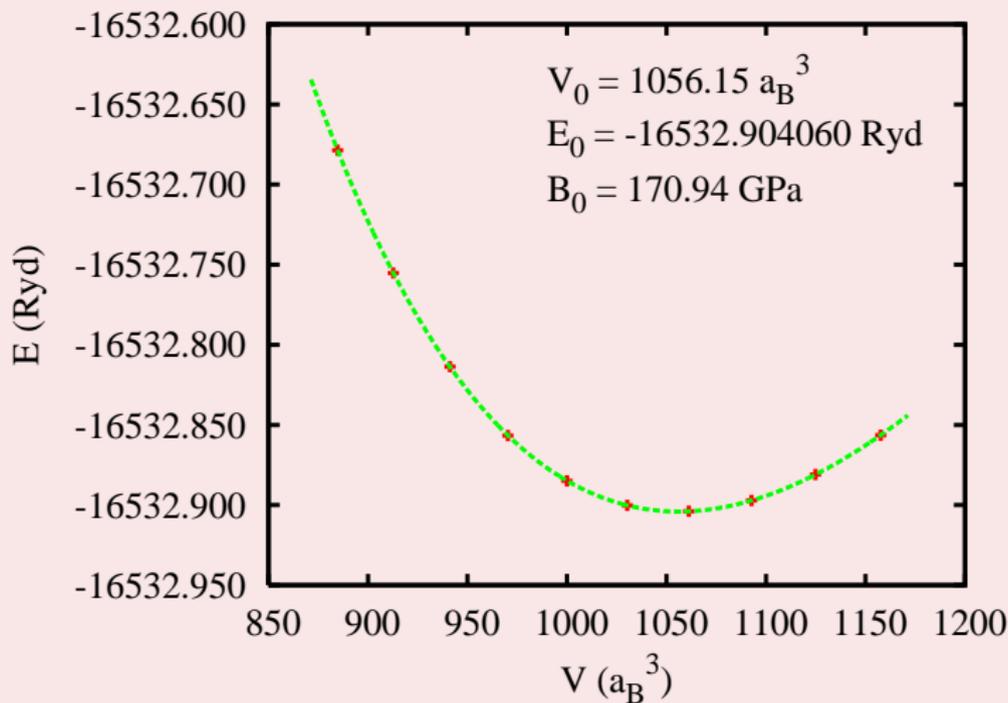
Iron Pyrite: FeS_2 

Pyrite

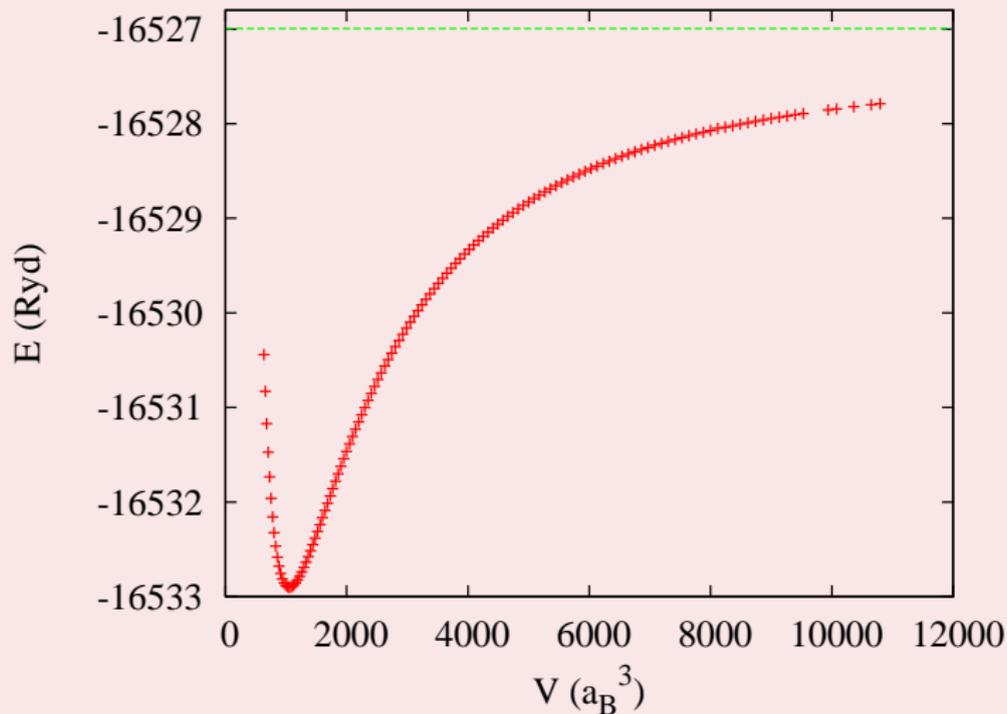
- $Pa\bar{3} (T_h^6)$
- $a = 5.4160 \text{ \AA}$
- “NaCl structure” sublattices occupied by
 - iron atoms
 - sulfur pairs
- sulfur pairs $\parallel \langle 111 \rangle$ axes
- $x_S = 0.38484$
- rotated FeS_6 octahedra



