All-Electron Full-Potential Calculations at $\mathcal{O}$(ASA) Speed

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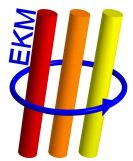
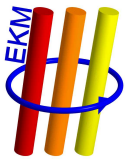
Institute for Physics, University of Augsburg

October 12, 2008



Outline



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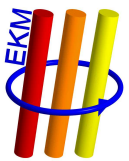

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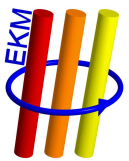

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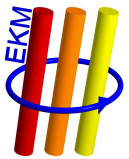

Back in the 1930's . . .

John C. Slater

Full Potential

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

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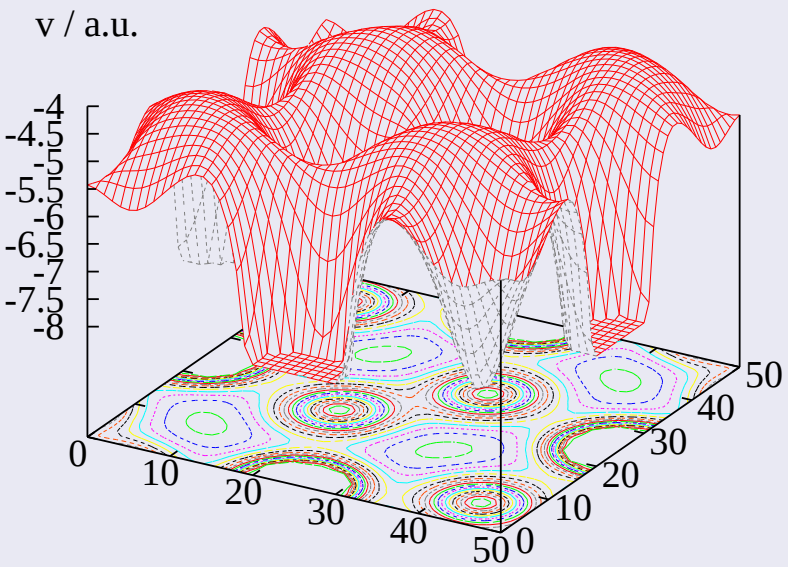
Muffin-Tin Approximation

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

Back in the 1930's . . .

Full Potential (FeS_2)



Muffin-Tin Potential

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Muffin-Tin Approximation

distinguish:

- atomic regions
- remainder

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Partial Waves

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    - plane waves
    - spherical waves

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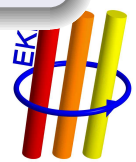
Basis Functions

- matched partial waves
  - augmented plane waves (APWs)
  - „muffin-tin orbitals" (MTOs), augmented spherical waves (ASWs)



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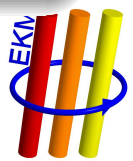

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Wave Function

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Core States

all-electron methods

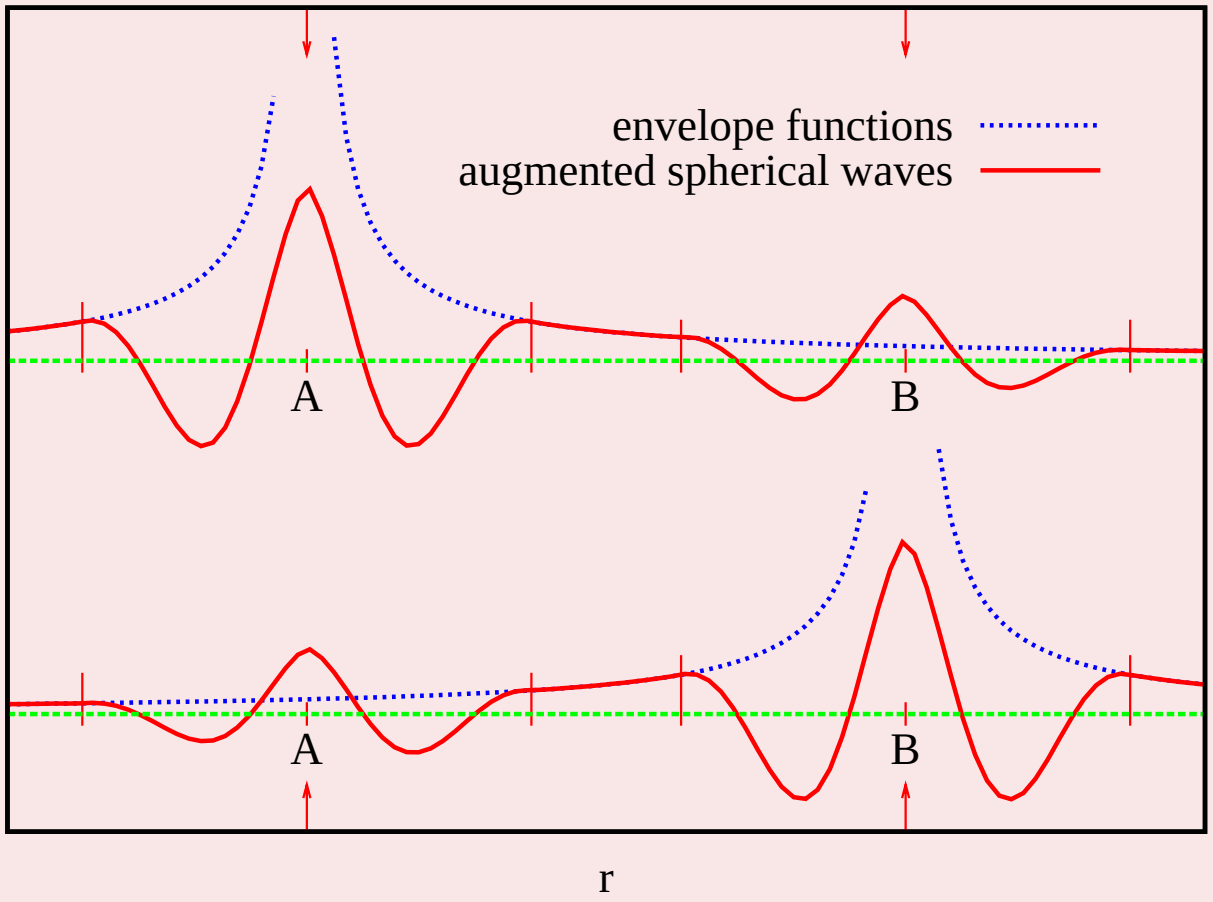
- fully included
- orthogonal to partial waves

Basis Functions

- matched partial waves
  - augmented plane waves (APWs)
  - „muffin-tin orbitals“ (MTOs), augmented spherical waves (ASWs)
- used to describe valence states

Back in the 1930's . . .

Augmented Spherical Waves



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"Linear Methods in Band Theory"

- energy dependence of basis functions almost linear $\rightarrow$ linearize $(\varphi, \dot{\varphi})$
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Linear Augmented Plane Wave (LAPW)

- muffin-tin approximation
- easy to implement — good!
- full-potential at a low price
  - basis functions from muffin-tin potential
  - wave functions from full potential
  - example: Wien2k
- large basis set ($\approx$ 100 pw's/atom) — bad!

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Linear Muffin-Tin Orbital (LMTO)

- based on spherical waves
  - does not require crystalline periodicity
  - natural interpretation of results
- difficult to implement bad!
- full-potential extension extremely difficult
- muffin-tin approximation (?)
  - finite interstitial region
  - large basis set:
    two functions per s-, p-, d-state
  - still inefficient bad!

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- atomic-sphere approximation (ASA)
  - make spheres space-filling!
    - interstitial region formally removed
    - only numerical functions in spheres
  - minimal basis set (s, p, d)
    - very high computational efficiency
      $\rightarrow \mathcal{O}$(ASA) speed!!!
  - makes potential more realistic
  - systematic error in total energy bad!

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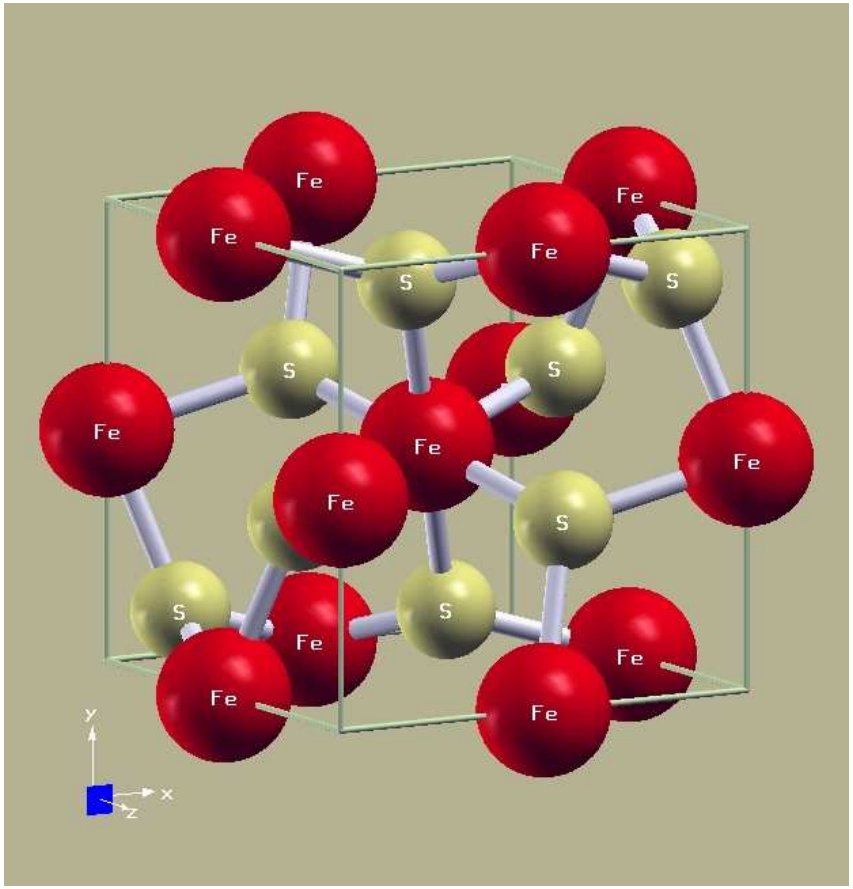
Iron Pyrite: FeS_2

