

From Quantum Mechanics to Materials Design

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Outline

- 1 Quantum Mechanics
 - Density Functional Theory
 - Full-Potential ASW Method
- 2 „Materials Design“



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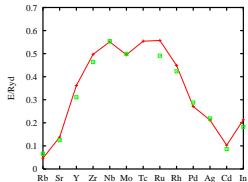
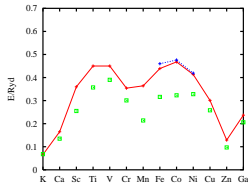
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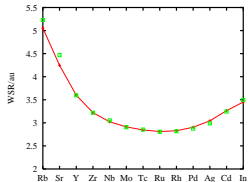
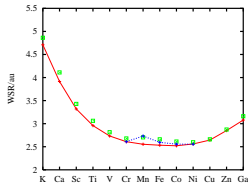


Calculated Electronic Properties

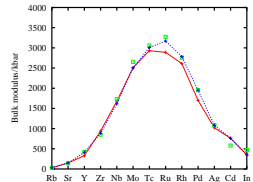
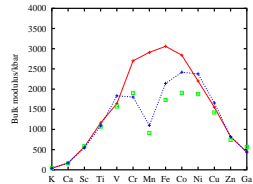
Moruzzi, Janak, Williams (IBM, 1978)



Cohesive Energies
 $\hat{=}$ **Stability**



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

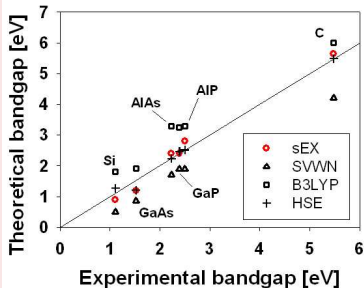


Compressibility
 $\hat{=}$ **Hardness**



Energy band structures from screened HF exchange

Si, AlP, AlAs, GaP, and GaAs



Experimental and
theoretical bandgap
properties

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



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

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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:

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

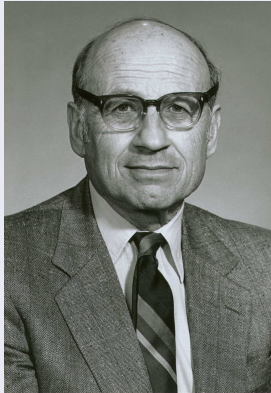


Authors

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

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Nota bene

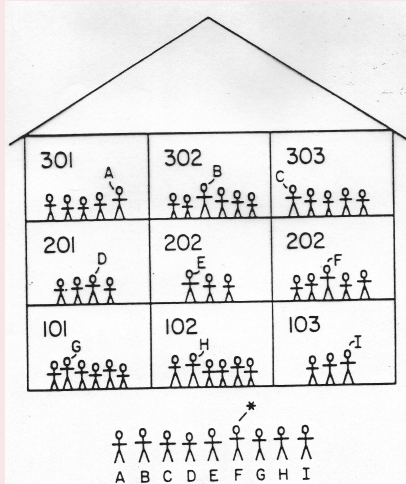
Both theorems are formulated for the ground state!

- Zero temperature!
- No excitations!



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



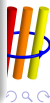
Levy, Lieb, 1979-1983: Constrained Search

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!**



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

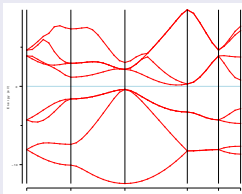
$$v_{xc}(\rho(\mathbf{r})) = \left[\frac{\partial}{\partial \rho} \{ \rho \varepsilon_{xc}(\rho) \} \right]_{\rho=\rho(\mathbf{r})}$$



Kohn and Sham, 1965: Local Density Approximation

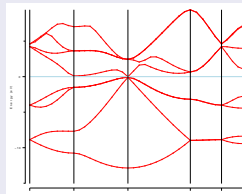
Limitations and Beyond

- LDA **exact** for homogeneous electron gas (within QMC)
- **Spatial variation** of ρ **ignored**
 - include $\nabla\rho(\mathbf{r}), \dots$
 - Generalized Gradient Approximation (GGA)
- **Self-interaction cancellation** in $V_{Hartree} + V_x$ **violated**

Si

Bandgaps

- Si, exp: 1.11 eV
- Si, GGA: 0.57 eV
- Ge, exp: 0.67 eV
- Ge, GGA: 0.09 eV

Ge

Muffin-Tin Approximation

John C. Slater



John C. Slater

Full Potential

$$v_{\sigma}(\mathbf{r}) : \begin{cases} \text{spherical symmetric near nuclei} \\ \text{flat outside the atomic cores} \end{cases}$$

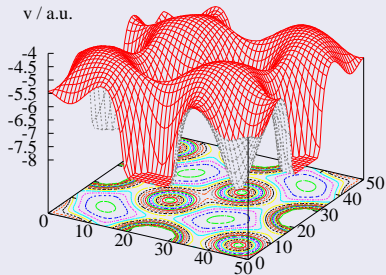
Muffin-Tin Approximation

$$v_{\sigma}^{MT}(\mathbf{r}) = \begin{cases} \text{spherical symmetric in spheres} \\ \text{constant in interstitial region} \end{cases}$$



Muffin-Tin Approximation

Full Potential (FeS₂)



Muffin-Tin Potential



Muffin-Tin Approximation

Wave Function

- 1 solve Schrödingers eq.
→ **partial waves**
- 2 match partial waves
→ basis functions,
„augmented“ partial waves
- 3 use to expand
→ **wave function**

Muffin-Tin Potential



Muffin-Tin Approximation

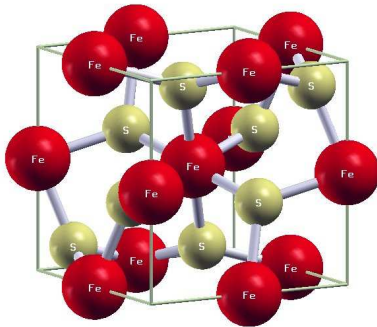
Flavors

- **Muffin-Tin Approximation**: touching spheres
- **Atomic Sphere Approximation**: space-filling spheres
 - interstitial region formally removed
 - only numerical functions in spheres
 - minimal basis set (s, p, d)
 - very high computational efficiency $\rightarrow \mathcal{O}(\text{ASA})$ speed!!!
 - makes potential more realistic
 - systematic error in total energy

bad!



Iron Pyrite: FeS_2



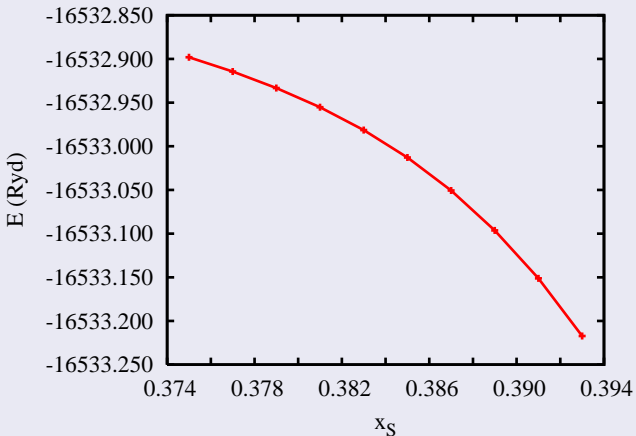
Pyrite

- $Pa\bar{3} (T_h^6)$
- $a = 5.4160 \text{ \AA}$
- “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: Structure Optimization

ASA+ Code



Basic Principles of the Full-Potential ASW Method

Steps to be Taken

- **remove total energy error** due to overlap of atomic spheres
 - reintroduce non-overlapping muffin-tin spheres
 - restore interstitial region



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- find representation of **electron density and full potential**
 - inside muffin-tin spheres
 - in the interstitial region



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 - **use spherical-harmonics expansions**
 - in the interstitial region