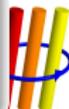
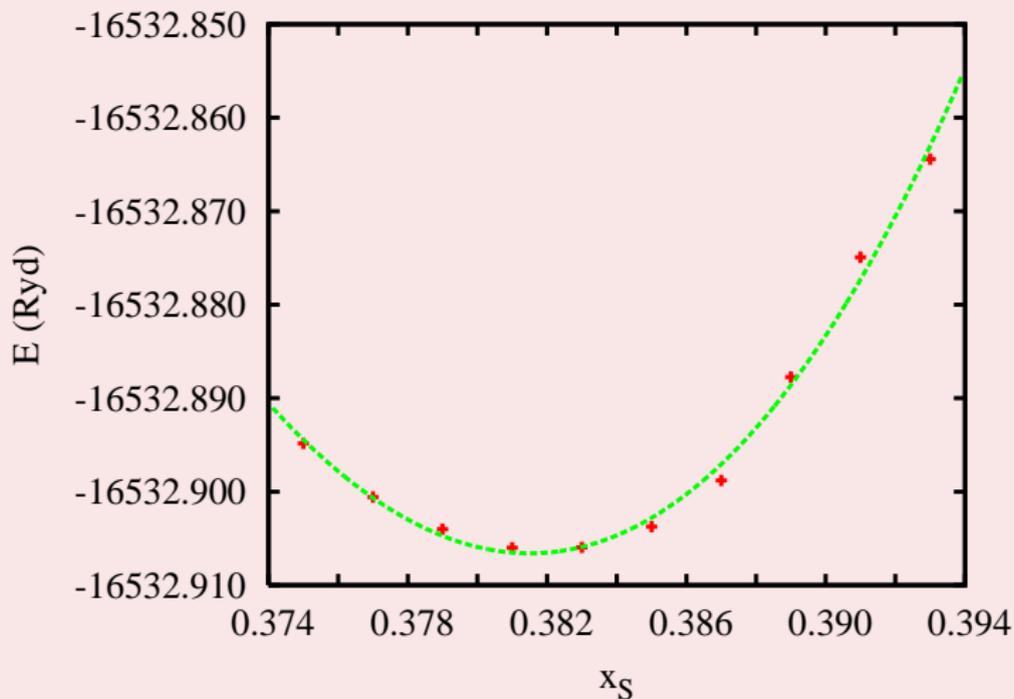
FeS₂: Equilibrium Volume and Bulk Modulus



