# All-Electron Full-Potential Calculations at $\mathcal{O}$(ASA) Speed — A Fata Morgana?

Volker Eyert

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

February 4, 2008

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

# Outline



INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

# Outline



INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

# Outline

# Outline

# Back in the 1930's . . .

## John C. Slater

## Full Potential

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

# Back in the 1930's . . .

## John C. Slater

## Full Potential

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

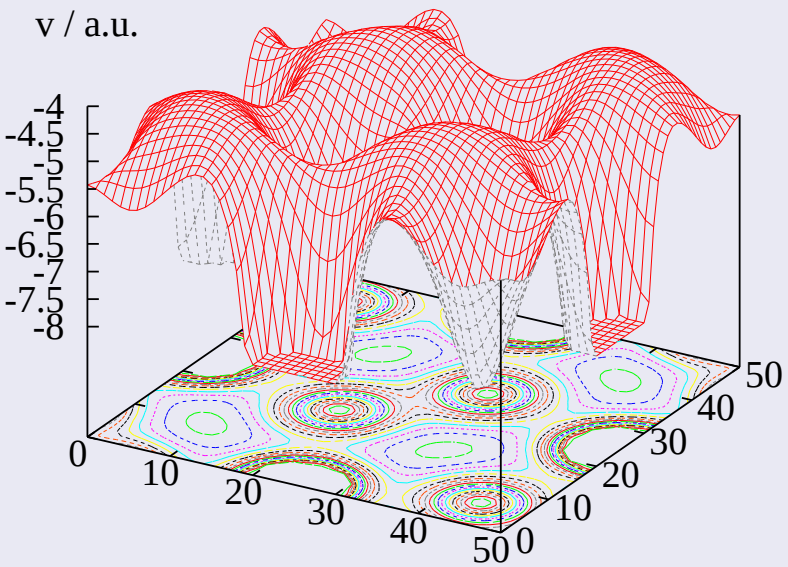
## Muffin-Tin Approximation

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

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

# Back in the 1930's . . .

## Full Potential ($FeS_2$)




## Muffin-Tin Potential

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

# Back in the 1930's . . .

## Muffin-Tin Approximation

distinguish:

- atomic regions
- remainder

## Muffin-Tin Potential

# Back in the 1930's . . .

## Muffin-Tin Approximation

distinguish:

- atomic regions
  - muffin-tin spheres
  - $v_{eff,\sigma}(\mathbf{r}) = v_{eff,\sigma}(|\mathbf{r}|)$
- remainder

## Muffin-Tin Potential

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

# Back in the 1930's . . .

## Muffin-Tin Approximation

distinguish:

- atomic regions
  - muffin-tin spheres
  - $v_{eff,\sigma}(\mathbf{r}) = v_{eff,\sigma}(|\mathbf{r}|)$
- remainder
  - interstitial region
  - $v_{eff,\sigma}(\mathbf{r}) = 0$

## Muffin-Tin Potential

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

# Back in the 1930's . . .

## Partial Waves

- muffin-tin spheres
  - $v_{eff,\sigma}(\mathbf{r}) = v_{eff,\sigma}(|\mathbf{r}|)$
- interstitial region
  - $v_{eff,\sigma}(\mathbf{r}) = 0$

## Muffin-Tin Potential

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

# Back in the 1930's . . .

## Partial Waves

- muffin-tin spheres
  - $v_{eff,\sigma}(\mathbf{r}) = v_{eff,\sigma}(|\mathbf{r}|)$
  - solve radial Schrödinger equation numerically
- interstitial region
  - $v_{eff,\sigma}(\mathbf{r}) = 0$

## Muffin-Tin Potential

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

# Back in the 1930's . . .

## Partial Waves

- muffin-tin spheres
  - $v_{eff,\sigma}(\mathbf{r}) = v_{eff,\sigma}(|\mathbf{r}|)$
  - solve radial Schrödinger equation numerically
- interstitial region
  - $v_{eff,\sigma}(\mathbf{r}) = 0$
  - exact solutions
    - plane waves
    - spherical waves

## Muffin-Tin Potential

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

# Back in the 1930's . . .

## Partial Waves

- muffin-tin spheres
  - $v_{eff,\sigma}(\mathbf{r}) = v_{eff,\sigma}(|\mathbf{r}|)$
  - solve radial Schrödinger equation numerically
- interstitial region
  - $v_{eff,\sigma}(\mathbf{r}) = 0$
  - exact solutions
    - plane waves
    - spherical waves
- match at sphere surface („augment“)

## Muffin-Tin Potential

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

# Back in the 1930's . . .

## Partial Waves

- muffin-tin spheres
  - $v_{eff,\sigma}(\mathbf{r}) = v_{eff,\sigma}(|\mathbf{r}|)$
  - solve radial Schrödinger equation numerically
- interstitial region
  - $v_{eff,\sigma}(\mathbf{r}) = 0$
  - exact solutions
    - plane waves
    - spherical waves
- match at sphere surface („augment“)

## Basis Functions

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

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

# Back in the 1930's . . .

## Wave Function

expand in basis functions

- expansion coefficients from variational principle

## Basis Functions

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

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

# Back in the 1930's . . .

## Wave Function

expand in basis functions

- expansion coefficients from variational principle

## Core States

all-electron methods

- fully included
- orthogonal to partial waves

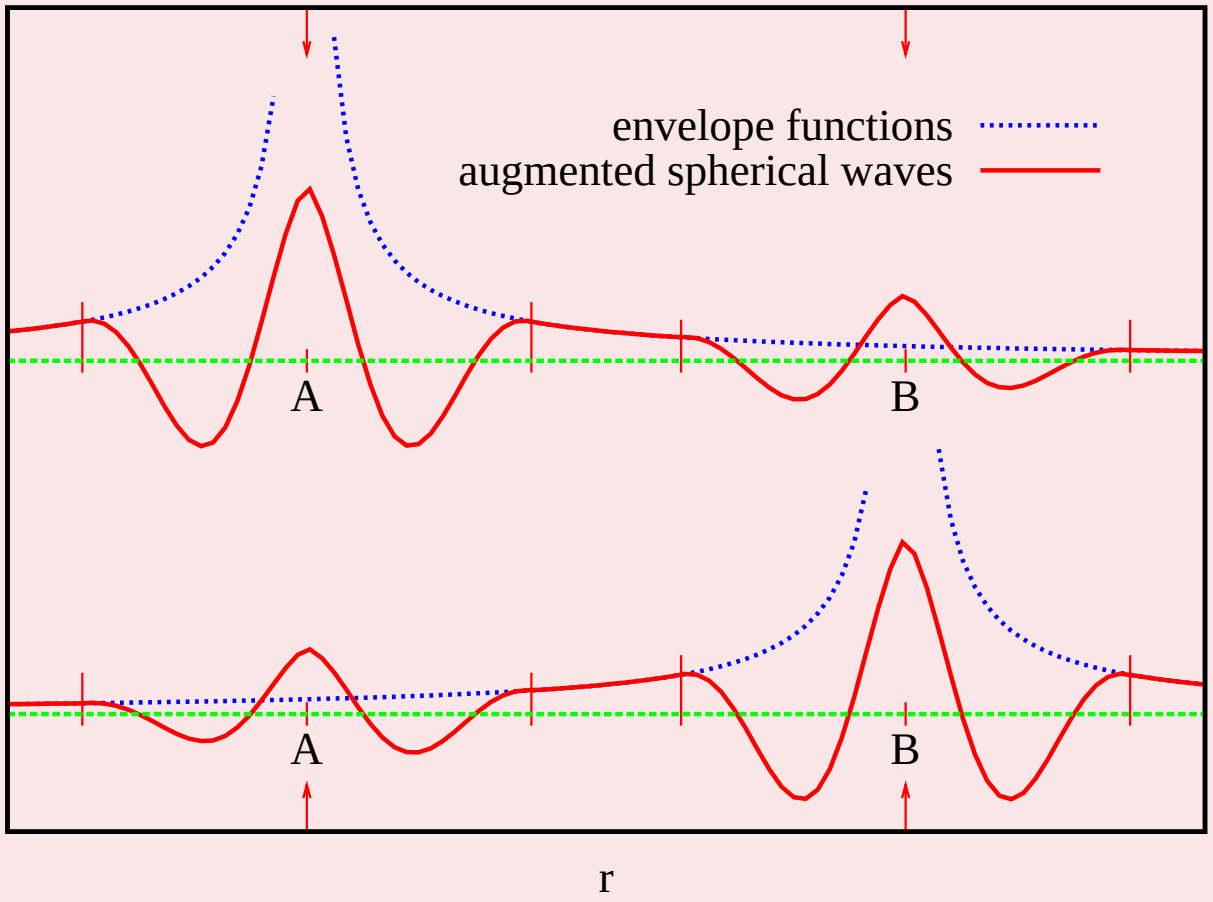
## Basis Functions

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

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

# Back in the 1930's . . .

## Augmented Spherical Waves



# Back in the 1970's . . .

## Ole K. Andersen

## "Linear Methods in Band Theory"

- energy dependence of basis functions almost linear $\rightarrow$ linearize $(\varphi, \dot{\varphi})$
  - huge increase in computat. efficiency!

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

# Back in the 1970's . . .

## Ole K. Andersen

## "Linear Methods in Band Theory"

- energy dependence of basis functions almost linear $\rightarrow$ linearize $(\varphi, \dot{\varphi})$
  - huge increase in computat. efficiency!

## 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!

# Back in the 1970's . . .

## Ole K. Andersen

## 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!

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

# Back in the 1970's . . .

## Ole K. Andersen

## 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!

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

# Back in the 1970's . . .

## Ole K. Andersen

## Linear Muffin-Tin Orbital (LMTO)

- based on spherical waves
  - does not require crystalline periodicity
  - natural interpretation of results
- 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!

# Back in the 1970's . . .

## Ole K. Andersen

## Linear Muffin-Tin Orbital (LMTO)

- based on spherical waves
  - does not require crystalline periodicity
  - natural interpretation of results
- 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!

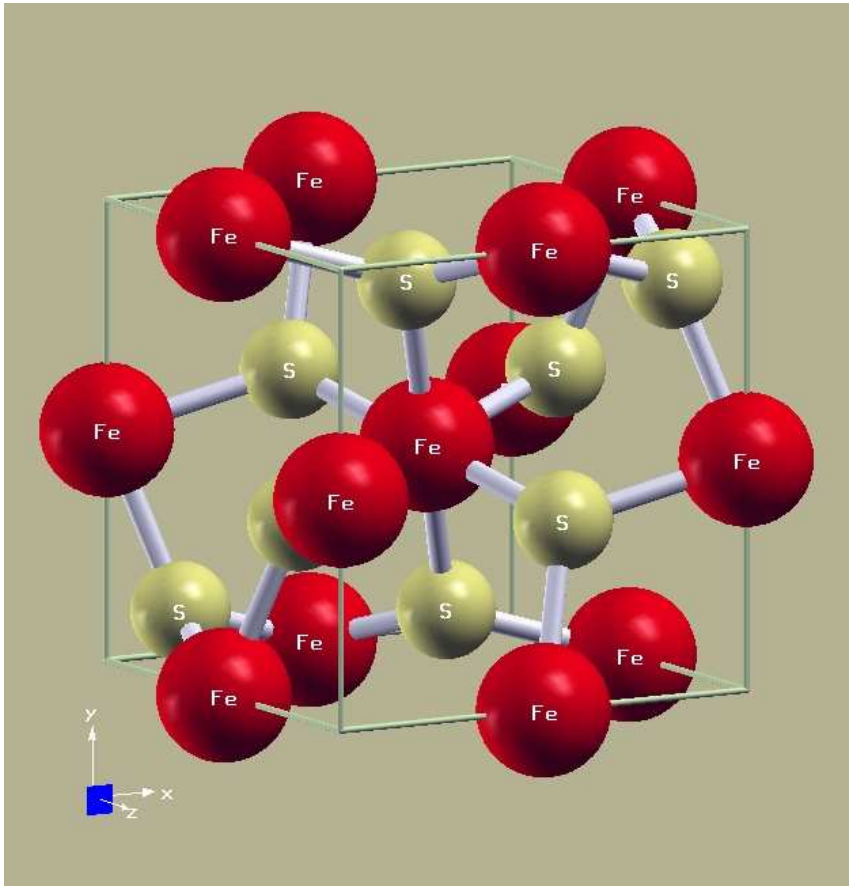
# Back in the 1970's . . .

## Ole K. Andersen

## Linear Muffin-Tin Orbital (LMTO)

- based on spherical waves
  - does not require crystalline periodicity
  - natural interpretation of results
- 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!

# Iron Pyrite: $FeS_2$



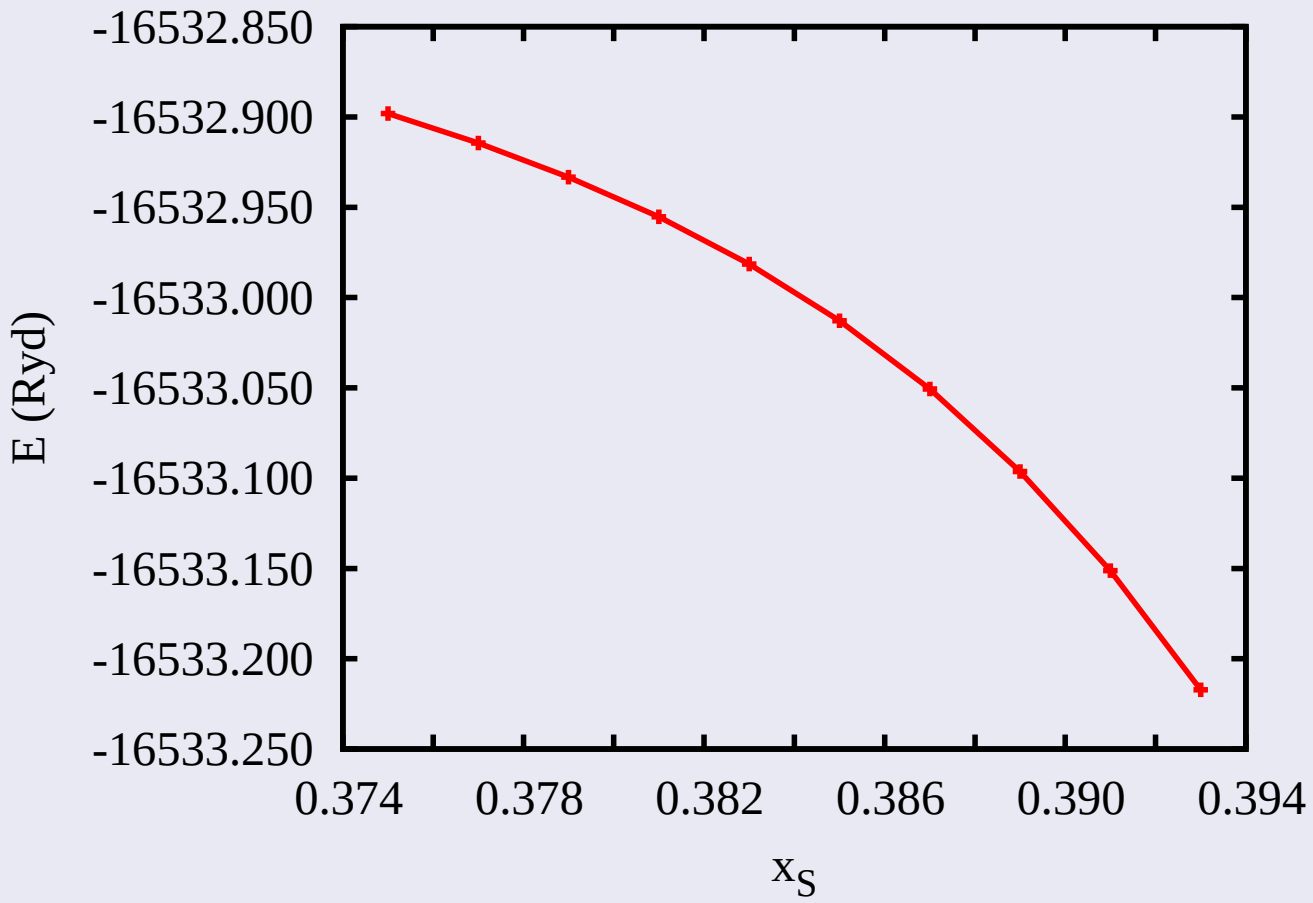

## Pyrite

- $Pa\bar{3}$ ($T_h^6$)
- 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

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

# $FeS_2$: Structure Optimization

## ASW Version 2.2



# 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 $\rightarrow$ inefficient

# 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 $\rightarrow$ inefficient

## Requirements

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

# 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 $\rightarrow$ inefficient

## Requirements

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

# Towards a Full-Potential Spherical-Wave Method

## 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

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

# Towards a Full-Potential Spherical-Wave Method

## 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

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

# ASW Method

## Characteristics

- similar to LMTO
  - different linearization scheme
  - different interstitial energy
  - different implementations