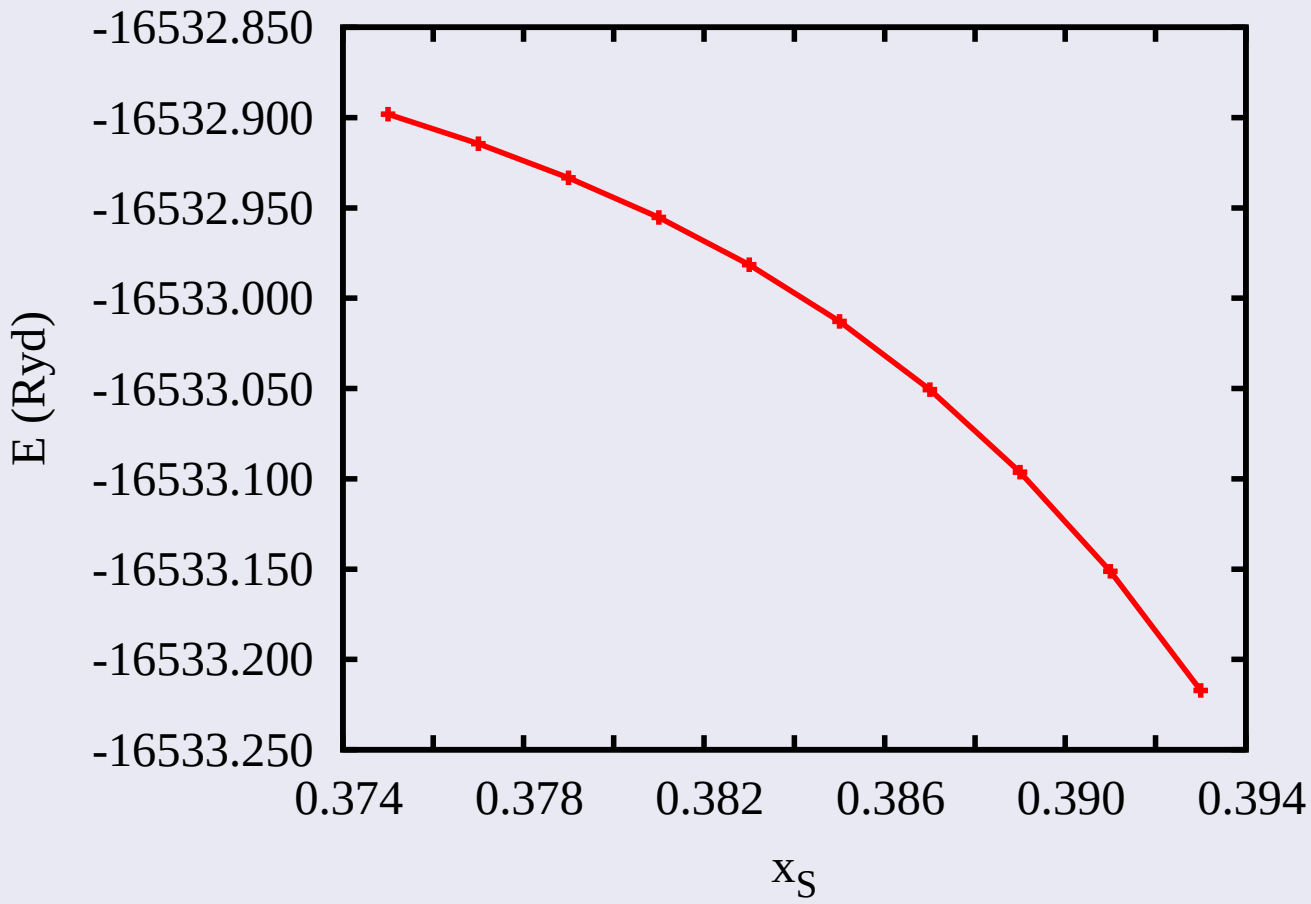


Pyrite

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

FeS_2: Structure Optimization

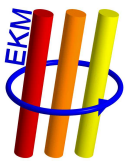
ASA^+ Code



Towards a Full-Potential Spherical-Wave Method

Conclusions

- ASA (space-filling atomic spheres)
  - $\mathcal{O}$(ASA) speed
  - systematic error in total energy
- non-overlapping muffin-tin spheres
  - prerequisite for accurate total energies
  - larger basis set $\longrightarrow$ inefficient



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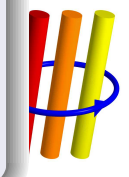
Requirements

- restore interstitial region
  - go to non-overlapping muffin-tin spheres
  - go beyond constant-potential approximation
- inside muffin-tin spheres
  - non-spherical contributions



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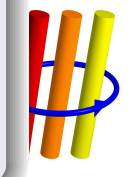

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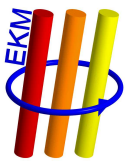
Guidelines

- interstitial quantities expanded in plane waves
  - straightforward to implement
  - inefficient
- interstitial quantities expanded in spherical waves
  - elegant, no periodicity required
  - efficient
  - difficult to implement



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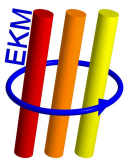
ASW Method

Characteristics

- “dialect” of LMTO
  - different linearization scheme
  - different interstitial energy
  - different implementations



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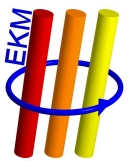
0th Generation (Williams, Kübler, Gelatt, 1970s)

PRB **19**, 6094 (1979)



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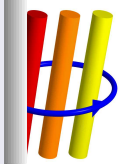
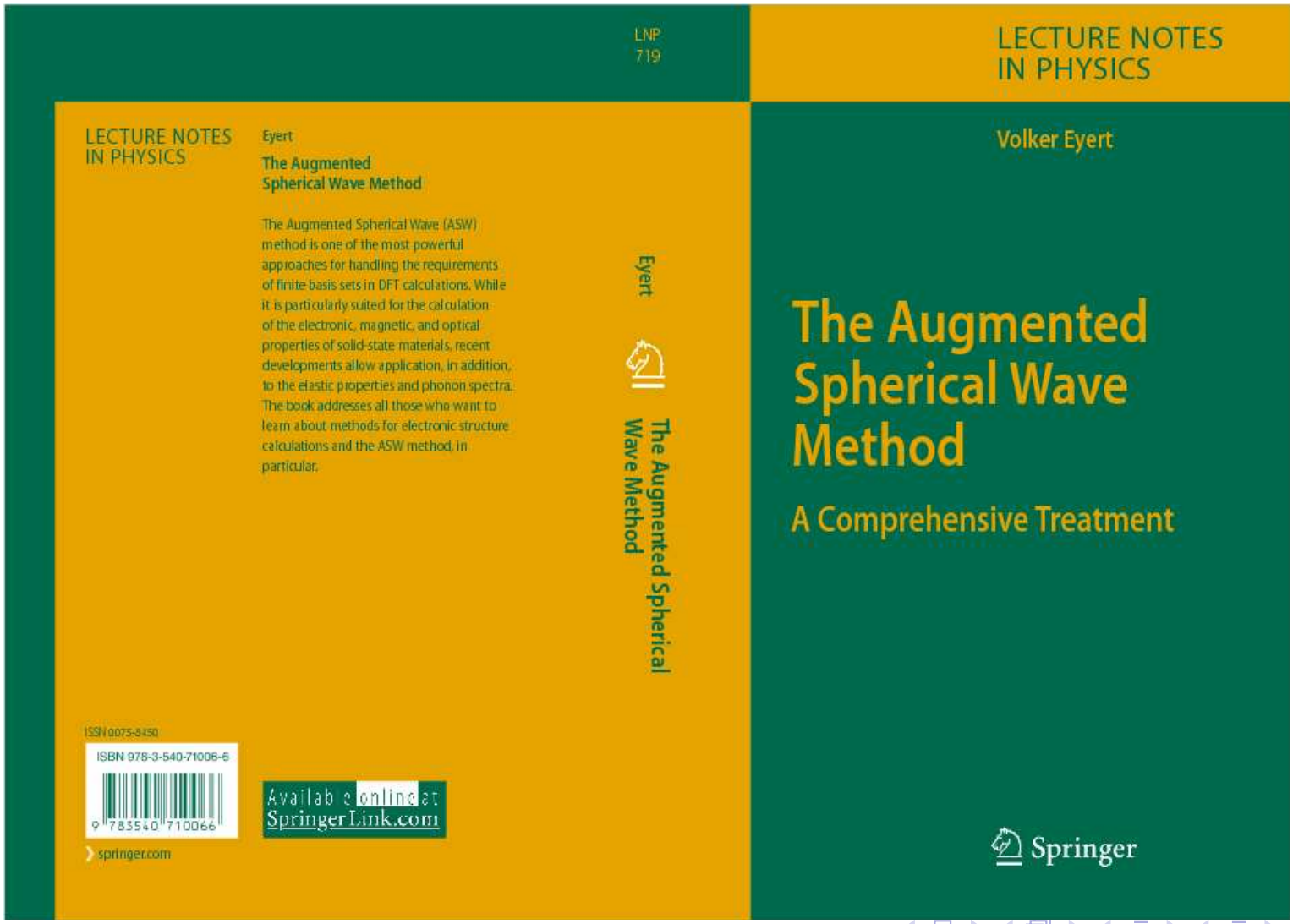
  - different interstitial energy
  - different implementations

1st Generation (VE, 1990s) IJQC **77**, 1007 (2000)

- completely new, monolithic implementation
- new algorithms $\longrightarrow$ improved accuracy, numerical stability
- much improved functionality, usability, and portability
- xAnderson convergence acceleration scheme
- all LDA-parametrizations, most GGA-schemes
- still based on atomic-sphere approximation



ASW Method: Further Reading



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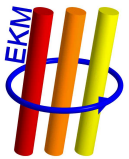

Basic Principles

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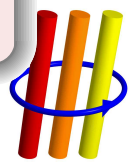
- remove total energy error due to overlap of atomic spheres
  - reintroduce non-overlapping muffin-tin spheres
  - restore interstitial region



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- remove total energy error due to overlap of atomic spheres
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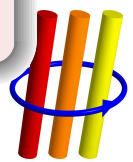
- find representation of electron density and full potential
  - inside muffin-tin spheres
  - in the interstitial region



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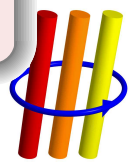

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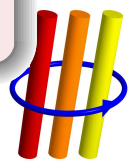

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    - use spherical-harmonics expansions
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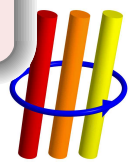

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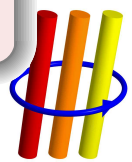
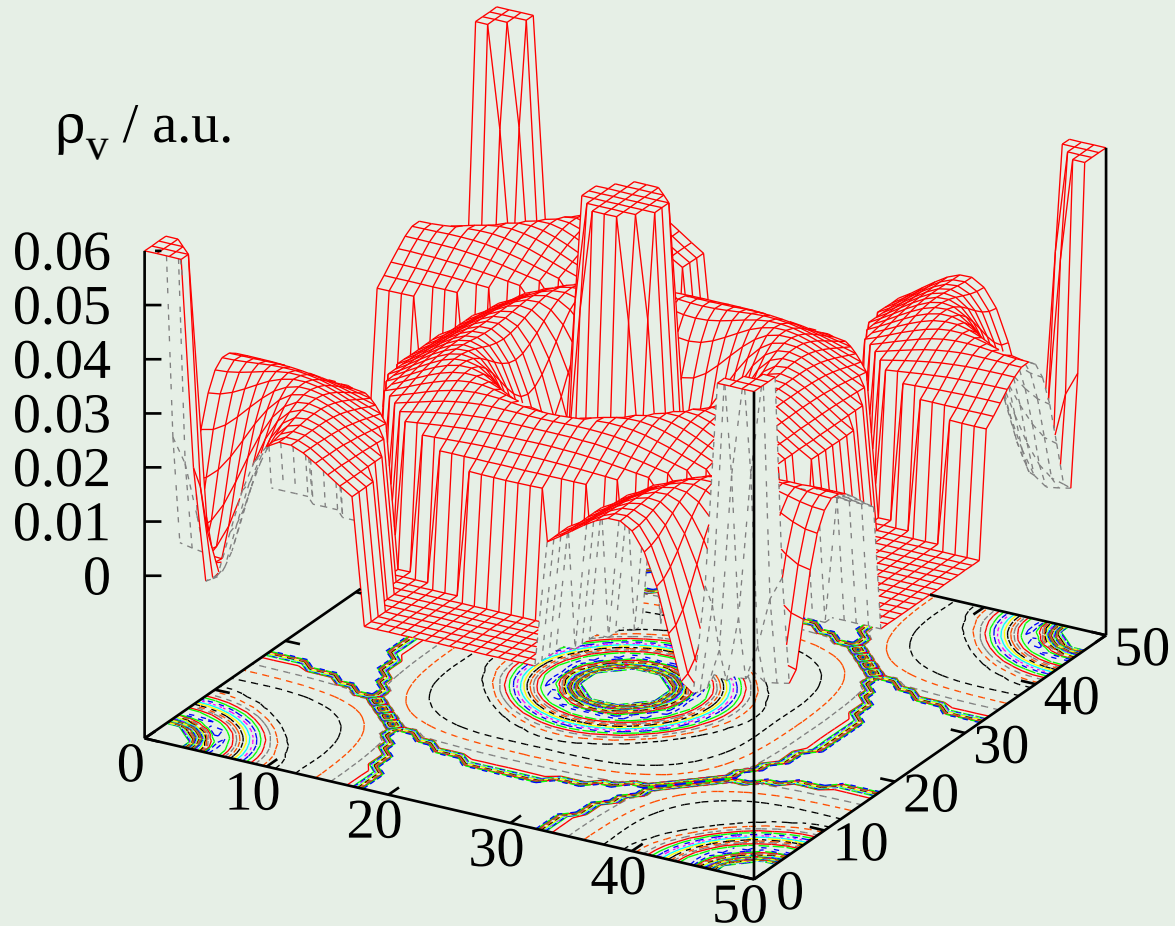
- find representation of products of the basis functions
  - inside muffin-tin spheres
    - use spherical-harmonics expansions
  - in the interstitial region
    - no exact spherical-wave representation available!