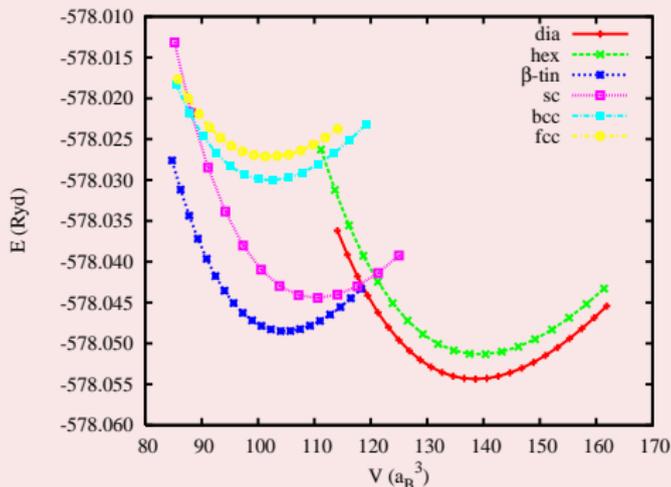
FeS₂: From Atoms to the Solid



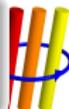
FeS₂: Structure Optimization

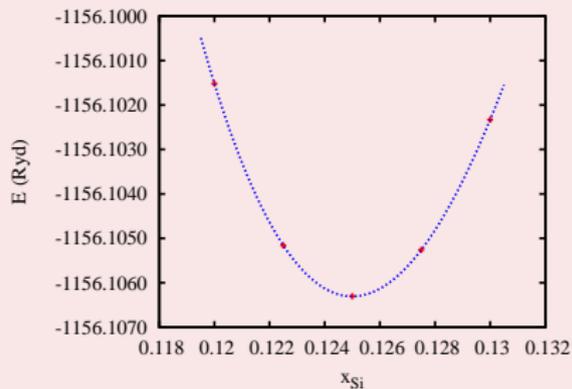
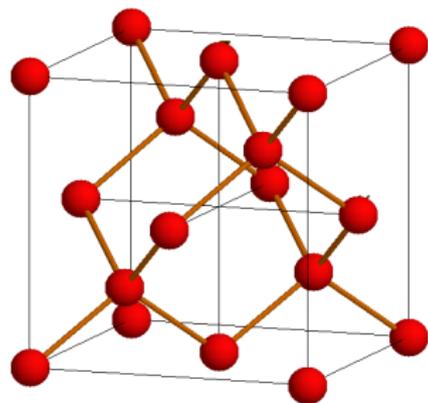


Phase Stability in Silicon



- diamond structure most stable
- pressure induced phase transition to β -tin structure



LTO(Γ)-Phonon in Silicon

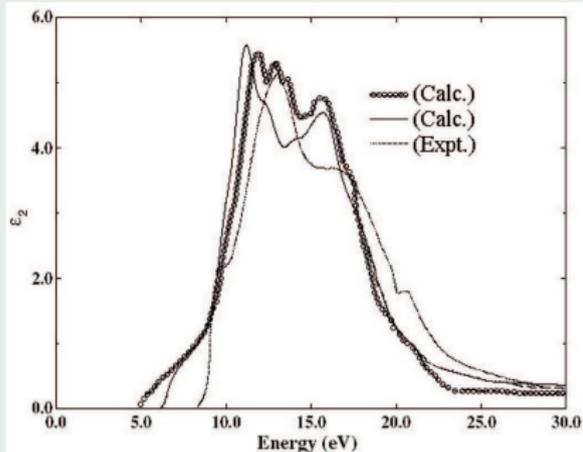
- phonon frequency: $f_{calc} = 15.34$ THz ($f_{exp} = 15.53$ THz)