Basic Principles of the Full-Potential ASW Method

Steps to be Taken

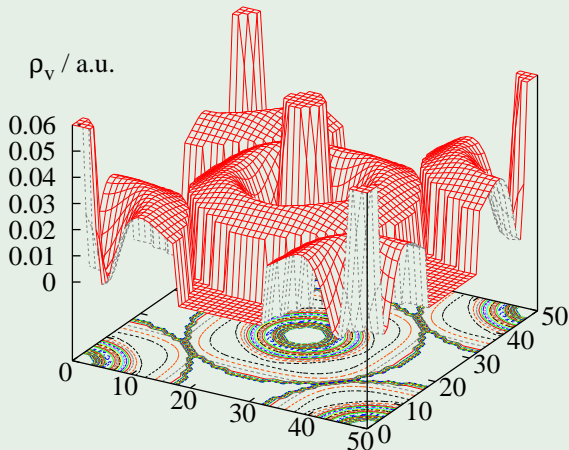
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- find representation of **electron density and full potential**
- find representation of **products of the wave function**
- find representation of **products of the basis functions**
 - inside muffin-tin spheres
 - **use spherical-harmonics expansions**
 - in the interstitial region
 - **no exact spherical-wave representation available!**



From Wave Functions to Electron Density

Density inside MT-Spheres

(A)



From Wave Functions to Electron Density

Products of Spherical Waves in Interstitial Region

- expand in **spherical waves**
 - would be efficient
 - coefficients/integrals not known analytically
 - Methfessel, 1988:
match values and slopes at MT-sphere surfaces

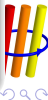
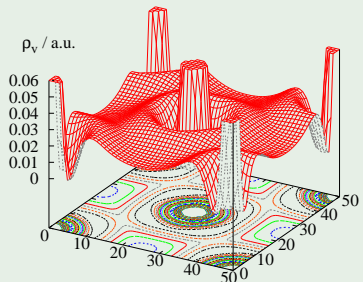
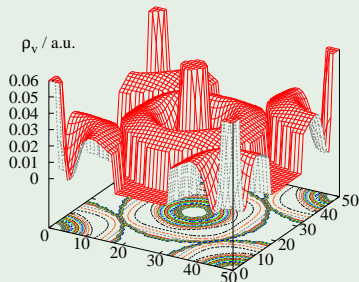


From Wave Functions to Electron Density

Products of Spherical Waves in Interstitial Region

- expand in **spherical waves**
- match values and slopes at **MT-sphere** surfaces

Density from Value/Slope Matching at MT-Radii (A)



Comparison of Approaches

Ole K. Andersen

1975

- ASA geometry used for basis functions
→ minimal basis set
- ASA geometry used for density and potential
→ error in total energy

good!

bad!



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- ASA geometry used for basis functions
→ **minimal basis set**
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→ **error in total energy**

good!**bad!**

Michael S. Methfessel

1988

- MT geometry used for density and potential
→ **accurate total energy**
- MT geometry used for basis functions
→ **large basis set**

good!**bad!**

Comparison of Approaches

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- ASA geometry used for basis functions
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good!

bad!

Michael S. Methfessel

1988

- MT geometry used for density and potential
- MT geometry used for basis functions

good!

bad!

present approach

2006

- ASA geometry used for basis functions
→ minimal basis set → $\mathcal{O}(\text{ASA})$ speed
- MT geometry used for density and potential
→ accurate total energy

great!

great!



Implementation: Augmented Spherical Wave Method

0th Generation ASW (Williams, Kübler, Gelatt, 1970s)

PRB **19**, 6094 (1979)

1st Generation (VE, 1990s)

- new implementation (accurate, stable, portable)
VE, Int. J. Quantum Chem. **77**, 1007 (2000)
VE, Lect. Notes Phys. **719** (Springer, 2007)
- xAnderson convergence acceleration scheme
VE, J. Comput. Phys. **124**, 271 (1996)
- all LDA- and GGA-parametrizations
- still based on atomic-sphere approximation
VE, Höck, PRB **57**, 12727 (1998)

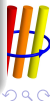


Implementation: Augmented Spherical Wave Method

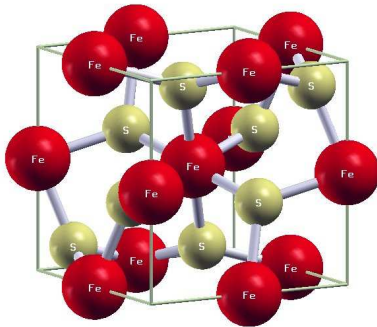
2nd Generation ASW (VE, 2000s)

- based on 1st generation code
- full-potential ASW method at $\mathcal{O}(\text{ASA})$ speed!
 - electron densities, spin densities
 - electric field gradients
 - elastic properties, phonon spectra
- optical properties
 - based on linear-response theory
 - direct calculation of $\Re\sigma$ and $\Im\sigma$
 - no Kramers-Kronig relations needed
- transport properties, thermoelectrics
- LDA+U method
 - all „flavors“ for double-counting terms (AMF, FLL, DFT)

VE, Lect. Notes Phys. (2nd ed., Springer, 2011)



Iron Pyrite: FeS_2



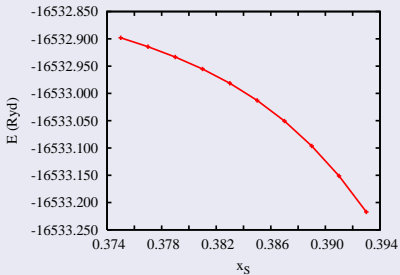
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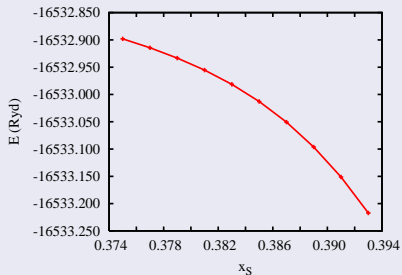
FeS₂: Structure Optimization

ASA+ Code

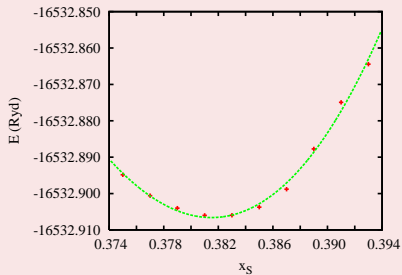


FeS₂: Structure Optimization

ASA+ Code



Full-Potential Code

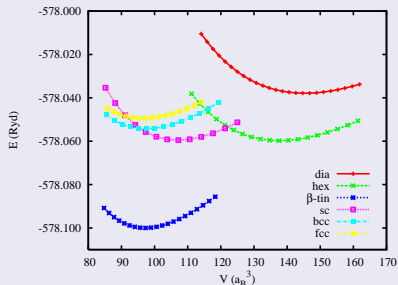


at $\mathcal{O}(\text{ASA})$ speed!



Phase Stability in Silicon

ASA+ Code



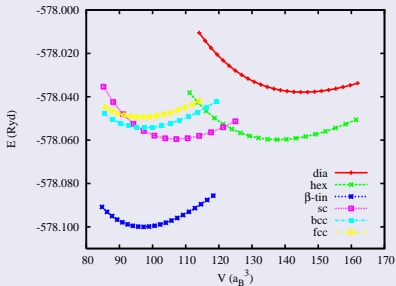
Bad

- β -tin structure most stable # nature (diamond structure)

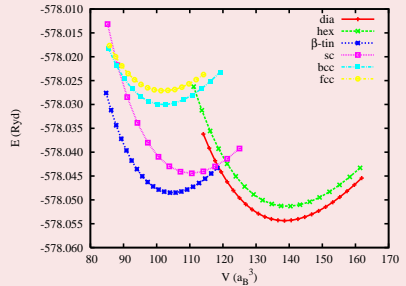


Phase Stability in Silicon

ASA+ Code



Full-Potential Code



New!

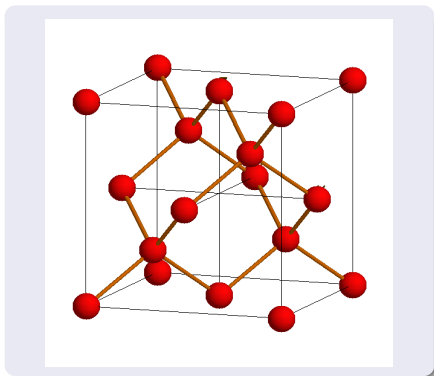
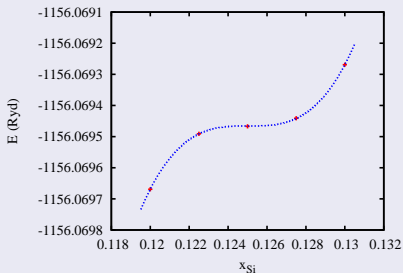
at $\mathcal{O}(\text{ASA})$ speed!

