From Quantum Mechanics to Materials Design

Volker Eyert

Institut für Physik, Universität Augsburg

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

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

Volker Eyert

Institut für Physik, Universität Augsburg

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

Outline

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

Outline

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

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

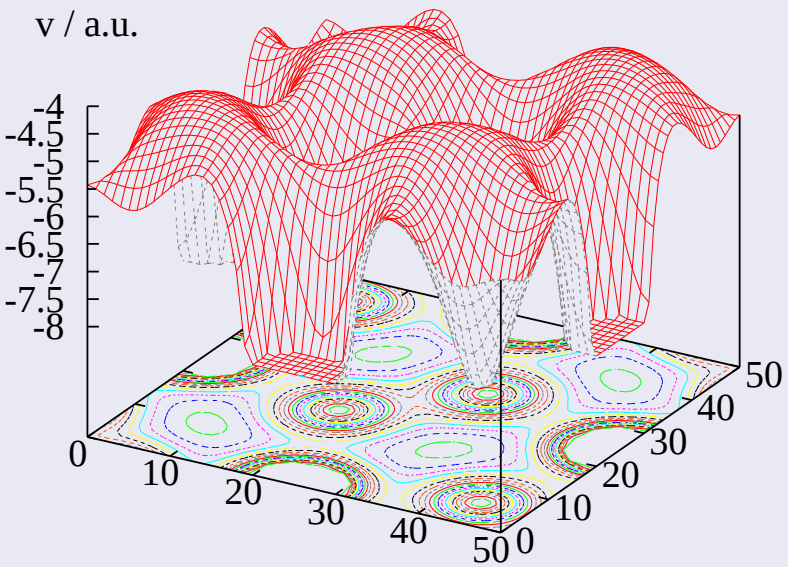
Muffin-Tin Approximation

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

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

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 1970's . . .

Ole K. Andersen

"Linear Methods in Band Theory"

- linearize energy dependence of basis functions
  - root tracing $\rightarrow$ eigenvalue problem
  - huge increase in computat. efficiency

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

Back in the 1970's . . .

Ole K. Andersen

"Linear Methods in Band Theory"

- linearize energy dependence of basis functions
  - root tracing $\longrightarrow$ eigenvalue problem
  - huge increase in computat. efficiency

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

Back in the 1970's . . .

Ole K. Andersen

"Linear Methods in Band Theory"

- linearize energy dependence of basis functions
  - root tracing $\longrightarrow$ eigenvalue problem
  - huge increase in computat. efficiency

Linear Augmented Plane Wave (LAPW)

- muffin-tin approximation
- easy to implement
- full-potential with moderate effort
  - basis functions from muffin-tin potential
  - wave functions from full potential
- large basis set

Back in the 1970's . . .

Ole K. Andersen

"Linear Methods in Band Theory"

- linearize energy dependence of basis functions
  - root tracing $\longrightarrow$ eigenvalue problem
  - huge increase in computat. efficiency

Linear Augmented Plane Wave (LAPW)

- muffin-tin approximation
- easy to implement
- full-potential with moderate effort
  - basis functions from muffin-tin potential
  - wave functions from full potential
- large basis set

Back in the 1970's . . .

Ole K. Andersen

"Linear Methods in Band Theory"

- linearize energy dependence of basis functions
  - root tracing $\longrightarrow$ eigenvalue problem
  - huge increase in computat. efficiency

Linear Augmented Plane Wave (LAPW)

- muffin-tin approximation
- easy to implement
- full-potential with moderate effort
  - basis functions from muffin-tin potential
  - wave functions from full potential
- large basis set

Back in the 1970's . . .

Ole K. Andersen

"Linear Methods in Band Theory"

- linearize energy dependence of basis functions
  - root tracing $\longrightarrow$ eigenvalue problem
  - huge increase in computat. efficiency

Linear Augmented Plane Wave (LAPW)

- muffin-tin approximation
- easy to implement
- full-potential with moderate effort
  - basis functions from muffin-tin potential
  - wave functions from full potential
- large basis set

Back in the 1970's . . .

Ole K. Andersen

Linear Muffin-Tin Orbital (LMTO)

- based on spherical waves
  - does not require crystalline periodicity
  - intuitive interpretation of results
- atomic-sphere approximation (ASA)
  - make spheres space-filling
  - more realistic
  - minimal basis set
    - very high computational efficiency
  - systematic error in total energy
- difficult to implement
- full-potential extension very difficult

Back in the 1970's . . .

Ole K. Andersen

Linear Muffin-Tin Orbital (LMTO)

- based on spherical waves
  - does not require crystalline periodicity
  - intuitive interpretation of results
- atomic-sphere approximation (ASA)
  - make spheres space-filling
  - more realistic
  - minimal basis set
    - very high computational efficiency
  - systematic error in total energy
- difficult to implement
- full-potential extension very difficult

Back in the 1970's . . .

Ole K. Andersen

Linear Muffin-Tin Orbital (LMTO)

- based on spherical waves
  - does not require crystalline periodicity
  - intuitive interpretation of results
- atomic-sphere approximation (ASA)
  - make spheres space-filling
  - more realistic
  - minimal basis set
    - very high computational efficiency
  - systematic error in total energy
- difficult to implement
- full-potential extension very difficult

Back in the 1970's . . .

Ole K. Andersen

Linear Muffin-Tin Orbital (LMTO)

- based on spherical waves
  - does not require crystalline periodicity
  - intuitive interpretation of results
- atomic-sphere approximation (ASA)
  - make spheres space-filling
  - more realistic
  - minimal basis set
    - very high computational efficiency
  - systematic error in total energy
- difficult to implement
- full-potential extension very difficult

Towards a Full-Potential Spherical-Wave Method

Requirements

- restore interstitial region
  - overlapping atomic spheres
    $\rightarrow$ non-overlapping muffin-tin spheres
  - go beyond constant-potential approximation

Towards a Full-Potential Spherical-Wave Method

Requirements

- restore interstitial region
  - overlapping atomic spheres
    $\longrightarrow$ non-overlapping muffin-tin spheres
  - go beyond constant-potential approximation
- inside muffin-tin spheres
  - non-spherical contributions

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

Towards a Full-Potential Spherical-Wave Method

Requirements

- restore interstitial region
  - overlapping atomic spheres
    $\rightarrow$ non-overlapping muffin-tin spheres
  - go beyond constant-potential approximation

Choices

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

Towards a Full-Potential Spherical-Wave Method

Requirements

- restore interstitial region
  - overlapping atomic spheres
    $\rightarrow$ non-overlapping muffin-tin spheres
  - go beyond constant-potential approximation

Choices

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

ASW Method

Naming

- Augmented Spherical Wave
  (for beginners)

ASW Method

Naming

- Augmented Spherical Wave
  (for beginners)
- Aussersinnliche Wahrnehmung
  (“extrasensory perception”, for the experienced)

ASW Method

Naming

- Augmented Spherical Wave
  (for beginners)
- Aussersinnliche Wahrnehmung
  (“extrasensory perception”, for the experienced)
- Always Slightly Wrong
  (for experts)

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
- all-electron method
  - core electrons fully included
  - full coverage of periodic table

ASW Method

Characteristics

- similar to LMTO
  - different linearization scheme
  - different interstitial energy
  - different implementations
- all-electron method
  - core electrons fully included
  - full coverage of periodic table
- minimal basis set
  - atomic-like (s, p, d, f) basis functions
  - intuitive interpretation of results
  - very high computational efficiency

ASW Method

Characteristics

- similar to LMTO
- all-electron method
- minimal basis set

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

PRB **19**, 6094 (1979)

ASW Method

Characteristics

- similar to LMTO
- all-electron method
- minimal basis set

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

- completely new implementation
- extended, more flexible basis set
- new algorithms $\longrightarrow$ accuracy, numerical stability
- all LDA-parametrizations, most GGA-schemes
- new interpretative tools
- 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