From Wave Functions to Electron Density

Density inside MT-Spheres (Al)

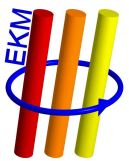


From Wave Functions to Electron Density

Products of Basis Functions in Interstitial Region

$$p^I(\mathbf{r}) = \sum_n d_n F_n(\mathbf{r})$$

$$\int d^3\mathbf{r}\, F^*_{n'}(\mathbf{r}) p^I(\mathbf{r}) = \sum_n d_n \int d^3\mathbf{r}\, F^*_{n'}(\mathbf{r}) F_n(\mathbf{r})$$



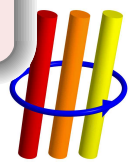
From Wave Functions to Electron Density

Products of Basis Functions in Interstitial Region

$$p^l(\mathbf{r}) = \sum_n d_n F_n(\mathbf{r})$$

$$\int d^3\mathbf{r}\, F^*_{n'}(\mathbf{r}) p^l(\mathbf{r}) = \sum_n d_n \int d^3\mathbf{r}\, F^*_{n'}(\mathbf{r}) F_n(\mathbf{r})$$

- $F_n(\mathbf{r})$: plane waves
  - integrals exact
  - inefficient
  - Weyrich 1988, Blöchl 1989, VE 1991, Savrasov 1992, Methfessel 2000



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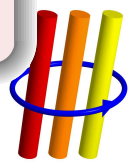
- $F_n(\mathbf{r})$: spherical waves
  - would be efficient
  - integrals not known analytically
  - Springborg/Andersen 1987, Methfessel 1988, VE 2002, VE 2006



From Wave Functions to Electron Density

Interstitial Products of Basis Functions

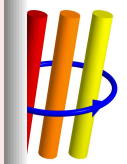
expand in atom-centered spherical waves (Hankel functions):

$$p^I(\mathbf{r}) := \left(H^{\infty}_{L\kappa_1\sigma}(\mathbf{r}_i)\right)^* H^{\infty}_{L'\kappa_2\sigma}(\mathbf{r}_j) \stackrel{!}{=} \sum_n \sum_{K\eta} d^{L\kappa_1 iL'\kappa_2 j}_{K\eta n\sigma} H_{K\eta}(\mathbf{r}_n)$$

- $H^{\infty}_{L'\kappa_2\sigma}(\mathbf{r}_j)$: orbital basis set (obs)
- $H_{K\eta}(\mathbf{r}_n)$: product basis set (pbs)

coefficients from projection $\mathcal{P}$:

$$\begin{aligned}\mathcal{P}\left[p^I(\mathbf{r})\right] &= \mathcal{P}\left[\left(H^{\infty}_{L\kappa_1\sigma}(\mathbf{r}_i)\right)^* H^{\infty}_{L'\kappa_2\sigma}(\mathbf{r}_j)\right] \\ &= \sum_n \sum_{K\eta} d^{L\kappa_1 iL'\kappa_2 j}_{K\eta n\sigma}\, \mathcal{P}\left[H_{K\eta}(\mathbf{r}_n)\right]\end{aligned}$$



From Wave Functions to Electron Density

Interstitial Products of Basis Functions

expand in atom-centered spherical waves (Hankel functions):

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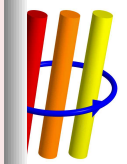

From Wave Functions to Electron Density

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projection $\mathcal{P}$:

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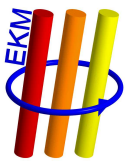

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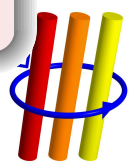
$$\mathcal{P}\left[\left(H^{\infty}_{L\kappa_1\sigma}(\mathbf{r}_i)\right)^* H^{\infty}_{L'\kappa_2\sigma}(\mathbf{r}_j)\right] = \sum_n \sum_{K\eta} d^{L\kappa_1 iL'\kappa_2 j}_{K\eta n\sigma}\, \mathcal{P}\left[H_{K\eta}(\mathbf{r}_n)\right]$$

- Springborg/Andersen 1987
  integrate over interstitial region, use one-center expansions

$$\mathcal{P}_{K'\eta' n'} \ldots \hat{=} \int_{\Omega_I} d^3\mathbf{r}\, H^*_{K'\eta'}(\mathbf{r}_{n'}) \ldots$$



From Wave Functions to Electron Density

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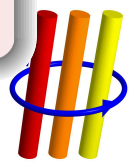
- Methfessel 1988
  match values and slopes at MT-sphere surfaces

$$\mathcal{P}_{K'\eta'n'} \ldots \hat{=} \int d^2\hat{\mathbf{r}}\, Y_{K'}(\hat{\mathbf{r}}) \left(\frac{\partial}{\partial r}\right)^{\eta'-1} \ldots \Big|_{|\mathbf{r}_{n'}|=s_{n'}}$$



From Wave Functions to Electron Density

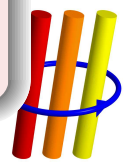
Interstitial Products of Basis Functions

projection $\mathcal{P}$:

$$\mathcal{P}\left[\left(H^{\infty}_{L\kappa_1\sigma}(\mathbf{r}_i)\right)^* H^{\infty}_{L'\kappa_2\sigma}(\mathbf{r}_j)\right] = \sum_n \sum_{K\eta} d^{L\kappa_1 iL'\kappa_2 j}_{K\eta n\sigma}\, \mathcal{P}\left[H_{K\eta}(\mathbf{r}_n)\right]$$

- VE 2002
  integrate over interstitial region, use one-center expansions
  (interstitial $\rightarrow$ shells between AS- and MT-spheres)

$$\mathcal{P}_{K'\eta'n'} \ldots \hat{=} \sum_m \int_{\Omega'_m} d^3\mathbf{r}_m\, H^*_{K'\eta'}(\mathbf{r}_{n'}) \ldots$$



From Wave Functions to Electron Density

Interstitial Products of Basis Functions

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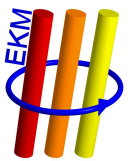
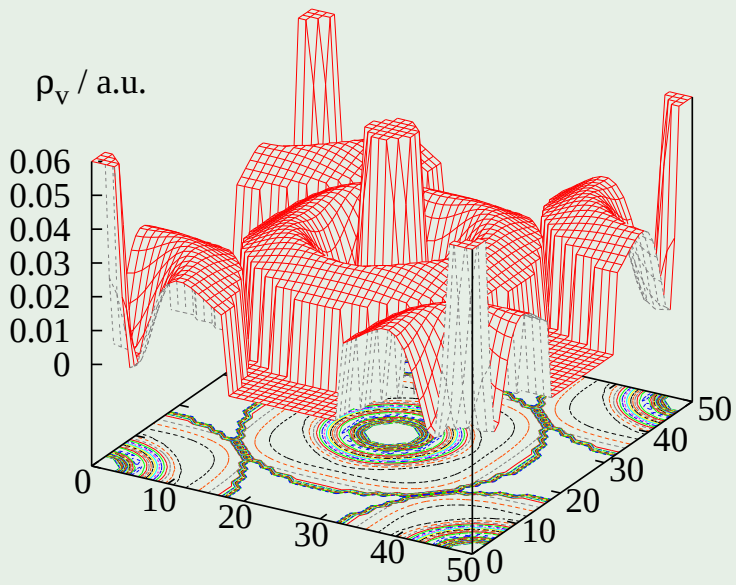
experience

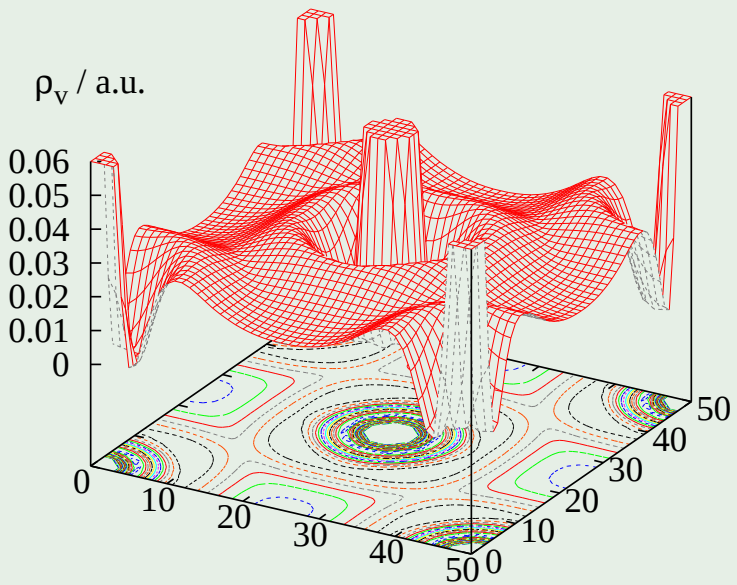
- product basis set almost overcomplete
- value/slope (Methfessel) matching most stable



From Wave Functions to Electron Density

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





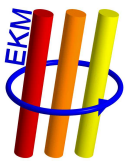
From Electron Density to Full Potential

Inside Muffin-Tin Spheres

- density, Hartree-potential and xc-potential numerically

Interstitial Region

- density from value/slope matching
- Hartree-potential analytically
- xc-potential from value/slope matching



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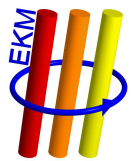


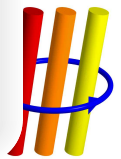
From Full Potential to Basis Functions

Previous Approaches

- project full potential to muffin-tin potential
- construct basis functions from muffin-tin potential
- no minimal basis set! (large basis set!)

Present Approach

- project full potential to ASA potential
- construct basis functions from ASA potential
- minimal basis set!
- future
  - use spheres larger than space-filling
  - remove linearization error



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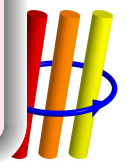
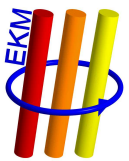


Comparison of Approaches

Ole K. Andersen

- ASA geometry used for basis functions
  $\longrightarrow$ minimal basis set — good!
- ASA geometry used for density and potential
  $\longrightarrow$ error in total energy — bad!



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Michael S. Methfessel

- MT geometry used for density and potential
  → accurate total energy — good!
- MT geometry used for basis functions
  → large basis set — bad!