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



LTO(Γ)-Phonon in Silicon

ASA⁺ Code



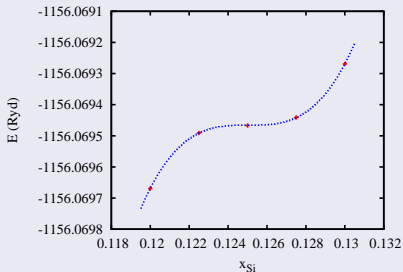
Bad

- no stable Si position # nature

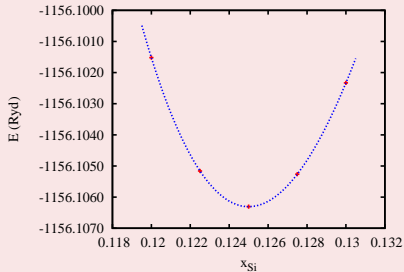


LTO(Γ)-Phonon in Silicon

ASA⁺ Code



Full-Potential Code



New!

at $\mathcal{O}(\text{ASA})$ speed!

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



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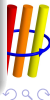
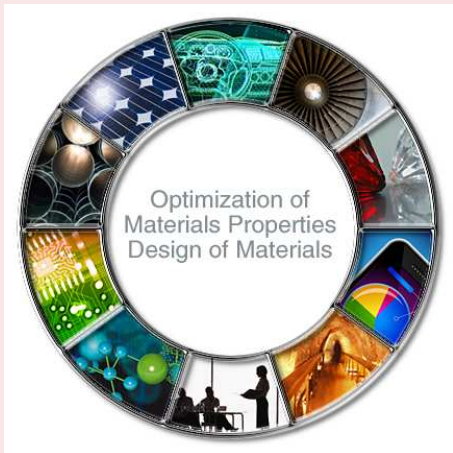
- 2 „Materials Design“



Industrial Applications

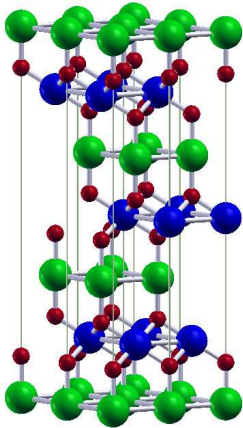
Computational Materials Engineering

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



Delafossites: ABO_2

Delafossite Structure



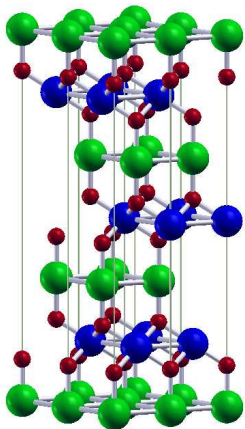
Building Blocks

- rhombohedral lattice
- triangular A-atom layers
- BO_2 sandwich layers
- B-atoms octahedrally coordinated
- linear O-A-O bonds



Delafossites: ABO_2

Delafossite Structure



Building Blocks

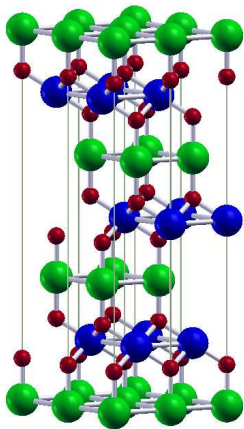
- rhombohedral lattice
- triangular A-atom layers
- BO_2 sandwich layers
- B-atoms octahedrally coordinated
- linear O-A-O bonds

Issues

- dimensionality
- geometric frustration
- play chemistry

Delafossites: ABO_2

Delafossite Structure



Prototype Materials

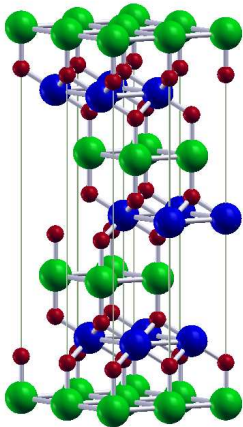
- $CuFeO_2$, $CuCrO_2$
- $CuCoO_2$, $CuRhO_2$
- $CuAlO_2$, $CuGaO_2$, $CuInO_2$, ...
- $PdCrO_2$, $PdCoO_2$, $PdRhO_2$, $PtCoO_2$

Properties

- semiconductors, AF interactions, (distorted) triangular
- non-magn. semicond., thermopower
- wide-gap semicond., p-type TCO
- very good metals, high anisotropy

Delafossites: ABO_2

Delafossite Structure



Prototype Materials

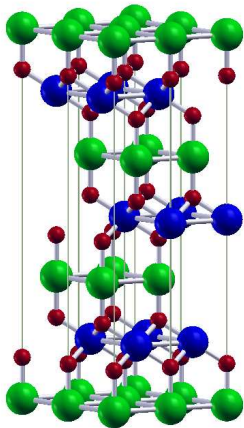
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Delafossite Structure



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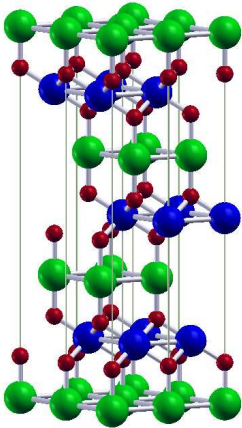
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PdCoO₂ and PtCoO₂

Delafossite Structure



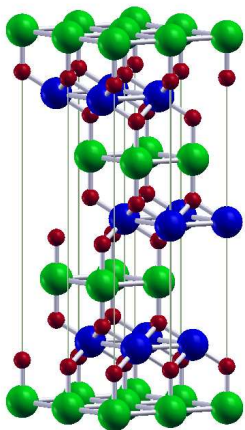
Experimental Results

- very low resistivity
- anisotropy ratio ≈ 200
- PES: only Pd 4d states at E_F
- PES/IPES: E_F in shallow DOS minimum
 - high thermopower on doping?



PdCoO₂ and PtCoO₂

Delafossite Structure



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 - high thermopower on doping?

Open Issues

role of Pd 4d, Co 3d, and O 2p orbitals?



Structure Optimization in PdCoO₂

Structural Data

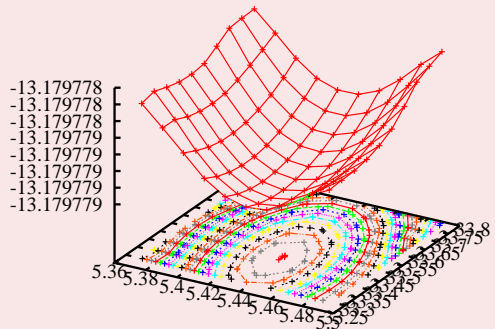
experiment

- $a = 2.83 \text{ \AA}$
- $c = 17.743 \text{ \AA}$
- $z_0 = 0.1112$

theory

- $a = 2.8767 \text{ \AA}$
- $c = 17.7019 \text{ \AA}$
- $z_0 = 0.1100$

Total energy surface

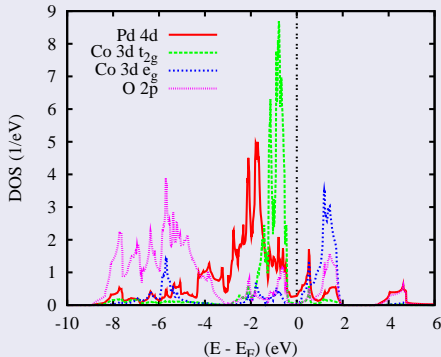


VE, R. Frésard, A. Maignan, Chem. Mat. **20**, 2370 (2008)



Electronic Properties of PdCoO_2

Partial Densities of States



Results

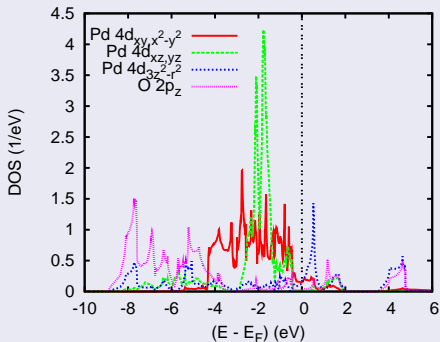
- Co 3d-O 2p hybridization
- CoO_6 octahedra:
Co 3d $\Rightarrow t_{2g}$ and e_g
- Co 3d⁶ (Co^{3+}) LS
- Pd 4d⁹ (Pd^{1+})
- Co 3d, O 2p: very small DOS at E_F