# ASW Method

## Characteristics

- similar to LMTO
  - different linearization scheme
  - different interstitial energy
  - different implementations

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

PRB **19**, 6094 (1979)

# ASW Method

## Characteristics

- similar to LMTO
  - different linearization scheme
  - 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: Basic Formalism

## Wave Function Expanded in Basis Functions

$$\psi_\sigma(\mathbf{r}) = \sum_{L\kappa i} c_{L\kappa i\sigma} H^{\infty}_{L\kappa\sigma}(\mathbf{r}_i)$$

$\longrightarrow$ $c_{L\kappa i\sigma}$ determined variationally

# ASW Method: Basic Formalism

## Wave Function Expanded in Basis Functions

$$\psi_\sigma(\mathbf{r}) = \sum_{L\kappa i} c_{L\kappa i\sigma} H^\infty_{L\kappa\sigma}(\mathbf{r}_i)$$

$\longrightarrow$ $c_{L\kappa i\sigma}$ determined variationally

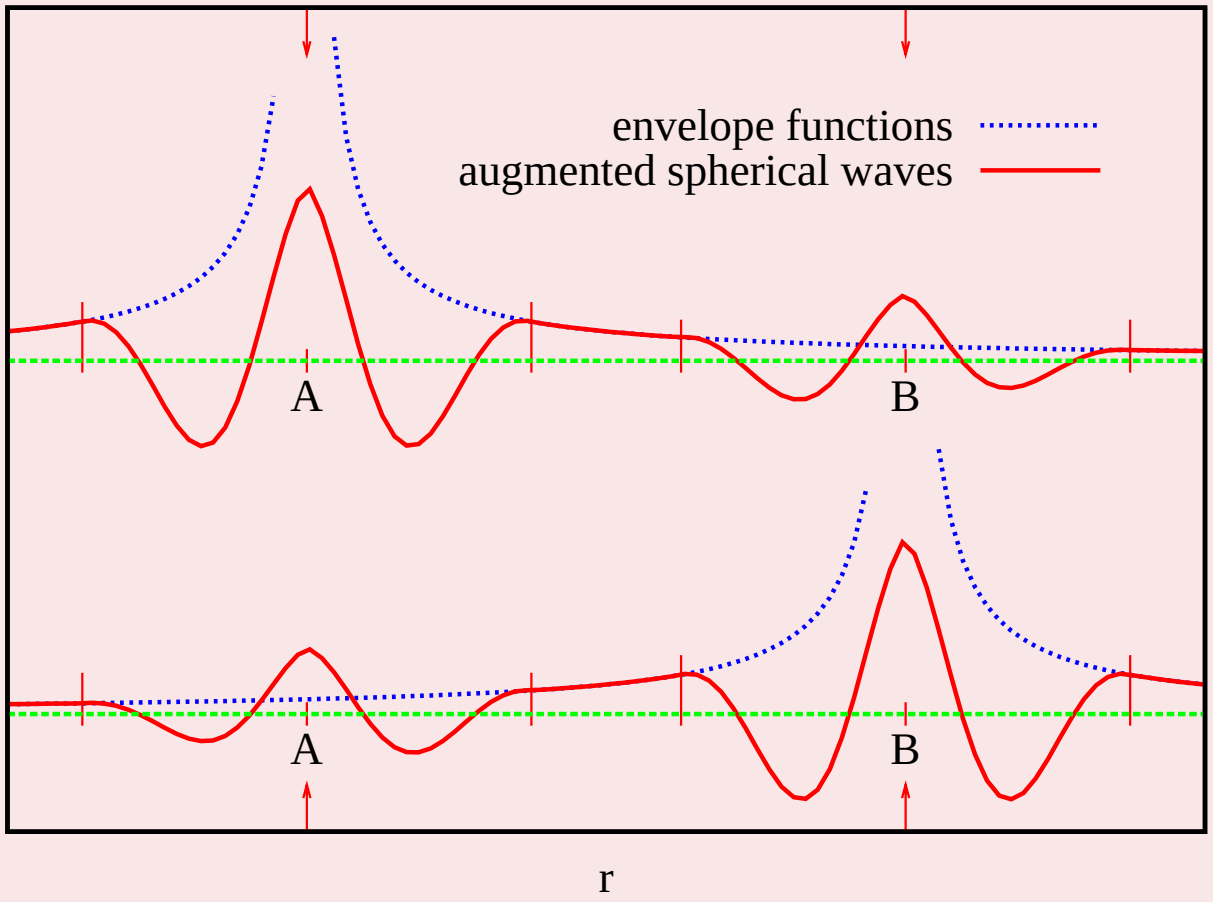
## Augmented Spherical Wave

$$H^\infty_{L\kappa\sigma}(\mathbf{r}_i) = \begin{cases} H^I_{L\kappa}(\mathbf{r}_i) & \text{interstitial region} \\ \tilde{H}_{L\kappa\sigma}(\mathbf{r}_i) & \text{on-centre sphere } i \\ \sum'_{L'j} \tilde{J}_{L'\kappa\sigma}(\mathbf{r}_j) B_{L'L\kappa} & \text{off-centre spheres } j \end{cases}$$

$B_{L'L\kappa}(\mathbf{R}_j - \mathbf{R}_i)$: structure constants
ASW classified by atomic site $\mathbf{R}_i$, $L = (l, m)$, decay $\kappa$, spin $\sigma$

# ASW Method: Basic Formalism

## Augmented Spherical Waves



# ASW Method: Basic Formalism

## Envelope Functions

$$H^l_{L\kappa}(\mathbf{r}_i) := i\kappa^{l+1} h^{(1)}_l(\kappa r_i) Y_L(\hat{\mathbf{r}}_i)$$

$h^{(1)}_l(\kappa r_i)$: spherical Hankel function

# ASW Method: Basic Formalism

## Envelope Functions

$$H^l_{L\kappa}(\mathbf{r}_i) := i\kappa^{l+1} h^{(1)}_l(\kappa r_i) Y_L(\hat{\mathbf{r}}_i)$$

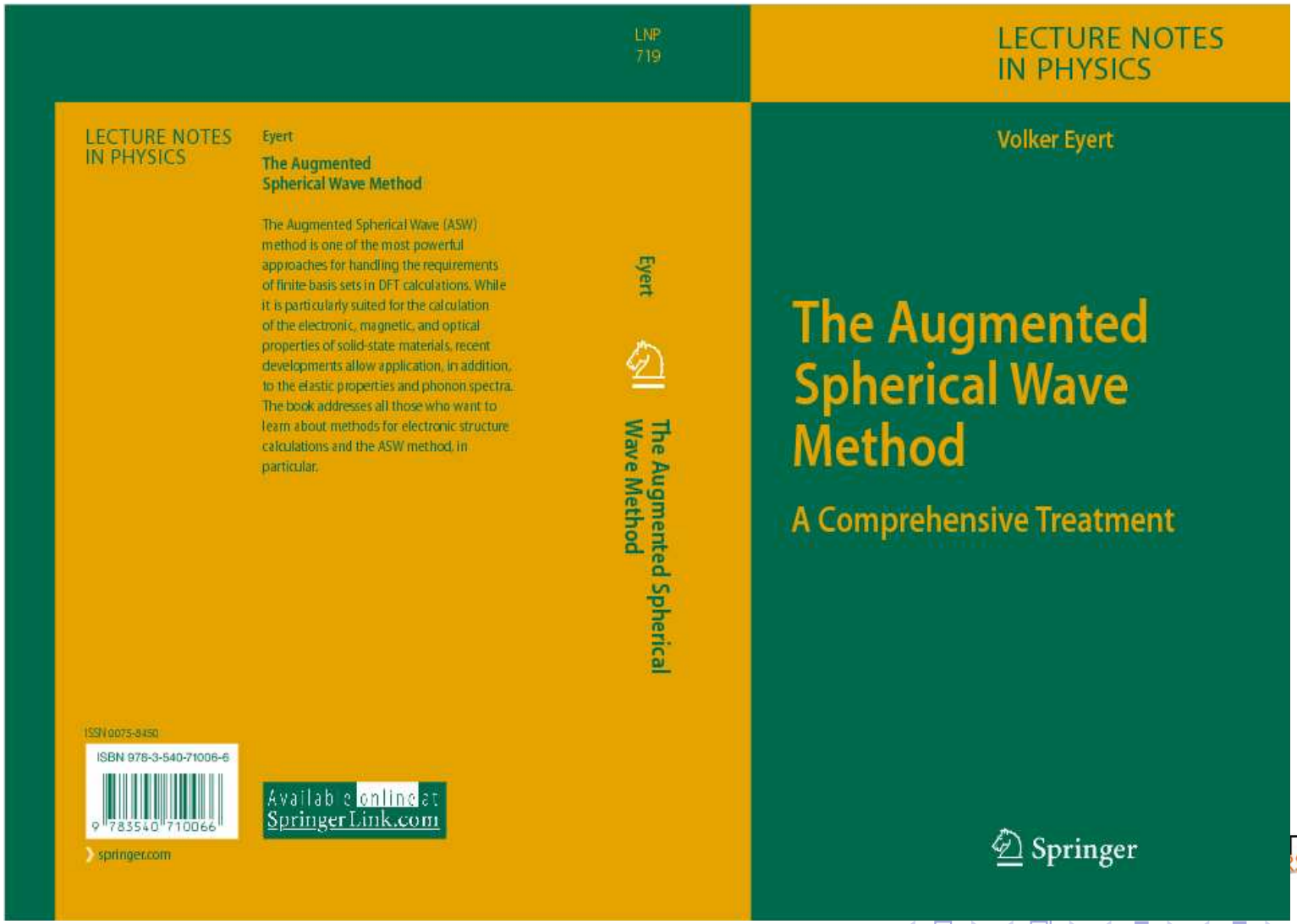
$h^{(1)}_l(\kappa r_i)$: spherical Hankel function

## Augmented Functions

$$\begin{aligned} \tilde{H}_{L\kappa\sigma}(\mathbf{r}_i) &:= \tilde{h}_{l\kappa\sigma}(r_i) Y_L(\hat{\mathbf{r}}_i) \\ \tilde{J}_{L'\kappa\sigma}(\mathbf{r}_j) &:= \tilde{j}_{l'\kappa\sigma}(r_j) Y_{L'}(\hat{\mathbf{r}}_j) \end{aligned}$$

$\tilde{h}$, $\tilde{j}$: numerical solutions of radial Kohn-Sham equation
boundary conditions from envelope functions
correspond to $\varphi$ and $\dot{\varphi}$ of LMTO

# ASW Method: Further Reading



# Outline

# Basic Principles

## Steps to be Taken

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

# Basic Principles

## Steps to be Taken

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

# Basic Principles

## Steps to be Taken

- remove total energy error due to overlap of atomic spheres
  - reintroduce non-overlapping muffin-tin spheres
  - restore interstitial region
- find representation of electron density and full potential
- find representation of products of the wave function
  - inside muffin-tin spheres
  - in the interstitial region

# Basic Principles

## Steps to be Taken

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

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

# Basic Principles

## Steps to be Taken

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

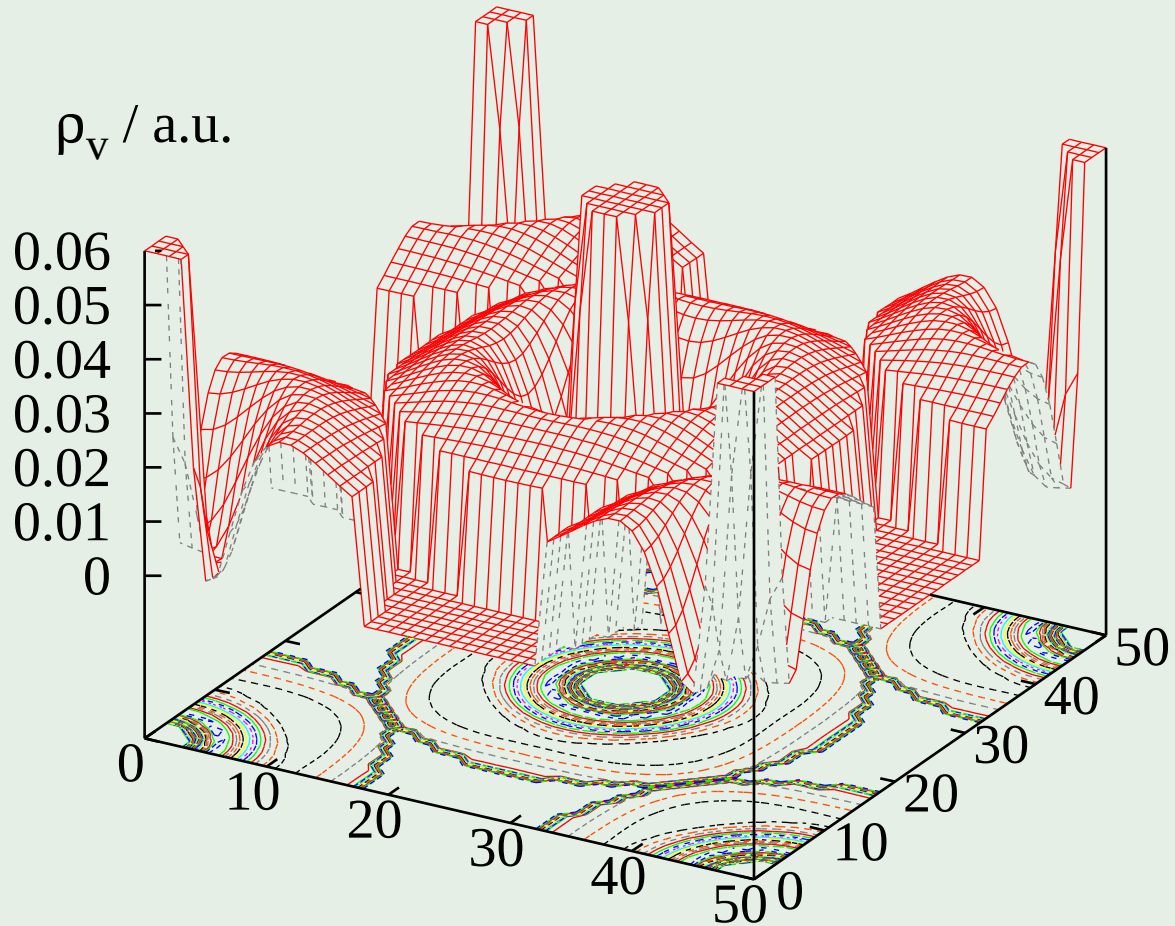
# Basic Principles

## Steps to be Taken

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

# From Wave Functions to Electron Density

## Products of Basis Functions in Interstitial Region

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

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

- $F_n(\mathbf{r})$: 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):