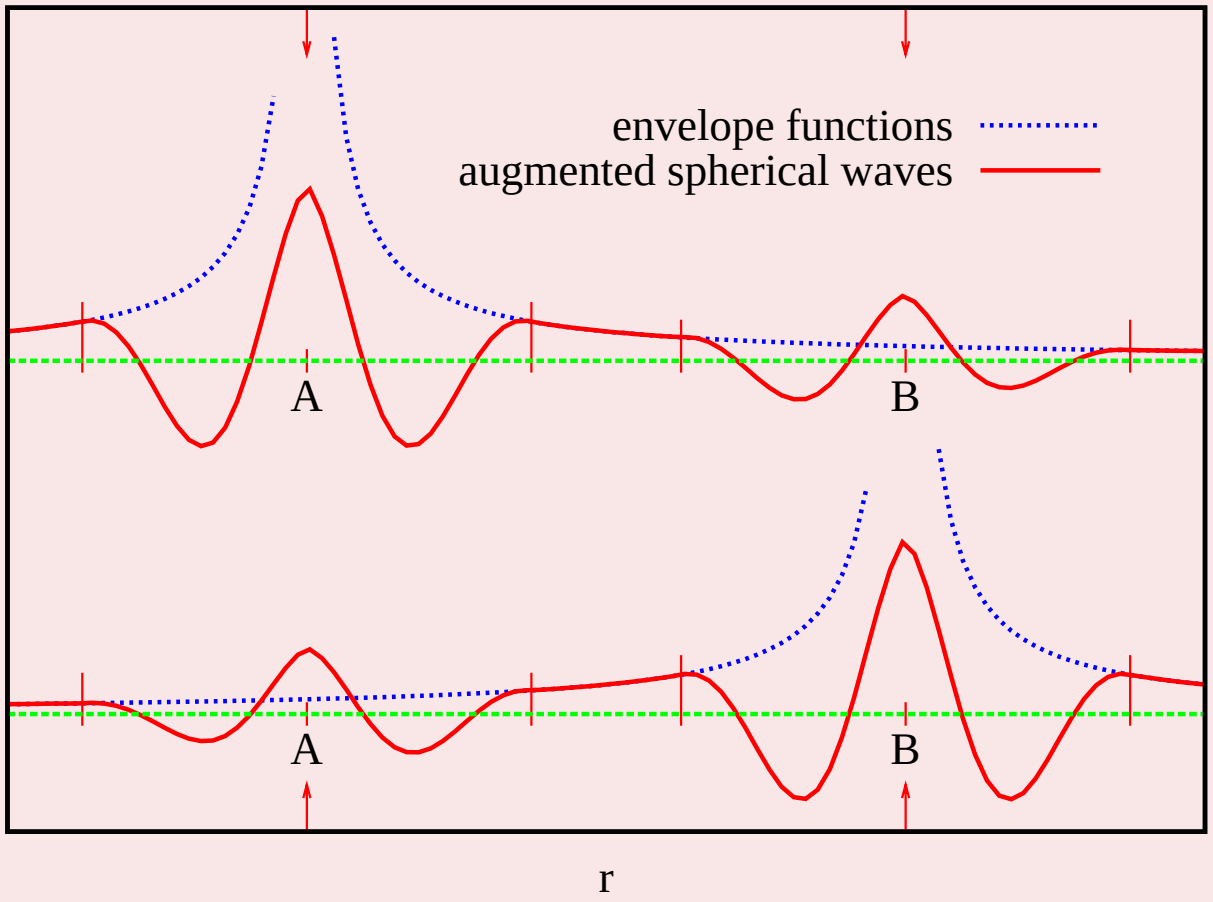
Augmented Spherical Wave

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

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

ASW Method: Basic Formalism

Augmented Spherical Waves



ASW Method: Basic Formalism

Envelope Functions

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

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

ASW Method: Basic Formalism

Envelope Functions

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

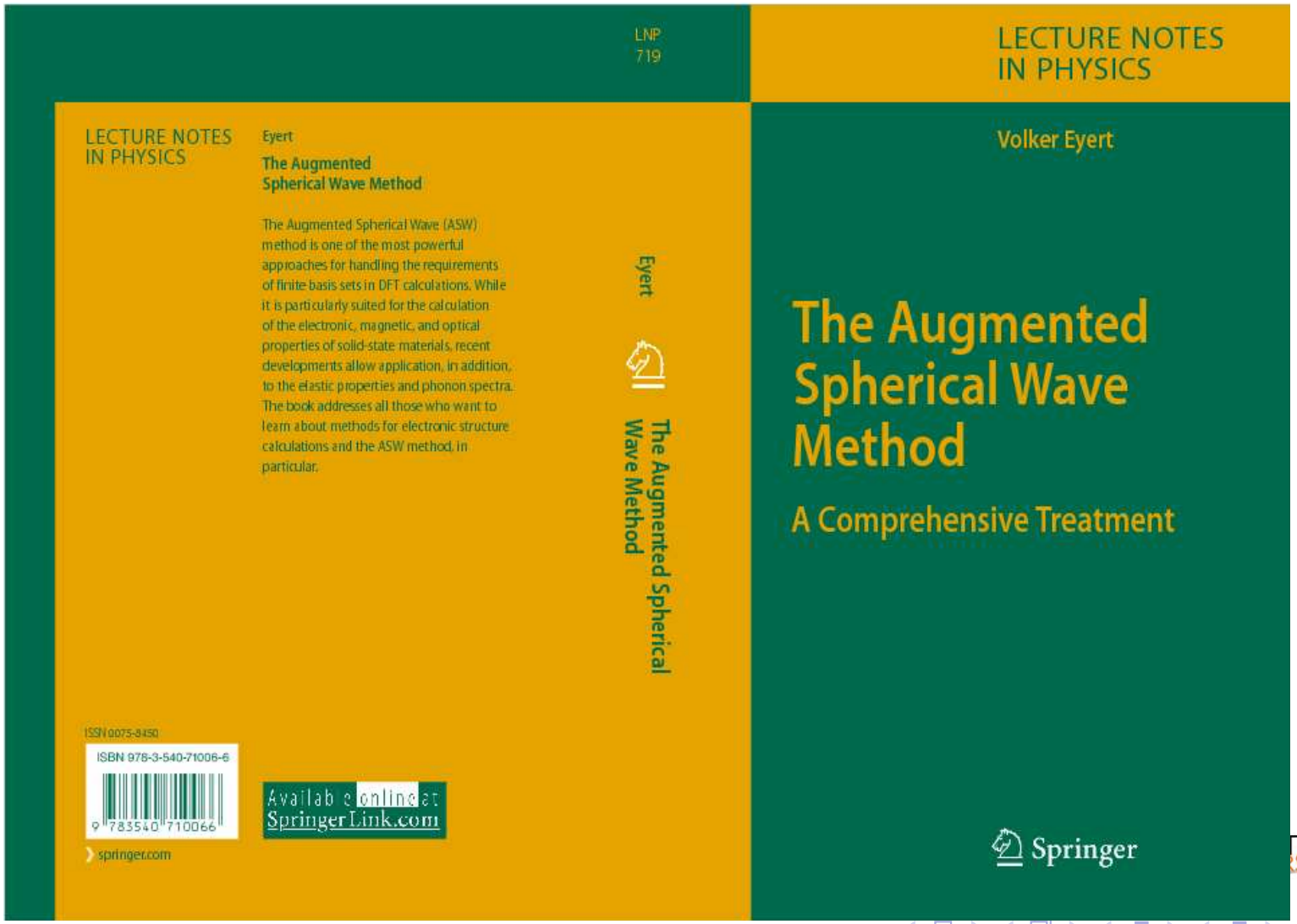
$h^{(1)}_l(\kappa r_i)$: spherical Hankel function

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 φ and $\dot{\varphi}$ of LMTO

Further Reading



Outline

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

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

From Wave Functions to Electron Density

Products of Basis Functions

$$p(\mathbf{r}) := \left(H^{\infty}_{L\kappa_1\sigma}(\mathbf{r}_i)\right)^* H^{\infty}_{L'\kappa_2\sigma}(\mathbf{r}_j) = p^I(\mathbf{r})\Theta_I + \tilde{p}(\mathbf{r})(1-\Theta_I)$$

- $\Theta_I = 0/1$ inside MT-spheres/in interstitial region

From Wave Functions to Electron Density

Products of Basis Functions

$$p(\mathbf{r}) := \left(H^{\infty}_{L\kappa_1\sigma}(\mathbf{r}_i)\right)^* H^{\infty}_{L'\kappa_2\sigma}(\mathbf{r}_j) = p^I(\mathbf{r})\Theta_I + \tilde{p}(\mathbf{r})(1-\Theta_I)$$

- $\Theta_I = 0/1$ inside MT-spheres/in interstitial region

Products of Basis Functions inside MT-Spheres

spherical-harmonics expansion

$$\tilde{p}(\mathbf{r}_m) = \sum_K \tilde{p}_K(r_m) Y_K(\hat{\mathbf{r}}_m)\Theta_m$$

From Wave Functions to Electron Density

Products of Basis Functions

$$p(\mathbf{r}) := \left(H^{\infty}_{L\kappa_1\sigma}(\mathbf{r}_i)\right)^* H^{\infty}_{L'\kappa_2\sigma}(\mathbf{r}_j) = p^I(\mathbf{r})\Theta_I + \tilde{p}(\mathbf{r})(1-\Theta_I)$$

- $\Theta_I = 0/1$ inside MT-spheres/in interstitial region

Products of Basis Functions inside MT-Spheres

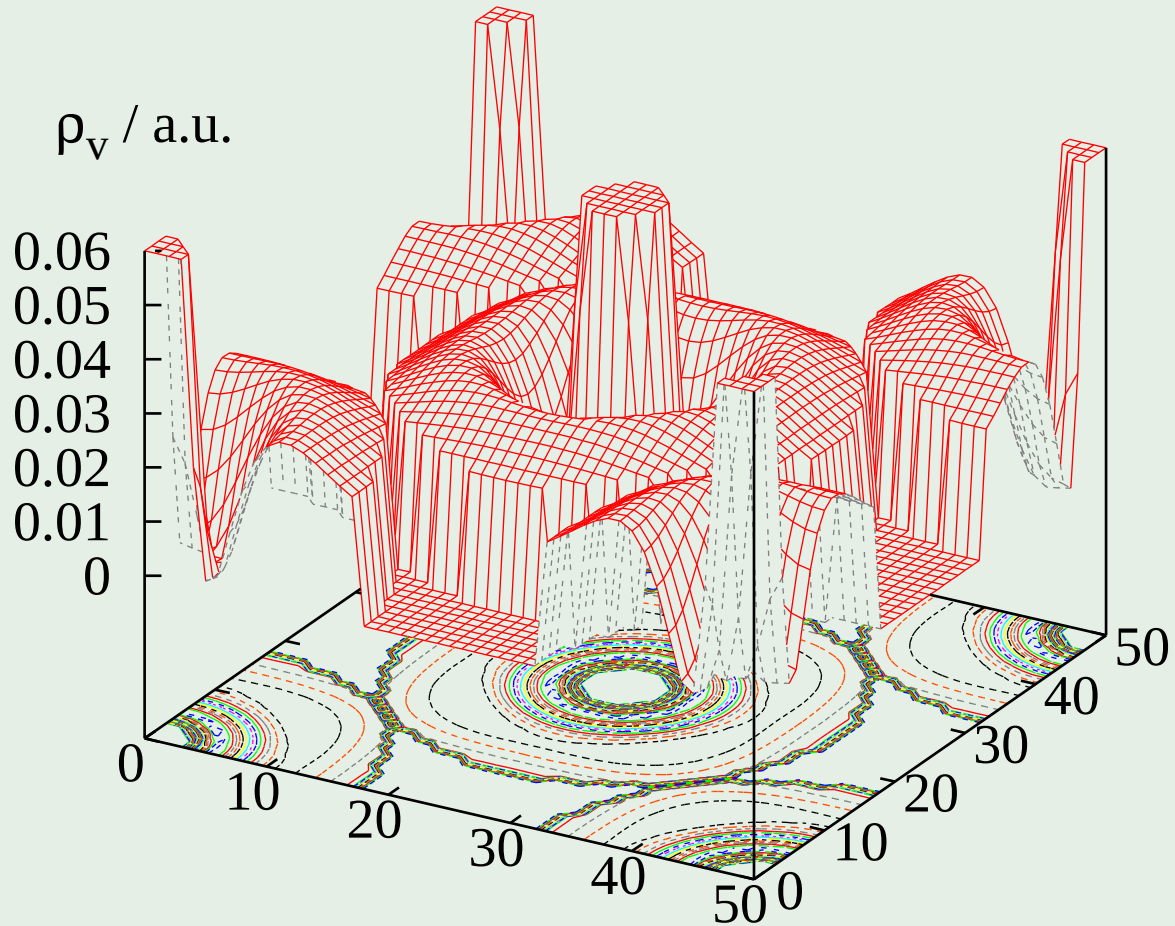
spherical-harmonics expansion

$$\tilde{p}(\mathbf{r}_m) = \sum_K \tilde{p}_K(r_m) Y_K(\hat{\mathbf{r}}_m)\Theta_m$$