VE, R. Frésard, A. Maignan, Chem. Mat. **20**, 2370 (2008)



Electronic Properties of PdCoO₂

Partial Densities of States



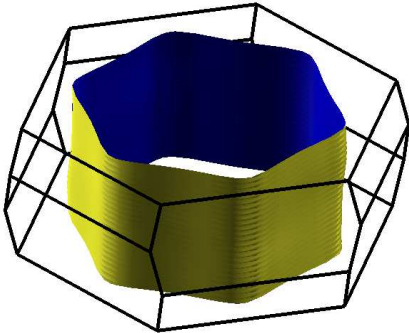
Results

- broad Pd d_{xy, x^2-y^2} bands
 - short in-plane Pd-Pd distance
- non-bonding Pd $d_{xz, yz}$ bands
- strong Pd $4d_{3z^2-r^2}$ -O $2p$ hybridization
- states at E_F :
Pd d_{xy, x^2-y^2} , $d_{3z^2-r^2}$

VE, R. Frésard, A. Maignan, Chem. Mat. **20**, 2370 (2008)

Electronic Properties of PdCoO₂

Fermi Surface



Results

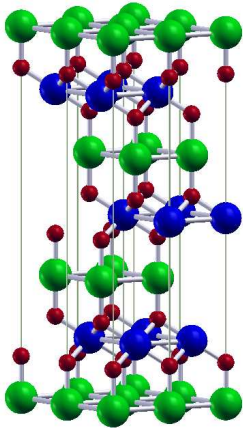
- quasi-2D
- single band crossing E_F
- but: bands below E_F disperse along Γ -A

VE, R. Frésard, A. Maignan, Chem. Mat. **20**, 2370 (2008)



CuFeO₂

Delafossite Structure



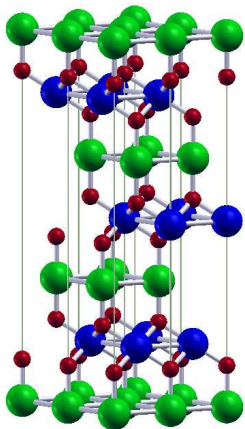
Basics

- semiconductor
- AF interactions
- triangular lattice



CuFeO₂

Delafossite Structure



Basics

- semiconductor
- AF interactions
- triangular lattice

Open Issues

- frustration vs. long-range order
- role of Cu 3d orbitals?
- role of Fe 3d and O 2p orbitals?



CuFeO₂

Previous Neutron Data

- $T_{N_1} = 16 \text{ K}$, $T_{N_2} = 11 \text{ K}$
- $\Theta_{CW} = -90 \text{ K}$
- magnetic supercells
- no structural distortion
- $m_{\text{Fe}^{3+}} = 4.4 \mu_B$



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Band Calculations

- rhombohedral structure
- $m_{\text{Fe}} = 0.9 \mu_B$, $m_{\text{Fe}} = 3.8 \mu_B$
- $E_g = 0$ in LDA, GGA
- # PES, XES



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New Neutron Data

- magnetic supercells
- monoclinic structure below 4 K

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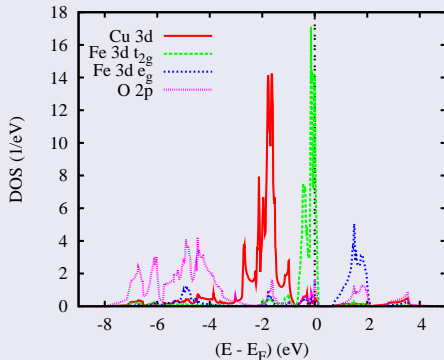
Open Issues

- spin-state of Fe?
- influence of monoc. structure?



Electronic Properties of CuFeO_2

Partial Densities of States



Results

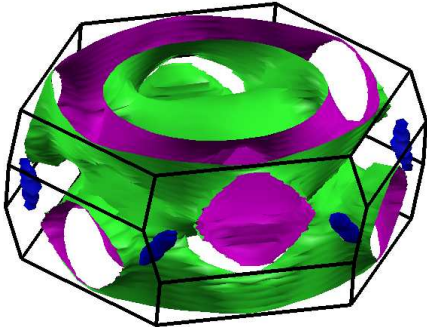
- Fe 3d-O 2p hybridization
- FeO₆ octahedra:
Fe 3d \Rightarrow t_{2g} and e_g
- Cu 4d¹⁰ (Cu¹⁺)
- Fe 3d t_{2g}
 - sharp peak at E_F

VE, R. Frésard, A. Maignan, PRB **78**, 052402 (2008)



Electronic Properties of CuFeO_2

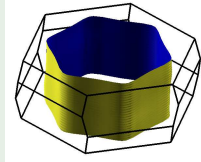
Fermi Surface



Results

- strongly 3D

FS PdCoO_2



VE, R. Frésard, A. Maignan, PRB **78**, 052402 (2008)



Magnetic Properties of CuFeO_2 Total Energies (mRyd/f.u.), Magn. Moms. (μ_B), Band Gaps (eV)

structure	magn. order	ΔE	m_{Fe}	m_{O}	E_g
rhomb.	spin-deg.	0.0			-
rhomb.	ferro (LS)	-16.7	1.03	-0.02	-
rhomb.	ferro (IS)	-12.0	2.02	-0.02	-
rhomb.	ferro (HS)	-19.2	3.73	0.21	-

VE, R. Frésard, A. Maignan, PRB **78**, 052402 (2008)

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rhomb.	ferro (HS)	-19.2	3.73	0.21	-
monoc.	spin-deg.	-6.0			-
monoc.	ferro (LS)	-21.5	1.04	-0.02	-
monoc.	ferro (IS)	-19.0	2.08	-0.02	-
monoc.	ferro (HS)	-32.0	3.62	0.19	-

VE, R. Frésard, A. Maignan, PRB **78**, 052402 (2008)

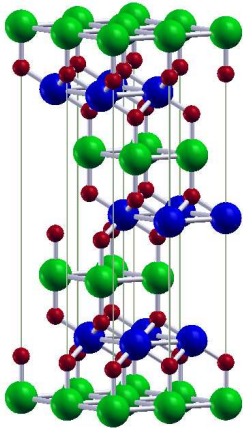
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monoc.	ferro (IS)	-19.0	2.08	-0.02	-
monoc.	ferro (HS)	-32.0	3.62	0.19	-
monoc.	antiferro	-46.0	± 3.72	± 0.08	0.05

VE, R. Frésard, A. Maignan, PRB **78**, 052402 (2008)

CuRhO₂

Delafossite Structure



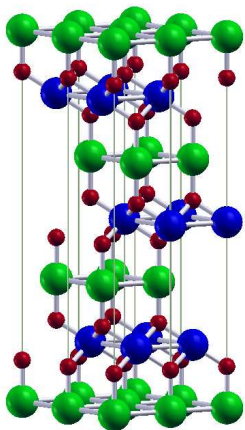
Experimental Findings

- semiconductor
- high thermopower on hole doping
 - Rh³⁺ → Mg²⁺ up to 12%
- high T -independent power factor



CuRhO₂

Delafossite Structure



Experimental Findings

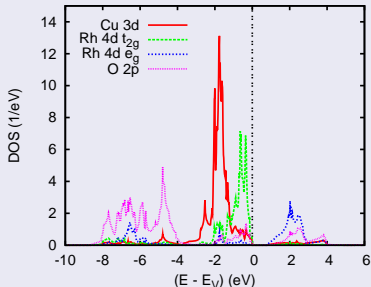
- semiconductor
- high thermopower on hole doping
 - Rh³⁺ → Mg²⁺ up to 12%
- high T -independent power factor

Open Issues

- origin of high thermopower
- role of Cu 3d orbitals?
- role of Rh 4d and O 2p orbitals?