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

- $H^{\infty}_{L'\kappa_2\sigma}(\mathbf{r}_j)$: 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

projection $\mathcal{P}$:

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

# From Wave Functions to Electron Density

## Interstitial Products of Basis Functions

projection $\mathcal{P}$:

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

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

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

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

# From Wave Functions to Electron Density

## Interstitial Products of Basis Functions

projection $\mathcal{P}$:

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

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

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

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

# 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

projection $\mathcal{P}$:

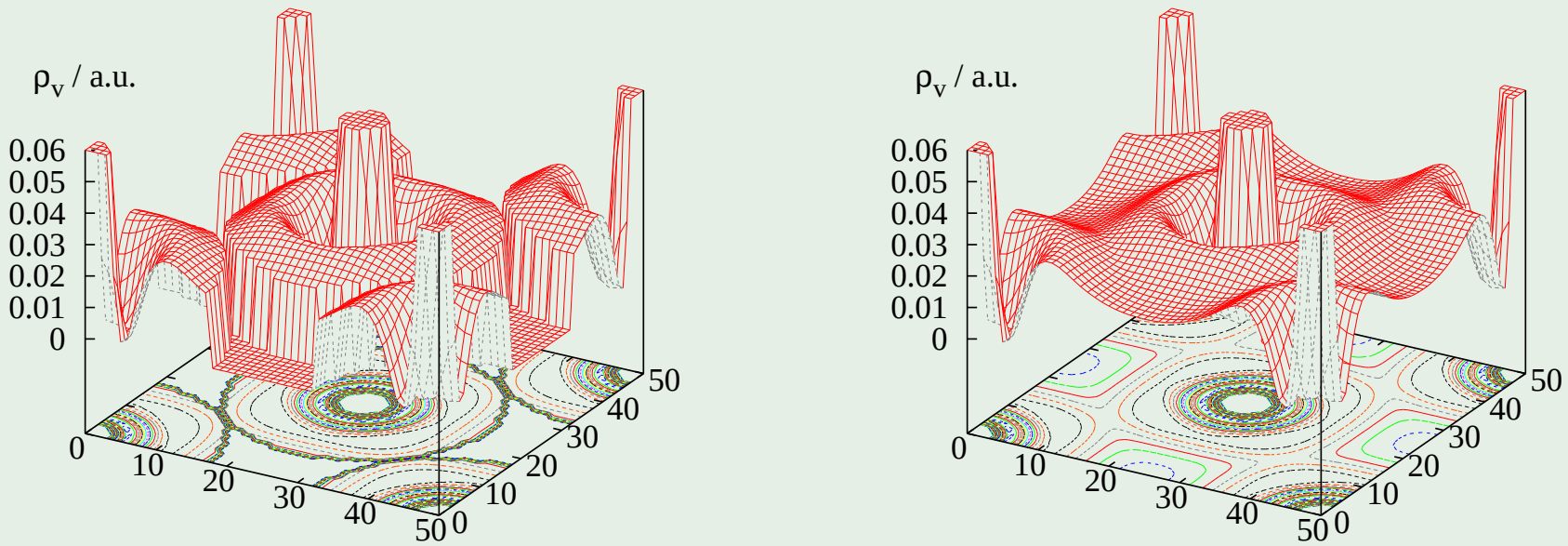
$$\mathcal{P}\left[\left(H^{\infty}_{L\kappa_1\sigma}(\mathbf{r}_i)\right)^* H^{\infty}_{L'\kappa_2\sigma}(\mathbf{r}_j)\right] = \sum_n \sum_{K\eta} d^{L\kappa_1 iL'\kappa_2 j}_{K\eta n\sigma}\ \mathcal{P}\left[H_{K\eta}(\mathbf{r}_n)\right]$$

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)




INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

# 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

# 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

# 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

# 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

# Comparison of Approaches

## Ole K. Andersen

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

# 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!

## Michael S. Methfessel

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

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

# Comparison of Approaches

## Ole K. Andersen

- ASA geometry used for basis functions — good!
- ASA geometry used for density and potential — bad!

## Michael S. Methfessel

- MT geometry used for density and potential — good!
- MT geometry used for basis functions — bad!

## 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
  $\rightarrow$ accurate total energy — great!

# 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)

# 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)

# Implementation

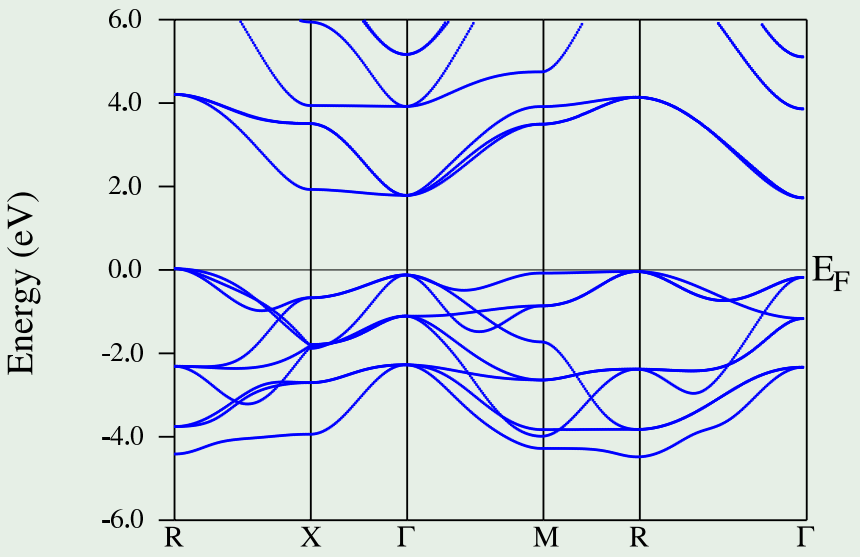
## 2nd Generation ASW (VE, 2000s)

- 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)