$\tilde{p}_K(r_m)$ from augmented functions ($\tilde{h}_{l\kappa\sigma}(r_m)$ and $\tilde{j}_{l\kappa\sigma}(r_m)$)

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

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

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

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

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

From Wave Functions to Electron Density

Products of Basis Functions in Interstitial Region

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

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

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

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

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 $\mathcal{P}$:

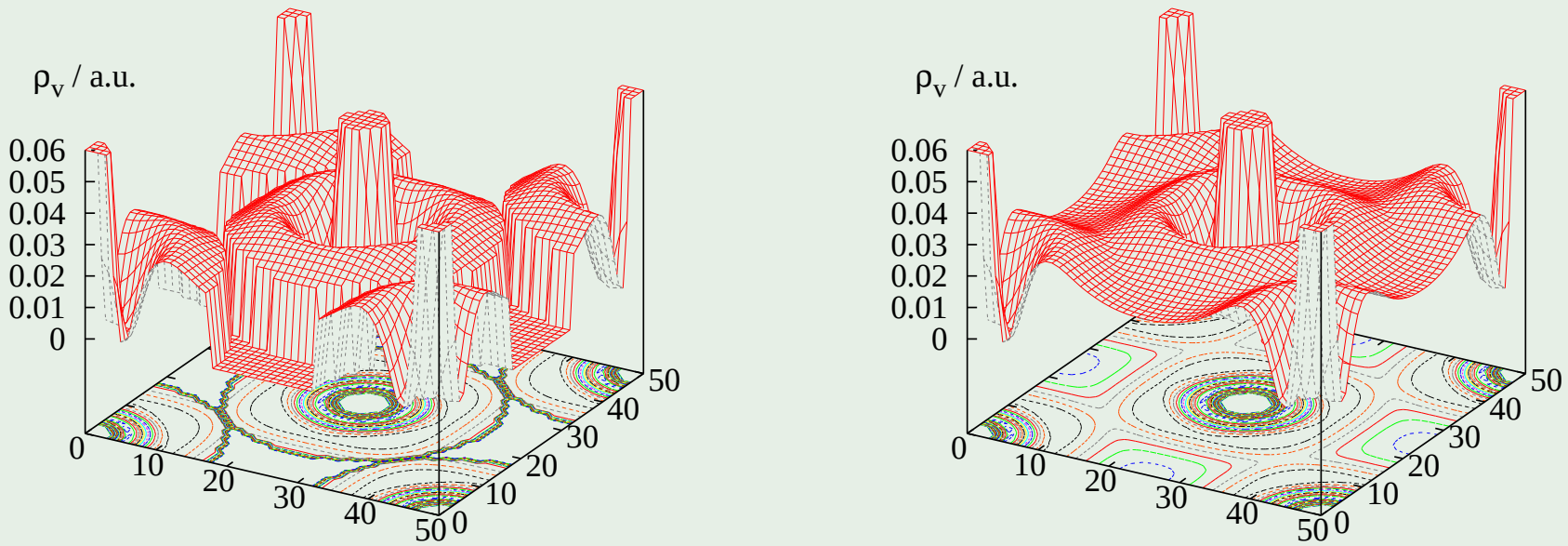
$$\mathcal{P}\left[\left(H^{\infty}_{L\kappa_1\sigma}(\mathbf{r}_i)\right)^* H^{\infty}_{L'\kappa_2\sigma}(\mathbf{r}_j)\right] = \sum_n \sum_{K\eta} d^{L\kappa_1 iL'\kappa_2 j}_{K\eta n\sigma}\ \mathcal{P}\left[H_{K\eta}(\mathbf{r}_n)\right]$$

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! (multiple-κ 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! (multiple-κ 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
  $\longrightarrow$ multiple-κ basis set — bad!

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

Implementation

2nd Generation (VE, 2000s)

- based on 1st generation code
- monolithic implementation
- full-potential ASW method — at $\mathcal{O}$(ASA) speed!
  - electron densities, spin densities
  - electric field gradients
  - elastic properties, phonon spectra
- optical properties

Implementation

2nd Generation (VE, 2000s)

- based on 1st generation code
- monolithic implementation
- full-potential ASW method — at $\mathcal{O}$(ASA) speed!
  - electron densities, spin densities
  - electric field gradients
  - elastic properties, phonon spectra
- optical properties

Implementation

2nd Generation (VE, 2000s)

- based on 1st generation code
- monolithic implementation
- full-potential ASW method — at $\mathcal{O}$(ASA) speed!
  - electron densities, spin densities
  - electric field gradients
  - elastic properties, phonon spectra
- optical properties

Implementation

2nd Generation (VE, 2000s)

- based on 1st generation code
- monolithic implementation
- full-potential ASW method — at $\mathcal{O}$(ASA) speed!
  - electron densities, spin densities
  - electric field gradients
  - elastic properties, phonon spectra
- optical properties

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

Implementation

2nd Generation (VE, 2000s)

- based on 1st generation code
- monolithic implementation
- full-potential ASW method — at $\mathcal{O}$(ASA) speed!
  - electron densities, spin densities
  - electric field gradients
  - elastic properties, phonon spectra
- optical properties

Implementation

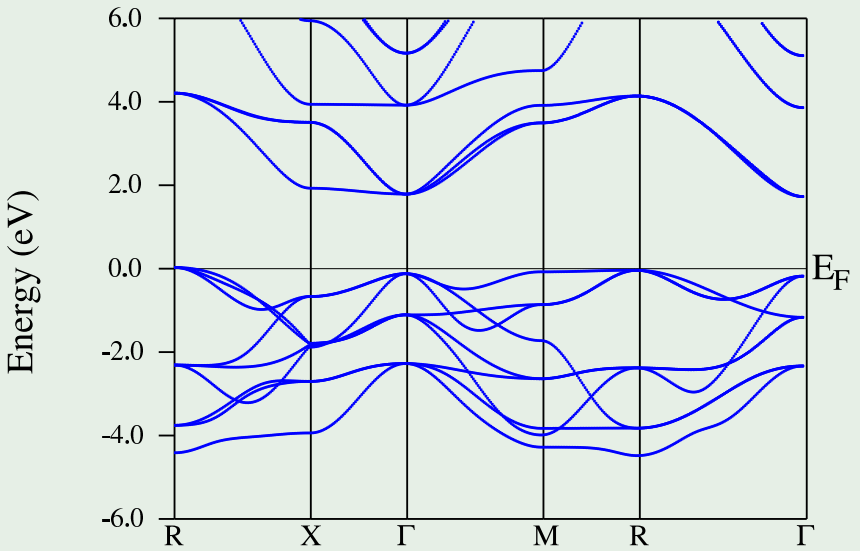
2nd Generation (VE, 2000s)

- based on 1st generation code
- monolithic implementation
- full-potential ASW method — at $\mathcal{O}$(ASA) speed!
  - electron densities, spin densities
  - electric field gradients
  - elastic properties, phonon spectra
- optical properties