Electronic Properties of CuRhO_2

Partial Densities of States



Results

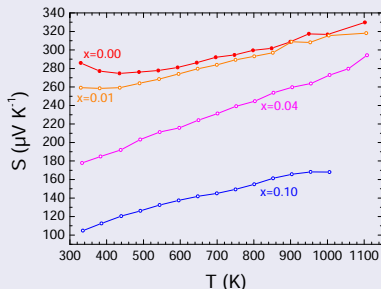
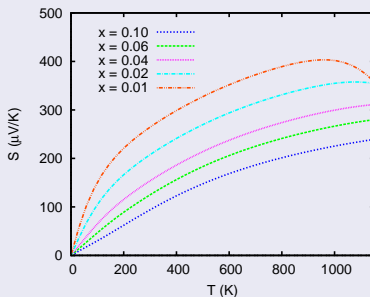
- Rh 4d-O 2p hybridization
- RhO_6 octahedra:
Rh 4d $\Rightarrow t_{2g}$ and e_g
- $E_g \approx 0.75$ eV
- Cu 4d¹⁰ (Cu^{1+})
- electronic structure:
strongly 3D

A. Maignan, VE *et al.*, PRB **80**, 115103 (2009)

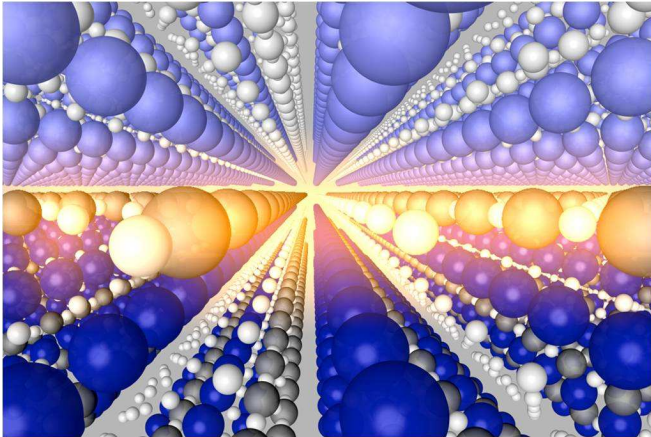


Thermoelectric Power of $\text{CuRh}_{1-x}\text{Mg}_x\text{O}_2$

Experiment

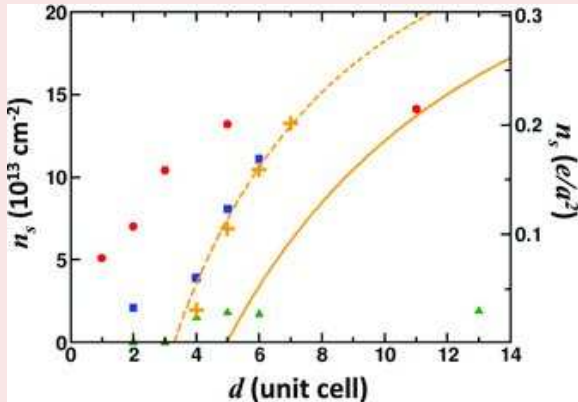
Theory: S_{xx} A. Maignan, VE *et al.*, PRB **80**, 115103 (2009)

2D Electron Gas at LaAlO₃-SrTiO₃ Interface



2D Electron Gas at LaAlO₃-SrTiO₃ Interface

Insulator-Metal Transition



Chen, Kolpak, Ismail-Beigi, Adv. Mater. **22**, 2881 (2010)

Slab Calculations for the LaAlO_3 - SrTiO_3 Interface



Structural setup of calculations

- central region: 5 layers SrTiO_3 , TiO_2 -terminated
- sandwiches: 2 to 5 layers LaAlO_3 , AlO_2 surface
- vacuum region $\approx 20 \text{ \AA}$
- inversion symmetry
- lattice constant of SrTiO_3 from GGA (3.944 \AA)



Slab Calculations for the LaAlO_3 - SrTiO_3 Interface



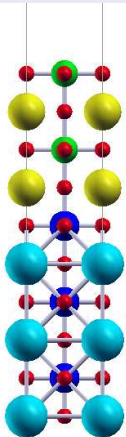
Calculational method

- Vienna Ab Initio Simulation Package (VASP)
- GGA-PBE
- Steps:
 - 1 optimization of SrTiO_3 lattice constant
 - 2 slab calculations
 - full relaxation of all atomic positions
 - $5 \times 5 \times 1$ \mathbf{k} -points
 - Γ -centered \mathbf{k} -mesh
 - Methfessel-Paxton BZ-integration



Slab Calculations for the LaAlO_3 - SrTiO_3 Interface

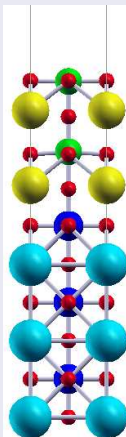
Ideal



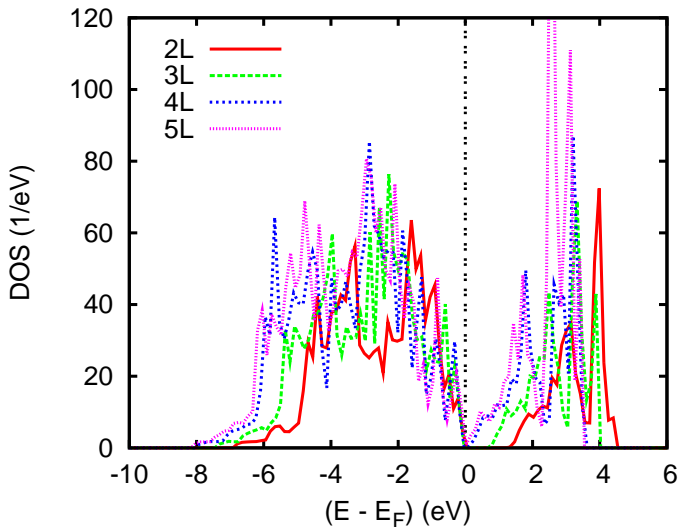
Structural relaxation

- AlO_2 surface layers
 - strong inward relaxation
 - weak buckling
- LaO layers
 - strong buckling
- AlO_2 subsurface layers
 - buckling
- TiO_2 interface layers
 - small outward relaxation

Optimized

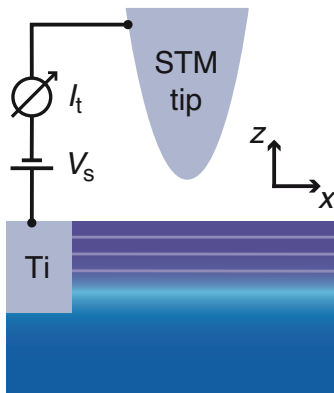


Slab Calculations for the $\text{LaAlO}_3\text{-SrTiO}_3$ Interface



Tunneling Spectroscopy of LaAlO₃-SrTiO₃ Interface

What is the origin of the 2-DEG?
Intrinsic mechanism or defect-doping?



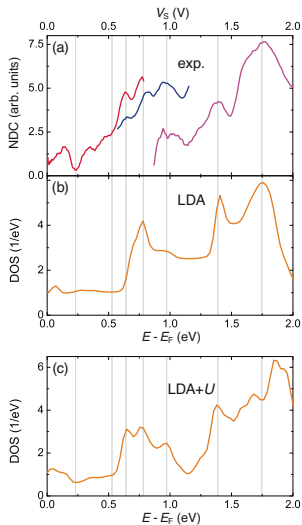
4 unit cells LaAlO₃
interface electron system
SrTiO₃

M. Breitschaft *et al.*, PRB **81**, 153414 (2010)



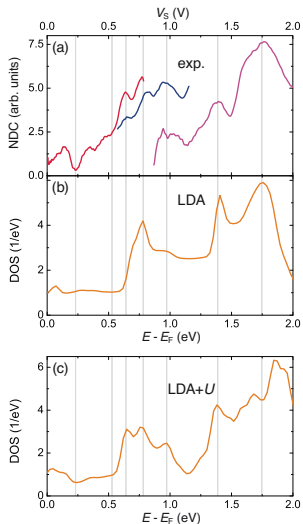
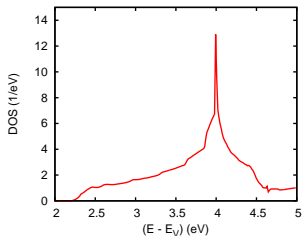
Tunneling Spectroscopy of LaAlO₃-SrTiO₃ Interface