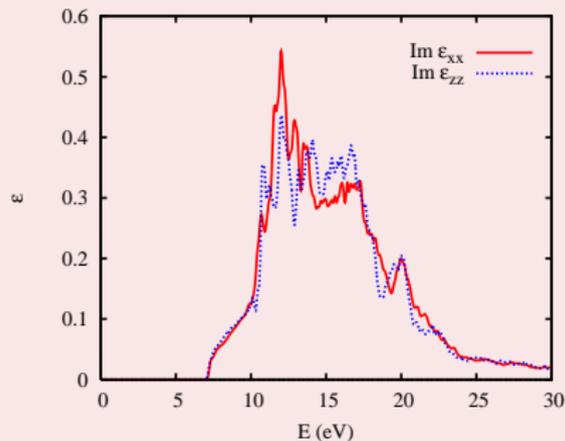
Dielectric Function of Al_2O_3

Imaginary Part

FLAPW, Hosseini *et al.*, 2005
FPLMTO, Ahuja *et al.*, 2004



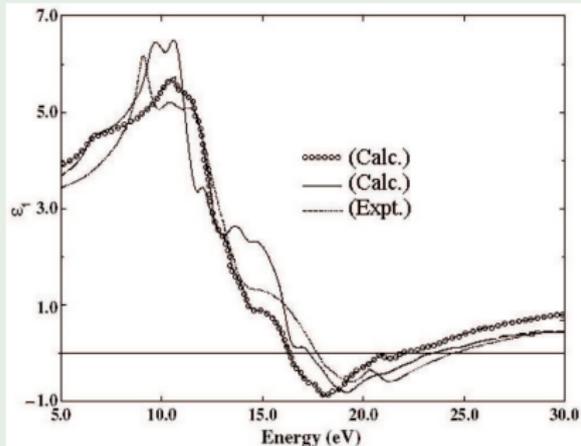
FPASW



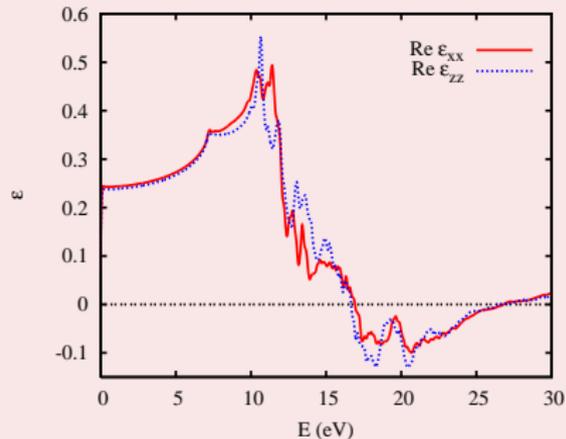
Dielectric Function of Al_2O_3

Real Part

FLAPW, Hosseini *et al.*, 2005
FPLMTO, Ahuja *et al.*, 2004

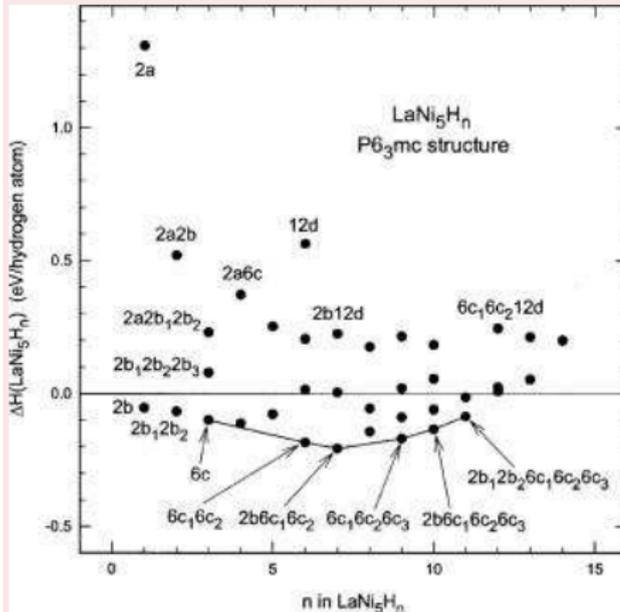


FPASW



Hydrogen site energetics in LaNi_5H_n and LaCo_5H_n

Enthalpy of hydride formation in LaNi_5H_n



$$\Delta H_{min} = -40 \text{ kJ/molH}_2$$

for H at $2b6c_16c_2$

agrees with

- neutron data

- calorimetry:

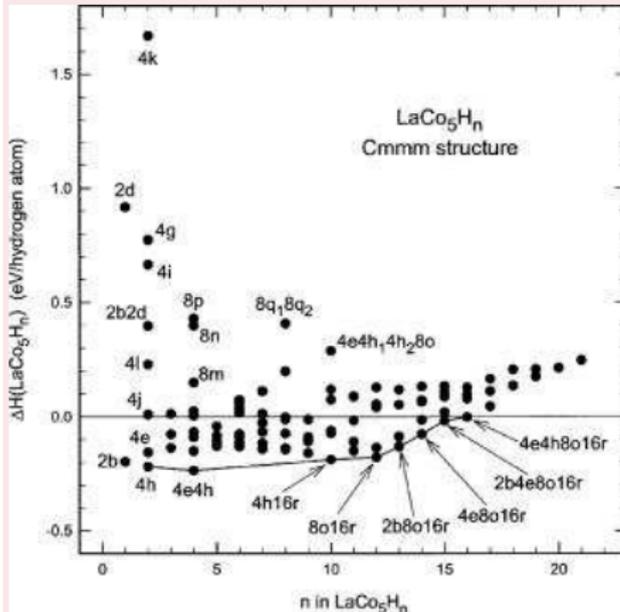
$$\Delta H_{min} = -\left(\frac{32}{37}\right) \text{ kJ/molH}_2$$