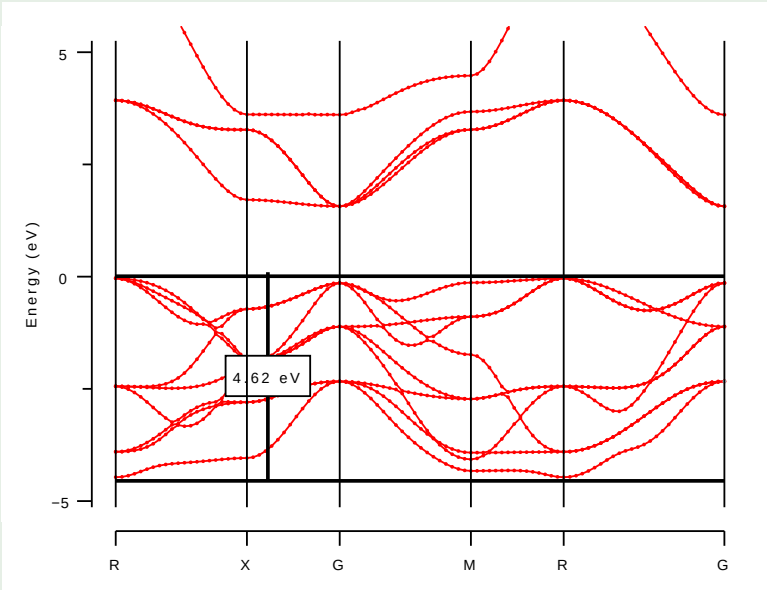
Outline

Electronic Structure of $BaTiO_3$

Wien2k



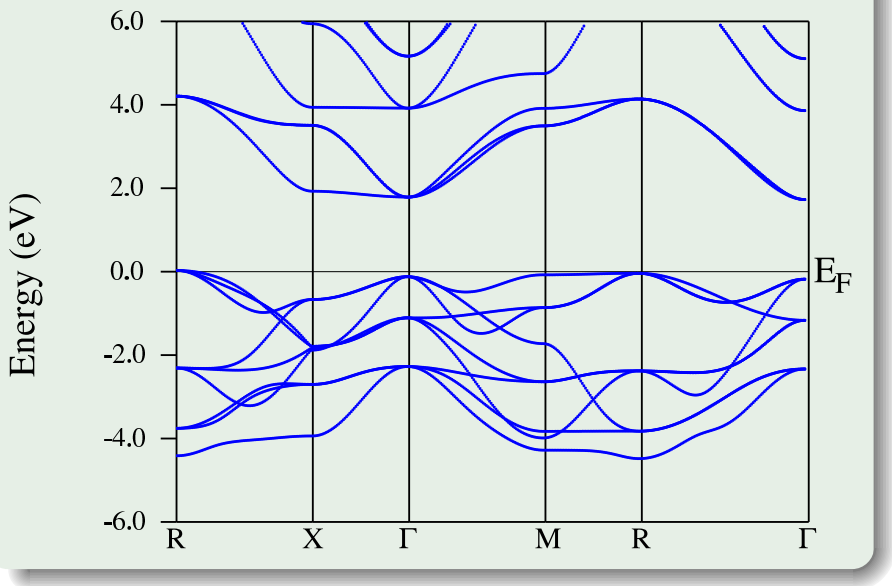
VASP



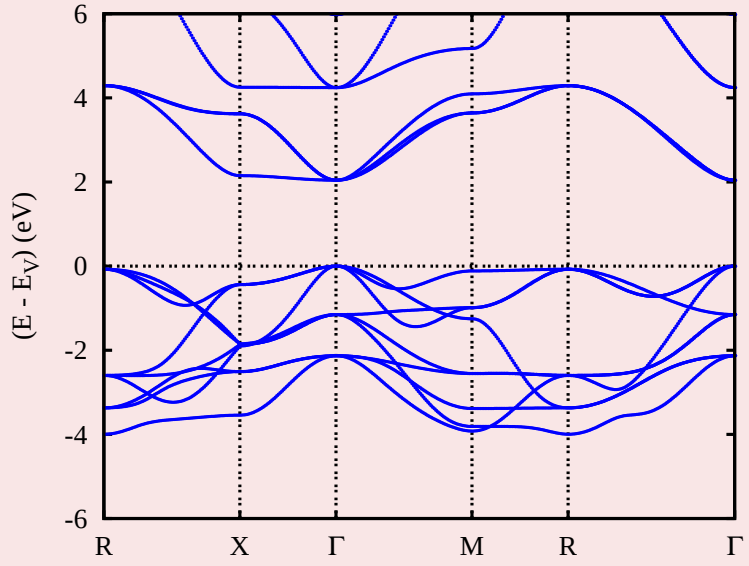
INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