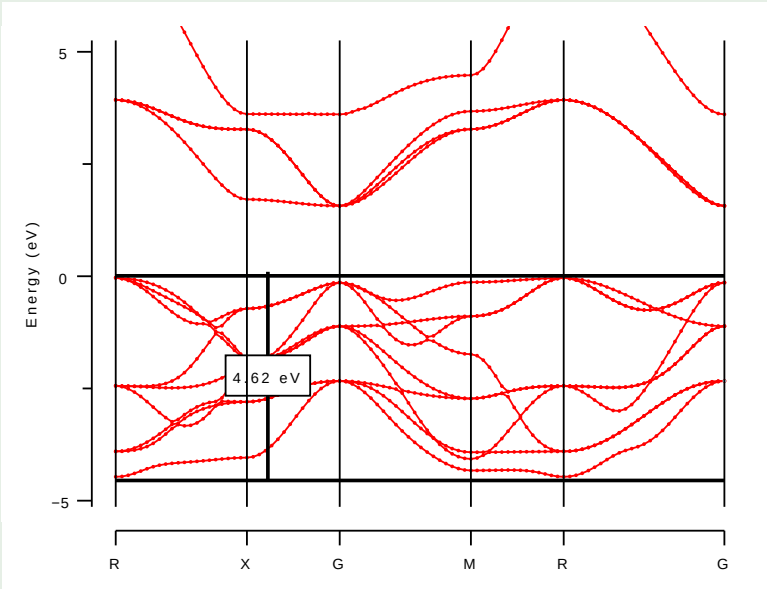
# Outline

# Electronic Structure of $BaTiO_3$

## Wien2k



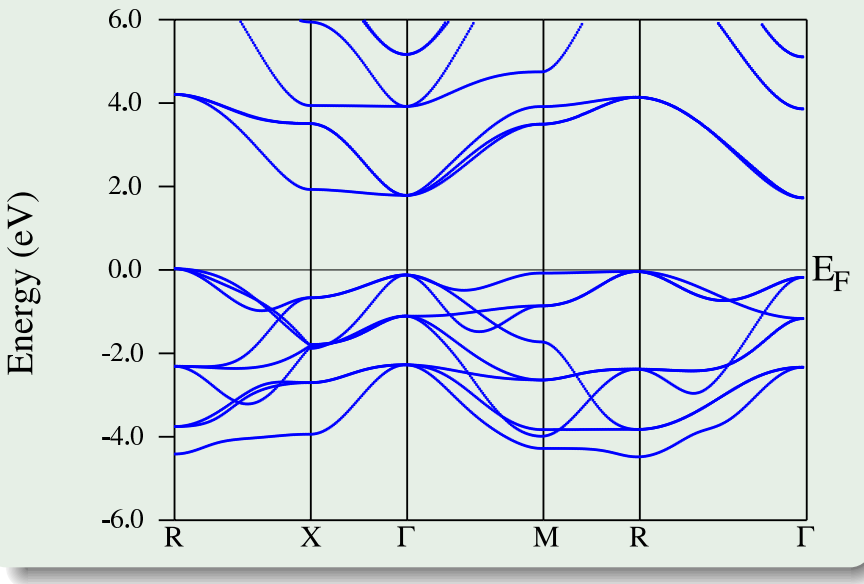

## VASP



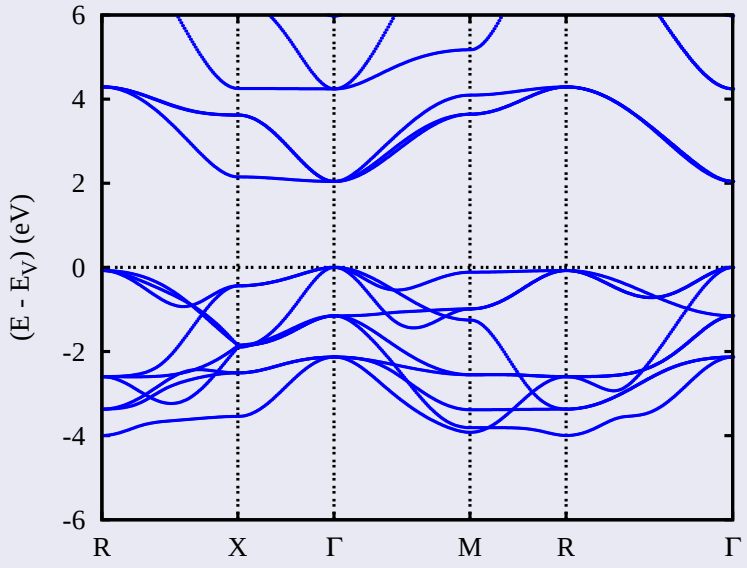

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

# Electronic Structure of $BaTiO_3$

## Wien2k

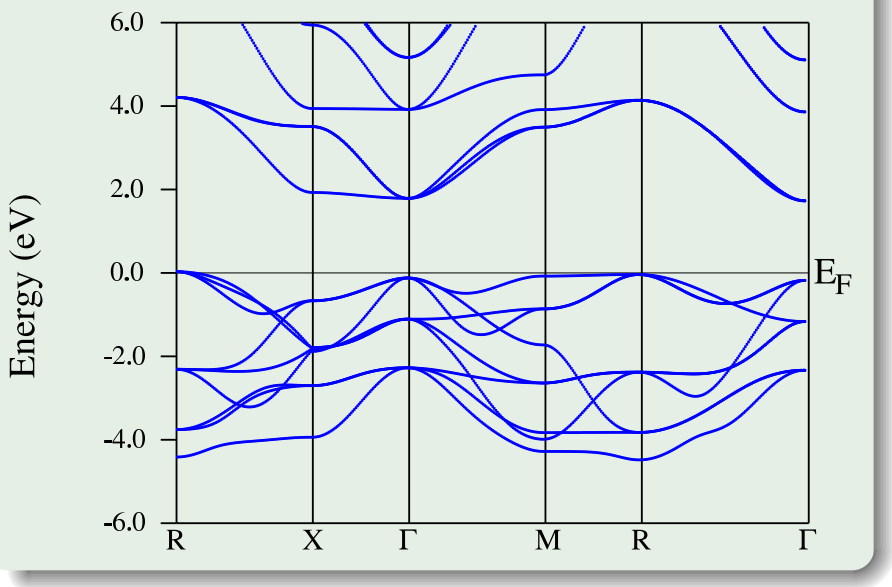



## ASW Version 2.2

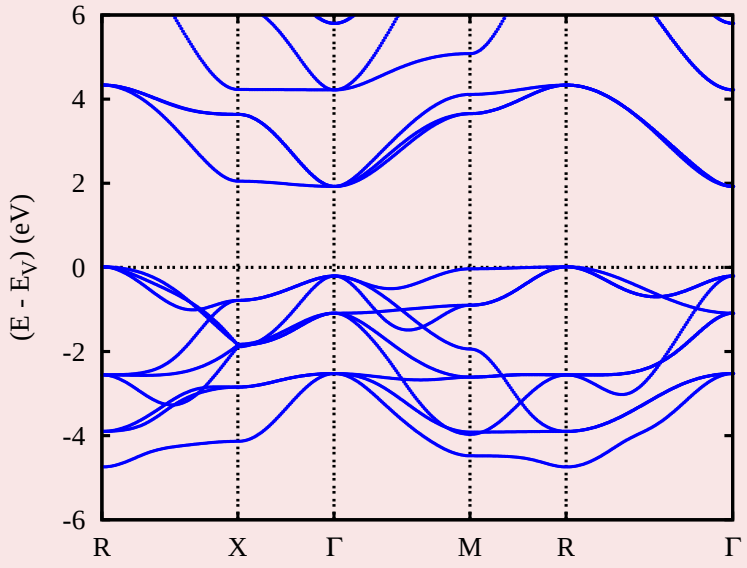


# Electronic Structure of $BaTiO_3$

## Wien2k




## FPASW Version 2.3

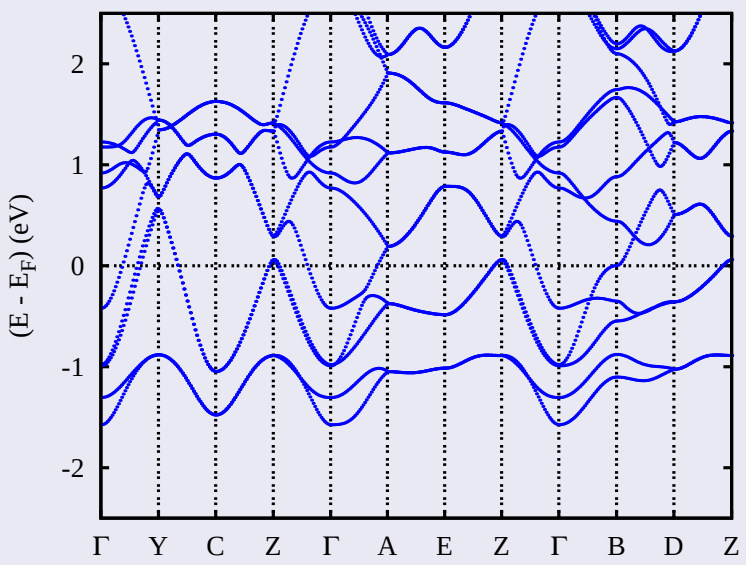



## New!

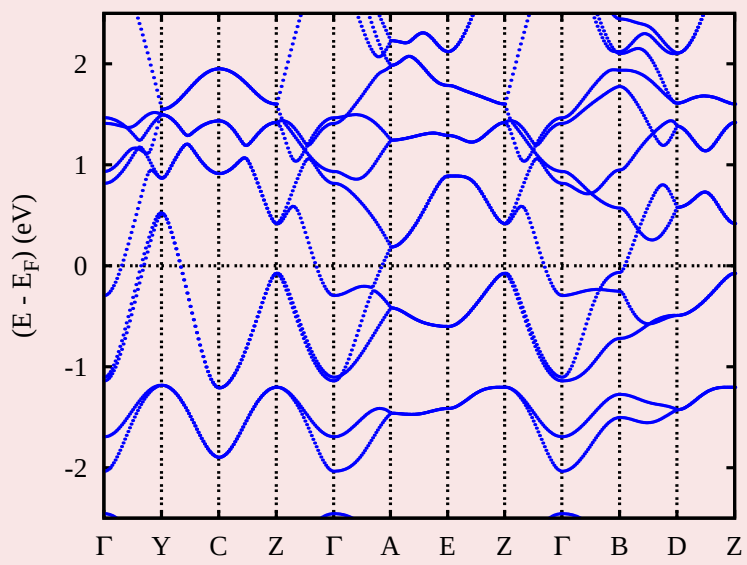
- much better agreement with other full-potential codes (valence-band width, valence states at M-point)

# Fermi Surface of $MoO_2$

## ASW Version 1.9



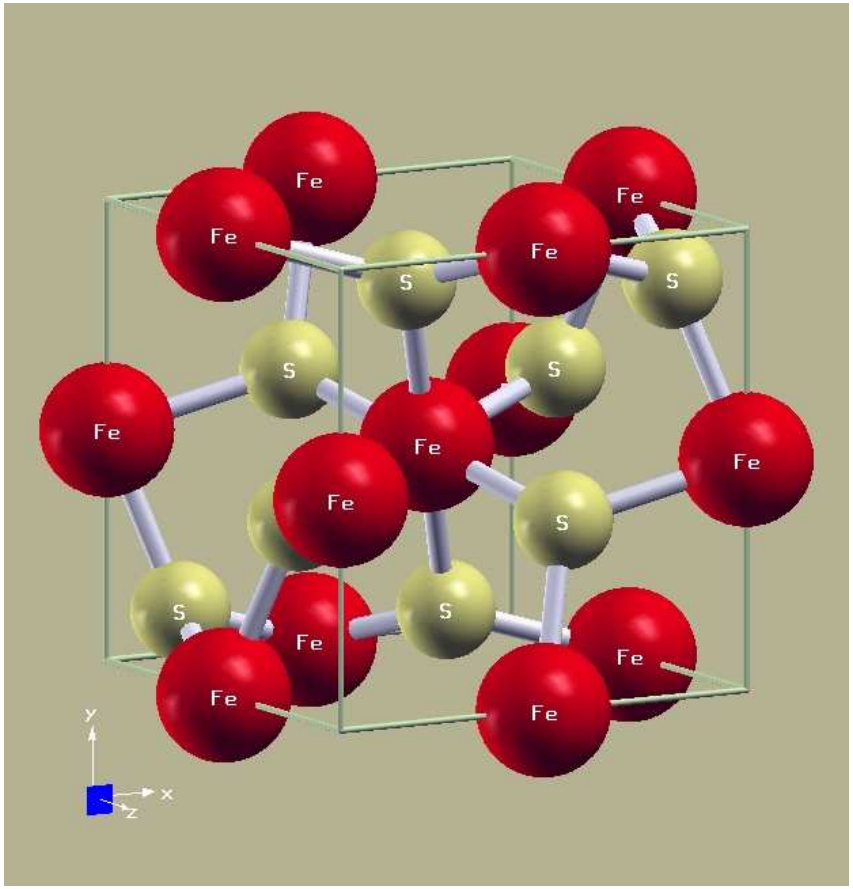

## FPASW Version 2.3




## New!

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

# Iron Pyrite: $FeS_2$

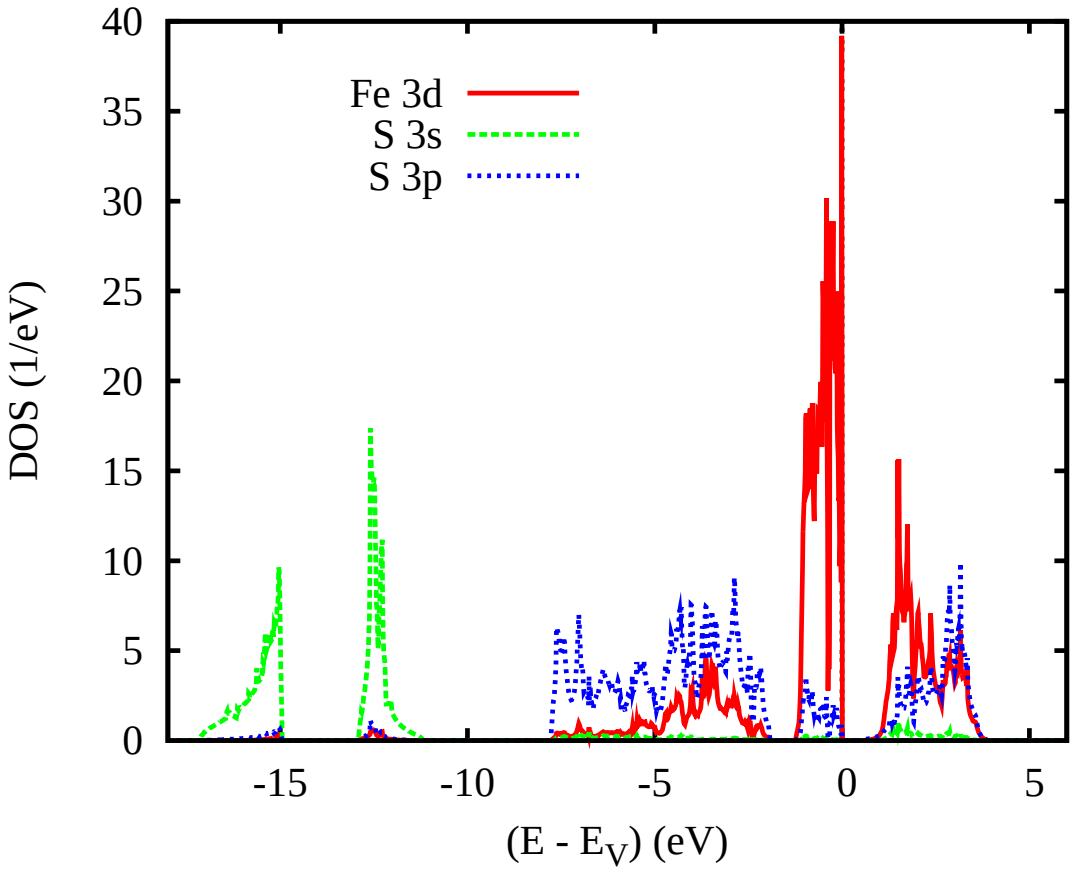



## Pyrite

- $Pa\bar{3}$ ($T_h^6$)
- 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

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

# $FeS_2$: Partial Densities of States

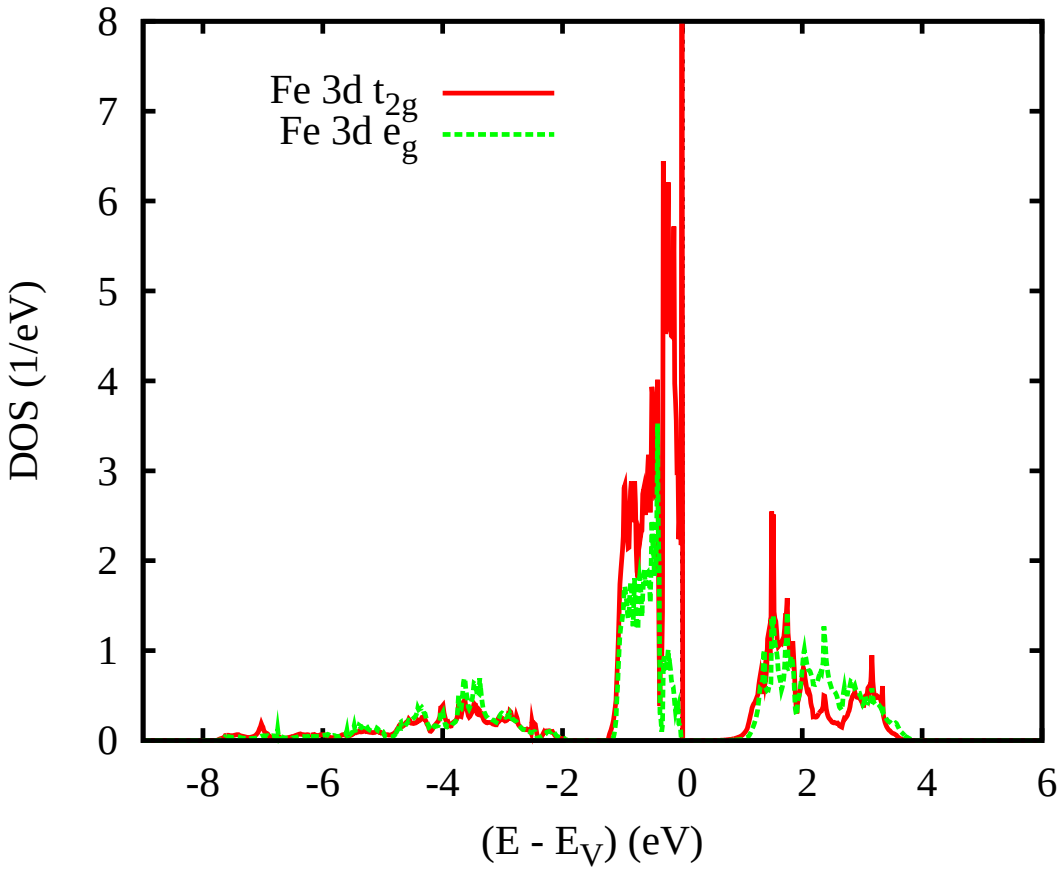



## Relevant states

- Fe 3*d*
- S 3*s*
- S 3*p*

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

# $FeS_2$: Partial Densities of States




## Crystal field splitting

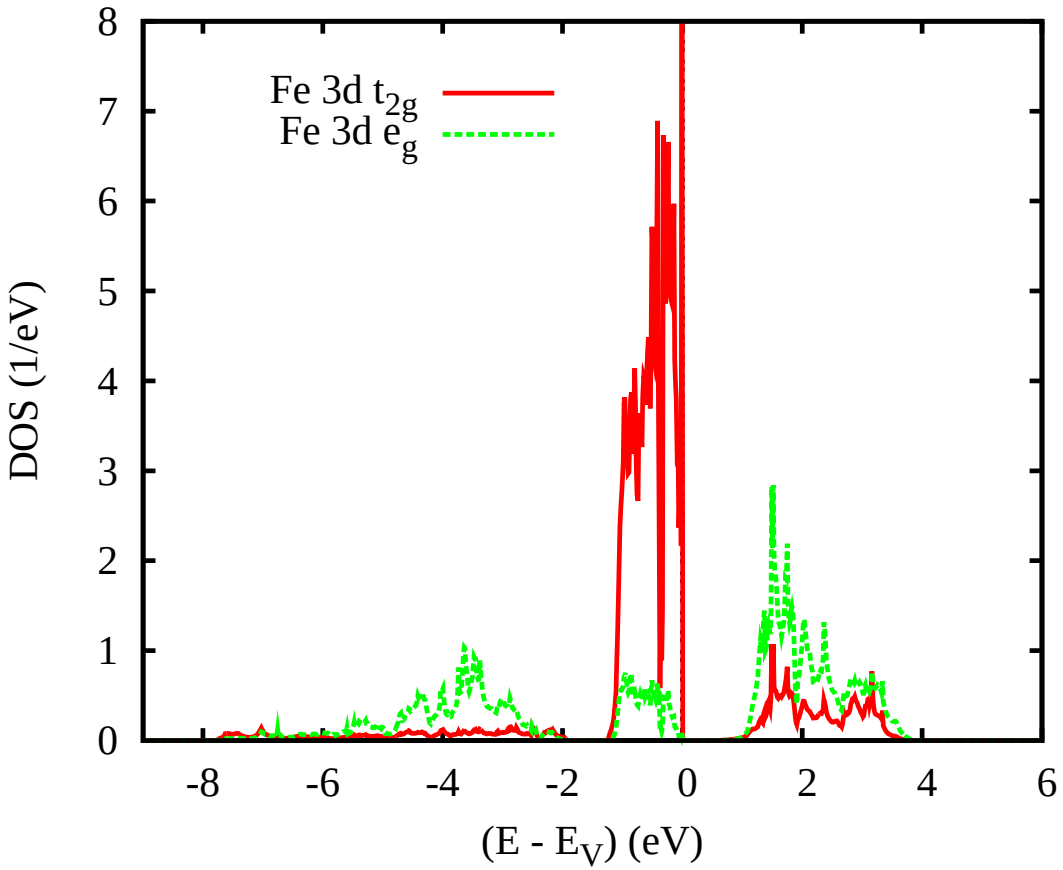
Fe 3*d* in octahedron:
$t_{2g}$ and $e_g$ states