Herbst, Hector,
APL **85**, 3465 (2004)



Hydrogen site energetics in LaNi_5H_n and LaCo_5H_n

Enthalpy of hydride formation in LaCo_5H_n



$$\Delta H_{min} = -45.6 \text{ kJ/molH}_2$$

for H at 4e4h

agrees with

- neutron data
- calorimetry:

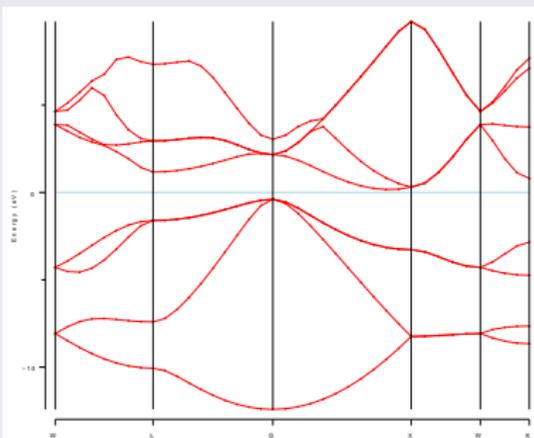
$$\Delta H_{min} = -45.2 \text{ kJ/molH}_2$$

Herbst, Hector,
APL **85**, 3465 (2004)



Problems of the Past

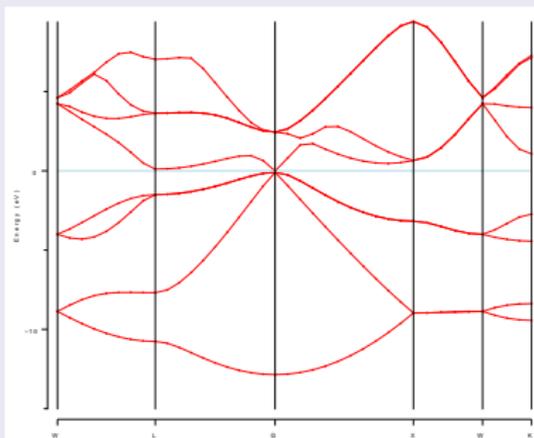
Si



Si bandgap

- exp: 1.11 eV
- GGA: 0.57 eV

Ge



Ge bandgap

- exp: 0.67 eV
- GGA: 0.09 eV

Critical review of the Local Density Approximation

Limitations and Beyond

- **Self-interaction cancellation** in $v_{Hartree} + v_x$ **violated**
- **Repair** using exact Hartree-Fock exchange functional
→ class of hybrid functionals

- PBE0

$$E_{xc}^{PBE0} = \frac{1}{4}E_x^{HF} + \frac{3}{4}E_x^{PBE} + E_c^{PBE}$$

- HSE03, HSE06

$$E_{xc}^{HSE} = \frac{1}{4}E_x^{HF, sr, \mu} + \frac{3}{4}E_x^{PBE, sr, \mu} + E_x^{PBE, lr, \mu} + E_c^{PBE}$$

based on decomposition of Coulomb kernel

$$\frac{1}{r} = S_\mu(r) + L_\mu(r) = \frac{\operatorname{erfc}(\mu r)}{r} + \frac{\operatorname{erf}(\mu r)}{r}$$

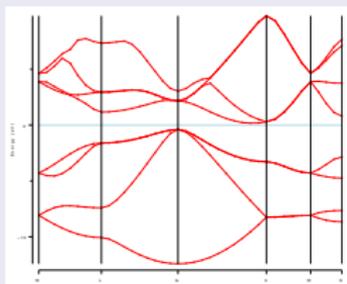


Critical review of the Local Density Approximation

Limitations and Beyond

- **Self-interaction cancellation** in $v_{Hartree} + v_x$ **violated**
- **Repair** using exact Hartree-Fock exchange functional
→ class of hybrid functionals

