From Quantum Mechanics to Materials Design

The Basics of Density Functional Theory

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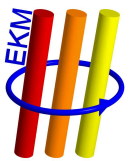

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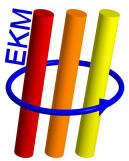

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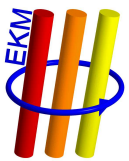

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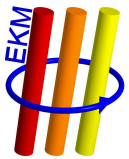


Key Players

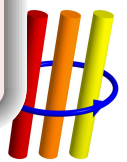
Hamiltonian (within Born-Oppenheimer approximation)

$$H_0 = \sum_i \left[-\frac{\hbar^2}{2m} \nabla_i^2 \right] + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\substack{i,j \\ j \neq i}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_i v_{ext}(\mathbf{r}_i)$$

where

$$\sum_i v_{ext}(\mathbf{r}_i) = \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{\substack{\mu\nu \\ \mu \neq \nu}} \frac{Z_{val,\mu} Z_{val,\nu}}{|\mathbf{R}_\mu - \mathbf{R}_\nu|} + \sum_i \left[\sum_\mu V_{ion-el}(\mathbf{r}_i - \mathbf{R}_\mu) \right]$$

$\mathbf{R}_\mu$: ionic positions, $\mathbf{r}_i$: positions of electrons
$Z_{val,\mu}$: number of valence electrons provided by μ'th ion

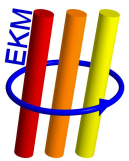


Key Players

Electron Density Operator

$$\begin{aligned}\hat{\rho}(\mathbf{r}) &= \sum_{\sigma}\hat{\rho}_{\sigma}(\mathbf{r}) = \sum_{\sigma}\sum_{\alpha\beta}\chi^{*}_{\alpha;\sigma}(\mathbf{r})\chi_{\beta;\sigma}(\mathbf{r})a^{+}_{\alpha}a_{\beta} \\ &= \sum_{\sigma}\sum_{i=1}^{N}\delta(\mathbf{r}-\mathbf{r}_i)\delta_{\sigma\sigma_i}\end{aligned}$$

χ_{α}: single particle state



Key Players

Electron Density

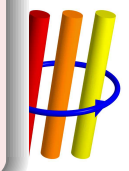
$$\rho(\mathbf{r}) = \sum_\sigma \rho_\sigma(\mathbf{r}) \quad = \quad \sum_\sigma \langle \Psi | \hat{\rho}_\sigma(\mathbf{r}) | \Psi \rangle = \sum_\sigma \sum_\alpha |\chi_{\alpha;\sigma}(\mathbf{r})|^2 n_\alpha$$

$|\Psi\rangle$: many-body wave function
χ_α: single particle state
n_α: occupation number

ground state, non-interacting particles:
$|\Psi\rangle \rightarrow$ Slater determinant, $n_\alpha = 0, 1$

normalization:

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



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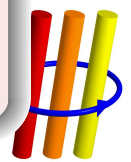
Universal Functional

$$F = \langle \Psi | H_{el,kin}(\{\mathbf{r}_i\}) + H_{el-el}(\{\mathbf{r}_i\}) | \Psi \rangle$$

Functional due to External Potential

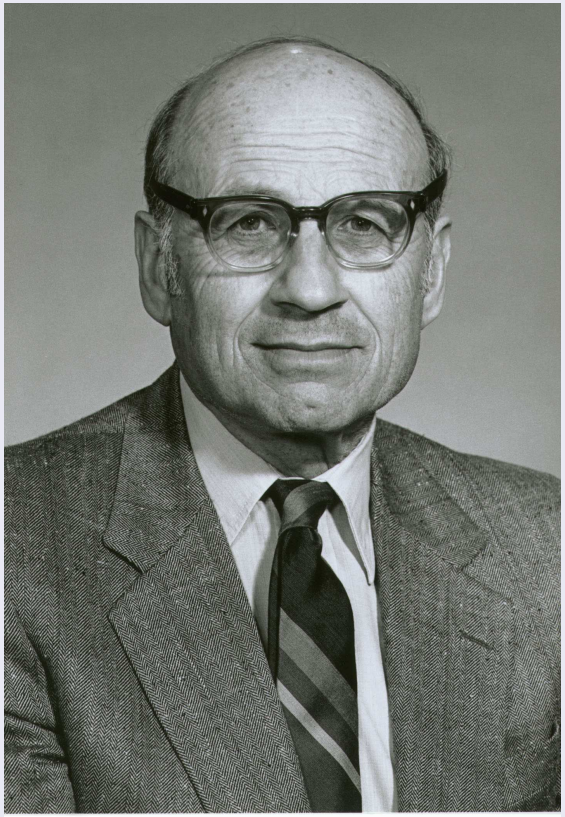
$$\langle \Psi | H_{ext}(\{\mathbf{r}_i\}) | \Psi \rangle = \int d^3\mathbf{r}\, v_{ext}(\mathbf{r}) \rho(\mathbf{r})$$



Density Functional Theory, Local Density Approx.

Pierre C. Hohenberg

Walter Kohn



Lu Jeu Sham

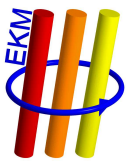
Hohenberg and Kohn, 1964: Theorems

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.



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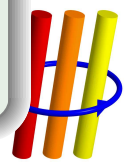
Nota bene

Both theorems are formulated for the ground state!

- Zero temperature!
- No excitations!