without rotation

with rotation

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

# $FeS_2$: Partial Densities of States




## Crystal field splitting

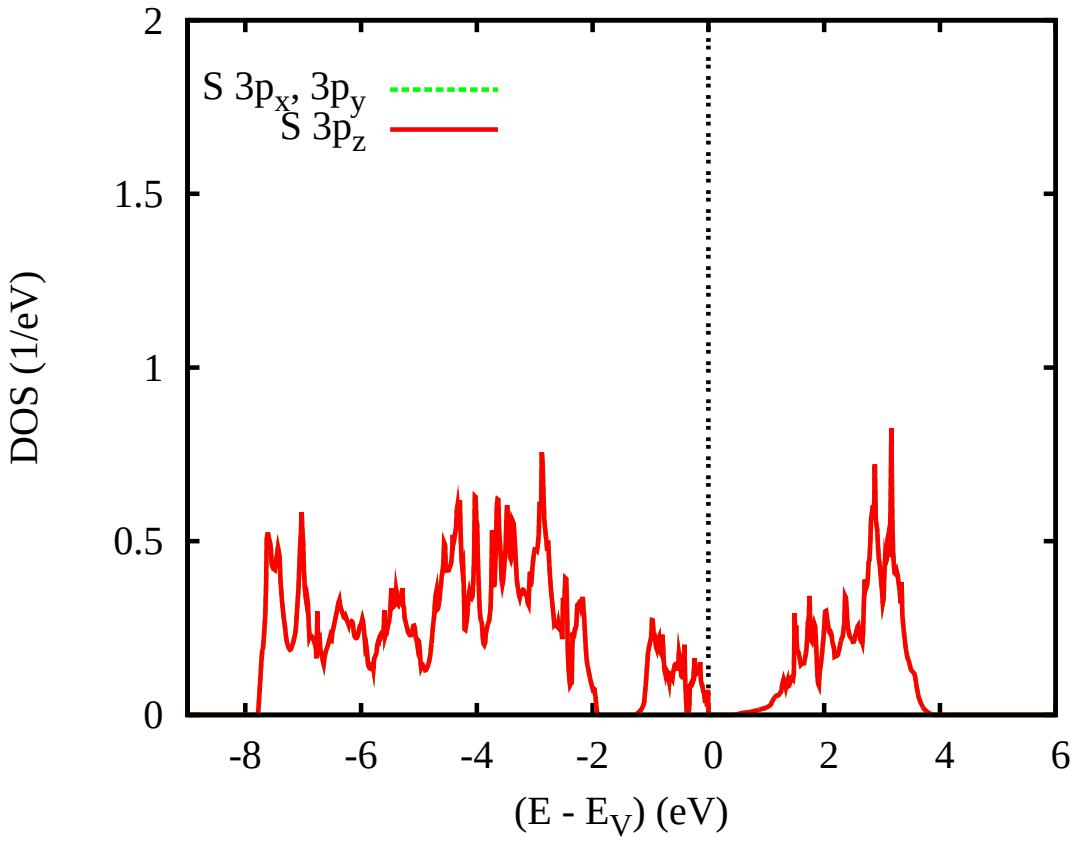
Fe 3*d* in octahedron:
$t_{2g}$ and $e_g$ states