Electronic Structure of $BaTiO_3$

Wien2k

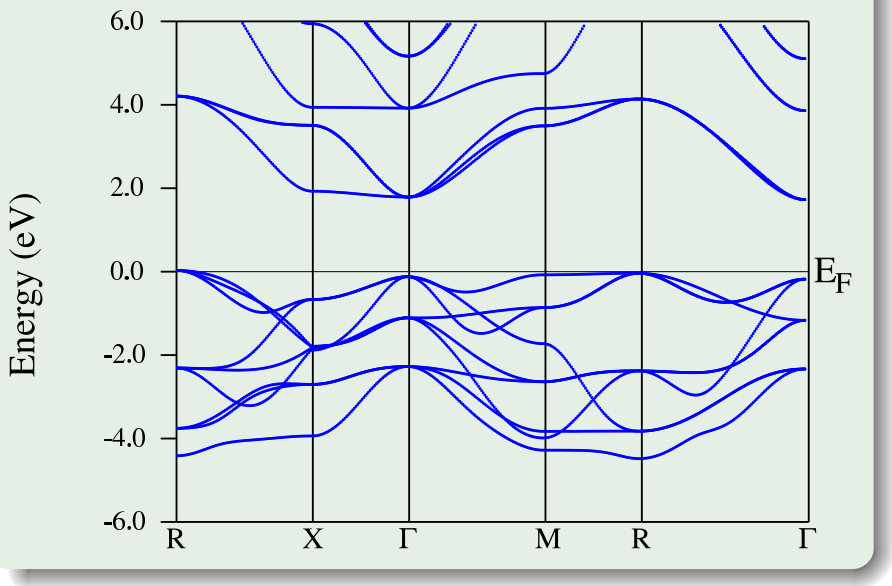


ASW Version 2.2

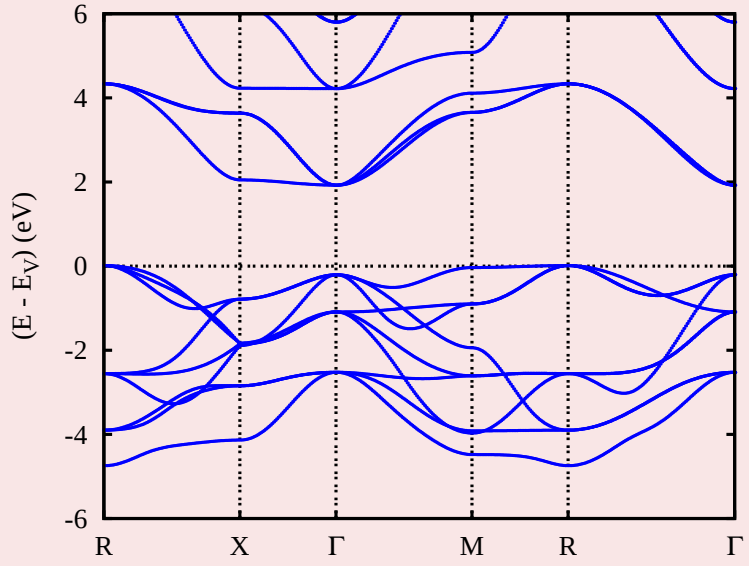


Electronic Structure of $BaTiO_3$

Wien2k

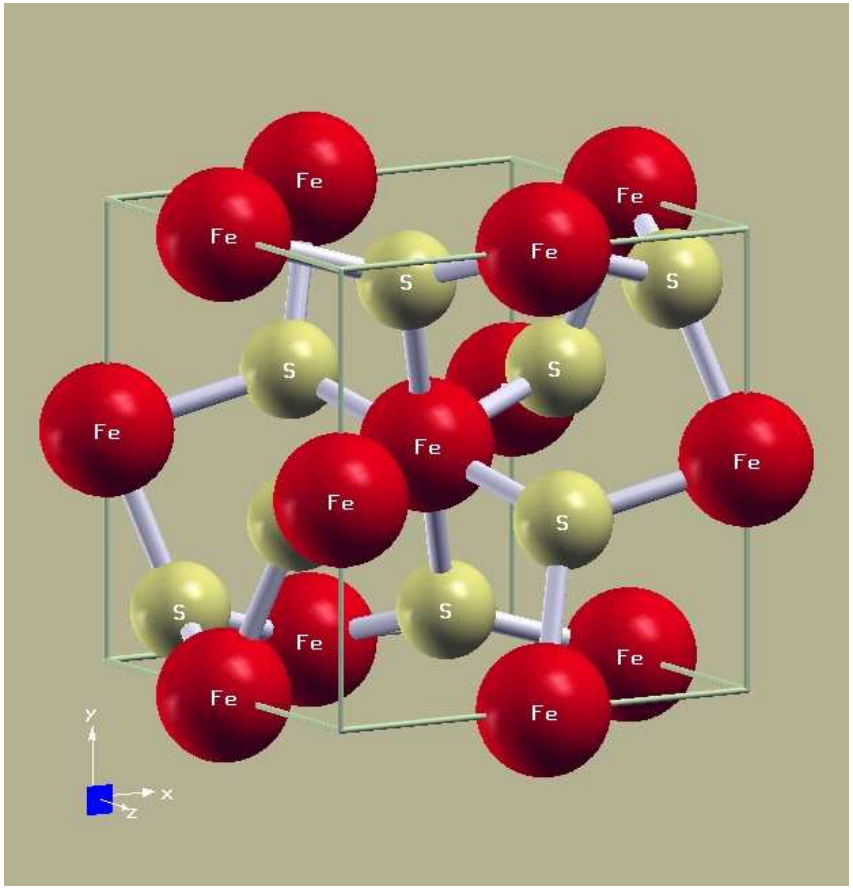


FPASW Version 2.3



INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

Iron Pyrite: FeS_2

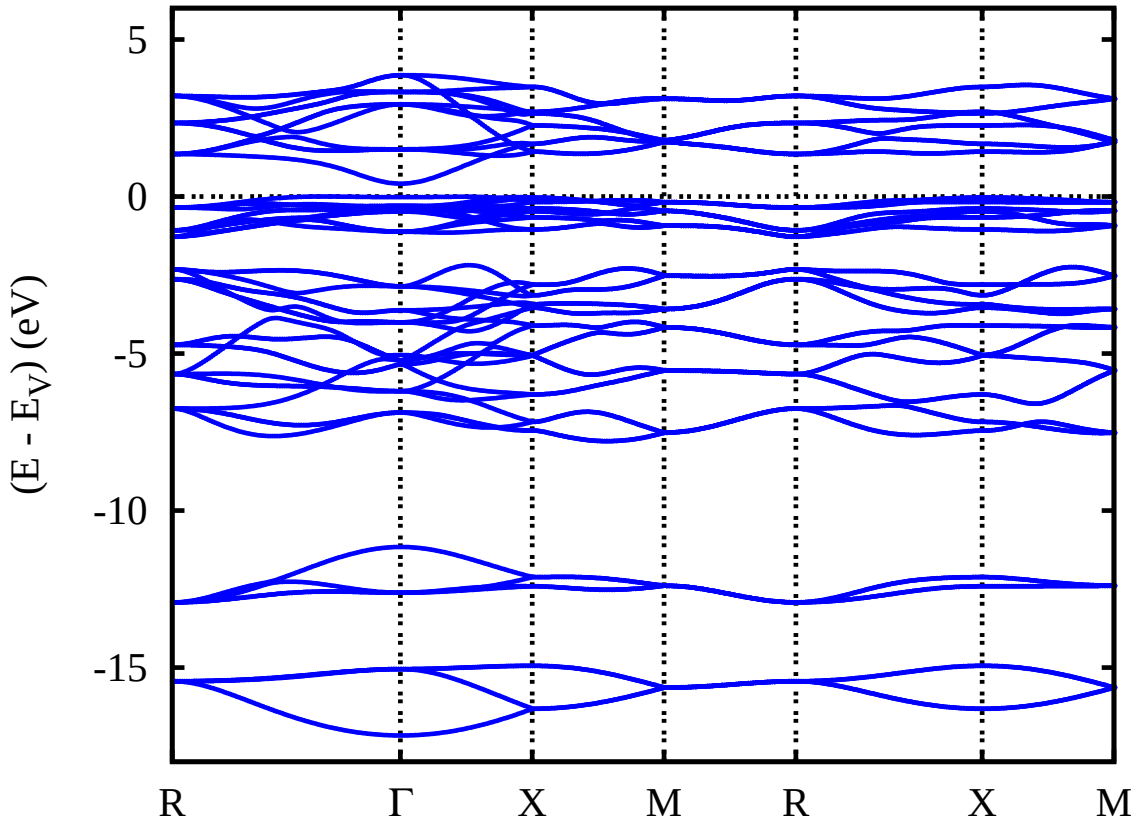


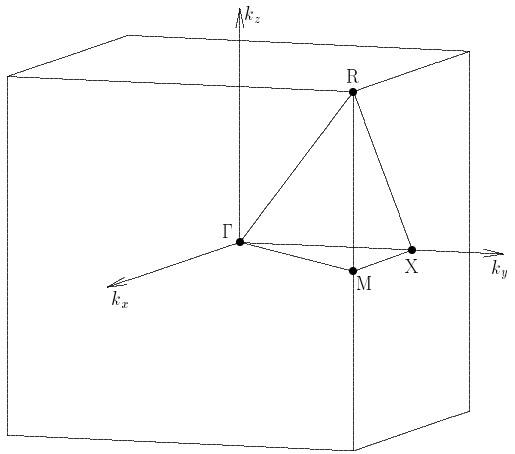
Pyrite

- $Pa\bar{3}$ (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

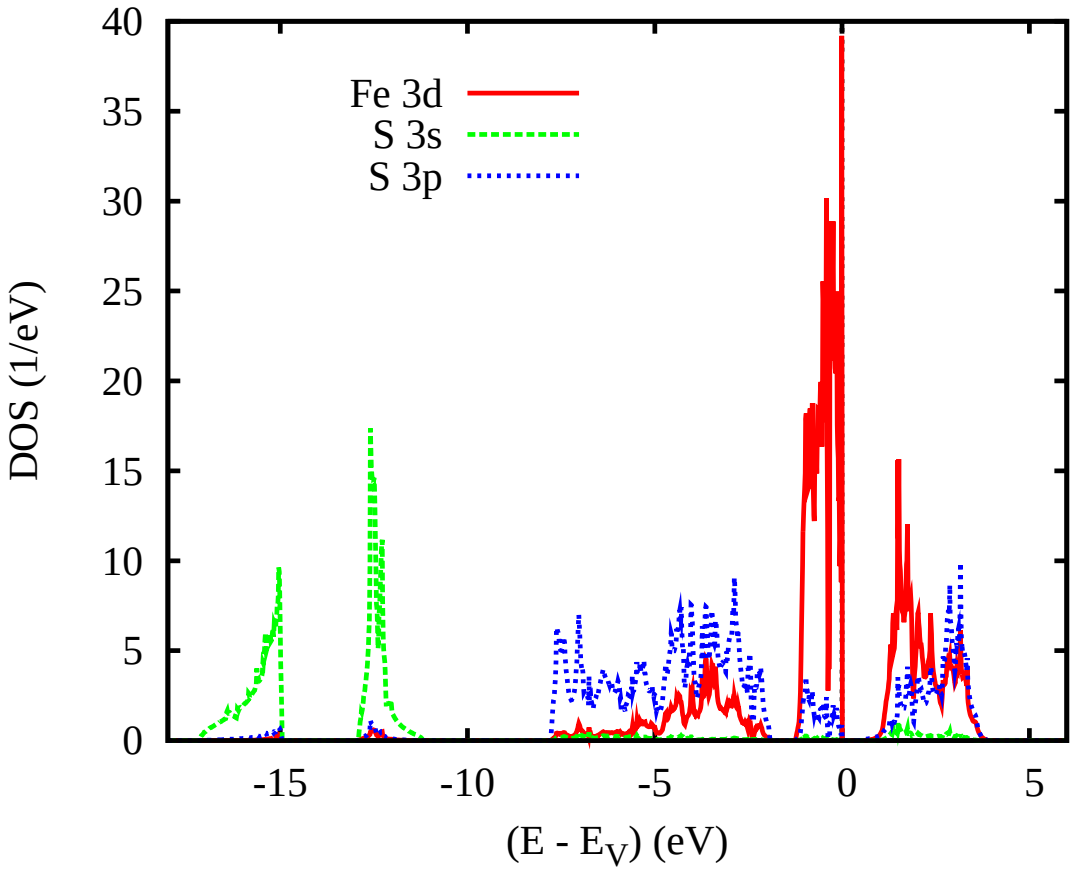
FeS_2: Band Structure





INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

FeS_2: Partial Densities of States

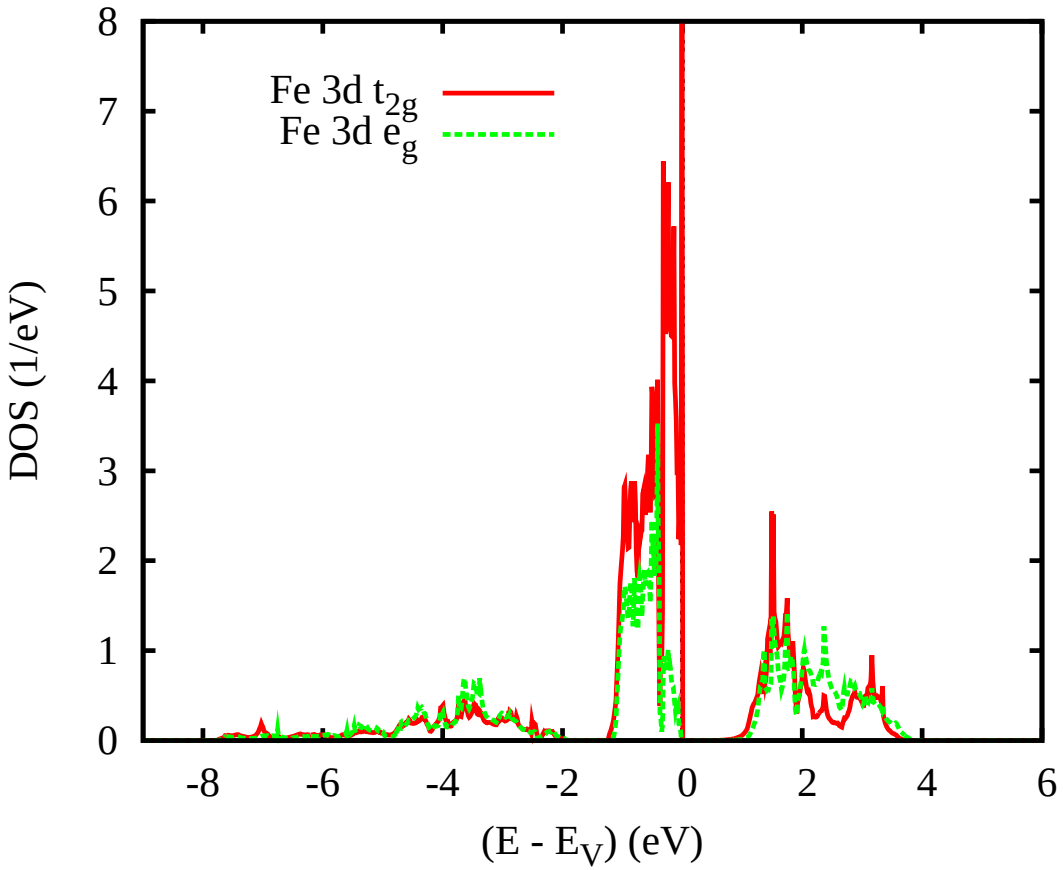


Relevant states

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

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

FeS_2: Partial Densities of States