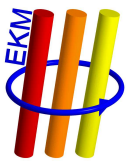


Hohenberg and Kohn, 1964: Theorems

Maps

Ground state $|\Psi_0\rangle$ (from minimizing $\langle\Psi_0|H_0|\Psi_0\rangle$):

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



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1st Theorem

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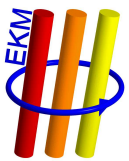
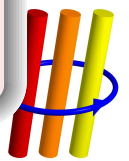


Levy, Lieb, 1979-1983: Constrained Search

Variational principle

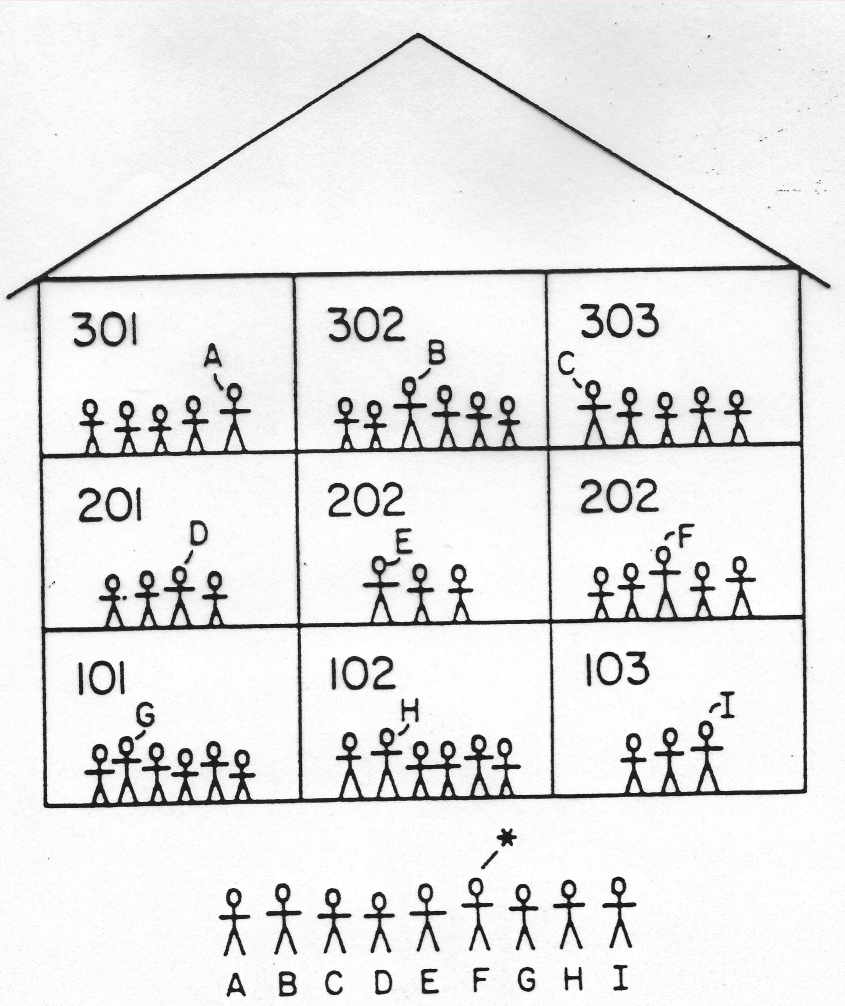
$$
\begin{aligned}
E_0 &= \inf_{|\Psi\rangle} \langle\Psi|H_0|\Psi\rangle \\
&= \inf_{|\Psi\rangle} \langle\Psi|H_{el,kin} + H_{el-el} + H_{ext}|\Psi\rangle \\
&= \inf_{\rho(\mathbf{r})} \left[\inf_{|\Psi\rangle\in S(\rho)} \langle\Psi|H_{el,kin} + H_{el-el}|\Psi\rangle + \int d^3\mathbf{r}\, v_{ext}(\mathbf{r})\rho(\mathbf{r}) \right] \\
&=: \inf_{\rho(\mathbf{r})} \left[F_{LL}[\rho] + \int d^3\mathbf{r}\, v_{ext}(\mathbf{r})\rho(\mathbf{r}) \right] = \inf_{\rho(\mathbf{r})} E[\rho]
\end{aligned}
$$

$S(\rho)$: 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

Percus-Levy partition



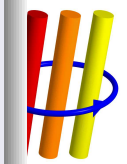
Levy, Lieb, 1979-1983: Constrained Search

Levy-Lieb functional

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

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:

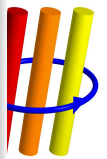
$$W_{xc}[\rho] \stackrel{!}{=} 0$$

- approximate kinetic energy functional:

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

Failures

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



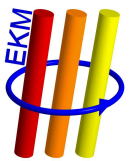
Kohn and Sham, 1965: Single-Particle Equations

Test-Case: Non-Interacting Electrons

$$E[\rho] = T_0[\rho] + \int d^3\mathbf{r}\, v_{ext}(\mathbf{r})\rho(\mathbf{r})$$

$$\rho_0(\mathbf{r}) = \sum_\sigma \sum_\alpha^{occ} |\chi_{\alpha;\sigma}(\mathbf{r})|^2$$

$$T_0[\rho] = \sum_\sigma \sum_\alpha^{occ} \int d^3\mathbf{r}\, \chi^*_{\alpha;\sigma}(\mathbf{r}) \left[-\frac{\hbar^2}{2m}\nabla^2\right] \chi_{\alpha;\sigma}(\mathbf{r})$$



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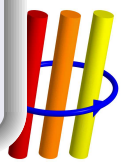
$$E[\rho] = T_0[\rho] + \int d^3\mathbf{r}\, v_{ext}(\mathbf{r})\rho(\mathbf{r})$$

Euler-Lagrange Equations

$$\frac{\delta E[\rho]}{\delta \rho} - \mu = \frac{\delta T_0[\rho]}{\delta \rho} + v_{ext}(\mathbf{r}) - \mu \stackrel{!}{=} 0$$

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

μ: charge conservation, „chemical potential“
ε_α: orthonormalization, „single-particle energies“



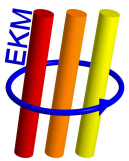
Kohn and Sham, 1965: Single-Particle Equations

Interacting Electrons

1. reintroduce single-particle wave functions
2. use different splitting of the functional $G[\rho]$

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

$T_0[\rho]$ is known, $E_{xc}[\rho]$ is not known!



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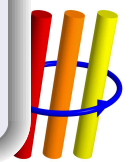
$T_0[\rho]$ is known, $E_{xc}[\rho]$ is not known!