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present approach

- ASA geometry used for basis functions
  $\rightarrow$ minimal basis set $\rightarrow$ $\mathcal{O}$(ASA) speed — great!
- MT geometry used for density and potential
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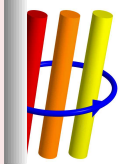
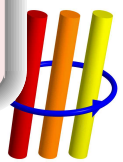


Implementation

2nd Generation ASW (VE, 2000s)

- based on 1st generation code
- full-potential ASW method — at $\mathcal{O}$(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
- LDA+U method
  - all „flavours“ for double-counting terms (AMF, FLL, DFT)



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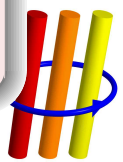

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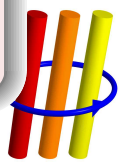
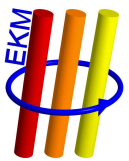
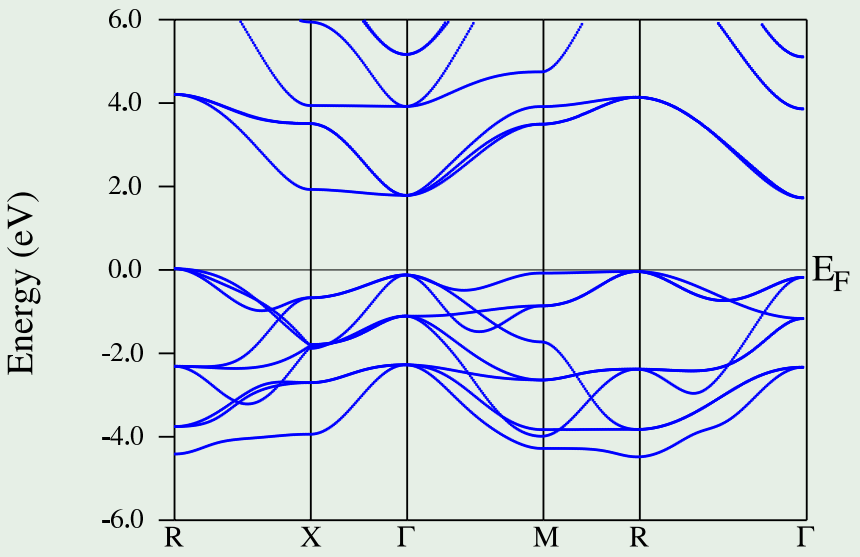


Outline

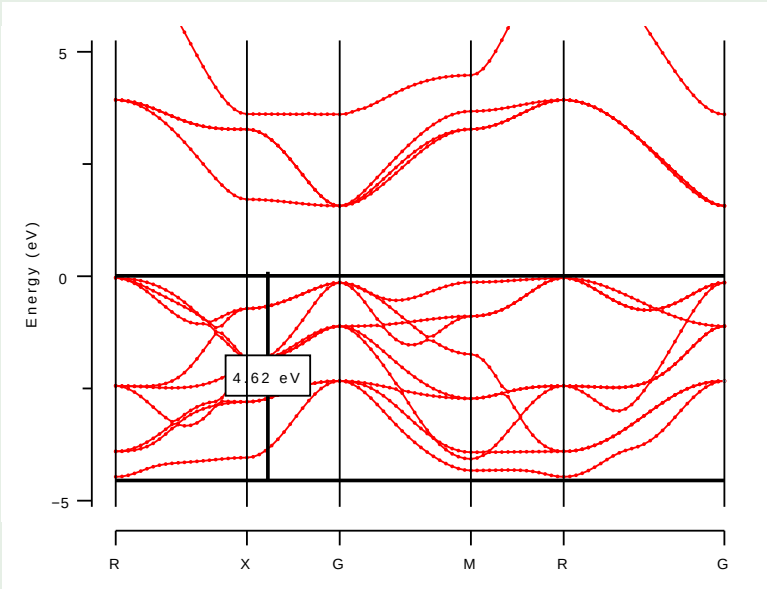


Electronic Structure of $BaTiO_3$

Wien2k



VASP



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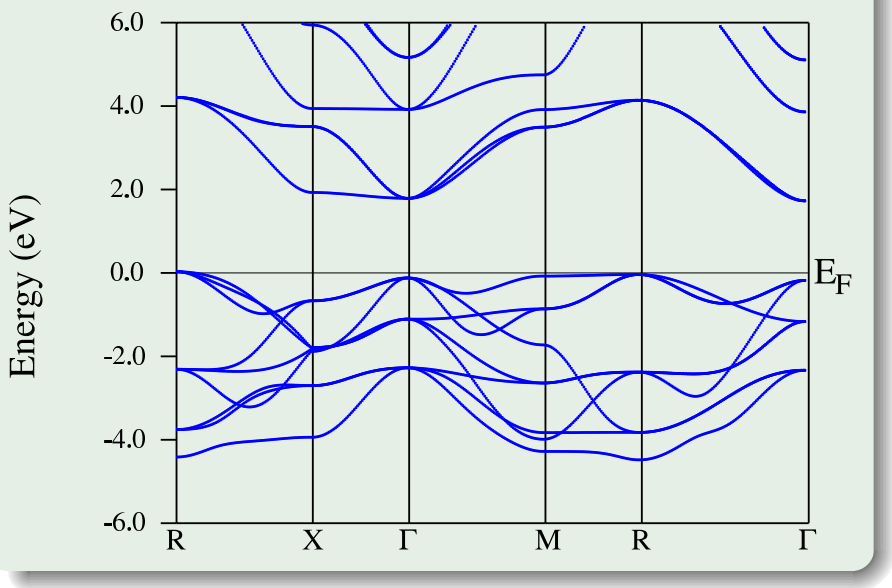
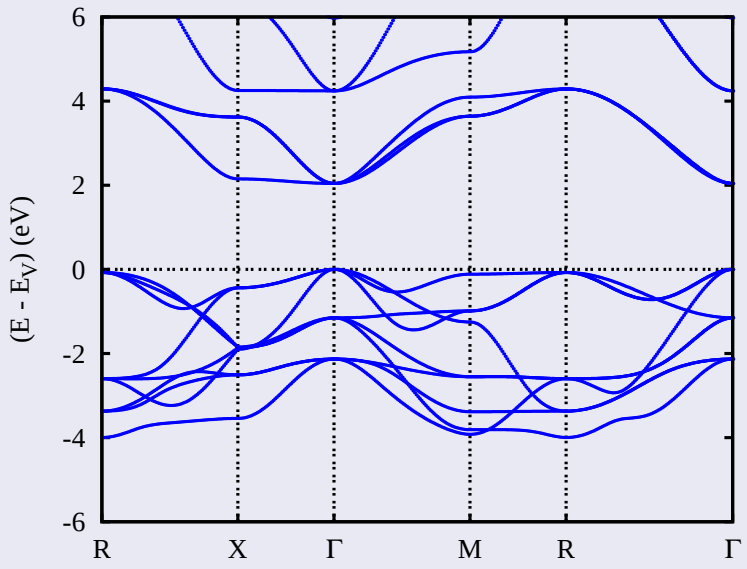


ASA$^+$ Code



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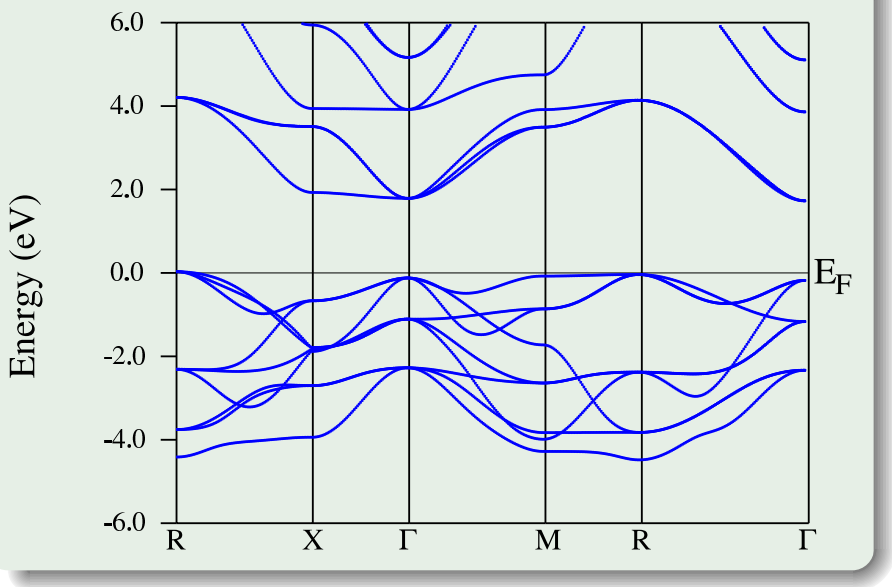
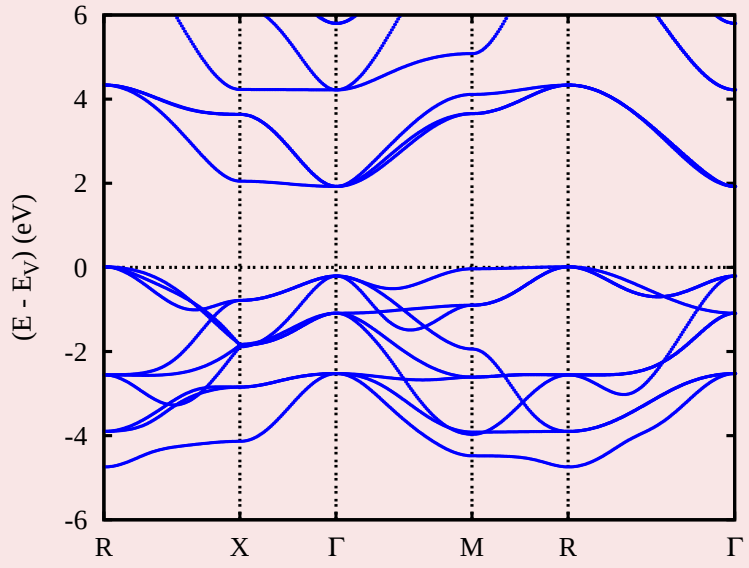
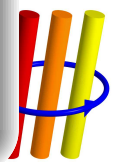


Full-Potential Code



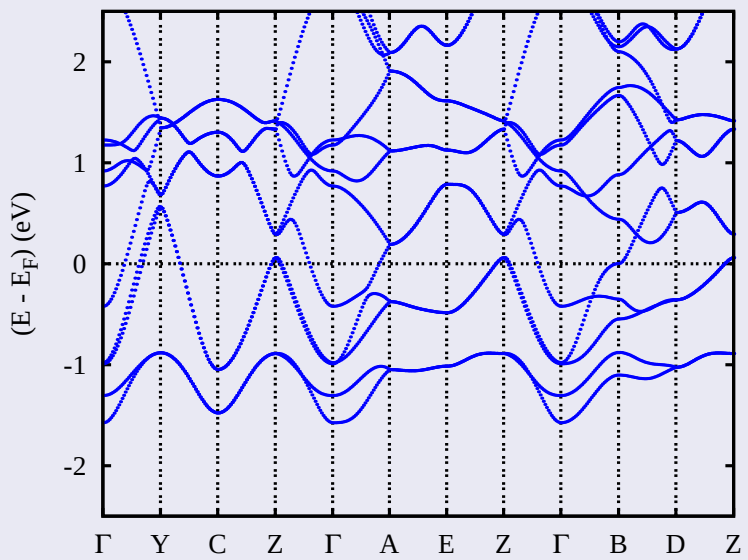
New!

- much better agreement with other full-potential codes (valence-band width, valence states at M-point)