Crystal field splitting

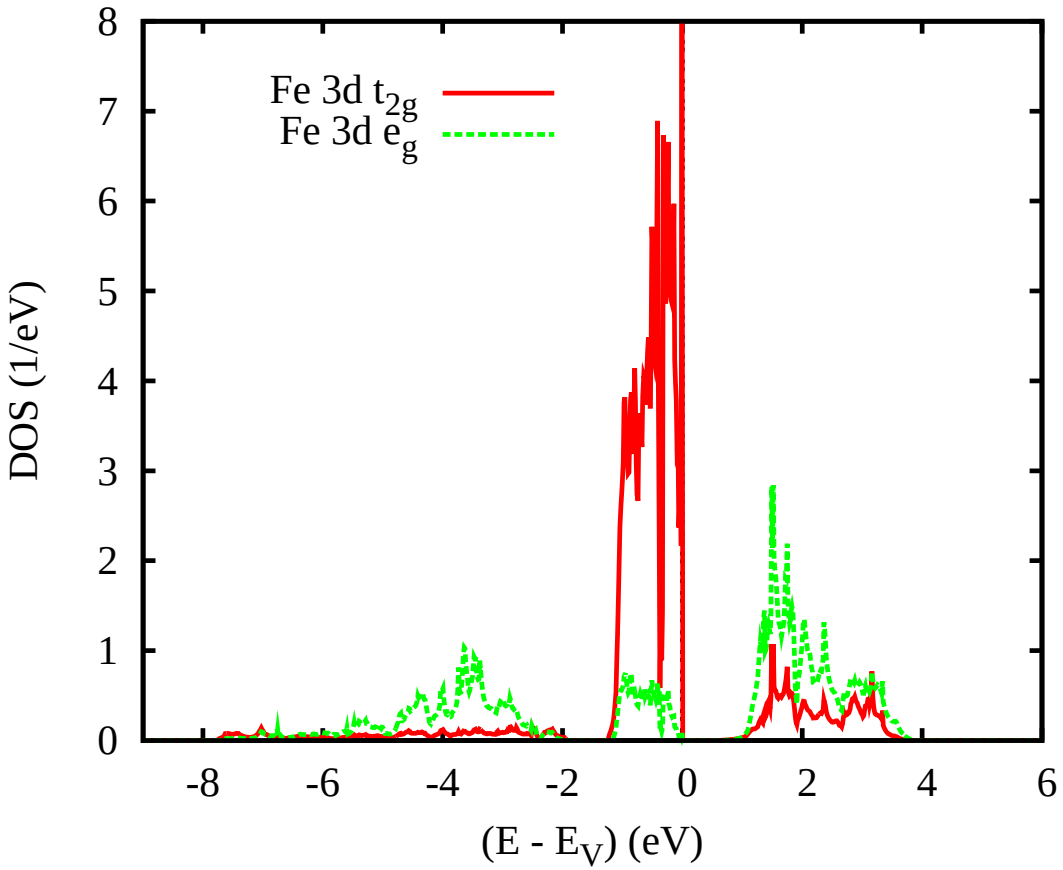
Fe 3*d* in octahedron: t_{2g} and e_g states

without rotation

with rotation
R(23)(1,1,0)
*R(17)(0,0,1)

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

FeS_2: Partial Densities of States



Crystal field splitting

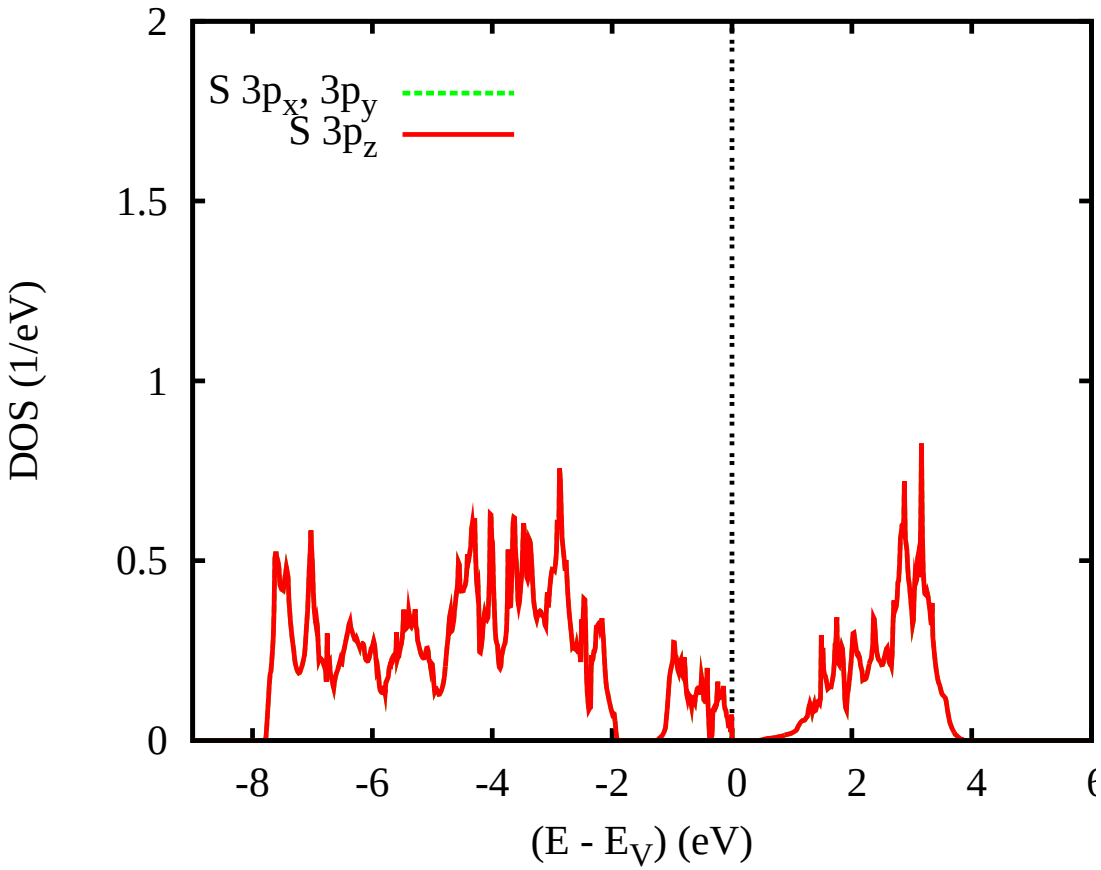
Fe 3*d* in octahedron:
t_{2g} and e_g states

without rotation

with rotation
R(23)(1,1,0)
*R(17)(0,0,1)

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

FeS_2: Partial Densities of States



Crystal field splitting

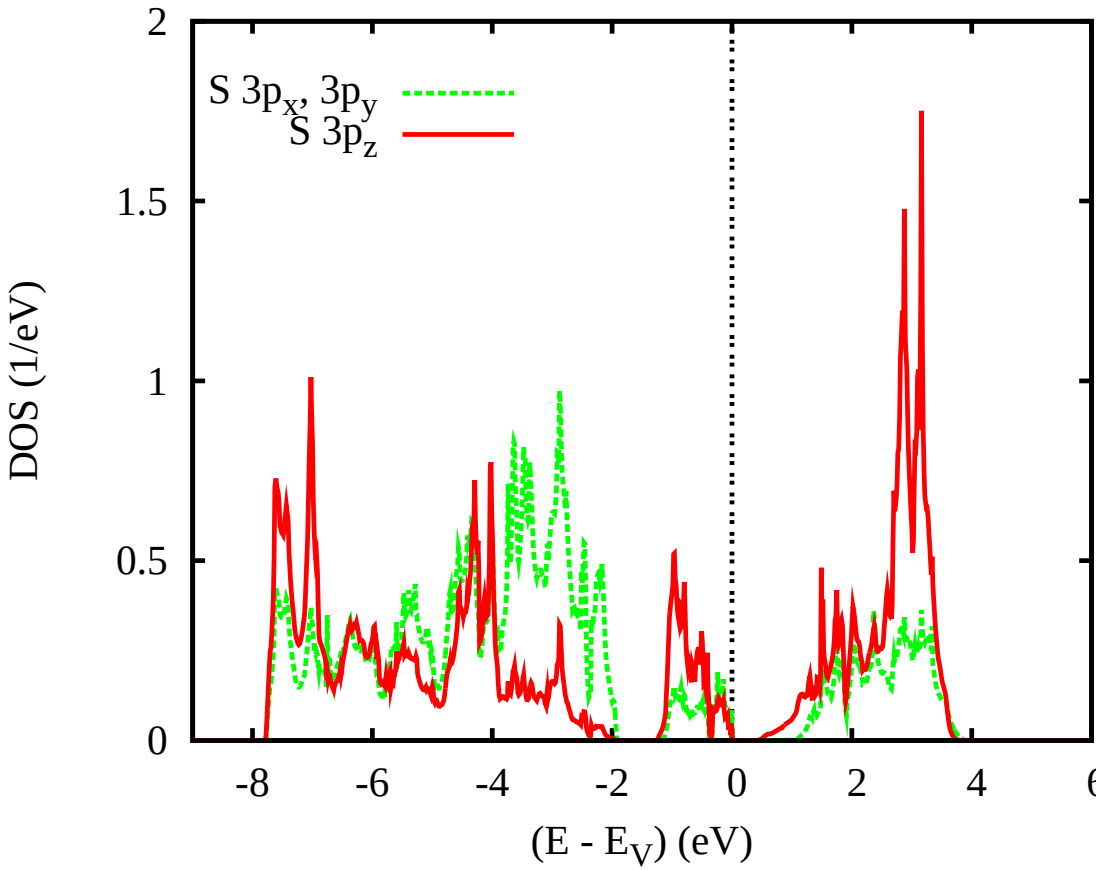
S 3*p*: p_x/p_y vs. p_z states

without rotation

with rotation
R8(-1,1,0)
≡ R(45)(-1,1,0)

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

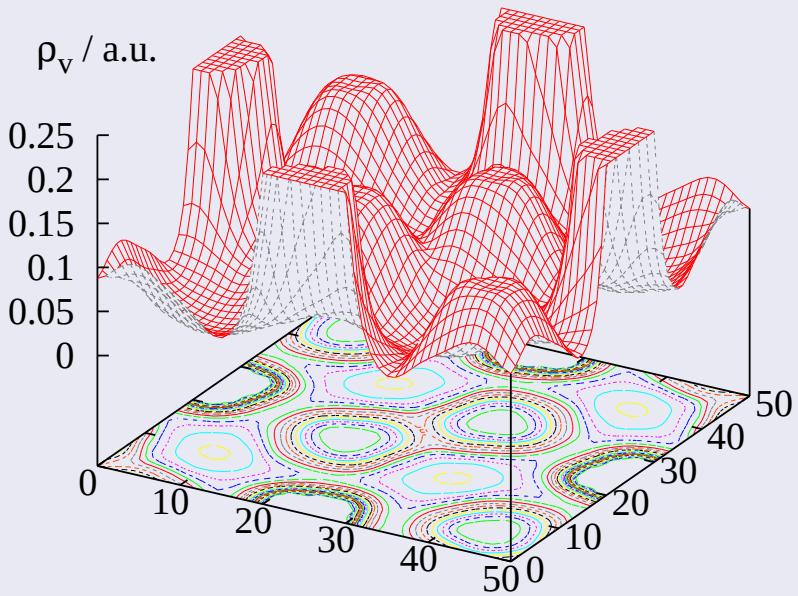
without rotation

with rotation
R8(-1,1,0)
$\equiv$ R(45)(-1,1,0)