Euler-Lagrange Equations

$$\frac{\delta E[\rho]}{\delta \rho} - \mu = \frac{\delta T_0[\rho]}{\delta \rho} + \underbrace{v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r})}_{v_{eff}(\mathbf{r})} - \mu \stackrel{!}{=} 0$$

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

μ: charge conservation, „chemical potential“



Kohn and Sham, 1965: Single-Particle Equations

Interacting Electrons

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

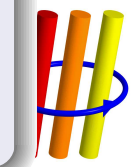
$T_0[\rho]$ is known, $E_{xc}[\rho]$ is not known!

Euler-Lagrange Equations (Kohn-Sham Equations)

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

$$v_{eff}(\mathbf{r}) := v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) \,, \qquad v_{xc}(\mathbf{r}) := \frac{\delta E_{xc}[\rho]}{\delta \rho}$$

ε_α: orthonormalization, „single-particle energies“



Kohn and Sham, 1965: Local Density Approximation

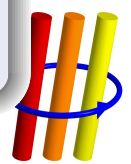
Be Specific!

- 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

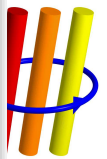
$$v_{xc}(\rho(\mathbf{r})) = \left[\frac{\partial}{\partial\rho}\{\rho\varepsilon_{xc}(\rho)\}\right]_{\rho=\rho(\mathbf{r})}$$



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)
$$\begin{aligned} \varepsilon_x(\rho) &= -\frac{3}{4\pi}\frac{e^2}{4\pi\epsilon_0}(3\pi^2\rho)^{\frac{1}{3}} \\ v_x(\rho) &= -\frac{1}{\pi}\frac{e^2}{4\pi\epsilon_0}(3\pi^2\rho)^{\frac{1}{3}} \end{aligned}$$
- Correlation energy density $\varepsilon_c(\rho)$
Calculate and parametrize
  - RPA (Hedin, Lundqvist; von Barth, Hedin)
  - QMC (Ceperley, Alder; Vosko, Wilk, Nusair; Perdew, Wang)

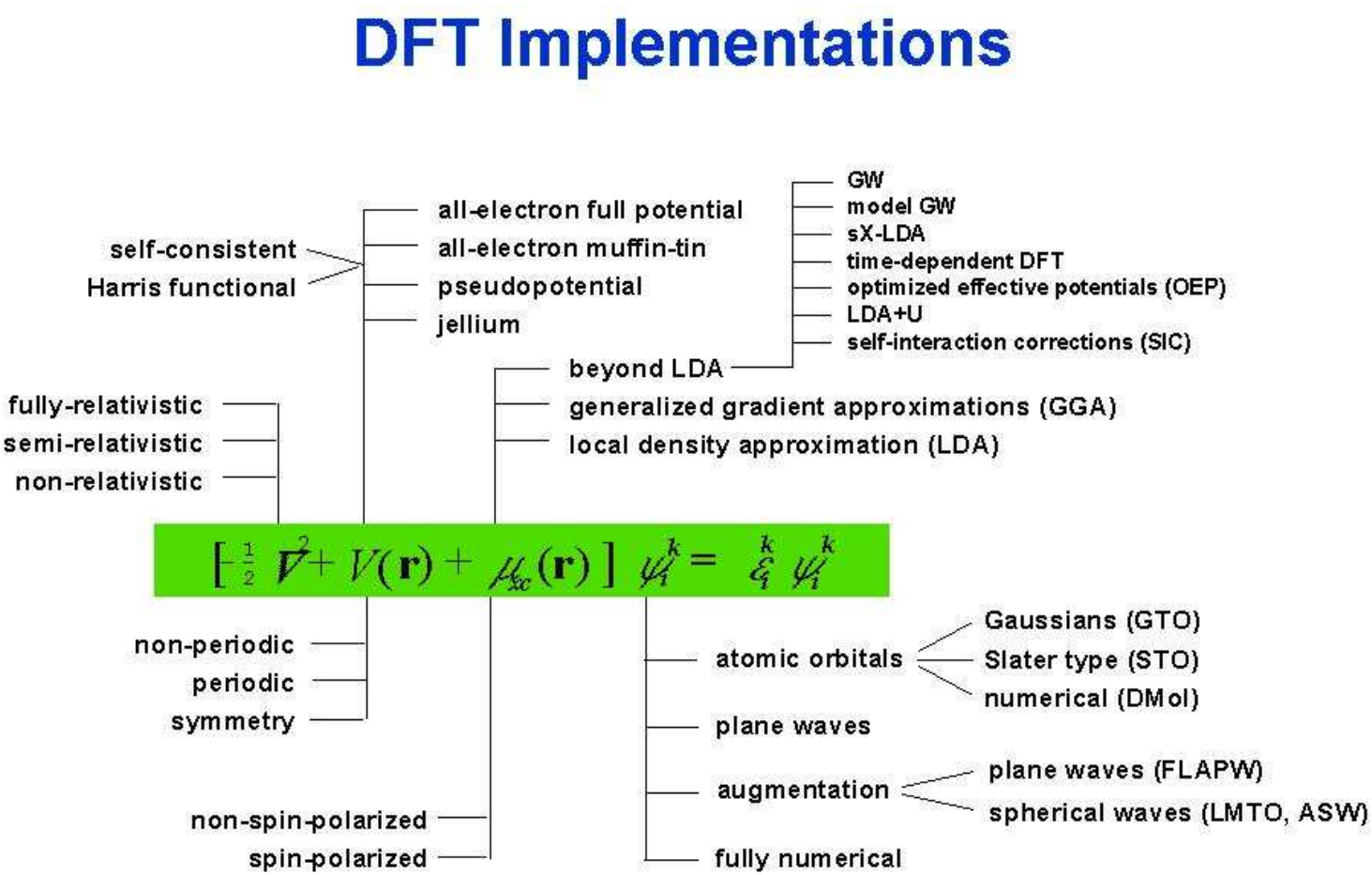


Kohn and Sham, 1965: Local Density Approximation

Limitations and Beyond

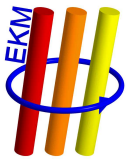
- LDA exact for homogeneous electron gas (within QMC)
- Spatial variation of ρ ignored
  - $\rightarrow$ include $\nabla\rho(\mathbf{r}), \ldots$
  - $\rightarrow$ Generalized Gradient Approximation (GGA)
- Cancellation of self-interaction in $v_{Hartree}(\rho(\mathbf{r}))$ and $v_x(\rho(\mathbf{r}))$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