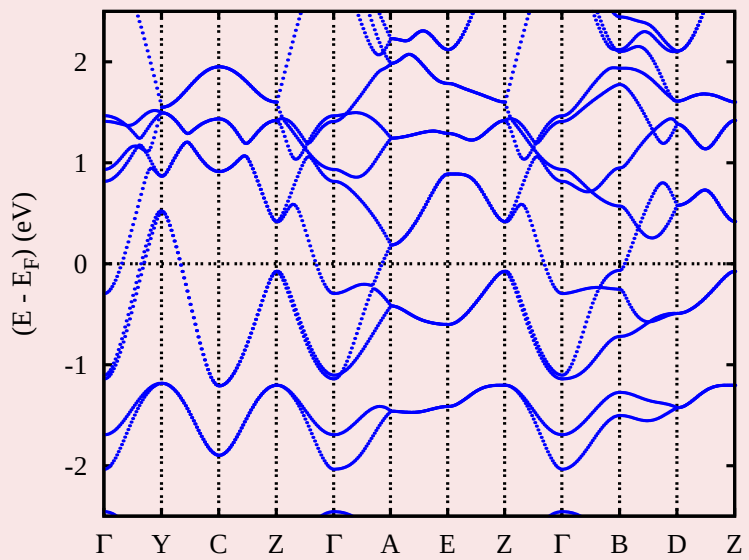


Fermi Surface of MoO_2

ASA Code

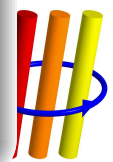


Full-Potential Code

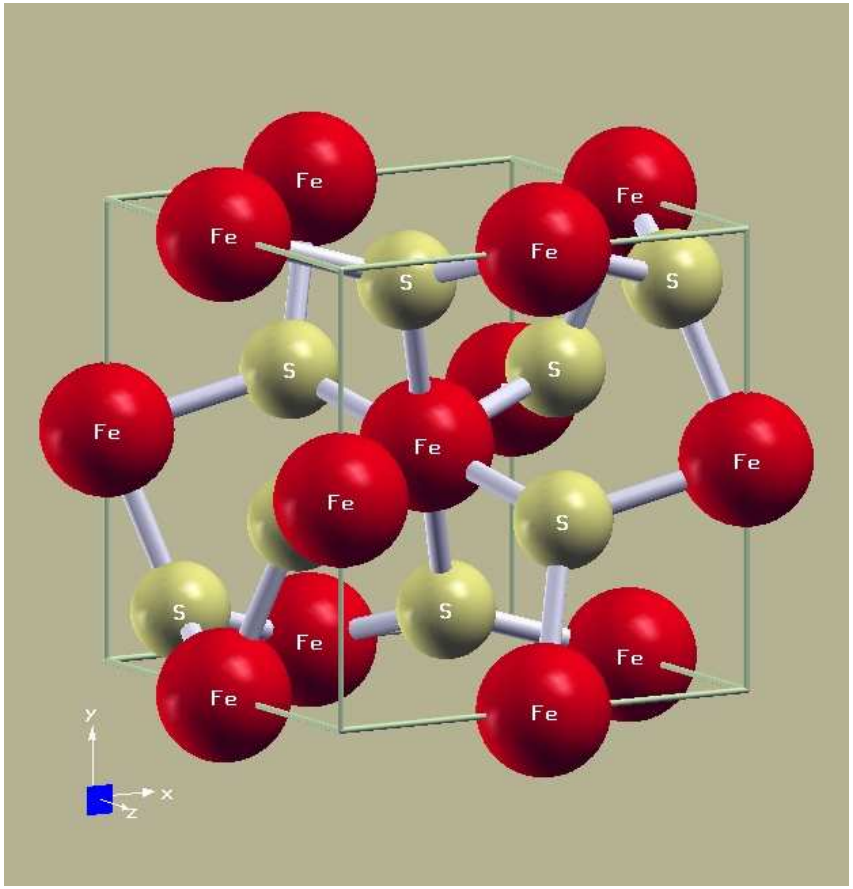


New!

- no hole pocket near Z-point
- much better agreement with ARPES, de Haas-van Alphen



Iron Pyrite: FeS_2

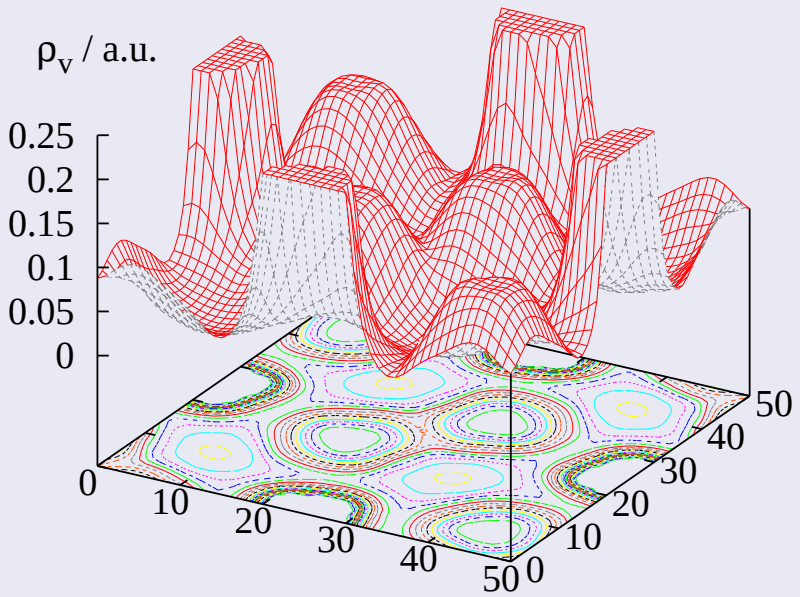


Pyrite

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

FeS_2: Density and Laplacian

Valence Electron Density



FeS_2: Density and Laplacian

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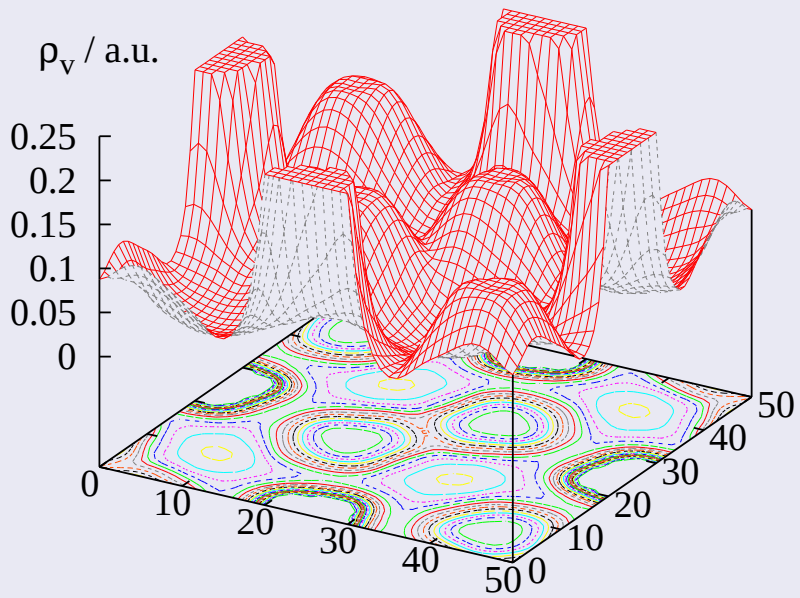
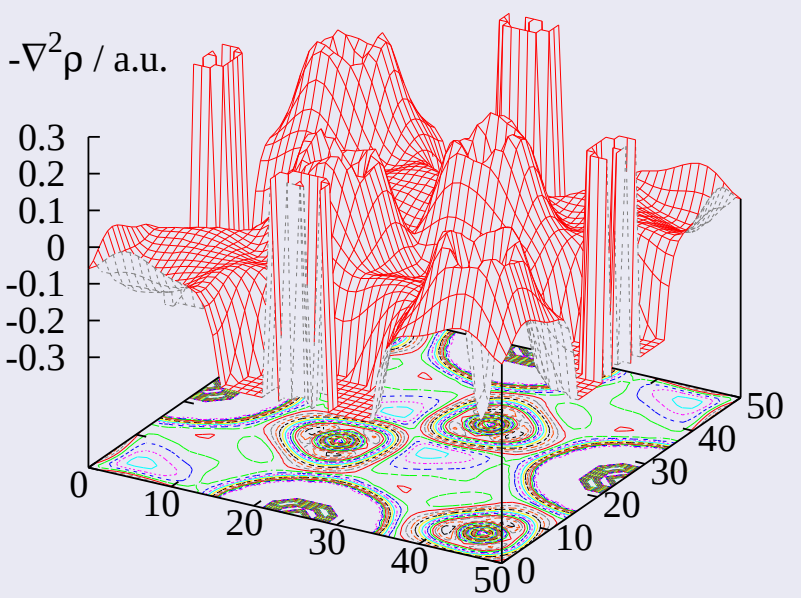


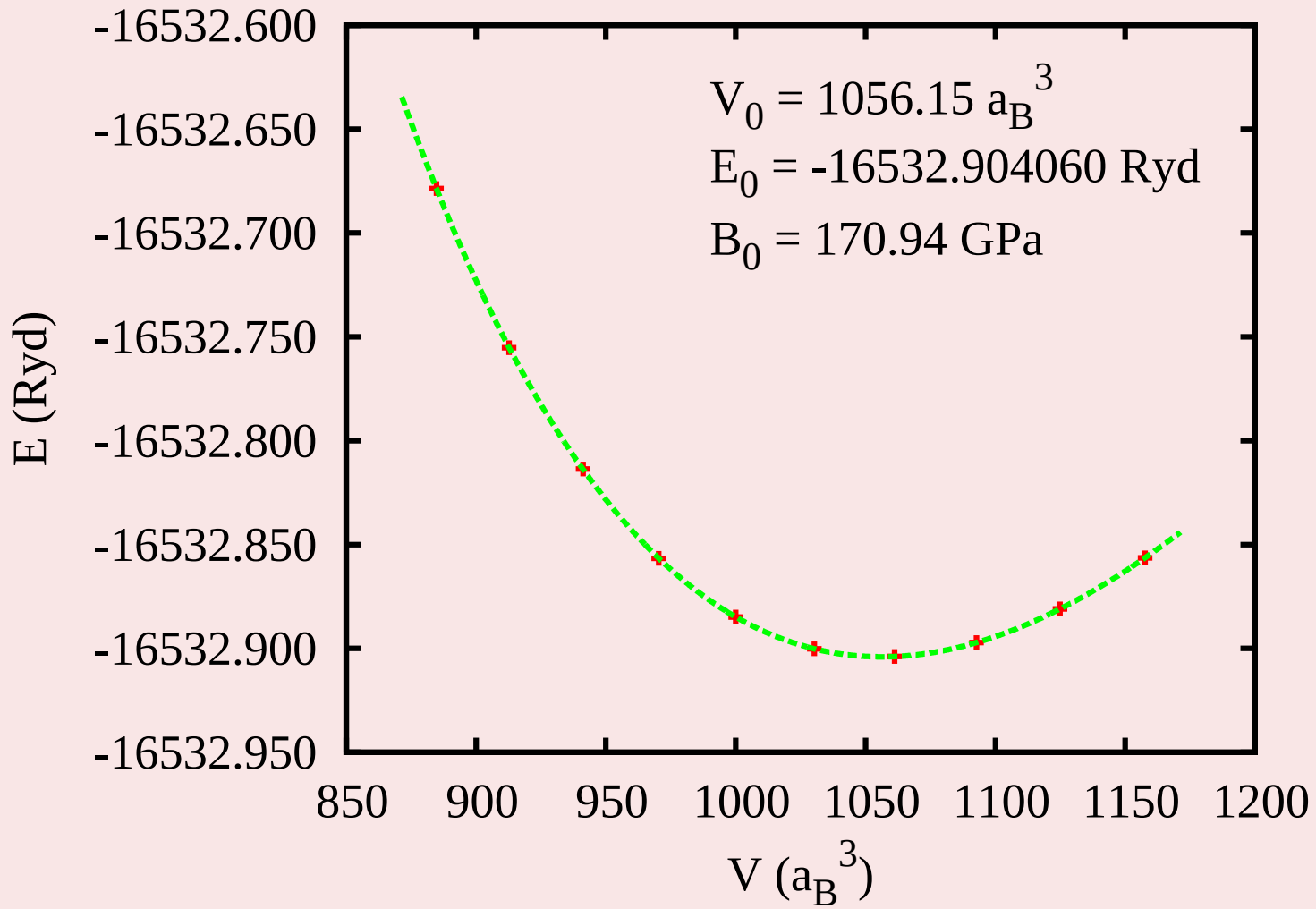
Laplacian of Electron Density



New!