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

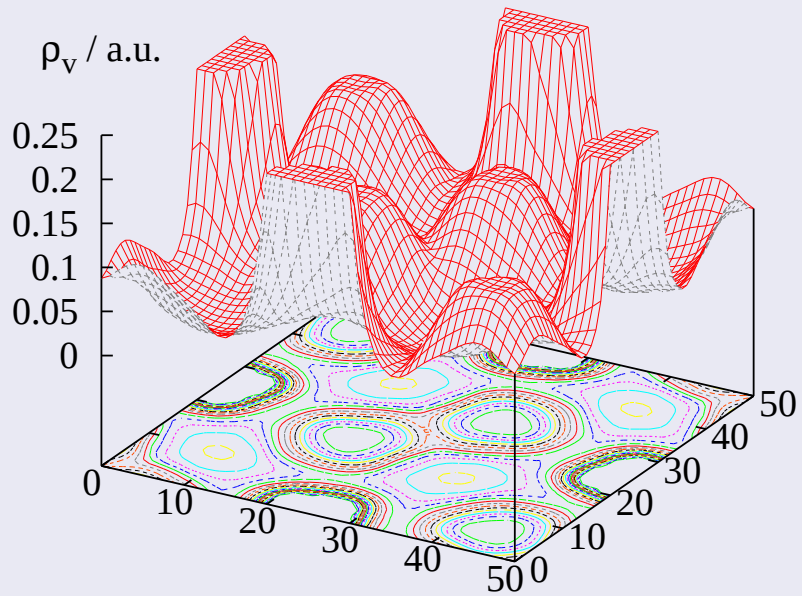
FeS_2: Density and Laplacian

Valence Electron Density

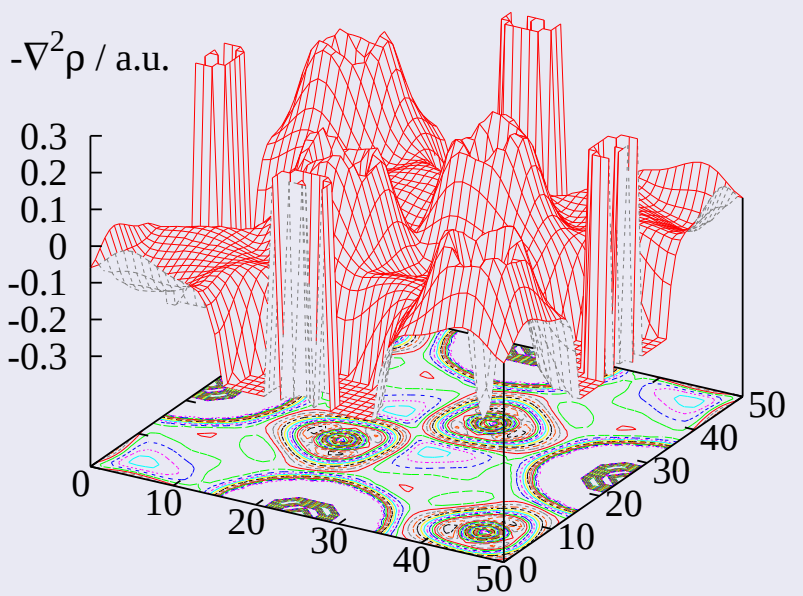


FeS_2: Density and Laplacian

Valence Electron Density

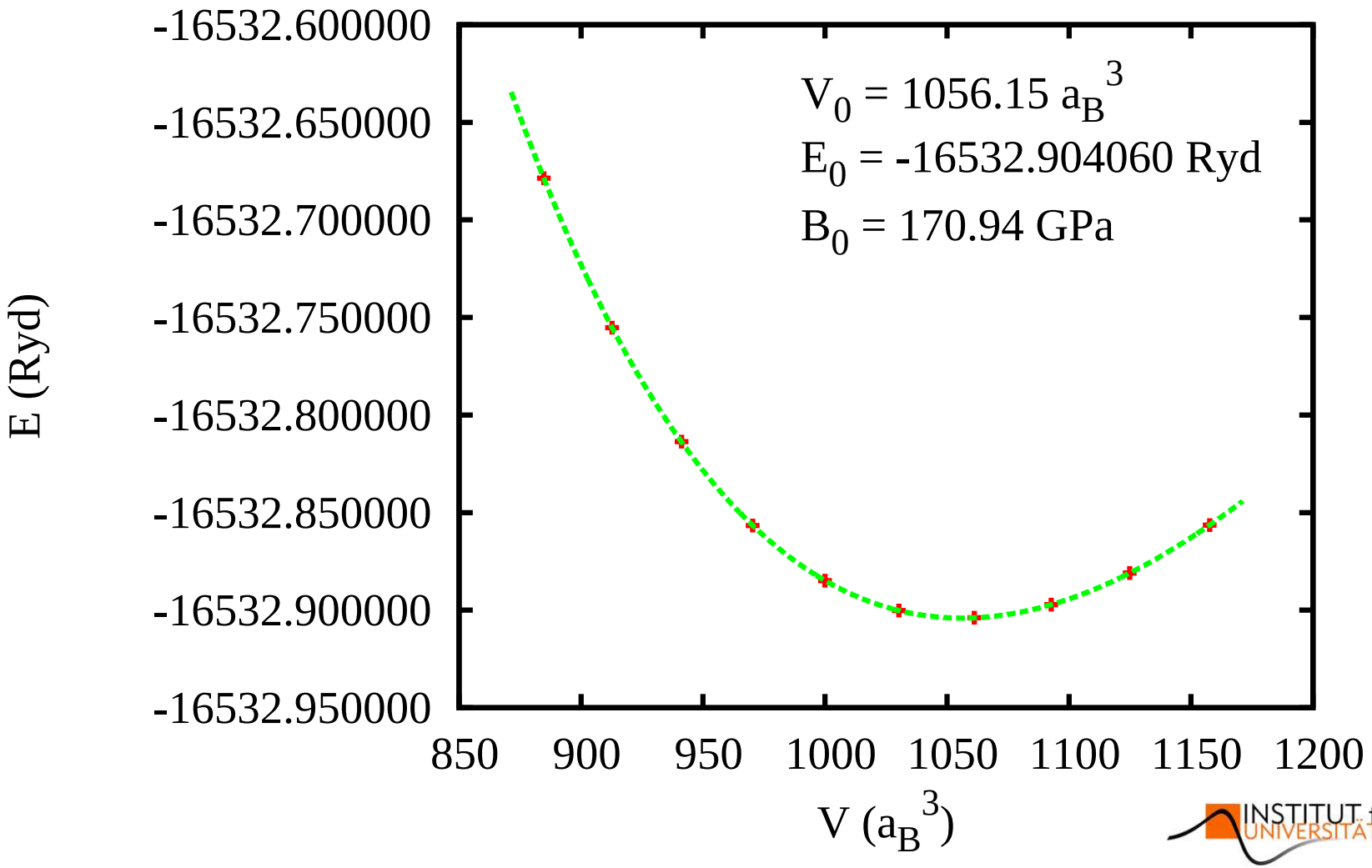


Laplacian of Electron Density



INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

FeS_2: Equilibrium Volume and Bulk Modulus



INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

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

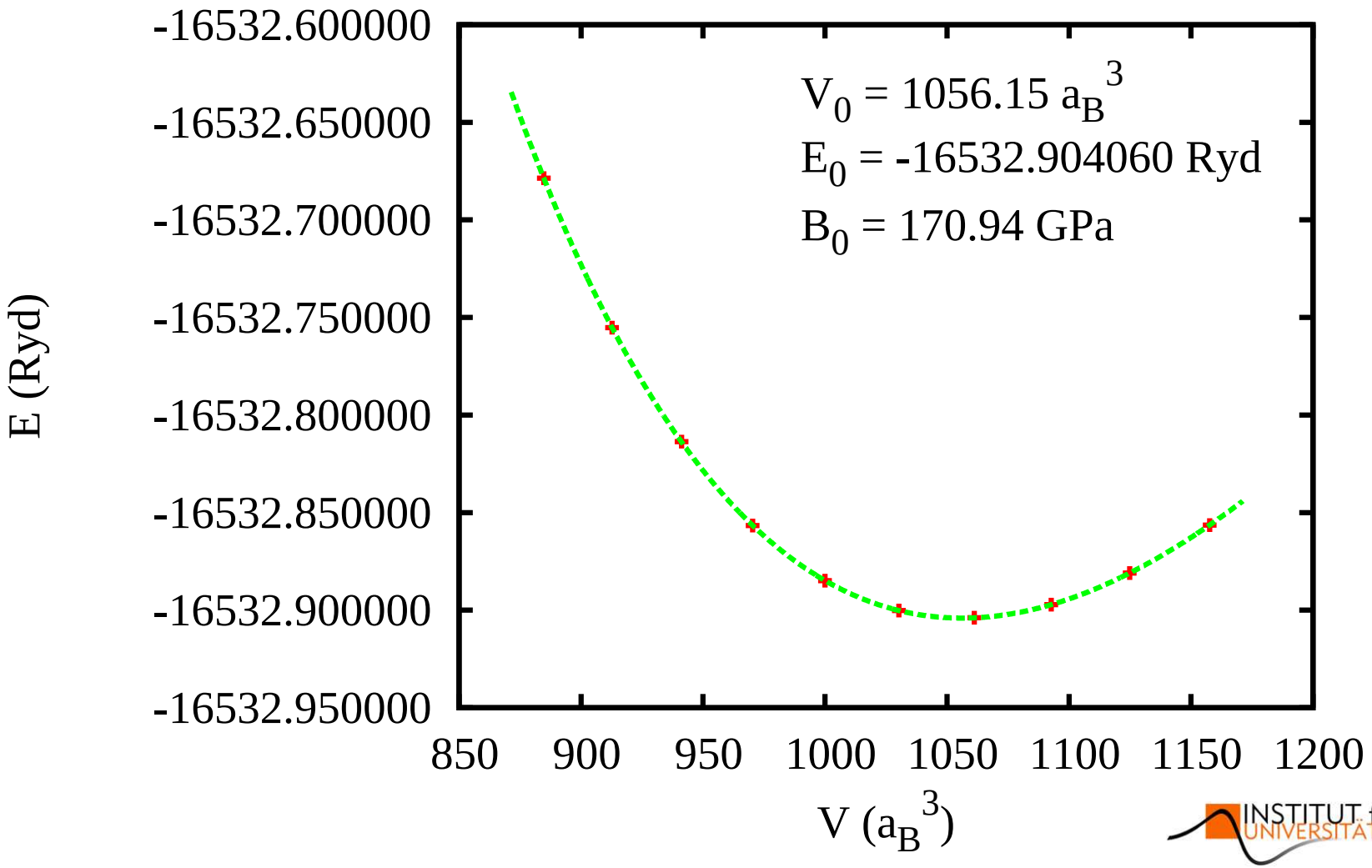
INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