Kohn/Sham Equations in Practice



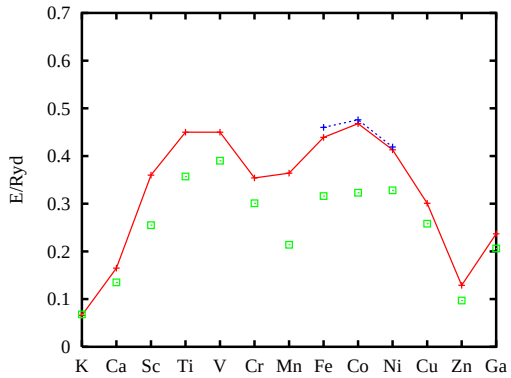
EW 1997-2000

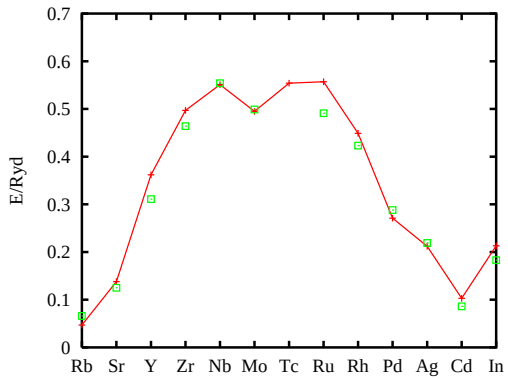
Outline



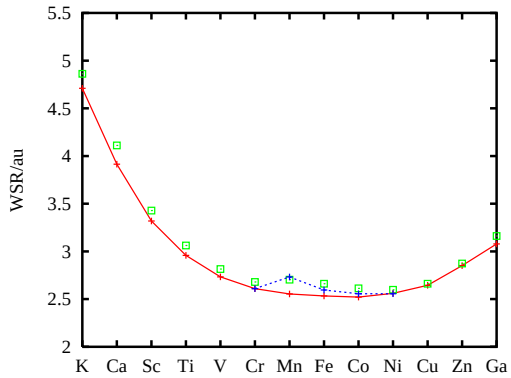
Calculated Electronic Properties

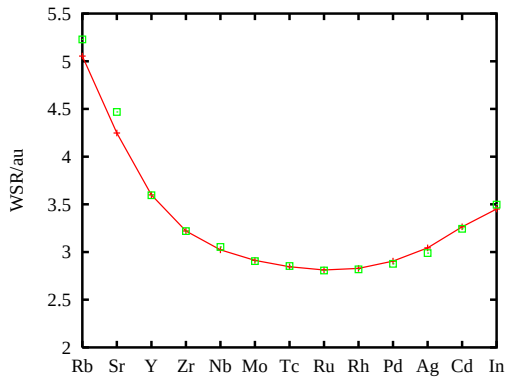
Moruzzi, Janak, Williams (IBM, 1978)