- topological analysis (Bader analysis)

FeS_2: Equilibrium Volume and Bulk Modulus



FeS_2: Equilibrium Volume and Bulk Modulus

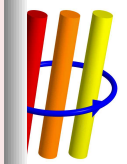
Lattice Constant

10.28	NCPP	Zeng and Holzwarth '94
10.02	FPLO	Opahle *et al.* '99
10.17	CRYSTAL98	Muscat *et al.* '02
9.92	CASTEP	Muscat *et al.* '02
10.18	FPASW	present work
10.23	exp.	Finklea *et al.* '76
10.22	exp.	Will *et al.* '84
10.23	exp.	Stevens *et al.* '91

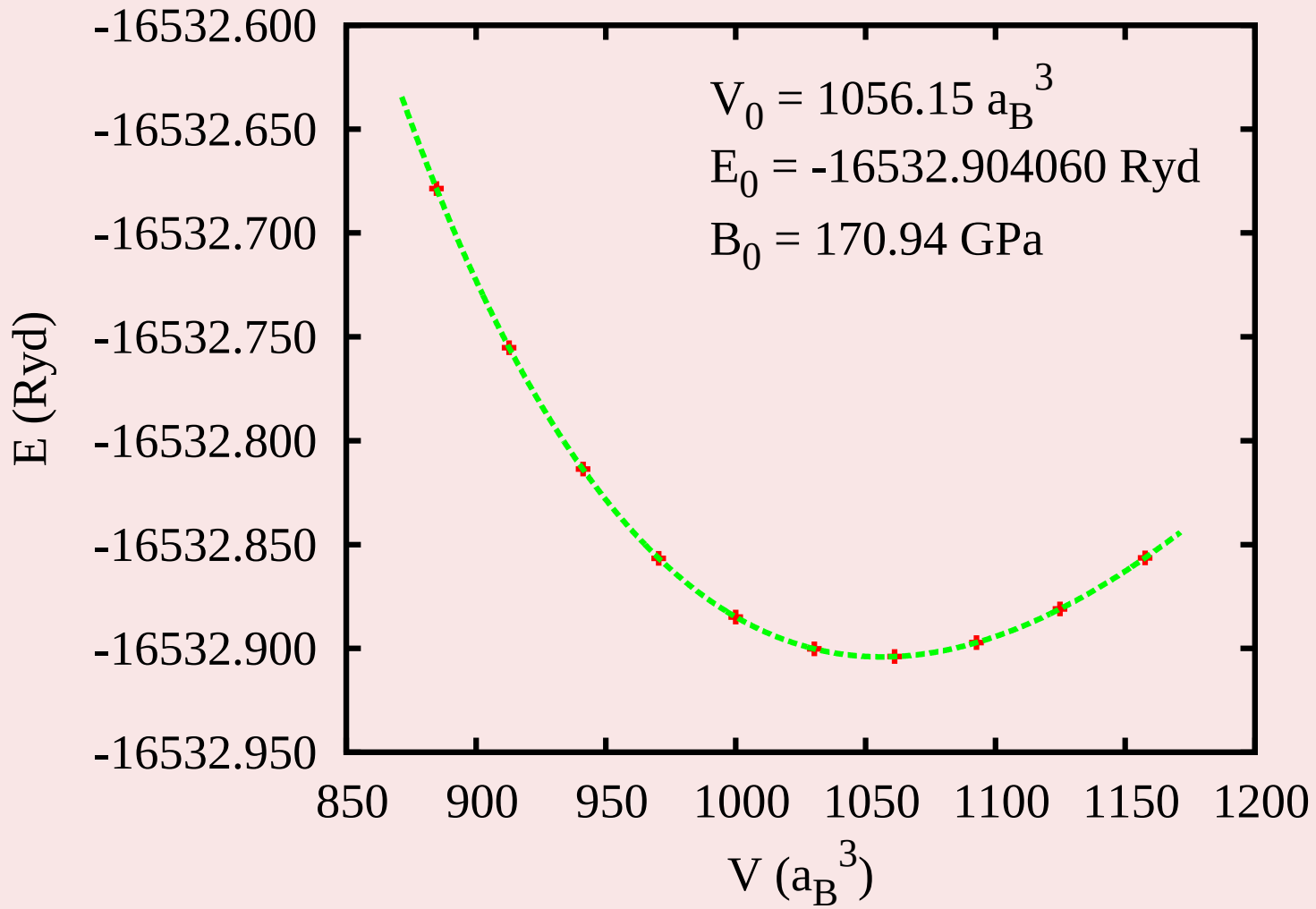
FeS_2: Equilibrium Volume and Bulk Modulus

Bulk Modulus

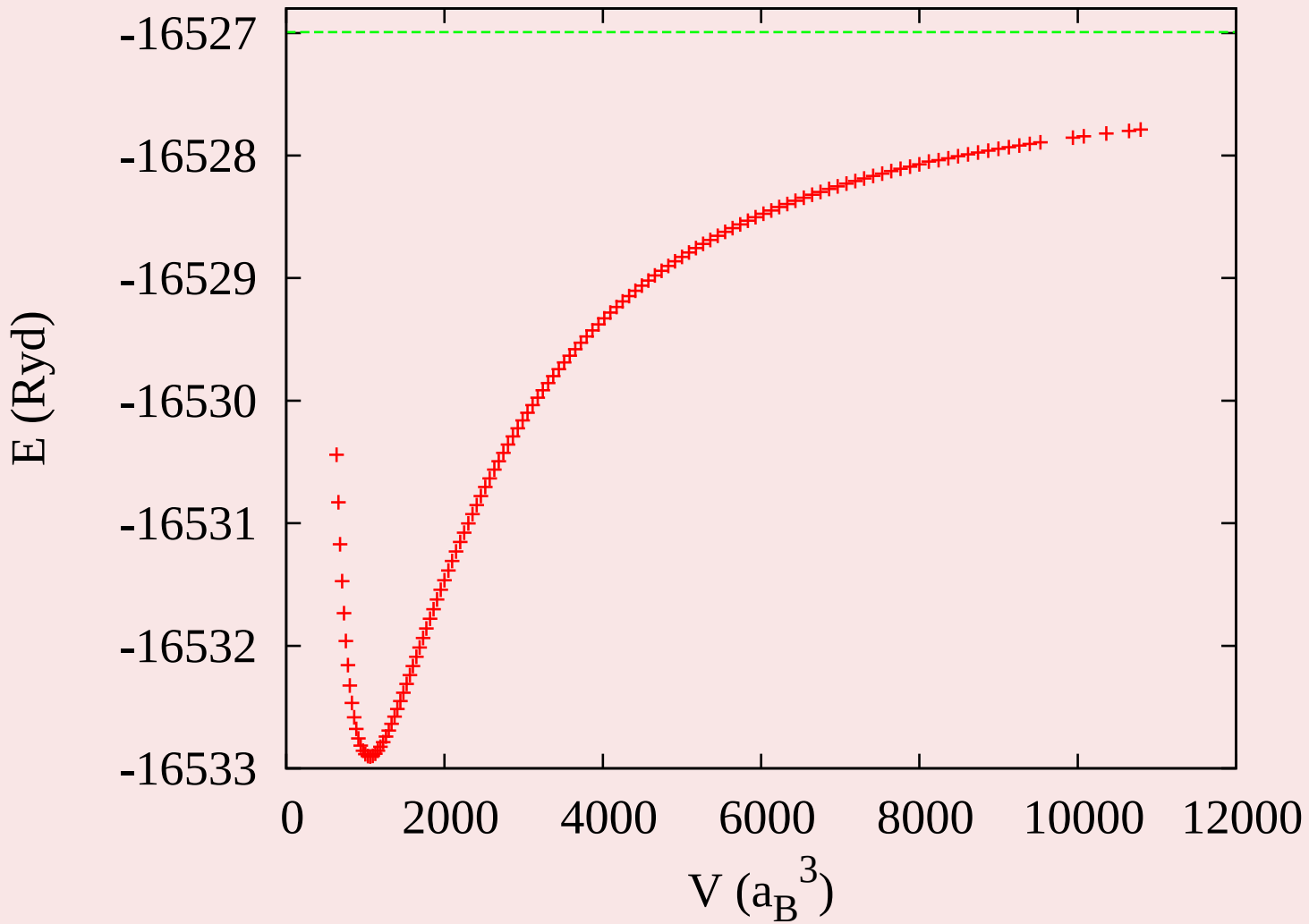
187	LMTO	Nguyen-Manh *et al.* ’98
185	FPLO	Opahle *et al.* ’99
209	CRYSTAL98	Muscat *et al.* ’02
208	CASTEP	Muscat *et al.* ’02
171	FPASW	present work
148	exp.	Drickamer *et al.* ’66
118	exp.	Will *et al.* ’84
215	exp.	Chattopadhyay and von Schnering ’85
157	exp.	Fujii *et al.* ’86
143	exp.	Jephcoat and Olson ’87
162	exp.	Ahrens and Jeanloz ’87
145	exp.	Blachnik *et al.* ’98