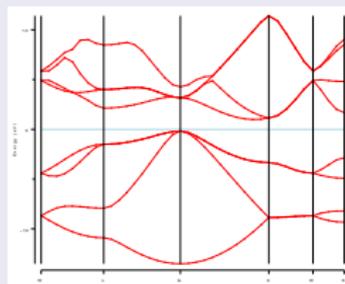
GGA



Si bandgap

- exp: 1.11 eV
- GGA: 0.57 eV
- HSE: 1.15 eV

HSE

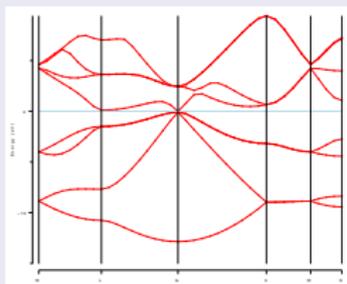


Critical review of the Local Density Approximation

Limitations and Beyond

- **Self-interaction cancellation** in $v_{Hartree} + v_x$ **violated**
- **Repair** using exact Hartree-Fock exchange functional
→ class of hybrid functionals

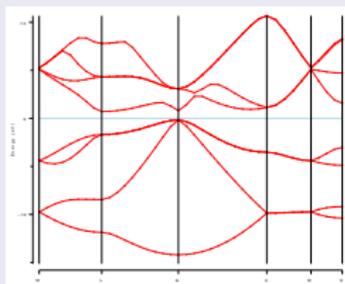
GGA



Ge bandgap

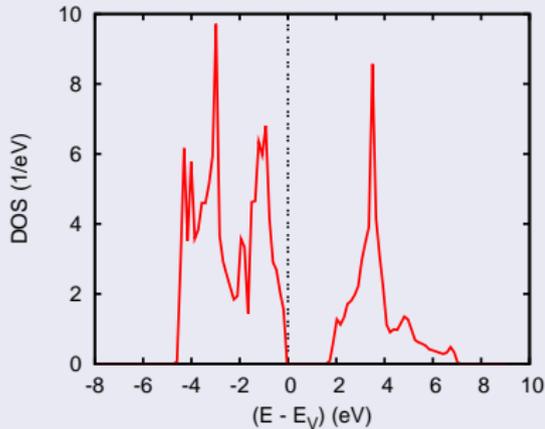
- exp: 0.67 eV
- GGA: 0.09 eV
- HSE: 0.66 eV