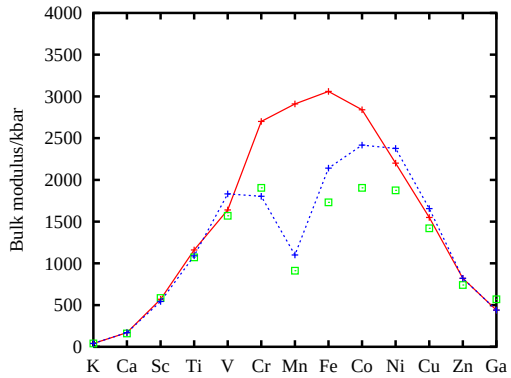


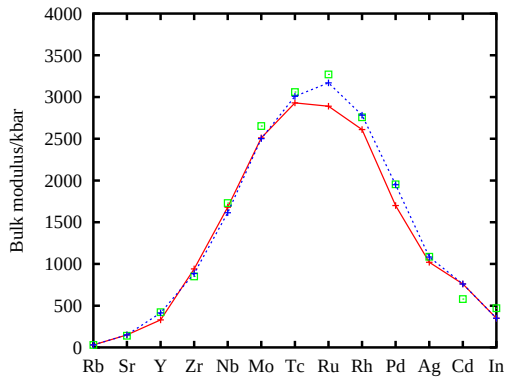
Cohesive Energies
≙ Stability





Wigner-Seitz-Rad.
≙ Volume

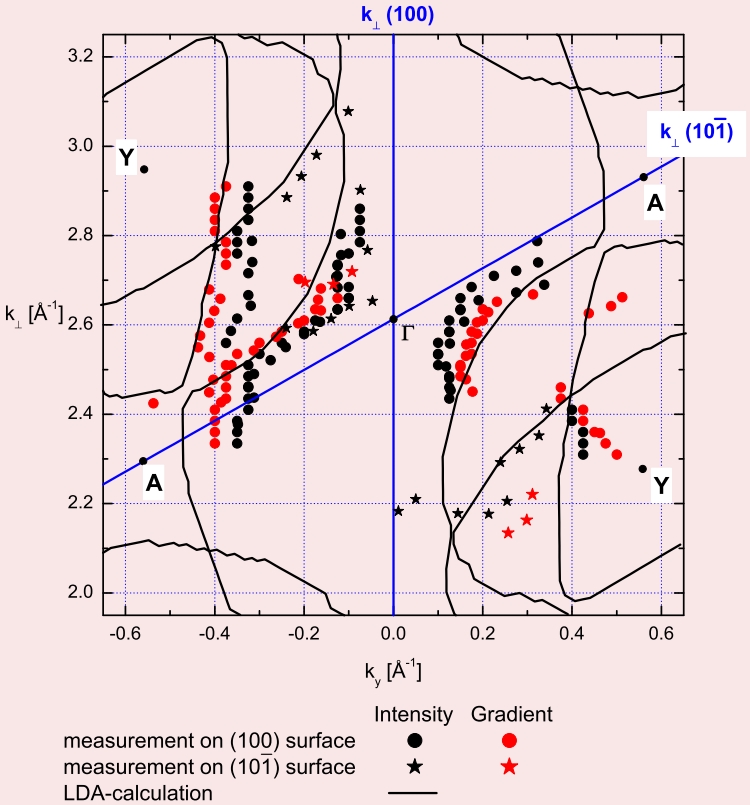


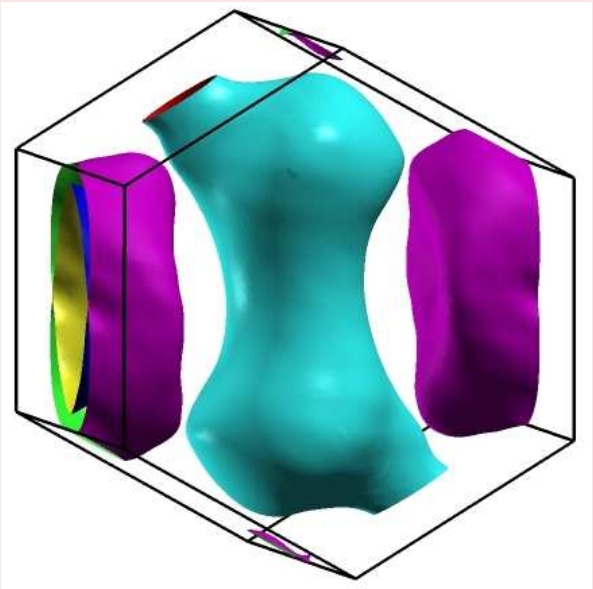


Compressibility
≙ Hardness

Fermi Surface of MoO_2

ARPES vs. DFT(LDA)



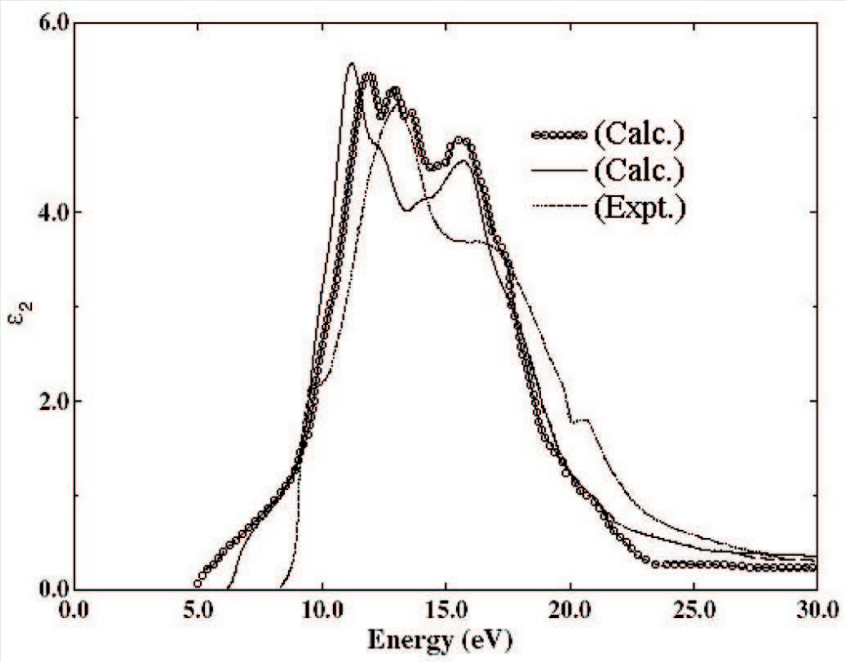


Moosburger *et al.*,
PRB **79**, 115113 (2009)