without rotation

with rotation

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

# $FeS_2$: Partial Densities of States




## Crystal field splitting

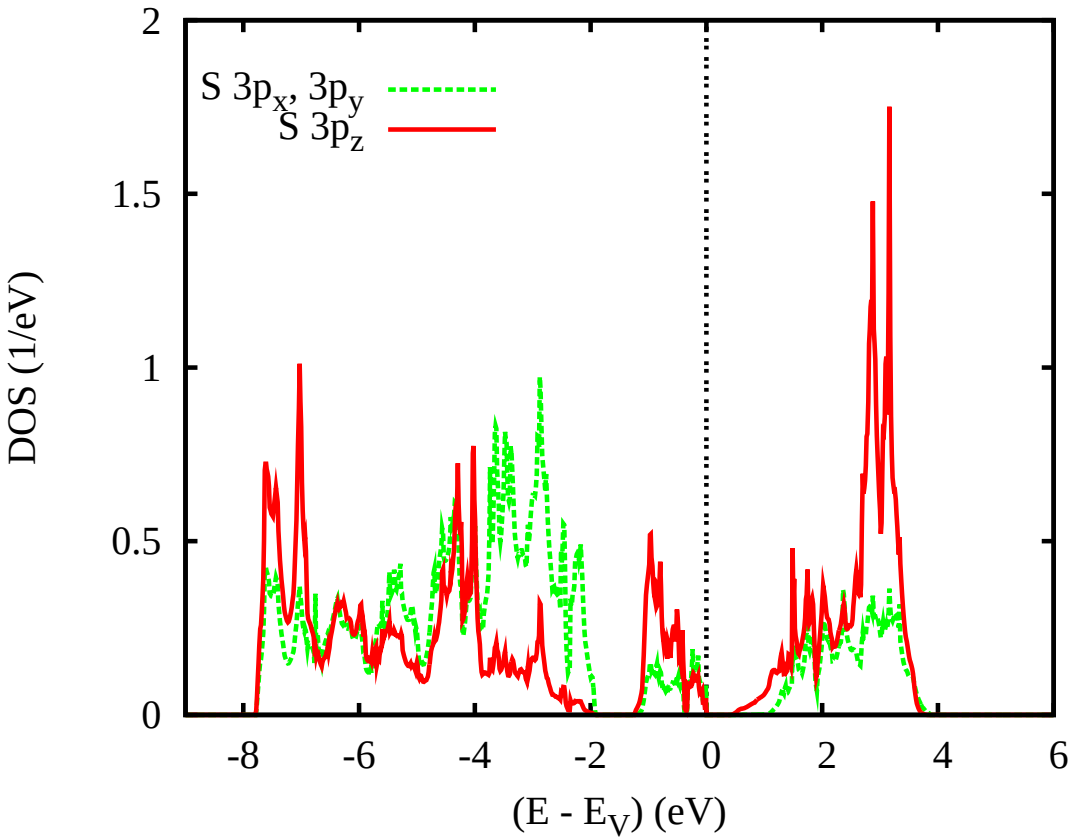
S 3*p*: $p_x/p_y$ vs. $p_z$ states

without rotation

with rotation:
$z$ axis $\parallel \langle 111 \rangle$

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

# $FeS_2$: Partial Densities of States




## Crystal field splitting

S 3*p*: $p_x/p_y$ vs. $p_z$ states

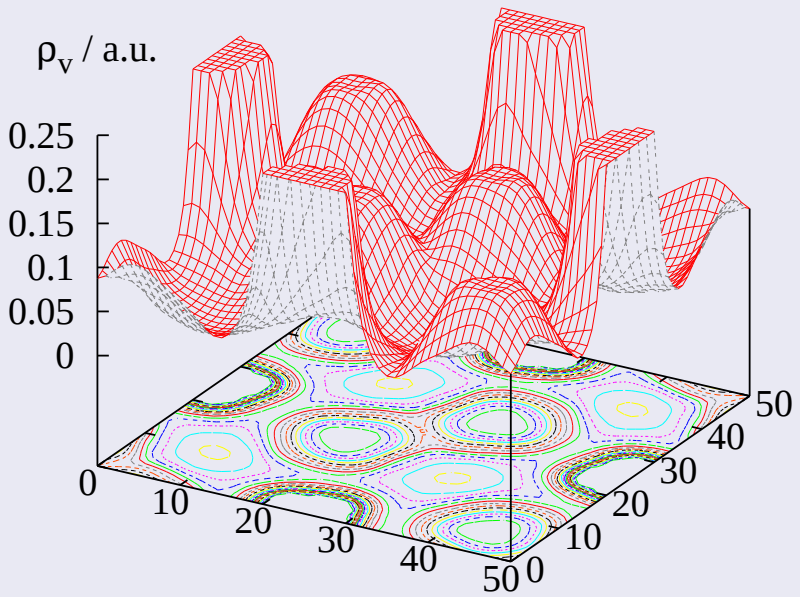
without rotation

with rotation:
*z* axis $\parallel \langle 111 \rangle$

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

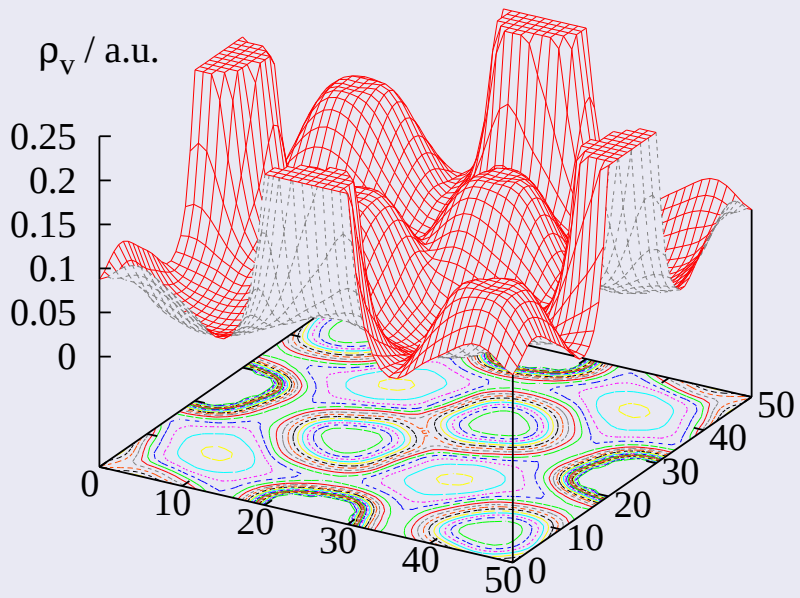
# $FeS_2$: Density and Laplacian

## Valence Electron Density

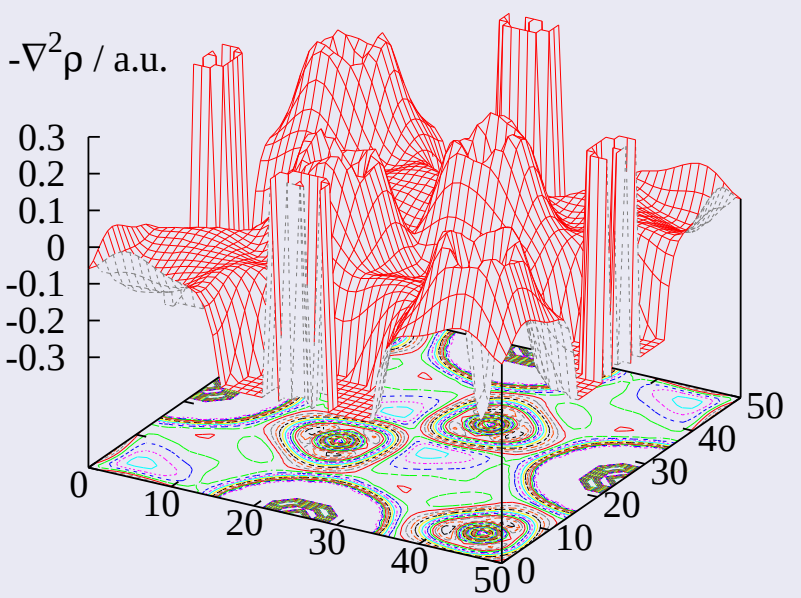


# $FeS_2$: Density and Laplacian

## Valence Electron Density



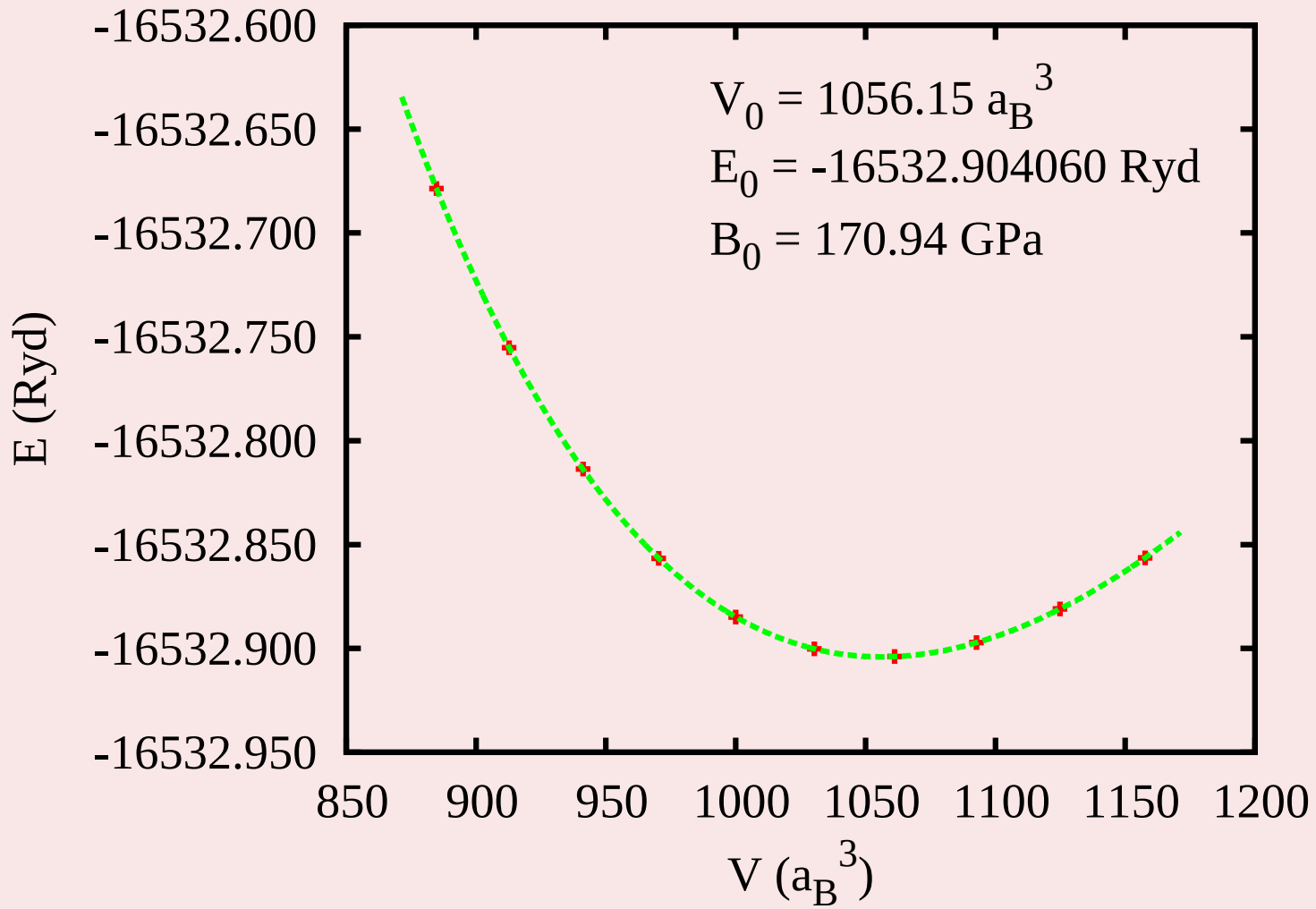

## Laplacian of Electron Density




## 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 |

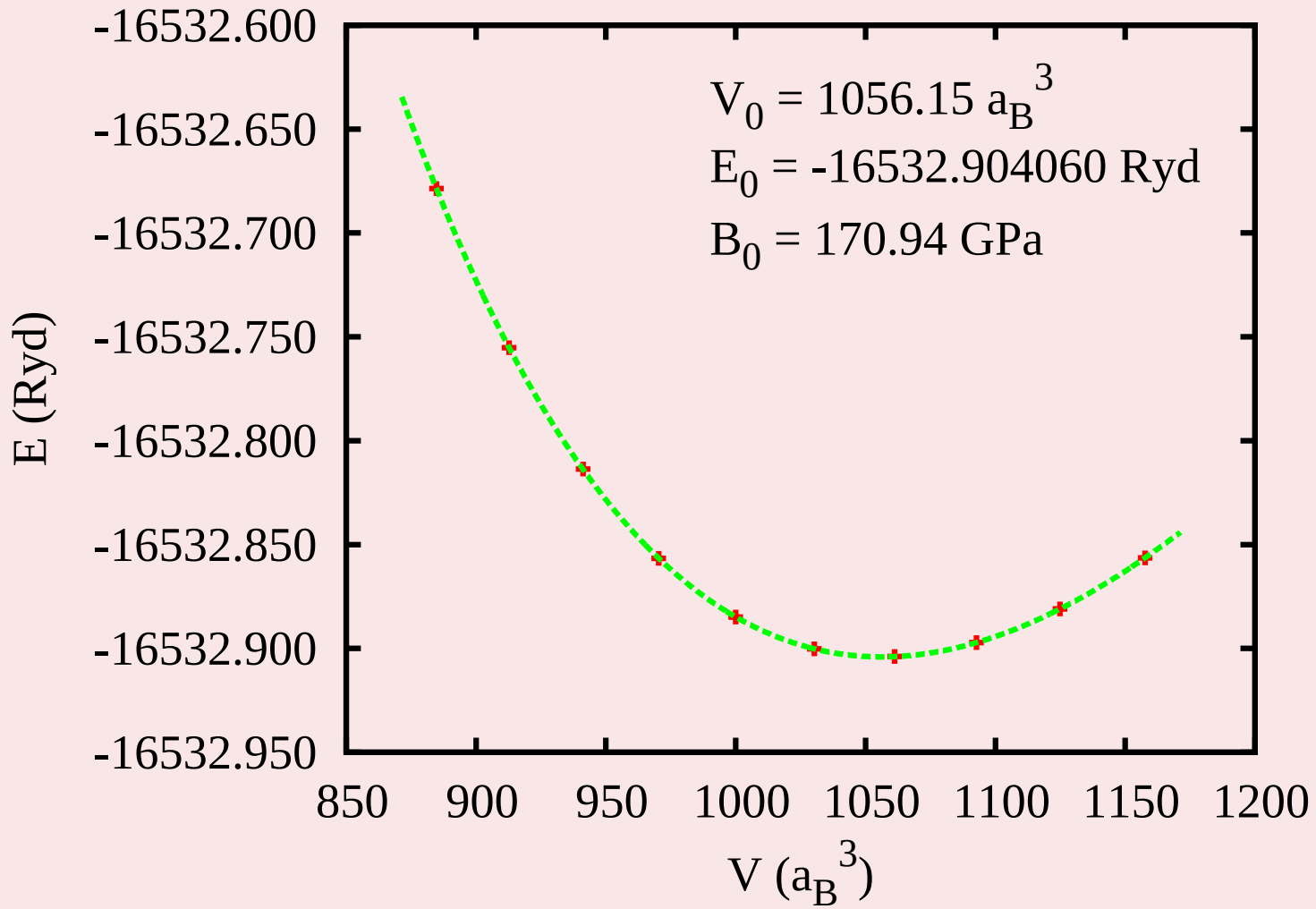
INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