HSE



Critical review of the Local Density Approximation

GGA



SrTiO₃ Bandgap

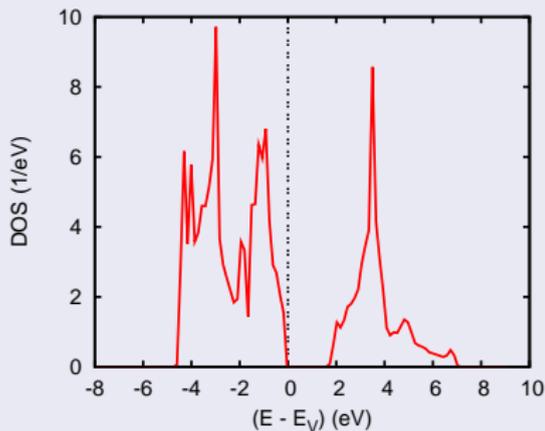
GGA: ≈ 1.6 eV,

exp.: 3.2 eV

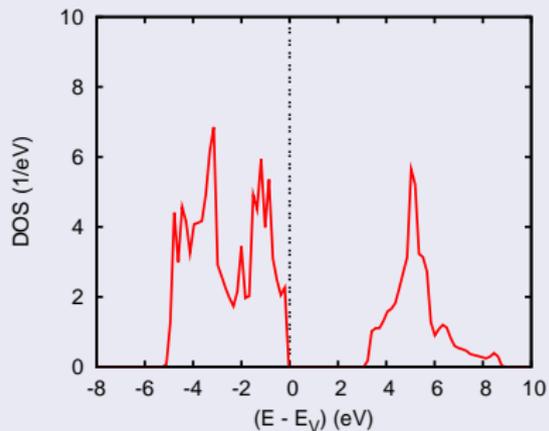


Critical review of the Local Density Approximation

GGA



HSE



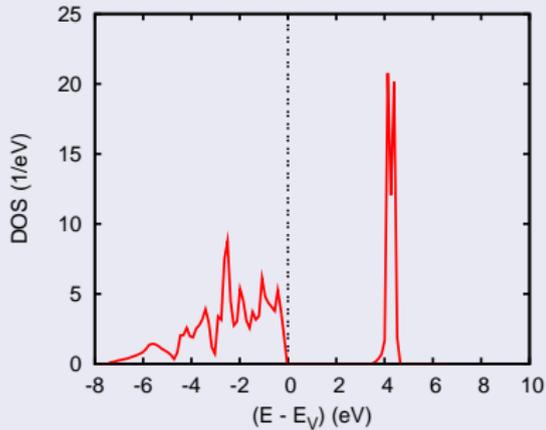
SrTiO₃ Bandgap

GGA: ≈ 1.6 eV, HSE: ≈ 3.1 eV, exp.: 3.2 eV



LaAlO₃

GGA

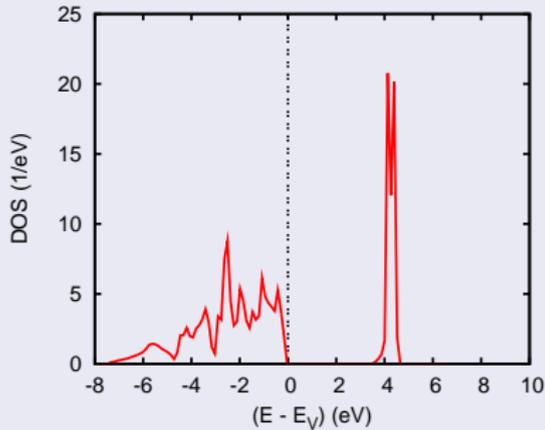
LaAlO₃ BandgapGGA: ≈ 3.5 eV,

exp.: 5.6 eV

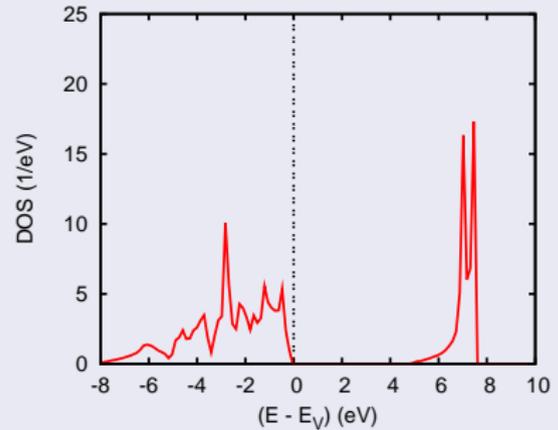


LaAlO₃

GGA



HSE

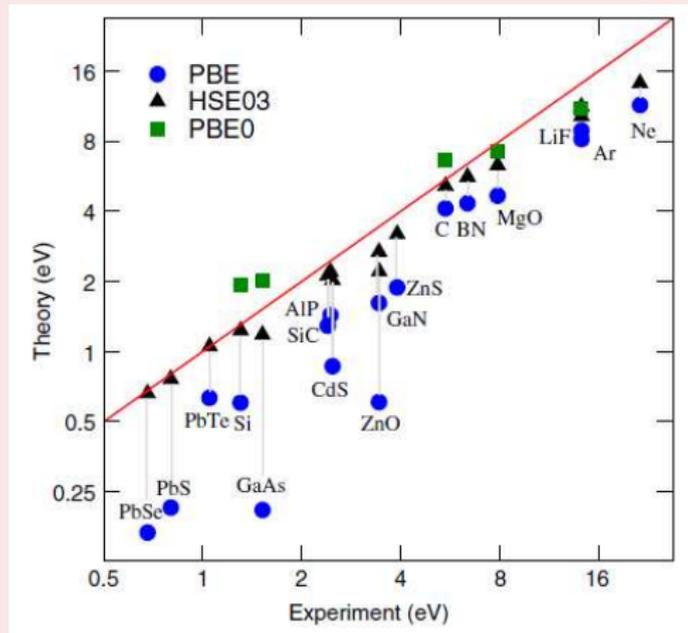
LaAlO₃ Bandgap

GGA: ≈ 3.5 eV, HSE: ≈ 5.0 eV, exp.: 5.6 eV



Critical review of the Local Density Approximation

Calculated vs. experimental bandgaps



Summary

Density Functional Theory

- exact (!) mapping of full many-body problem to an effective single-particle problem