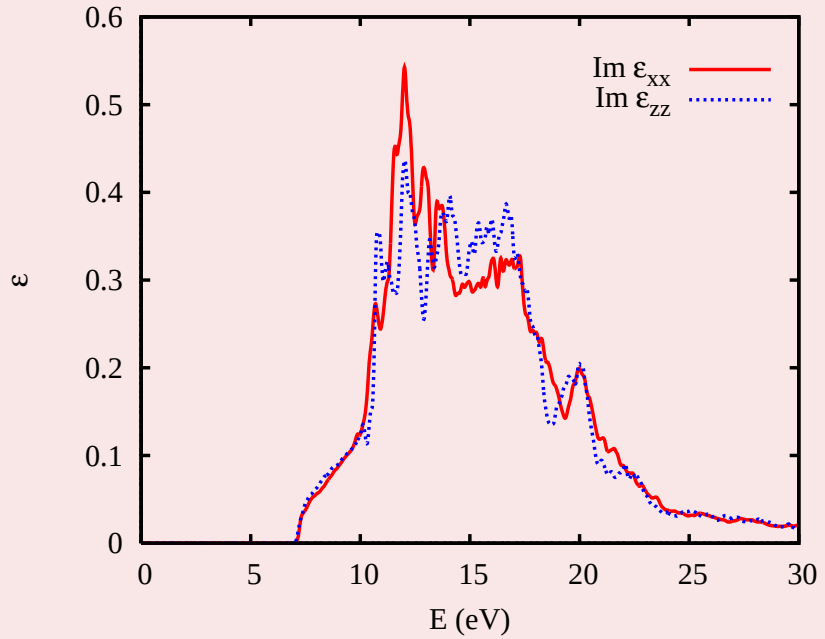
Dielectric Function of Al_2O_3

Imaginary Part

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



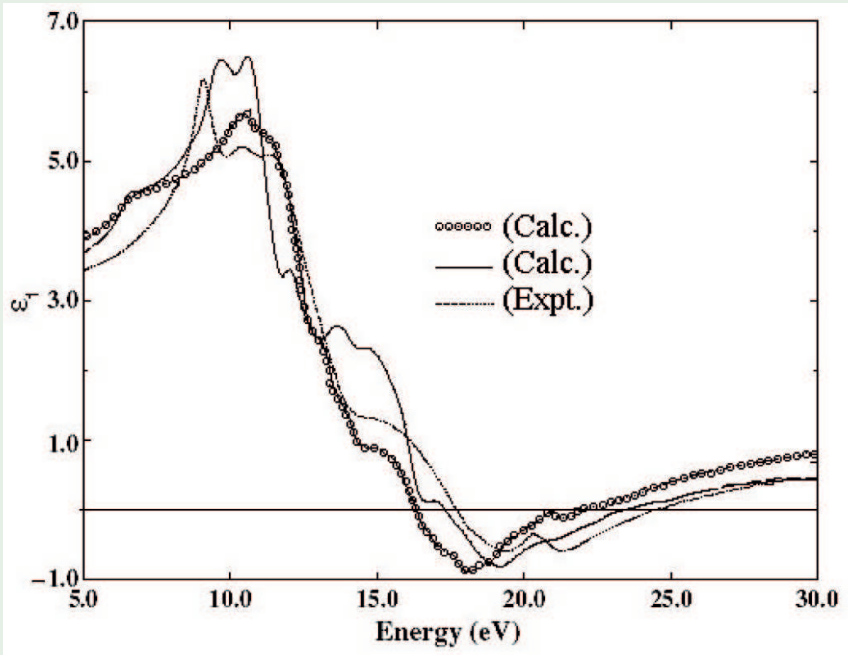
FPASW



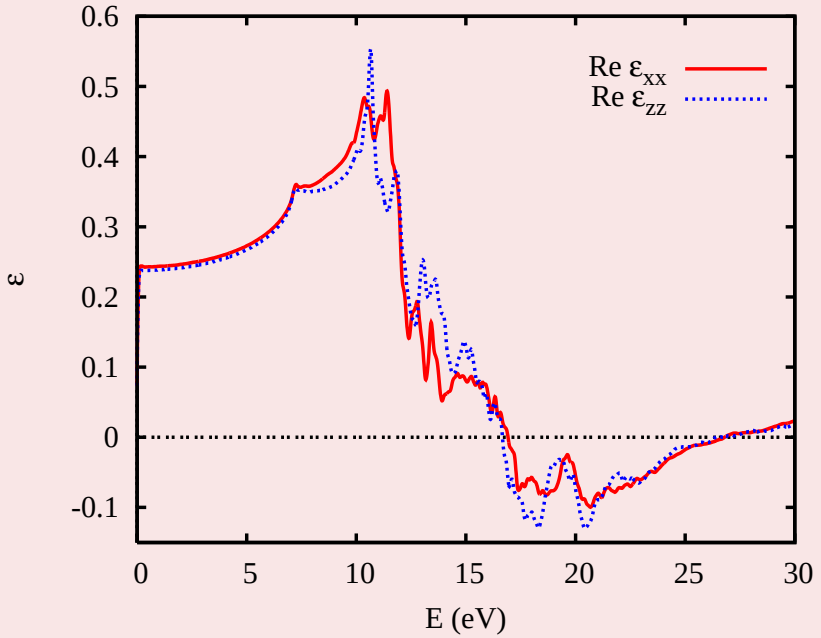
Dielectric Function of Al_2O_3

Real Part

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

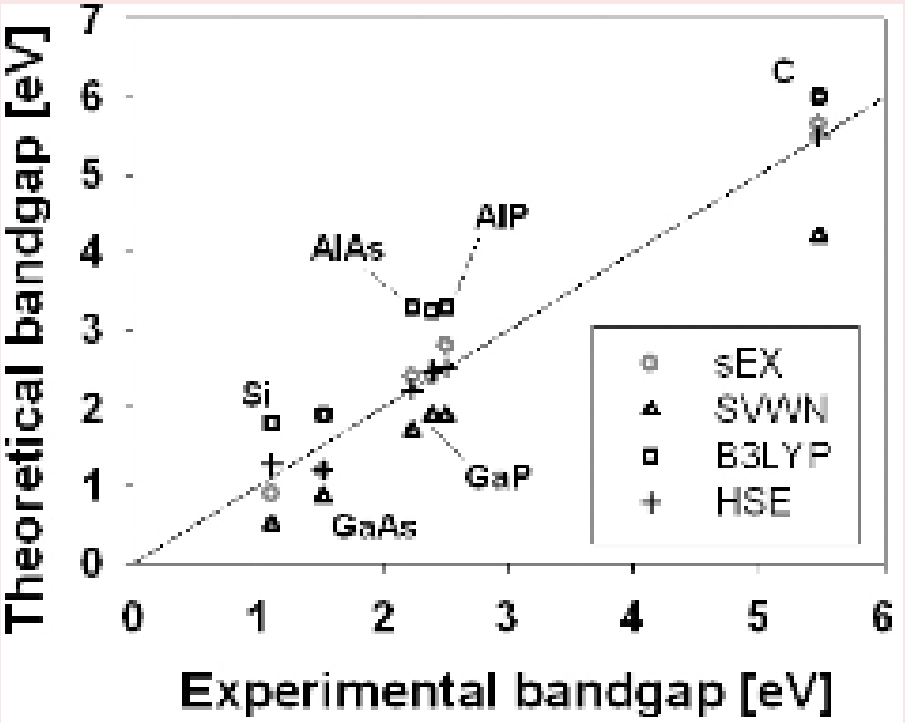


FPASW



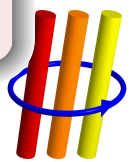
Energy band structures from screened HF exchange