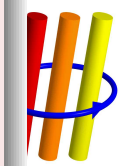


FeS_2: From Atoms to the Solid



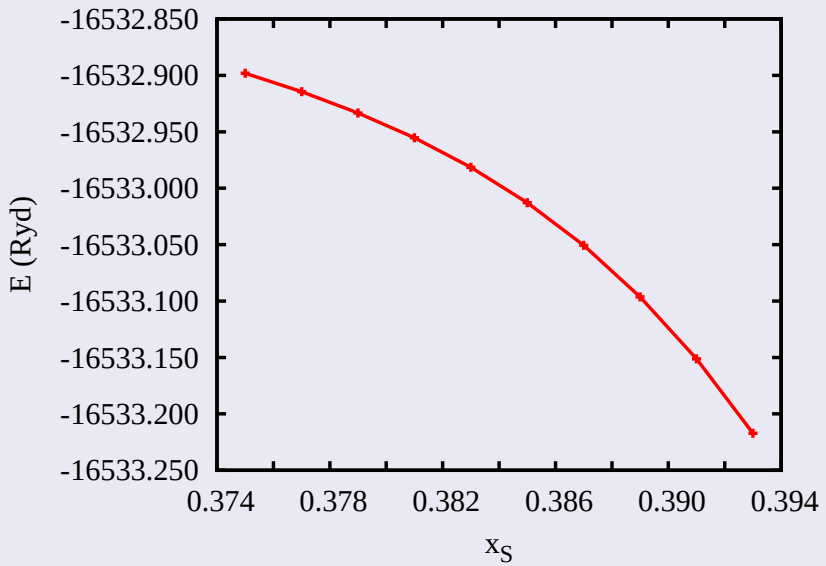
FeS_2: From Atoms to the Solid





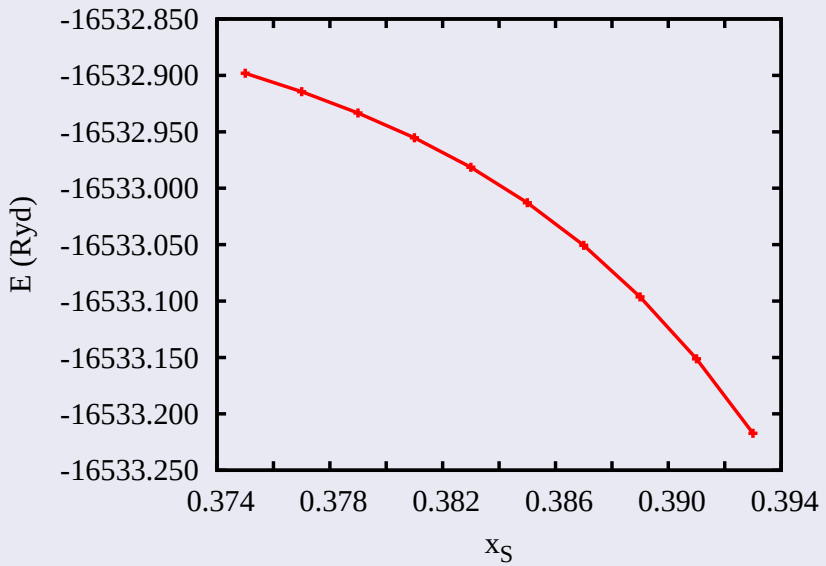
FeS_2: Structure Optimization

ASA^+ Code

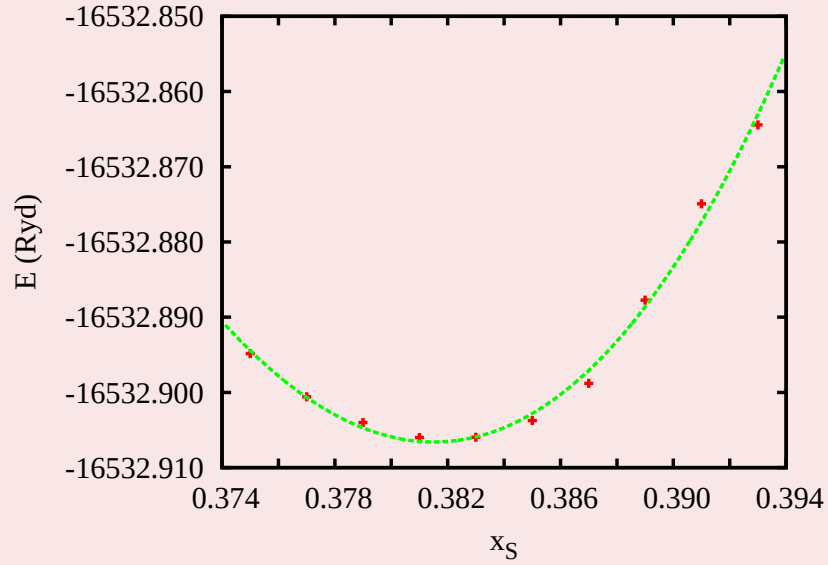


FeS_2: Structure Optimization

ASA^+ Code



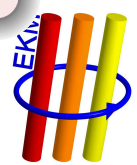
Full-Potential Code



FeS_2: Structure Optimization

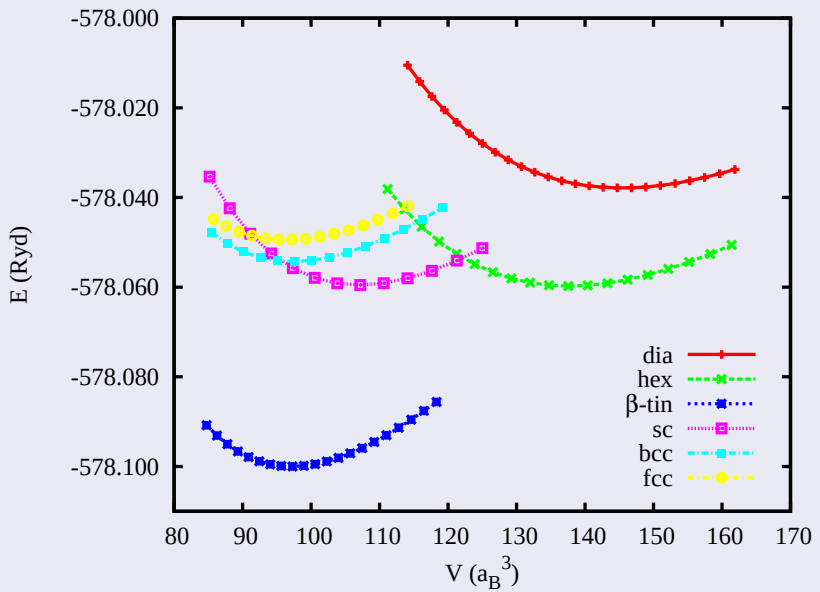
Sulfur Position

0.378	NCPP	Zeng and Holzwarth '94
0.377	FPLO	Opahle *et al.* '99
0.378	CRYSTAL98	Muscat *et al.* '02
0.382	CASTEP	Muscat *et al.* '02
0.382	FPASW	present work
0.386	exp.	Finklea *et al.* '76
0.386	exp.	Will *et al.* '84
0.385	exp.	Stevens *et al.* '91



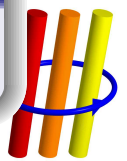
Phase Stability in Silicon

ASA$^+$ Code



Bad

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



Phase Stability in Silicon

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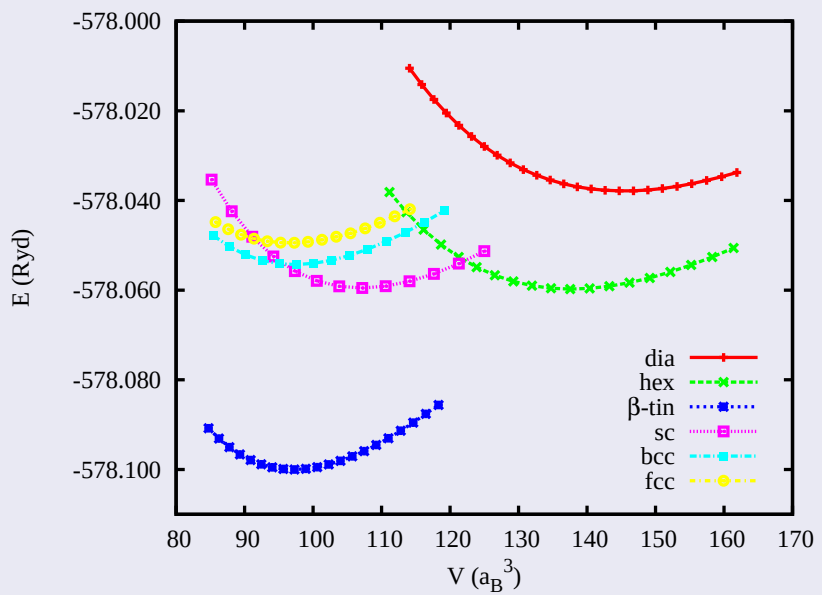
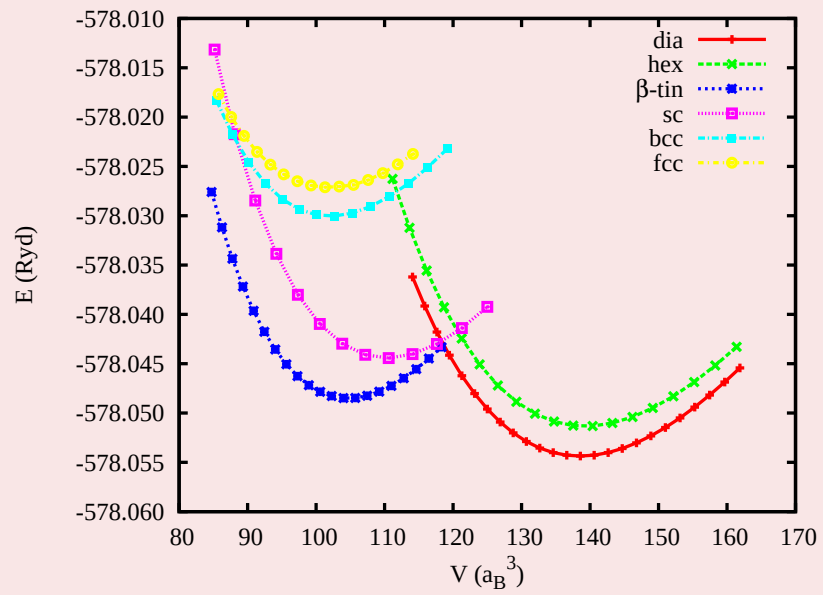
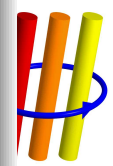


Full-Potential Code



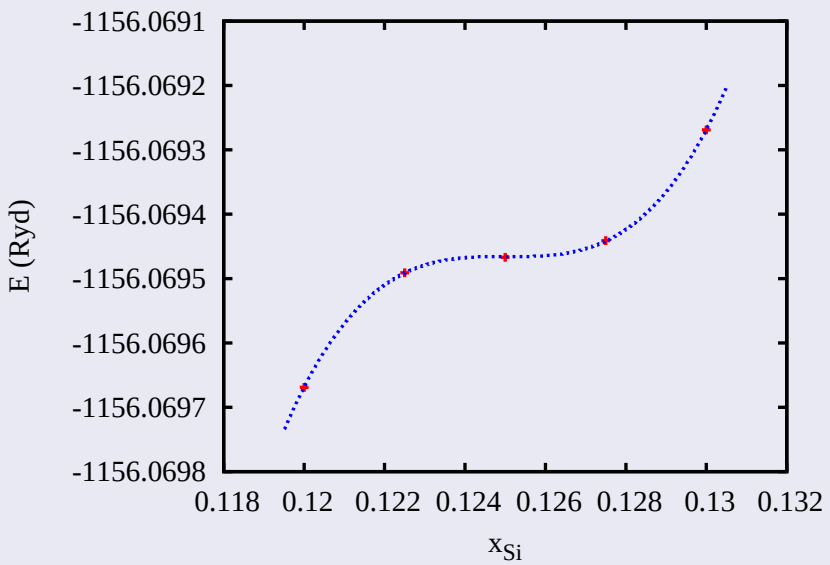
New!

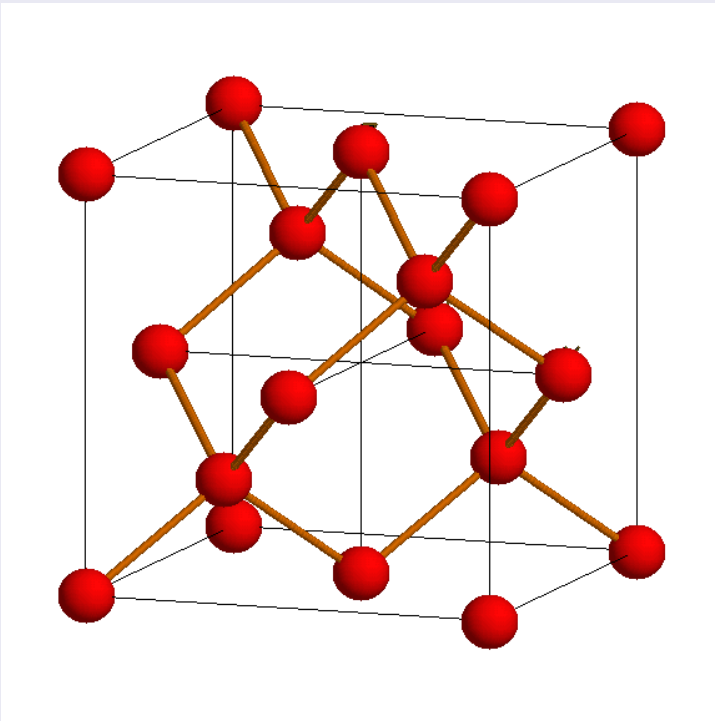
- diamond structure most stable
- pressure induced phase transition to β-tin structure



LTO(Γ)-Phonon in Silicon

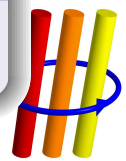
ASA$^+$ Code





Bad

- no stable Si position # nature



LTO(Γ)-Phonon in Silicon

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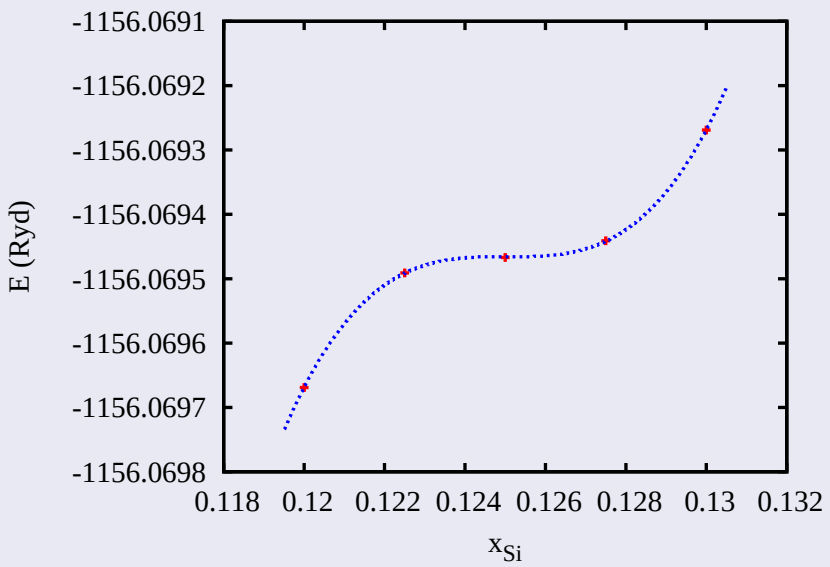
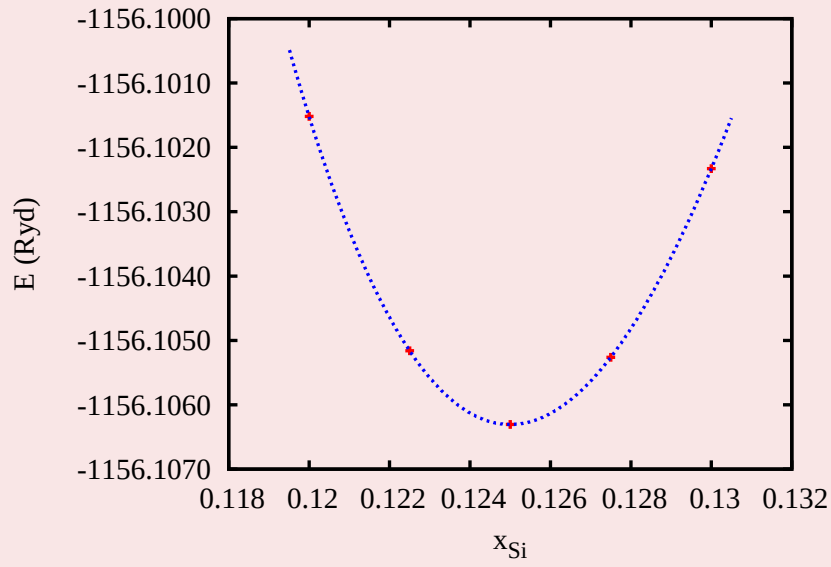