Local Density Approximation

- approximative treatment of exchange (!) and correlation
- considerable improvement: exact treatment of exchange

Applications

- very good agreement DFT/Exp. in numerous cases
- theory meets industry

Further Reading

- V. Eyert and U. Eckern, *PhiuZ* **31**, 276 (2000)



Summary

Density Functional Theory

- exact (!) mapping of full many-body problem to an effective single-particle problem

Local Density Approximation

- approximative treatment of exchange (!) and correlation
- considerable improvement: exact treatment of exchange

Applications

- very good agreement DFT/Exp. in numerous cases
- theory meets industry

Further Reading

- V. Eyert and U. Eckern, *Phys. Rev. Lett.* **31**, 276 (2000)



Summary

Density Functional Theory

- exact (!) mapping of full many-body problem to an effective single-particle problem

Local Density Approximation

- approximative treatment of exchange (!) and correlation
- considerable improvement: exact treatment of exchange

Applications

- very good agreement DFT/Exp. in numerous cases
- theory meets industry

Further Reading

- V. Eyert and U. Eckern, *Phys. Rev. Lett.* **31**, 276 (2000)



Summary

Density Functional Theory

- exact (!) mapping of full many-body problem to an effective single-particle problem

Local Density Approximation

- approximative treatment of exchange (!) and correlation
- considerable improvement: exact treatment of exchange

Applications

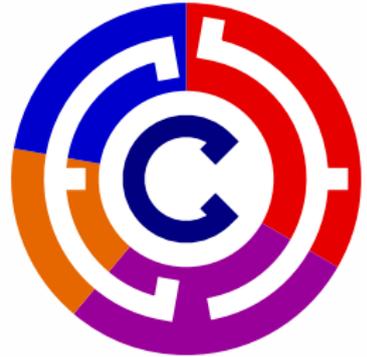
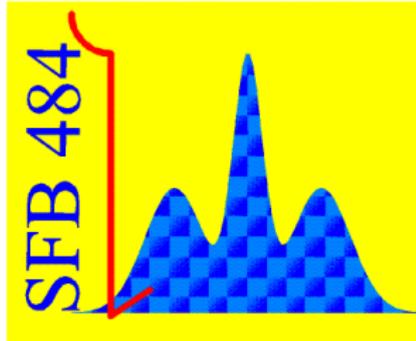
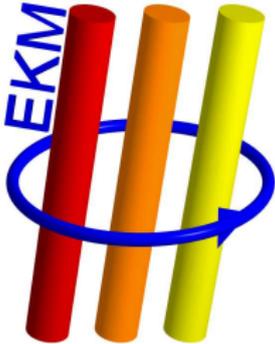
- very good agreement DFT/Exp. in numerous cases
- theory meets industry

Further Reading

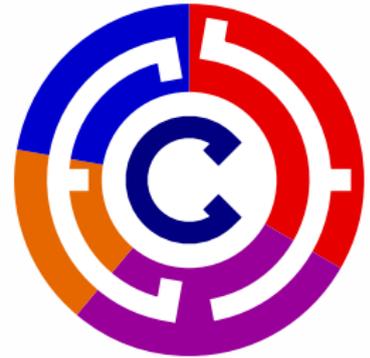
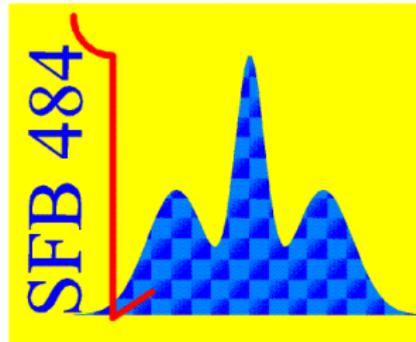
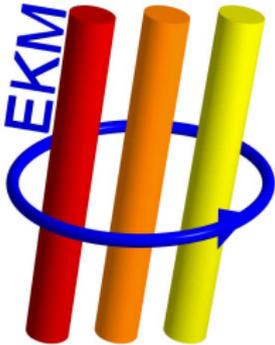
- V. Eyert and U. Eckern, *PhiuZ* **31**, 276 (2000)



Acknowledgments



Acknowledgments



Augsburg/München

Thank You for Your Attention!