Si, AlP, AlAs, GaP, and GaAs



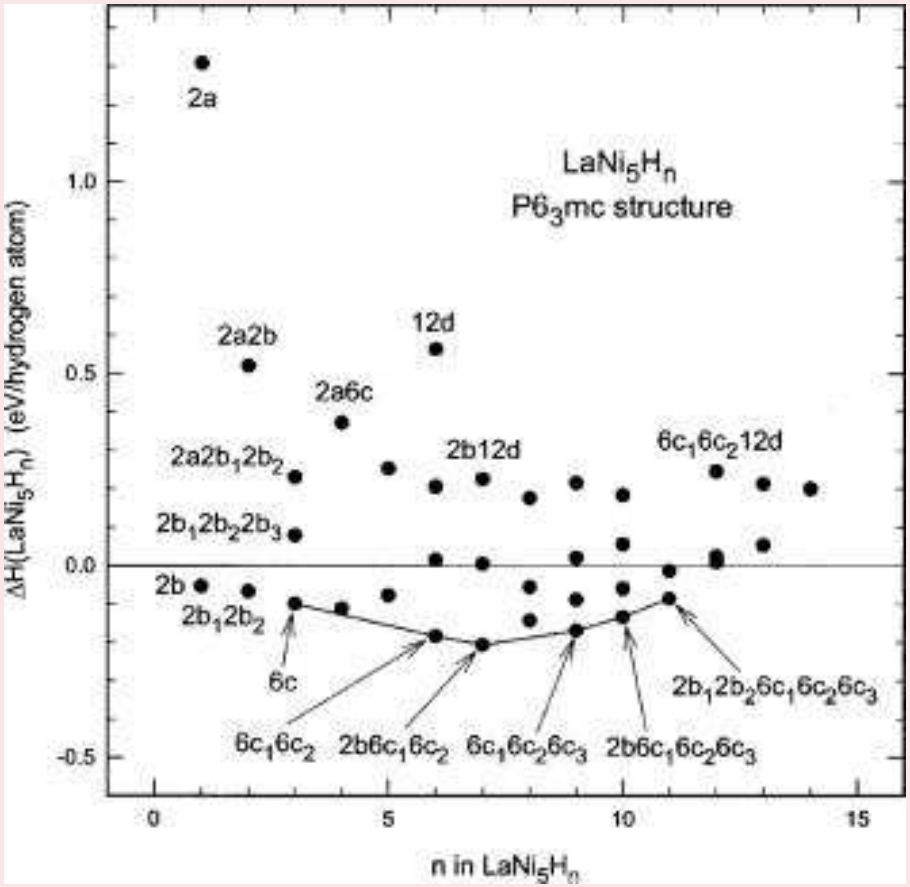
Experimental and theoretical bandgap properties

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



Hydrogen site energetics in $LaNi_5H_n$ and $LaCo_5H_n$

Enthalpy of hydride formation in $LaNi_5H_n$

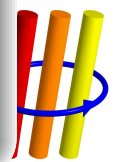


$\Delta H_{min} = -40\text{kJ/molH}_2$
for H at $2b6c_16c_2$

agrees with

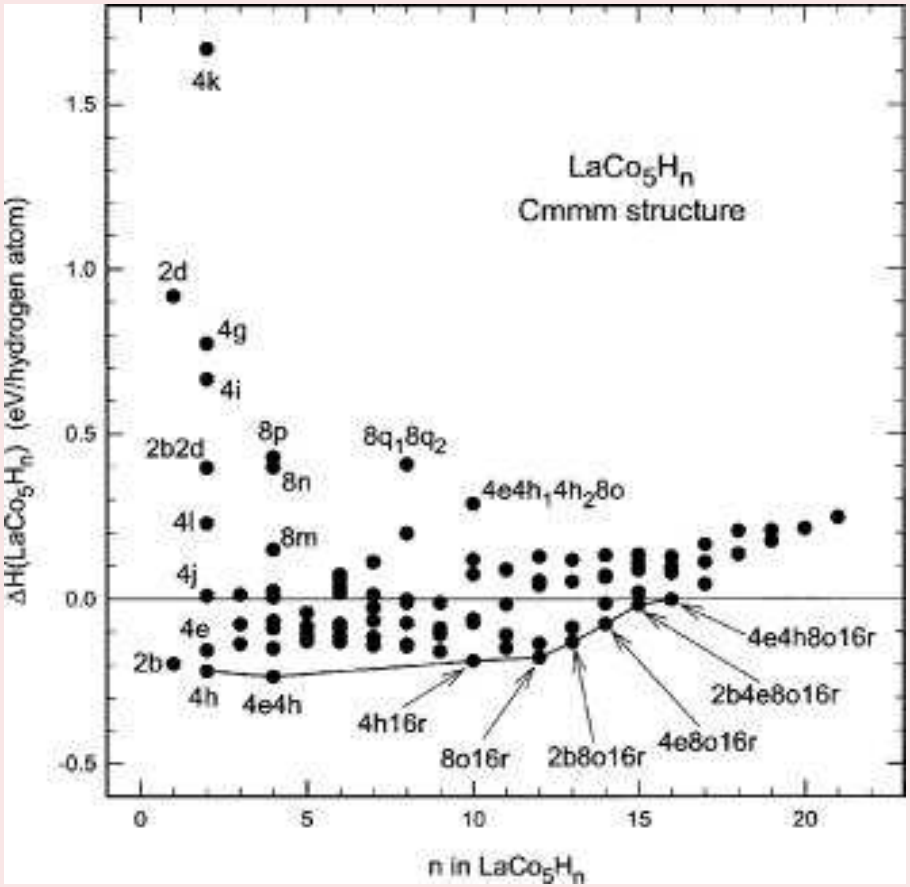
- neutron data
- calorimetry:
  $\Delta H_{min} = -(32/37)\text{kJ/molH}_2$

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



Hydrogen site energetics in $LaNi_5H_n$ and $LaCo_5H_n$

Enthalpy of hydride formation in $LaCo_5H_n$



$\Delta H_{min} = -45.6 \mathrm{kJ/molH_2}$
for H at $4e4h$

agrees with

- neutron data
- calorimetry:
  $\Delta H_{min} = -45.2 \mathrm{kJ/molH_2}$

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

Industrial Applications

Computational Materials Engineering

- Automotive
- Energy & Power Generation
- Aerospace
- Steel & Metal Alloys
- Glass & Ceramics
- Electronics
- Display & Lighting
- Chemical & Petrochemical
- Drilling & Mining