# $FeS_2$: Equilibrium Volume and Bulk Modulus

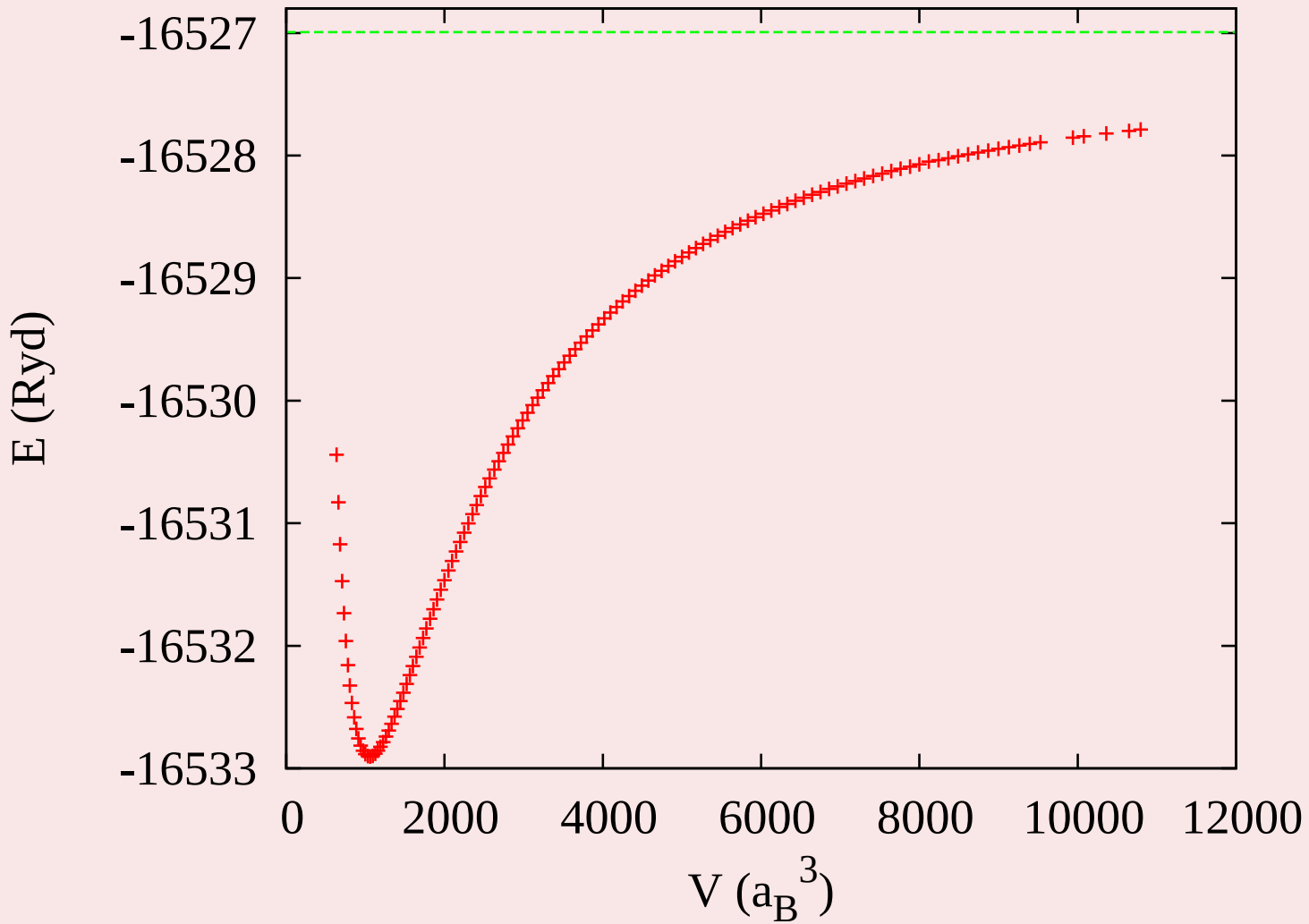
## Bulk Modulus

| | | |
|---|---|---|
| 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

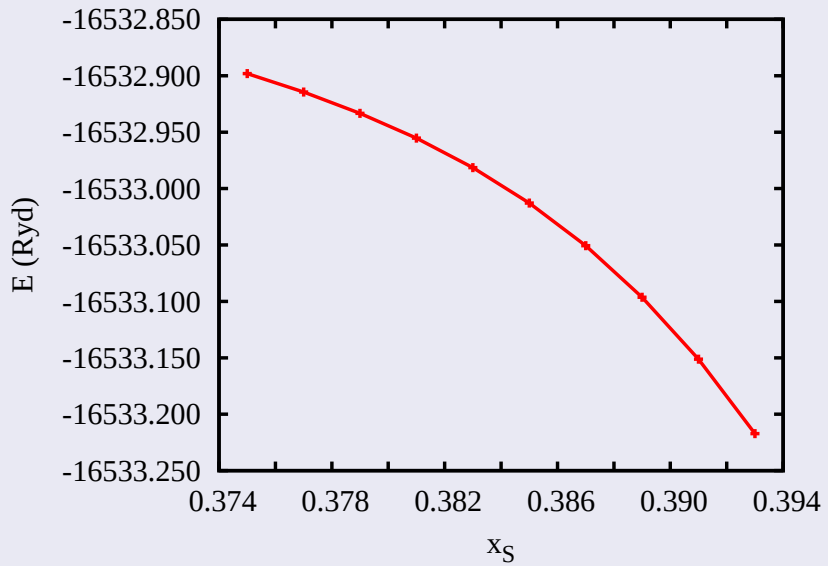


# $FeS_2$: From Atoms to the Solid



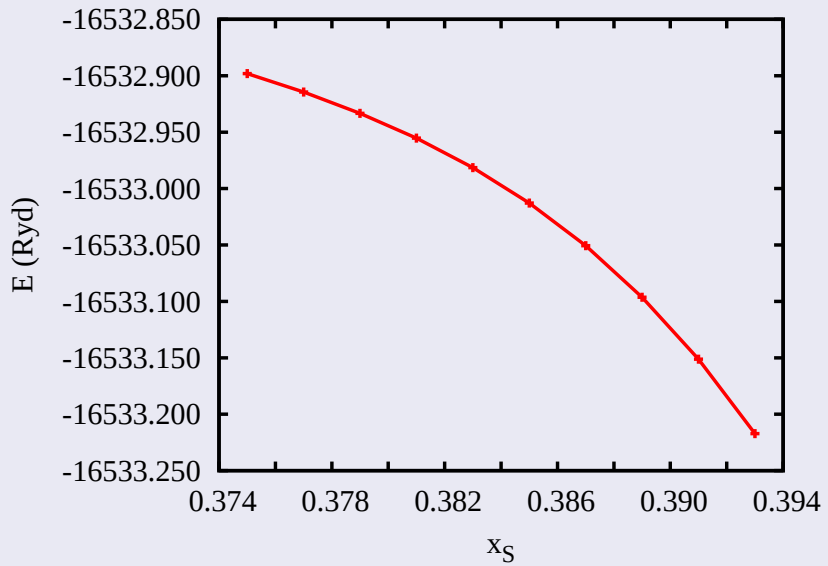
# $FeS_2$: Structure Optimization

## ASW Version 2.2

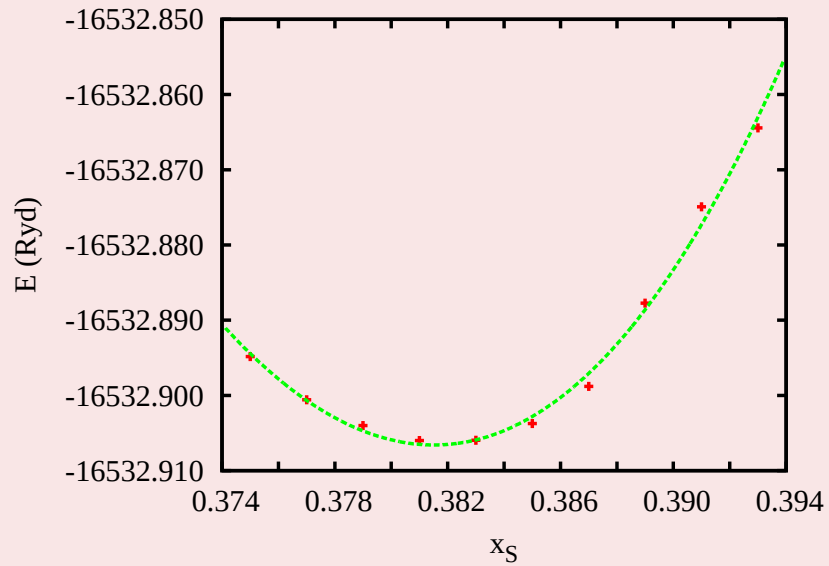


# $FeS_2$: Structure Optimization

## ASW Version 2.2




## FPASW Version 2.3




INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

# $FeS_2$: Structure Optimization

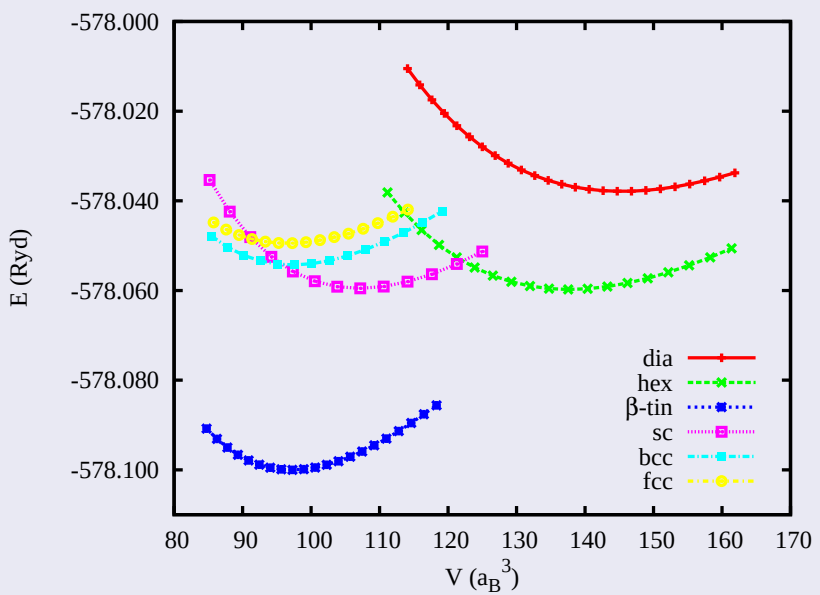
## Sulfur Position

| | | |
|---|---|---|
| 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 |

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

# Phase Stability in Silicon

## ASW Version 2.2

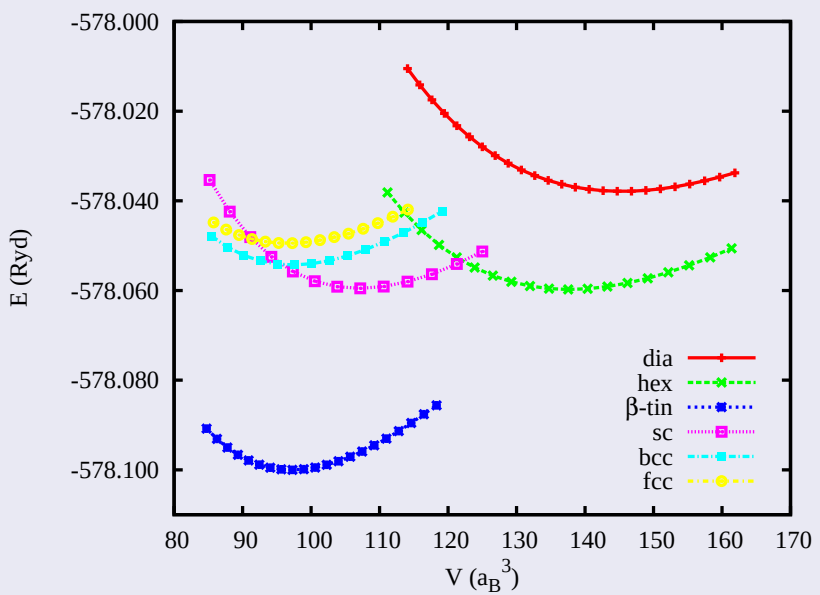



## Bad

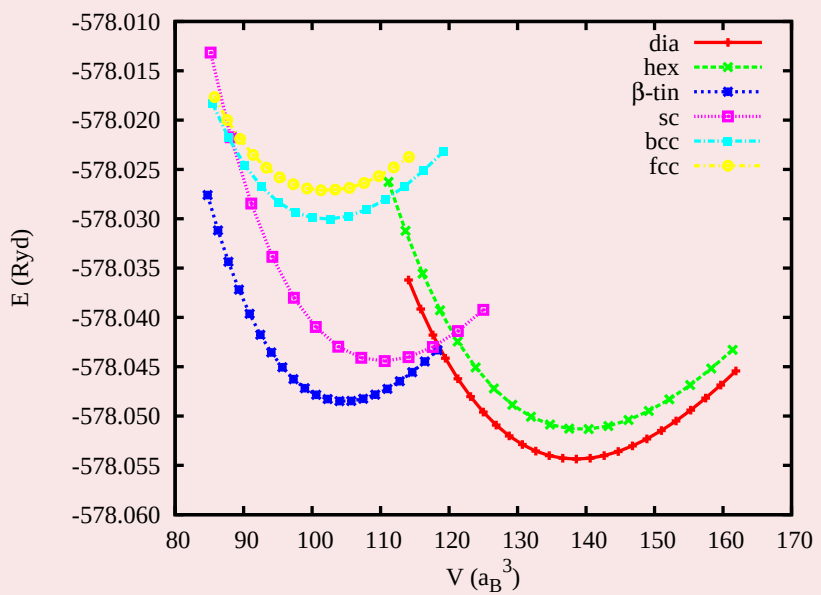
- $\beta$-tin structure most stable # nature (diamond structure)

# Phase Stability in Silicon

## ASW Version 2.2




## FPASW Version 2.4

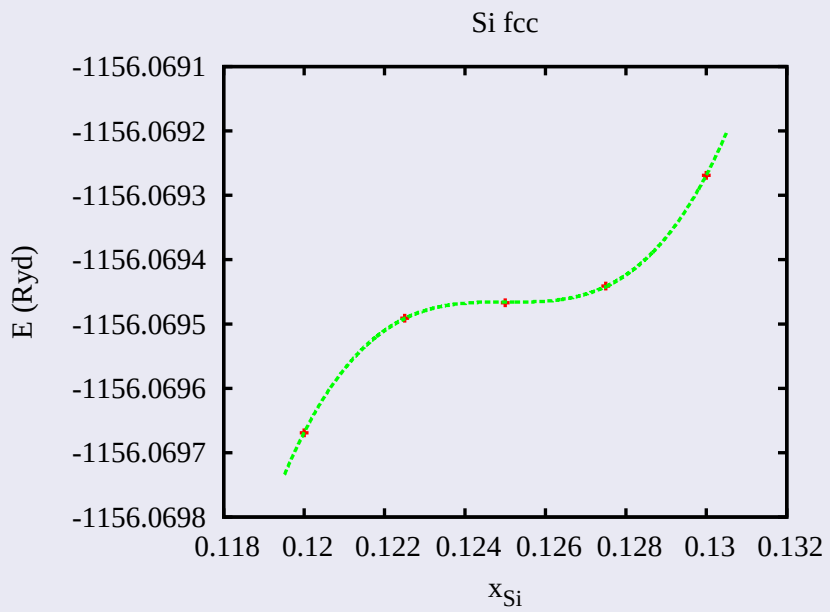


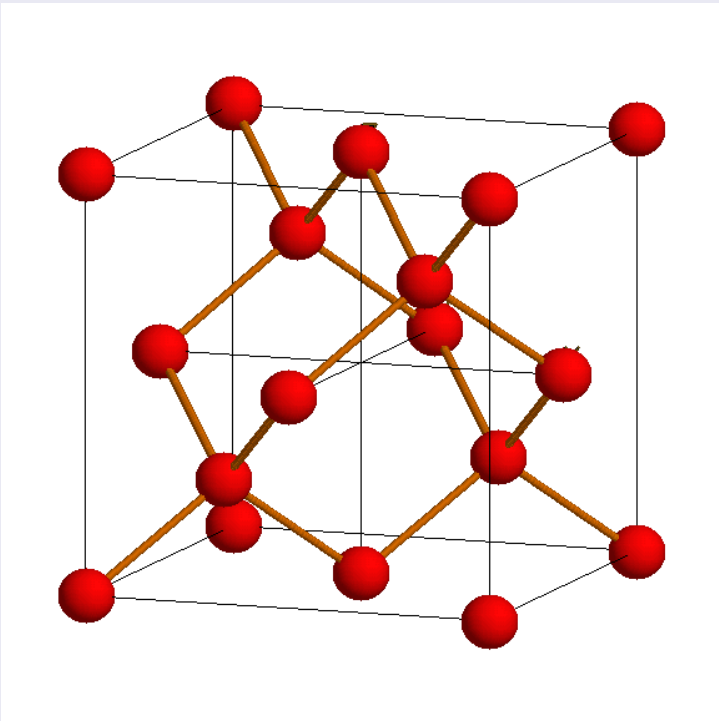

## New!

- diamond structure most stable
- pressure induced phase transition to $\beta$-tin structure

# LTO(Γ)-Phonon in Silicon

## ASW Version 2.2



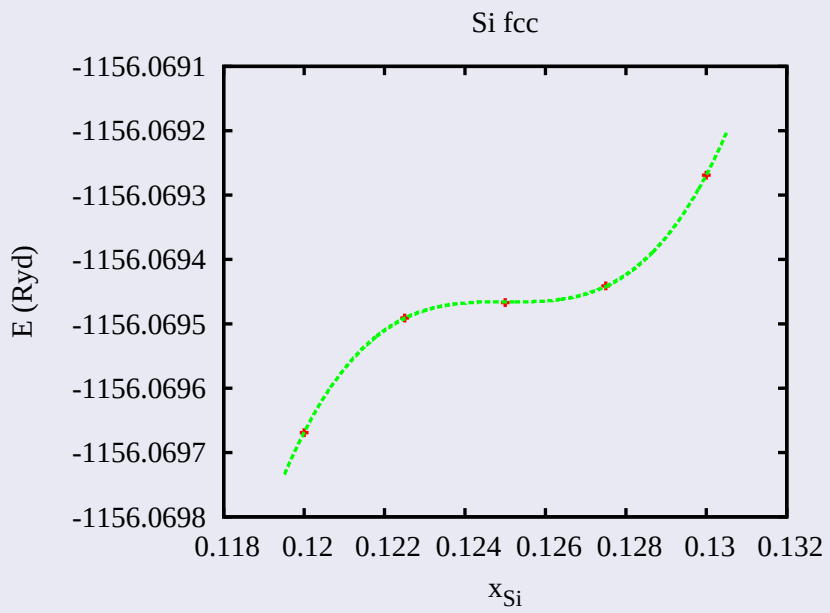



## Bad

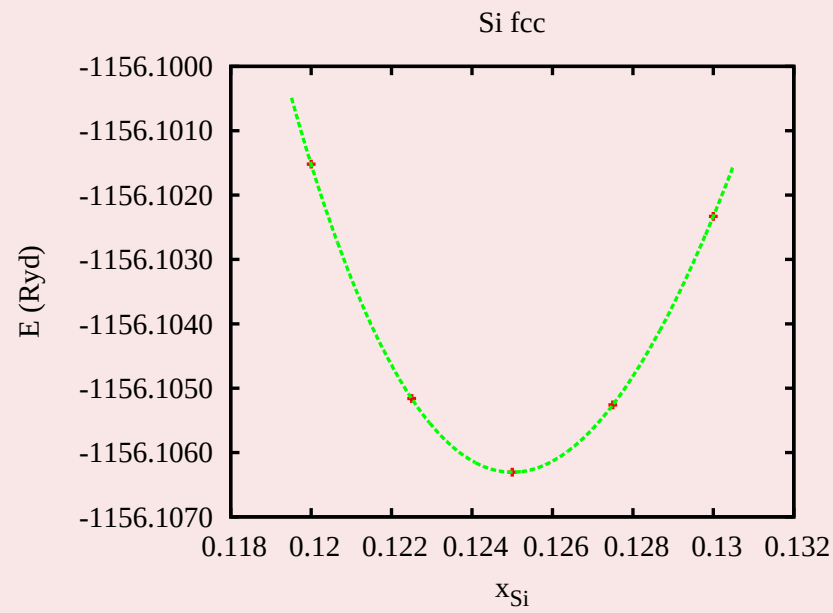
- no stable Si position # nature

# LTO(Γ)-Phonon in Silicon

## ASW Version 2.2




## FPASW Version 2.4

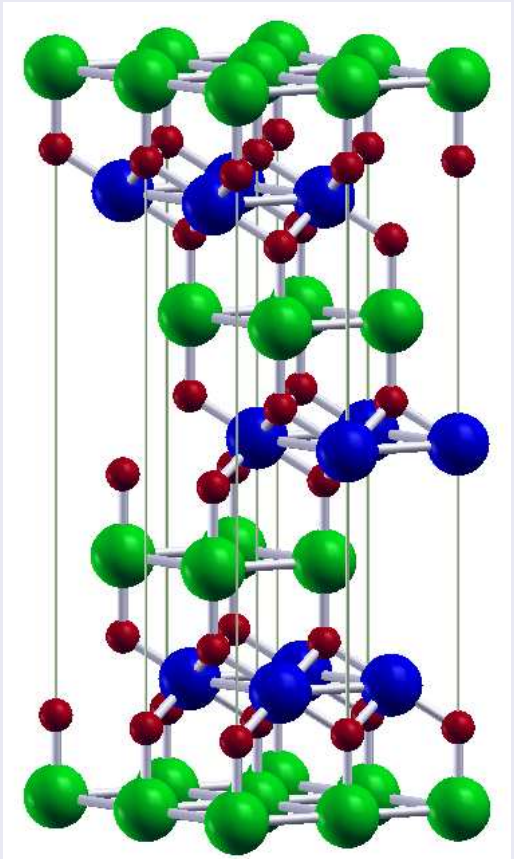



## New!

- phonon frequency: $f_{calc} = 15.26\,\text{THz}$ ($f_{exp} = 15.53\,\text{THz}$)