- 4uc LaAlO₃ on SrTiO₃, tunneling data
- 4uc LaAlO₃ on SrTiO₃, LDA calculations, DOS of interface Ti
- 4uc LaAlO₃ on SrTiO₃, LDA+*U* calculations, DOS of interface Ti

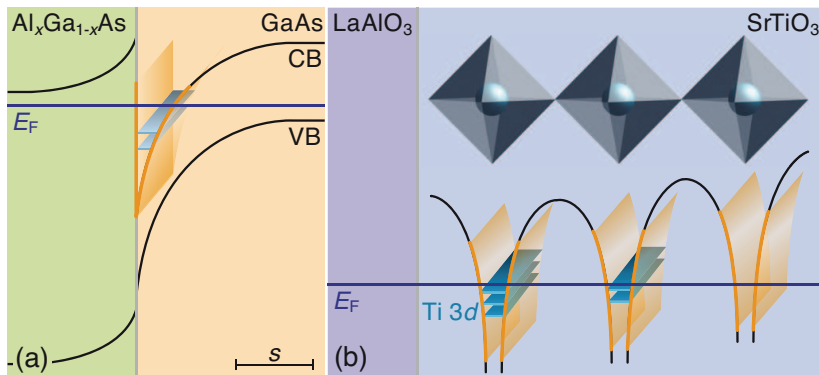


Tunneling Spectroscopy of LaAlO₃-SrTiO₃ Interface

- bulk SrTiO₃,
LDA calculations,
conduction band DOS



“2D Electron Liquid State” at LaAlO₃-SrTiO₃ Interface



M. Breitschaft *et al.*, PRB **81**, 153414 (2010)



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

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

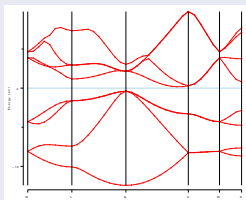


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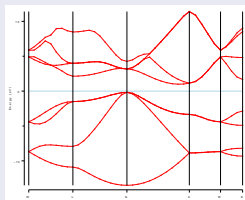
GGA



Si bandgap

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

HSE

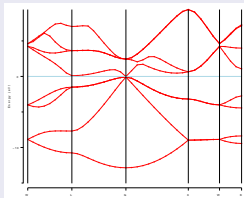


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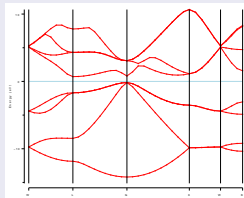
GGA



Ge bandgap

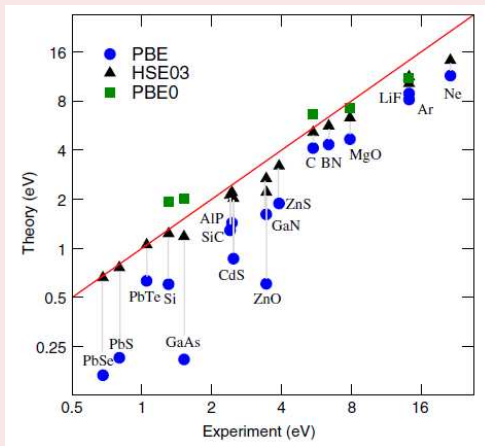
- exp: 0.67 eV
- GGA: 0.09 eV
- HSE: 0.66 eV

HSE



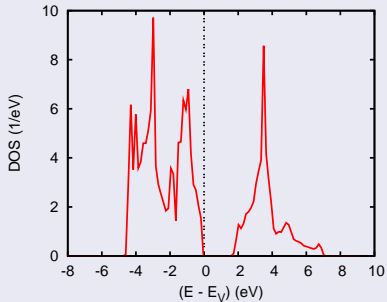
Critical review of the Local Density Approximation

Calculated vs. experimental bandgaps



SrTiO₃

GGA



Bandgap

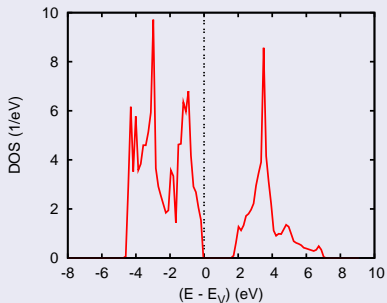
GGA: ≈ 1.6 eV,

exp.: 3.2 eV

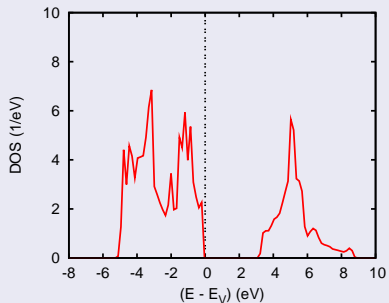


SrTiO₃

GGA



HSE



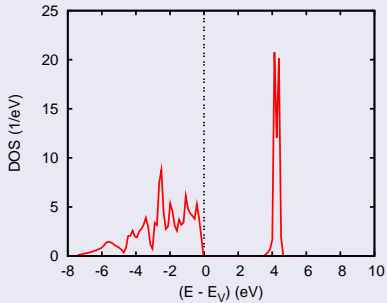
Bandgap

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



LaAlO₃

GGA



Bandgap

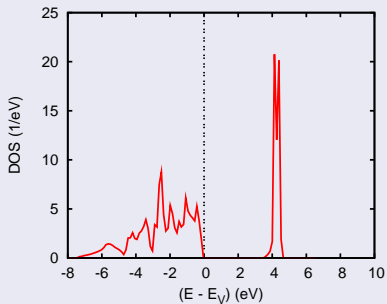
GGA: ≈ 3.5 eV,

exp.: 5.6 eV

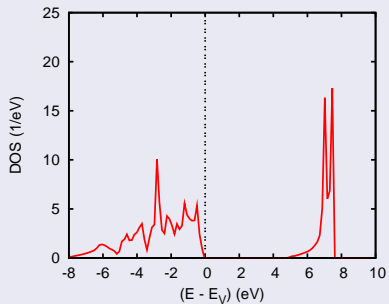


LaAlO₃

GGA



HSE



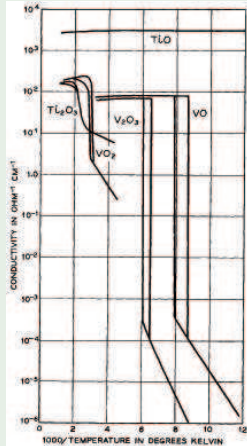
Bandgap

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



Metal-Insulator Transition of VO_2

Morin, PRL 1959



Metal-Insulator Transitions (MIT)

- VO_2 (d^1)
 - 1st order, 340 K, $\Delta\sigma \approx 10^4$
 - rutile \rightarrow M_1 (monoclinic)
- V_2O_3 (d^2)
 - 1st order, 170 K, $\Delta\sigma \approx 10^6$
 - corundum \rightarrow monoclinic
 - paramagn. \rightarrow AF order

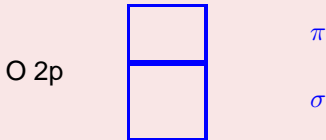
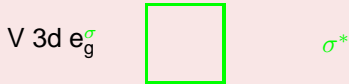
Origin of the MIT???

- Structural Changes?
- Electron Correlations?