Summary

Density Functional Theory

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

Local Density Approximation

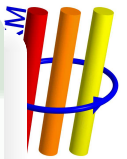
- approximative treatment of exchange (!) and correlation
- considerable improvement: exact treatment of exchange

Applications

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

Further Reading

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



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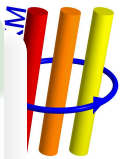

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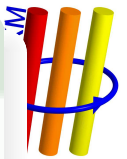

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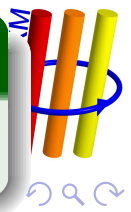

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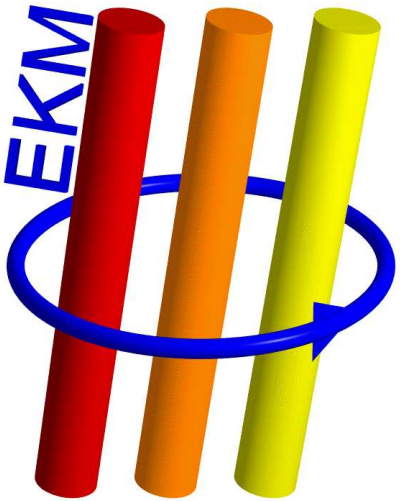

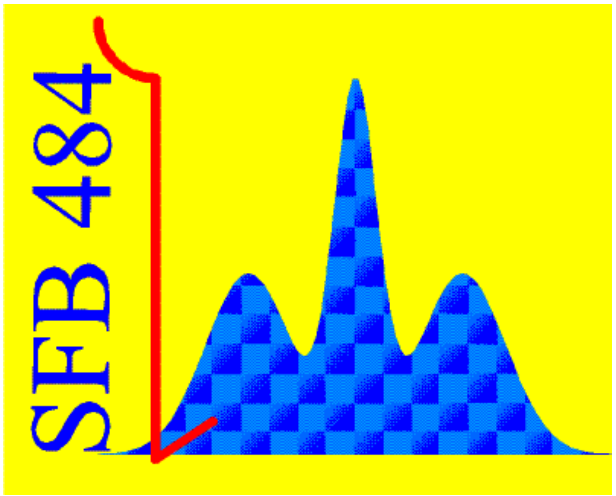

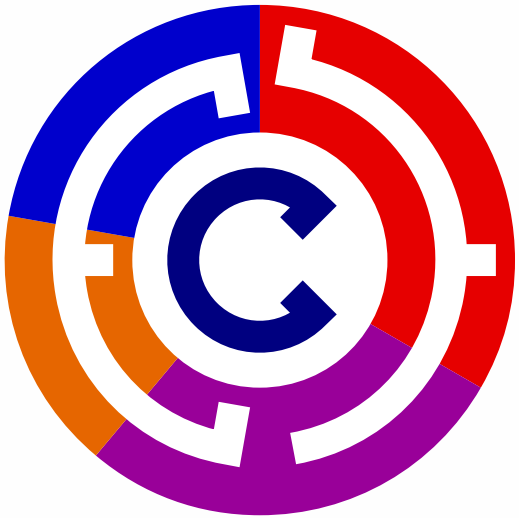

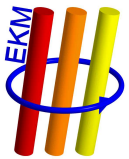

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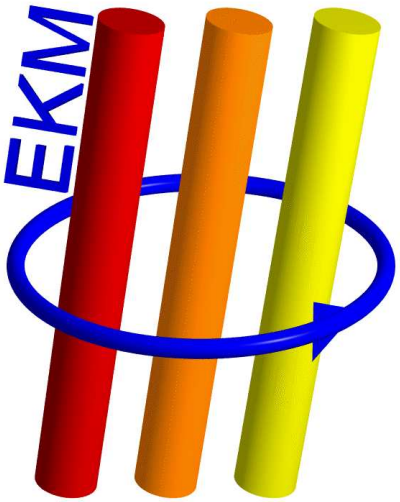

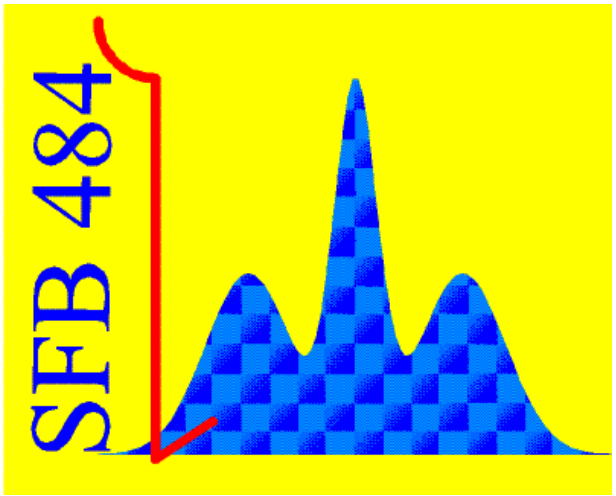

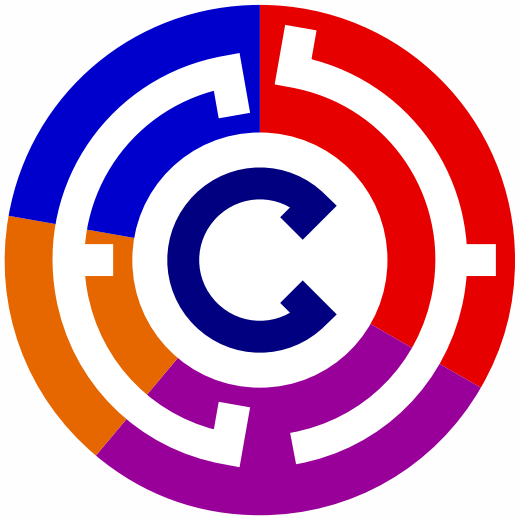

ACIT Workshop

Thank You for Your Attention!