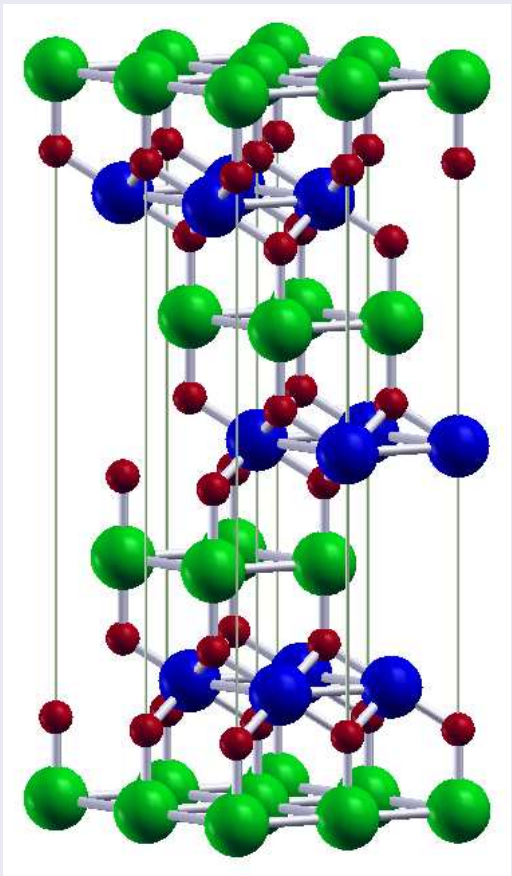
# Structure Optimization in $PdCoO_2$

## Delafossite Structure

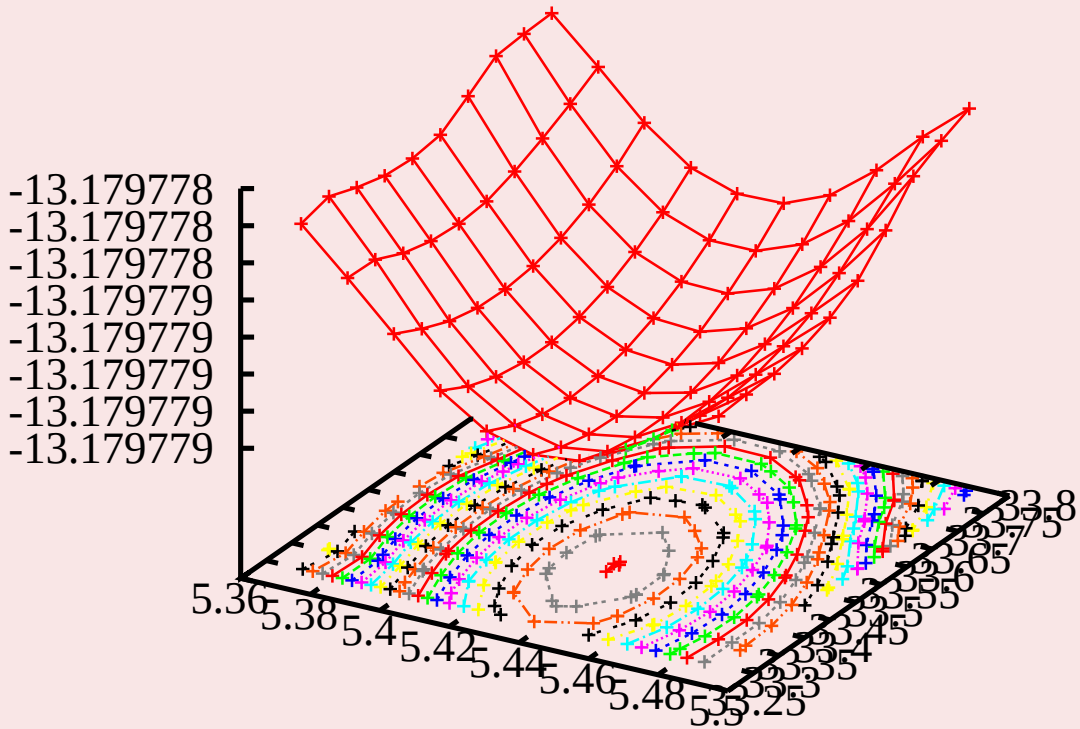


# Structure Optimization in $PdCoO_2$

## Delafossite Structure



## Total energy surface



# Structure Optimization in $PdCoO_2$

## Structural Data

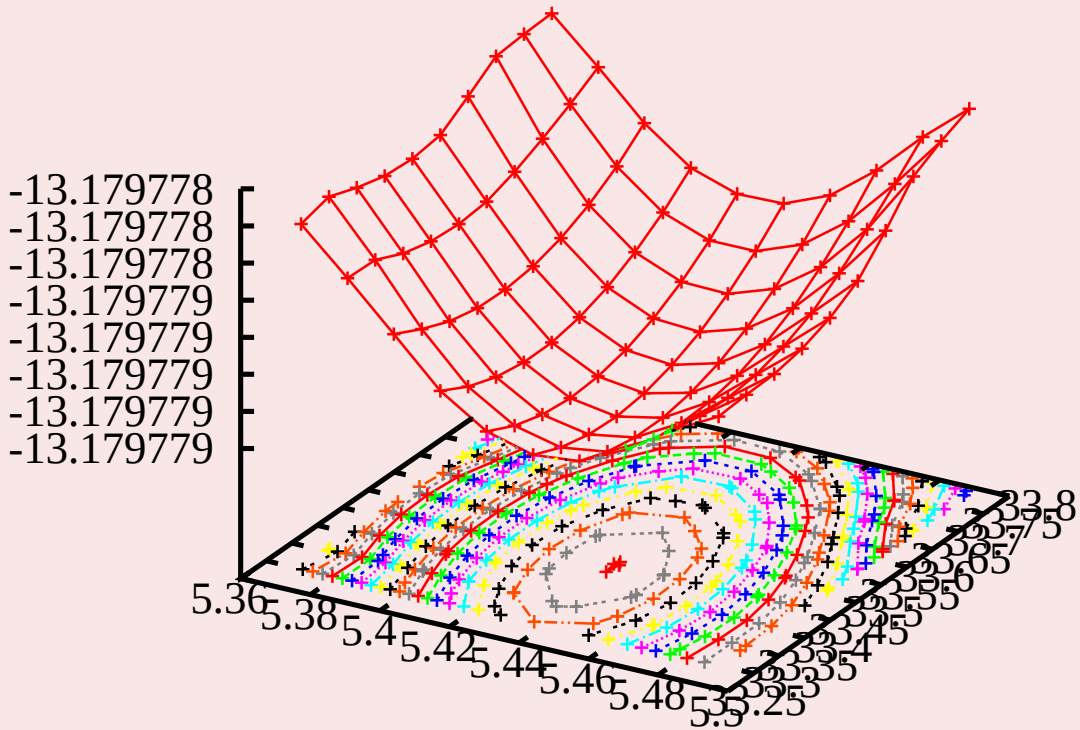
experiment

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

theory

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

## Total energy surface

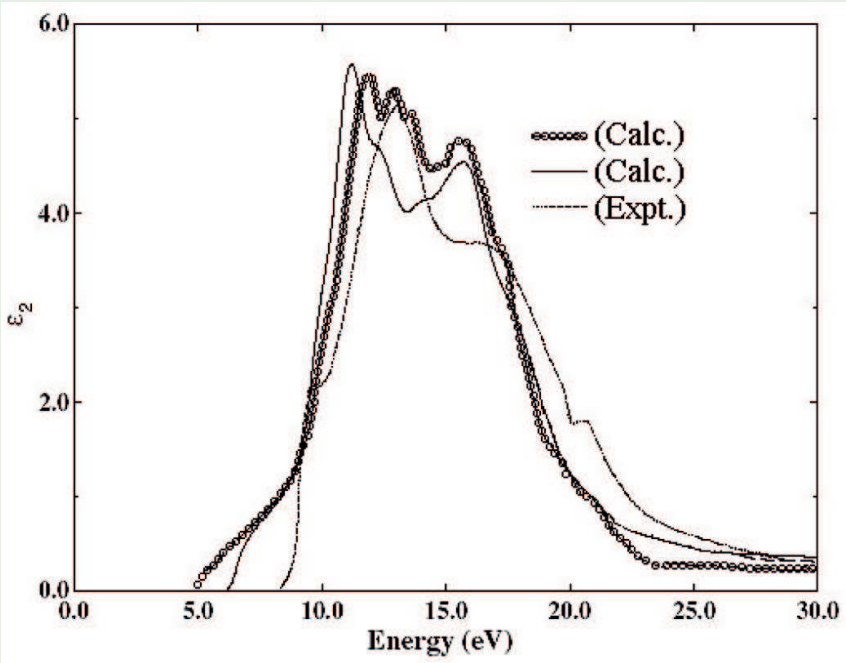



VE, R. Frésard, A. Maignan, Chem. Mat. (2008), in press

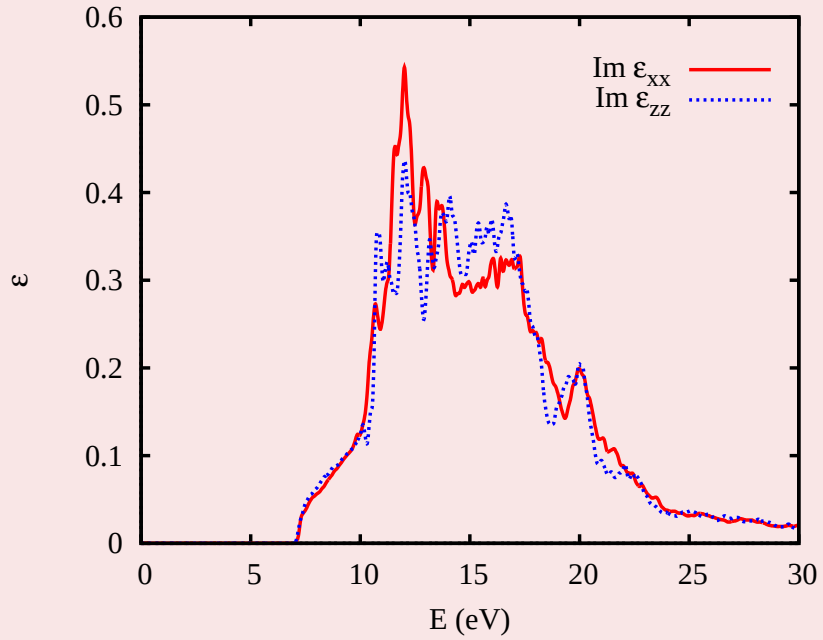
# Dielectric Functions of Corundum

## Imaginary Part

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




### FPASW

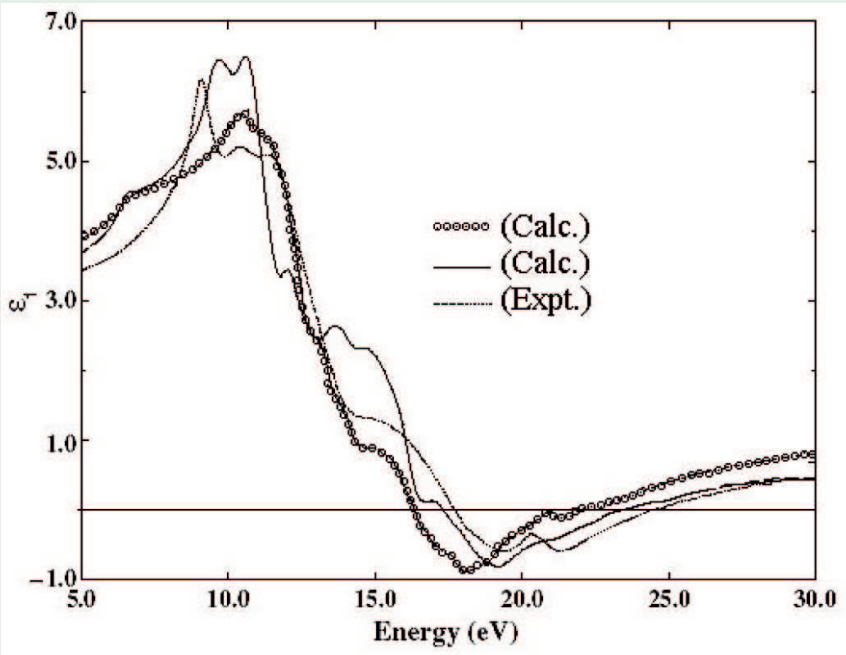



INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

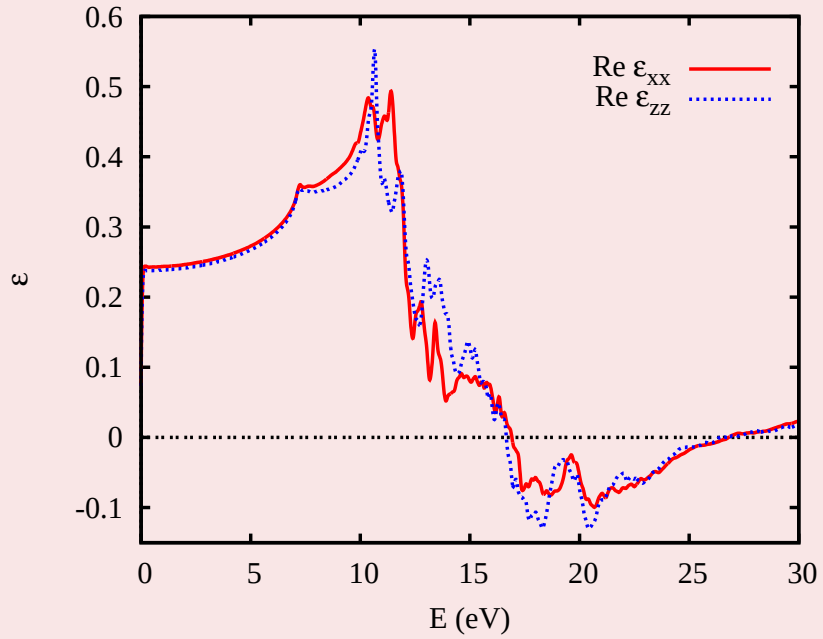
# Dielectric Functions of Corundum

## Real Part

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



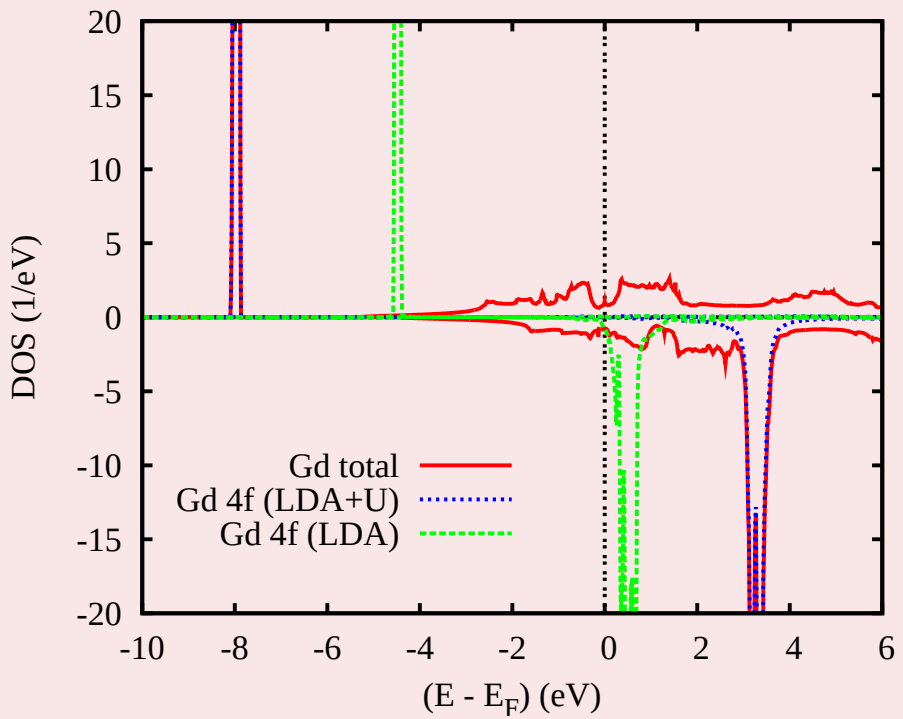

### FPASW




INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

# LDA+U-Calculations for Gadolinium

## DOS of ferromagnetic Gd




## Energetics

| | $E_{AF} - E_{FE}$ |
|---|---|
| LDA | -1.601 |
| LDA+U | 8.425 |

(in mRyd/atom)

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

# Summary

## Full-Potential ASW Method (Versions 2.3/2.4)

- 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?

# Summary

## Full-Potential ASW Method (Versions 2.3/2.4)

- 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?

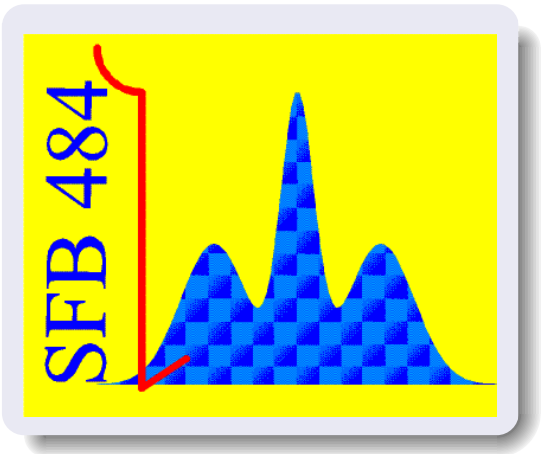
- Forces? Automated Structure Optimization?
- Exact Exchange (EXX)? at $\mathcal{O}$(ASA) speed?

# Acknowledgments

**Darmstadt**
SFB 252

**Stuttgart**
O. K. Andersen

**Augsburg**
T. Kopp, J. Mannhart,
K.-H. Höck, W. Scherer




**Darmstadt**
J. Sticht †

**Darmstadt**
P. C. Schmidt, M. Stephan

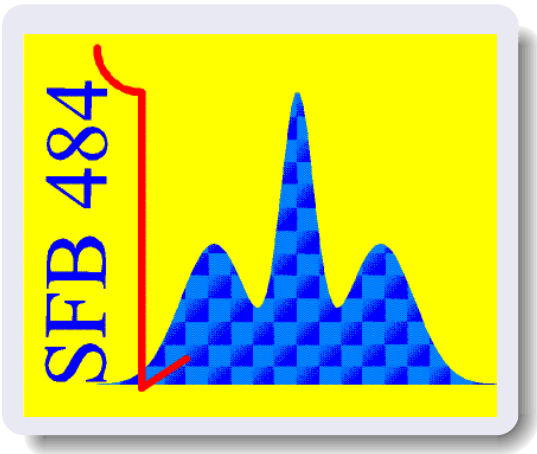
INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

# Acknowledgments

**Darmstadt**
SFB 252

**Stuttgart**
O. K. Andersen

**Augsburg**
T. Kopp, J. Mannhart,
K.-H. Höck, W. Scherer




**Darmstadt**
J. Sticht †

**Darmstadt**
P. C. Schmidt, M. Stephan

**Cocoyoc**
Thank You for Your Attention!