Metal-Insulator Transition of VO_2

Octahedral Coordination



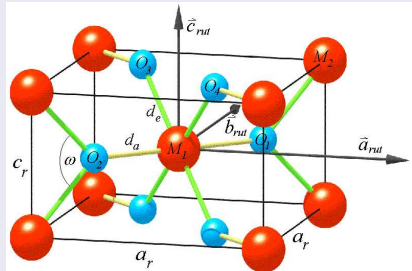
● V 3d-O 2p hybridization

● σ, σ^* ($p-de_g^\sigma$)

● π, π^* ($p-dt_{2g}$)

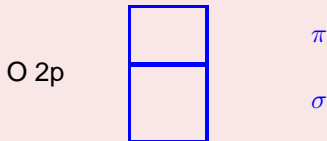
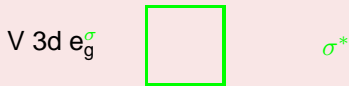
Rutile Structure

- simple tetragonal
- $P4_2/mnm$ (D_{4h}^{14})



Metal-Insulator Transition of VO_2

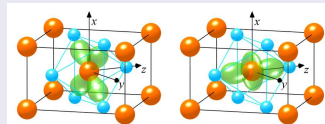
Octahedral Coordination



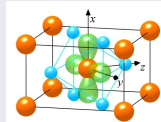
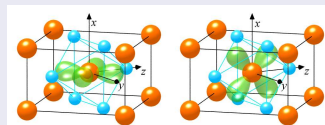
● V 3d-O 2p hybridization

- σ, σ^* ($p-de_g^{\sigma}$)
- π, π^* ($p-dt_{2g}$)

e_g^{σ} Orbitals

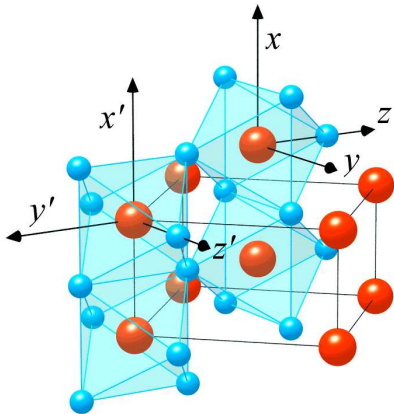


t_{2g} Orbitals



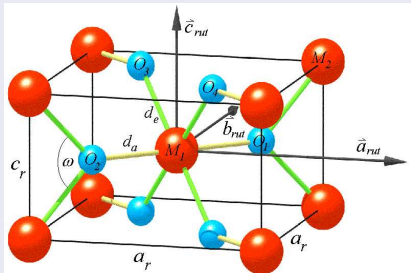
Metal-Insulator Transition of VO_2

Octahedral Chains



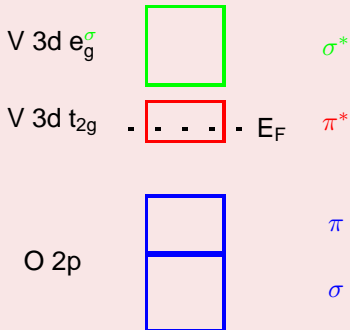
Rutile Structure

- simple tetragonal
- $P4_2/mnm$ (D_{4h}^{14})

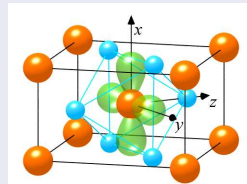
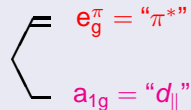
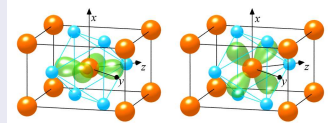


Metal-Insulator Transition of VO_2

Octahedral Coordination

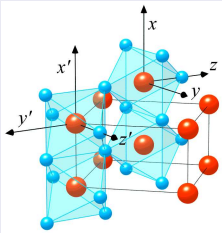


t_{2g} Orbitals

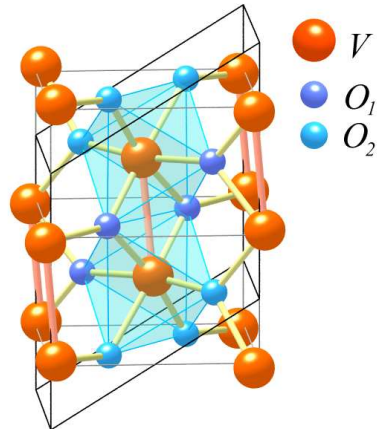


Metal-Insulator Transition of VO_2

Rutile Structure



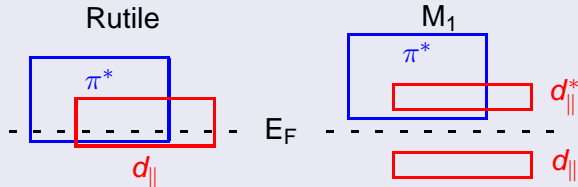
M_1 -Structure



Structural Changes

- V-V dimerization $\parallel c_R$
- antiferroelectric displacement $\perp c_R$

Metal-Insulator Transition of VO_2

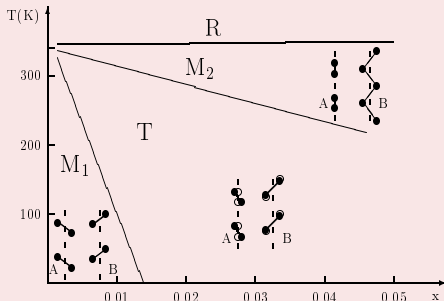


- Goodenough, 1960-1972
 - metal-metal dimerization $\parallel c_R \rightarrow$ **splitting into d_{\parallel} , d_{\parallel}^***
 - antiferroelectric displacement $\perp c_R \rightarrow$ **upshift of π^***
- Zylbersztein and Mott, 1975
 - **splitting of d_{\parallel}** by electronic correlations
 - **upshift of π^*** unscreens d_{\parallel} electrons



Metal-Insulator Transition of VO_2

Other Phases



- doping with Cr, Al, Fe, Ga
- uniaxial pressure $\parallel \langle 110 \rangle$

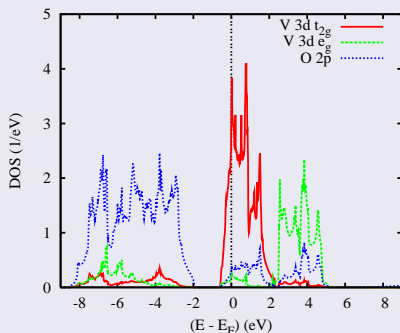
$\text{Cr}_x\text{V}_{1-x}\text{O}_2$
Pouget, Launois, 1976



Electronic Structure in Detail

Rutile Structure

- molecular-orbital picture ✓
- octahedral crystal field
⇒ V 3d t_{2g}/e_g
- V 3d–O 2p hybridization



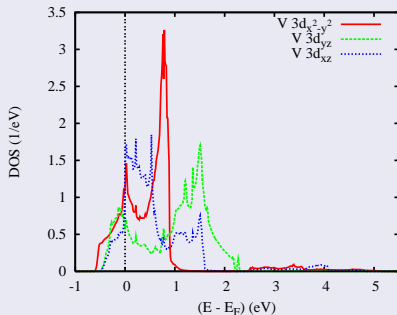
Ann. Phys. (Leipzig) **11**, 650 (2002)



Electronic Structure in Detail

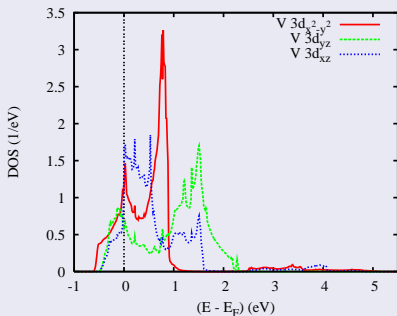
Rutile Structure

- molecular-orbital picture ✓
- octahedral crystal field
 $\implies V\ 3d\ t_{2g}/e_g$
- $V\ 3d-O\ 2p$ hybridization
- t_{2g} at E_F : $d_{x^2-y^2}$, d_{yz} , d_{xz}
- $n(d_{x^2-y^2}) \approx n(d_{yz}) \approx n(d_{xz})$

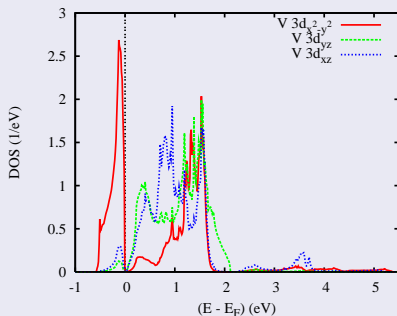
Ann. Phys. (Leipzig) **11**, 650 (2002)

Electronic Structure in Detail

Rutile Structure



M₁ Structure



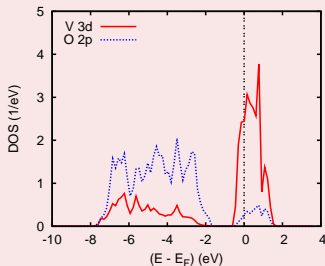
- bonding-antibonding splitting of $d_{||}$ bands
- energetical upshift of π^* bands \implies orbital ordering
- optical band gap on the verge of opening