Full-Potential Code

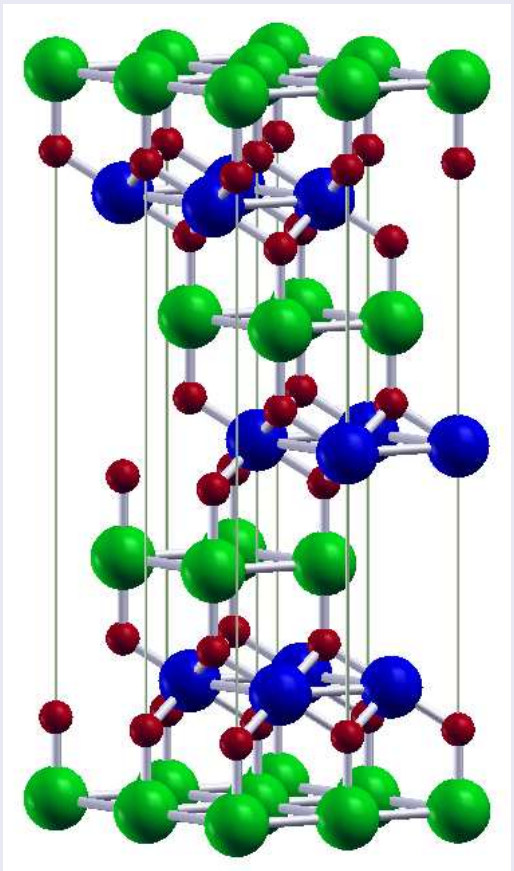


New!

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

Structure Optimization in $PdCoO_2$

Delafossite Structure



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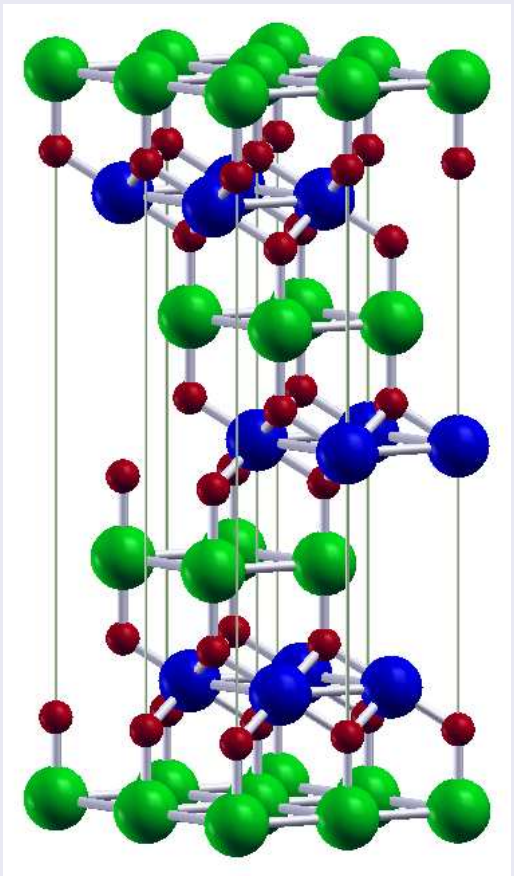
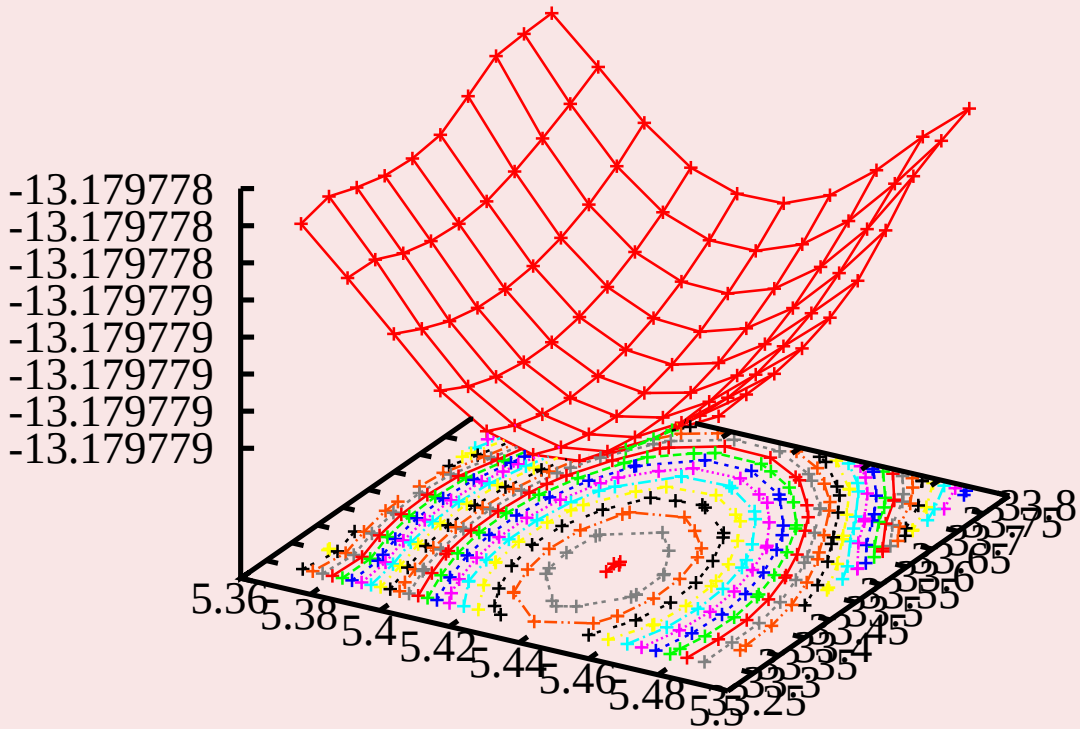


Total energy surface



Structure Optimization in $PdCoO_2$

Structural Data

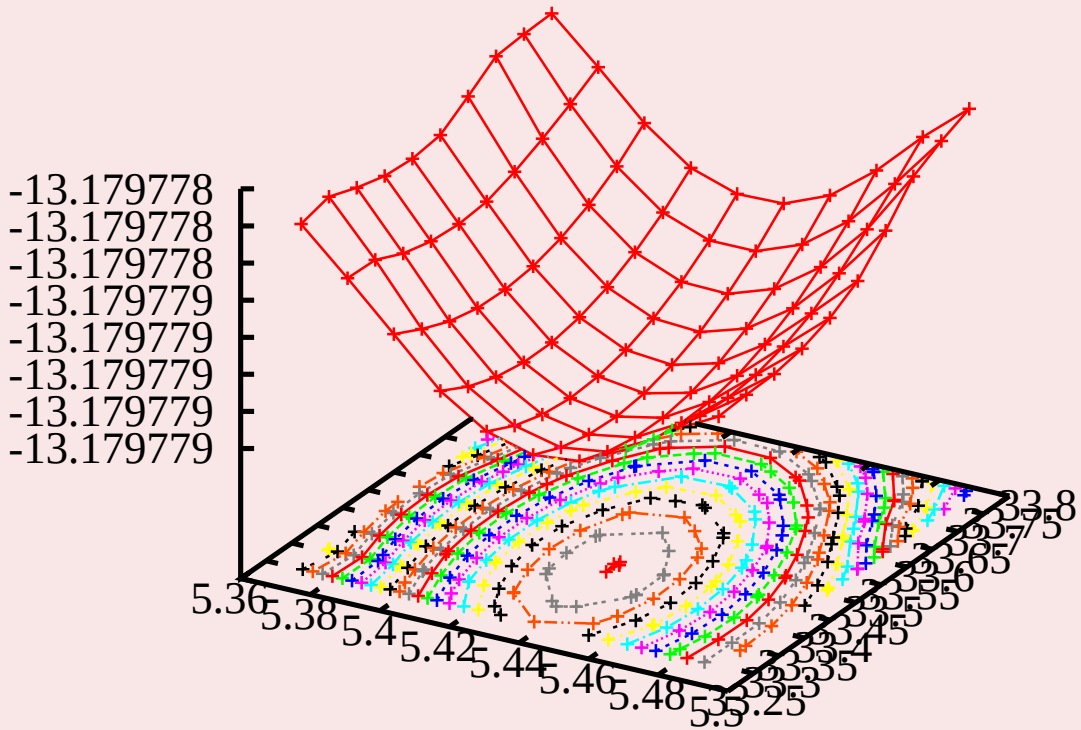
experiment

- $a = 2.83\,\text{Å}$
- $c = 17.743\,\text{Å}$
- $z_O = 0.1112$

theory

- $a = 2.8767\,\text{Å}$
- $c = 17.7019\,\text{Å}$
- $z_O = 0.1100$

Total energy surface



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

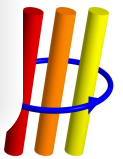
Summary

Full-Potential ASW Method

- ASA Geometry used for Basis Functions
- MT Geometry used for Density and Potential
- Accurate Total Energies
- $\mathcal{O}$(ASA) Speed!
- Optical Properties implemented
- LDA+U-Method implemented

What's Next?

- Forces? Automated Structure Optimization?
- Exact Exchange (EXX)? at $\mathcal{O}$(ASA) speed?



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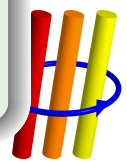

Acknowledgments

Darmstadt
SFB 252

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Augsburg
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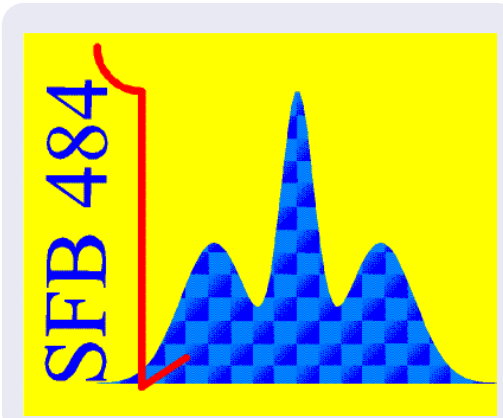

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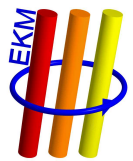
J. Sticht †

Darmstadt/Jülich
P. C. Schmidt, M. Stephan



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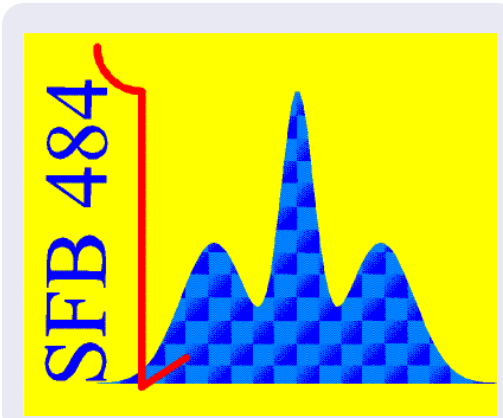

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Oran
Thank You for Your Attention!