New Calculations: GGA vs. HSE

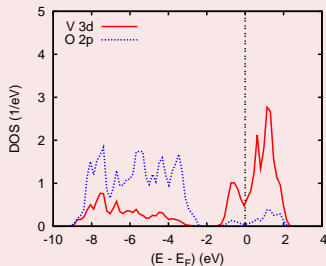
Rutile Structure

GGA



Rutile Structure

HSE



Rutile Structure: GGA \implies HSE

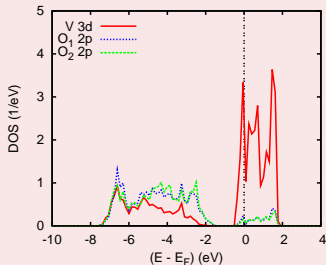
- broadening of O 2p and V 3d t_{2g} (!) bands
- splitting within V 3d t_{2g} bands



New Calculations: GGA vs. HSE

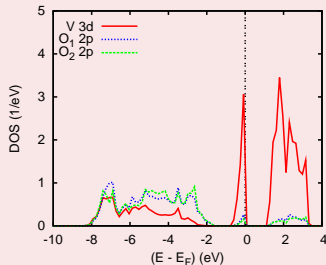
M_1 Structure

GGA



M_1 Structure

HSE



M_1 Structure: GGA \implies HSE

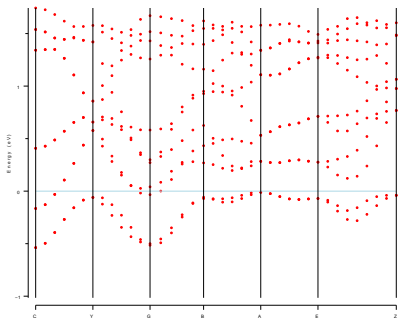
- splitting of $d_{||}$ bands, upshift of π^* bands
- optical bandgap of ≈ 1 eV



New Calculations: GGA vs. HSE

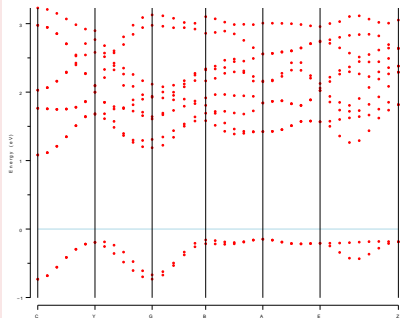
M₁ Structure

GGA



M₁ Structure

HSE



M₁ Structure: GGA \implies HSE

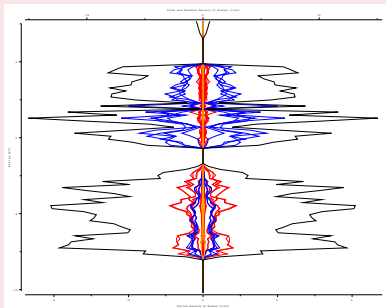
- splitting of $d_{||}$ bands, upshift of π^* bands
- optical bandgap of ≈ 1 eV



New Calculations: GGA vs. HSE

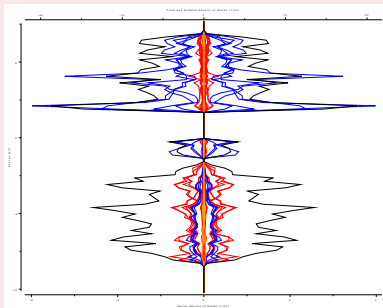
M₂ Structure

GGA



M₂ Structure

HSE



M₂ Structure: GGA \Rightarrow HSE

- localized magnetic moment of 1 μ_B
- optical bandgap of ≈ 1.6 eV



Unified Picture

Rutile-Related Transition-Metal Dioxides

VO_2 ($3d^1$), NbO_2 ($4d^1$), MoO_2 ($4d^2$)
(WO_2 ($5d^2$), TcO_2 ($4d^3$), ReO_2 ($5d^3$))

- instability against similar local distortions
 - metal-metal dimerization $\parallel c_R$
 - antiferroelectric displacement $\perp c_R$
- („accidental“) metal-insulator transition of the d^1 -members

VE *et al.*, J. Phys.: CM **12**, 4923 (2000)

VE, Ann. Phys. **11**, 650 (2002)

VE, EPL **58**, 851 (2002)

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

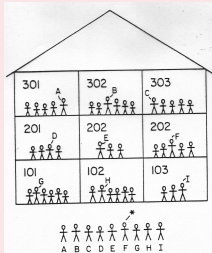


Success Stories

Basics

- DFT (exact, ground state)
- LDA, GGA, ...

Percus-Levy partition



Success Stories

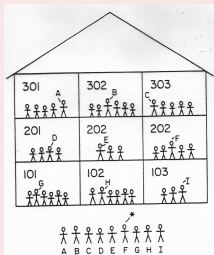
Basics

- DFT (exact, ground state)
- LDA, GGA, ...

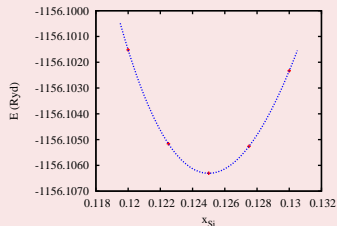
Implementation

- Muffins and beyond
- Full-Potential ASW

Percus-Levy partition



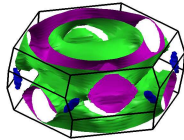
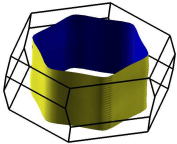
Full-Potential Code



Success Stories

Delafossites

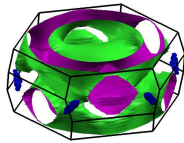
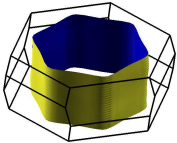
2D \rightarrow 3D



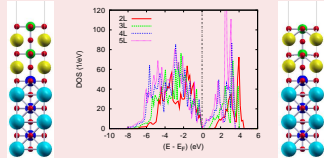
Success Stories

Delafossites

2D \rightarrow 3D



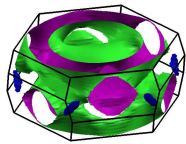
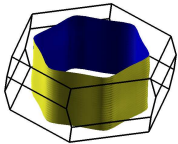
LaAlO₃/SrTiO₃



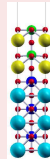
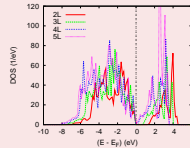
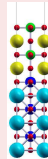
Success Stories

Delafossites

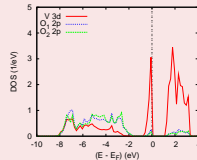
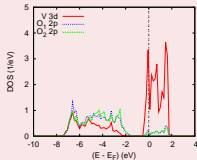
2D → 3D



LaAlO₃/SrTiO₃

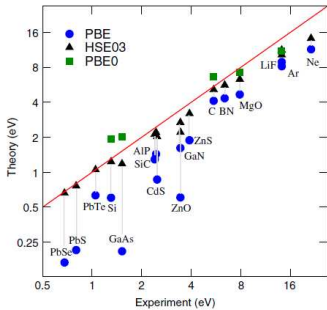


Metal-Insulator Transitions in VO₂

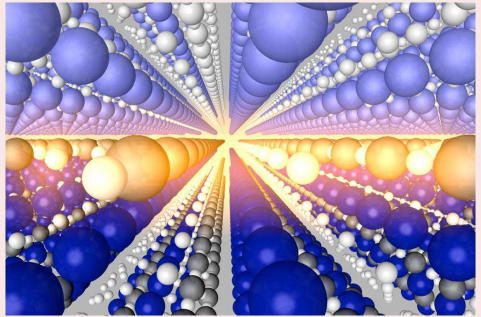


Visions

Methods



Materials



Acknowledgments

Augsburg

M. Breitschaft, U. Eckern,
K.-H. Höck, S. Horn, R. Horny,
T. Kopp, J. Kündel, J. Mannhart,
J. Moosburger-Will, N. Pavlenko,
W. Scherer, D. Vollhardt

TRR 80



Caen

R. Frésard,
S. Hébert,
A. Maignan,
C. Martin

Darmstadt/Jülich

P. C. Schmidt, M. Stephan,
J. Sticht †

Europe/USA

E. Wimmer, A. Mavromaras,
P. Saxe, R. Windiks, W. Wolf



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Würzburg

Thank You for Your Attention!