FeS_2: Equilibrium Volume and Bulk Modulus

Bulk Modulus

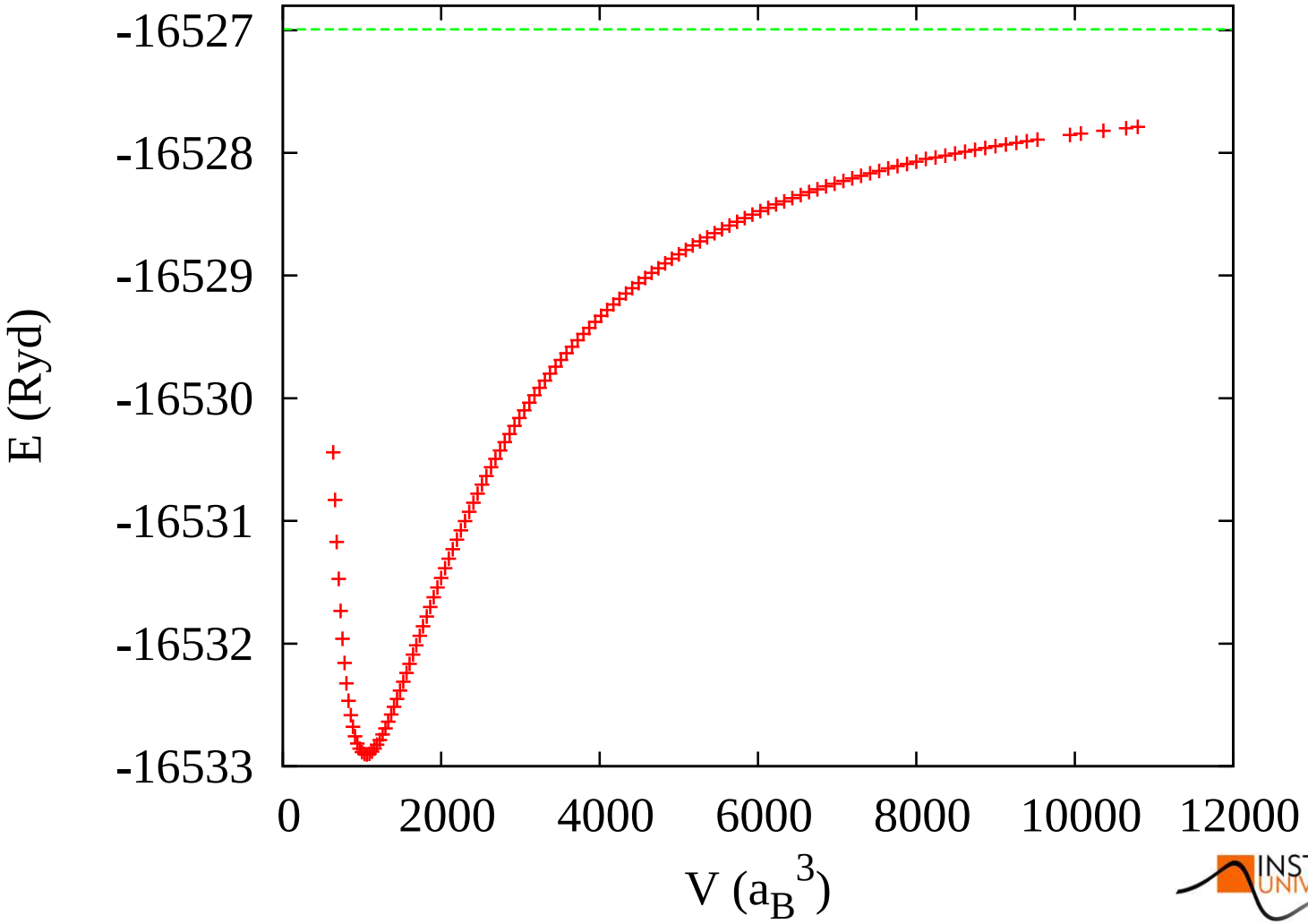
187	LMTO	Nguyen-Manh *et al.* ’98
185	FPLO	Opahle *et al.* ’99
209	CRYSTAL98	Muscat *et al.* ’02
208	CASTEP	Muscat *et al.* ’02
171	FPASW	present work
148	exp.	Drickamer *et al.* ’66
118	exp.	Will *et al.* ’84
215	exp.	Chattopadhyay and von Schnering ’85
157	exp.	Fujii *et al.* ’86
143	exp.	Jephcoat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

FeS_2: From Atoms to the Solid



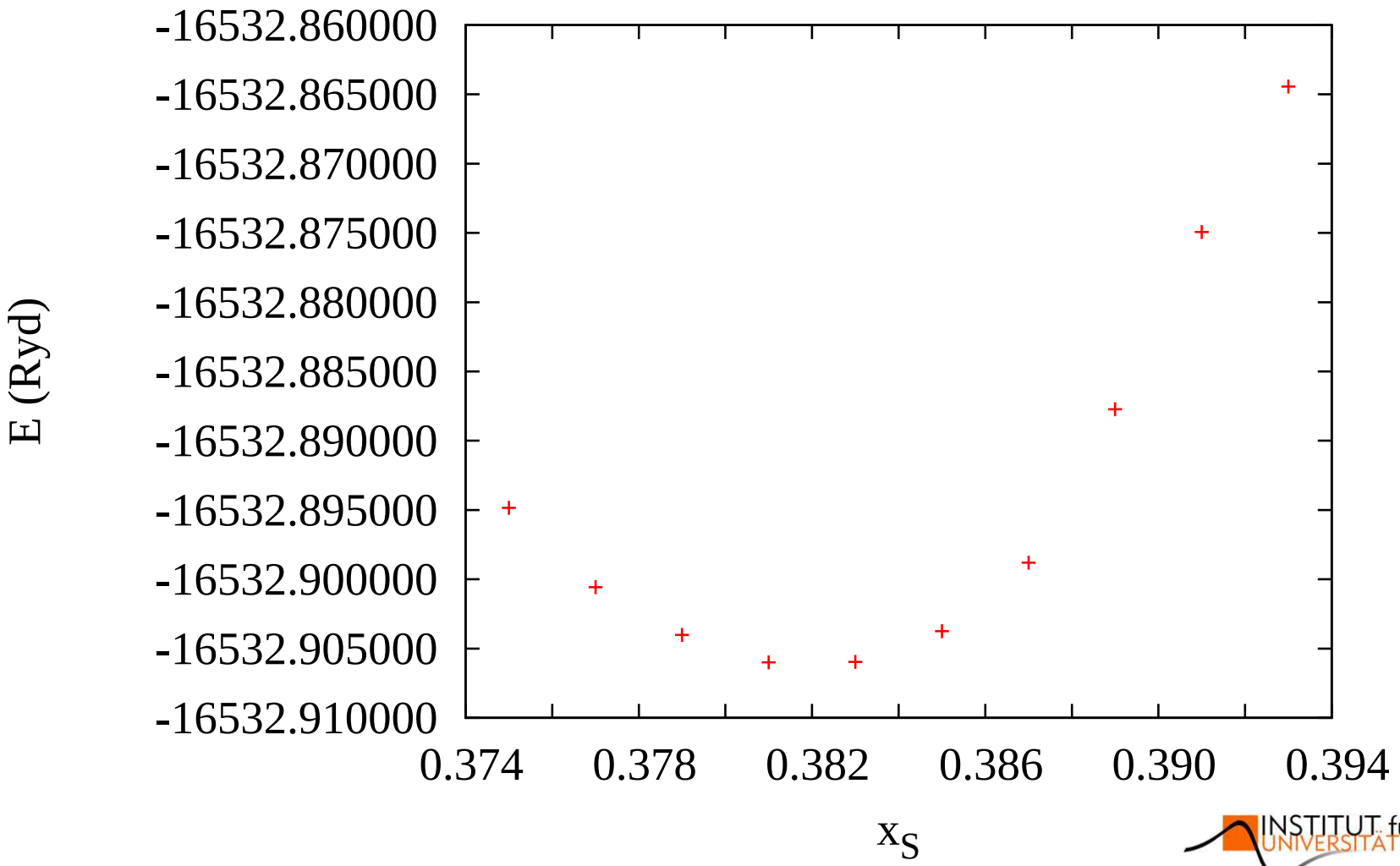
INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

FeS_2: From Atoms to the Solid



INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

FeS_2: Frozen Phonon Calculation



INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

FeS_2: Frozen Phonon Calculation

Sulfur Position

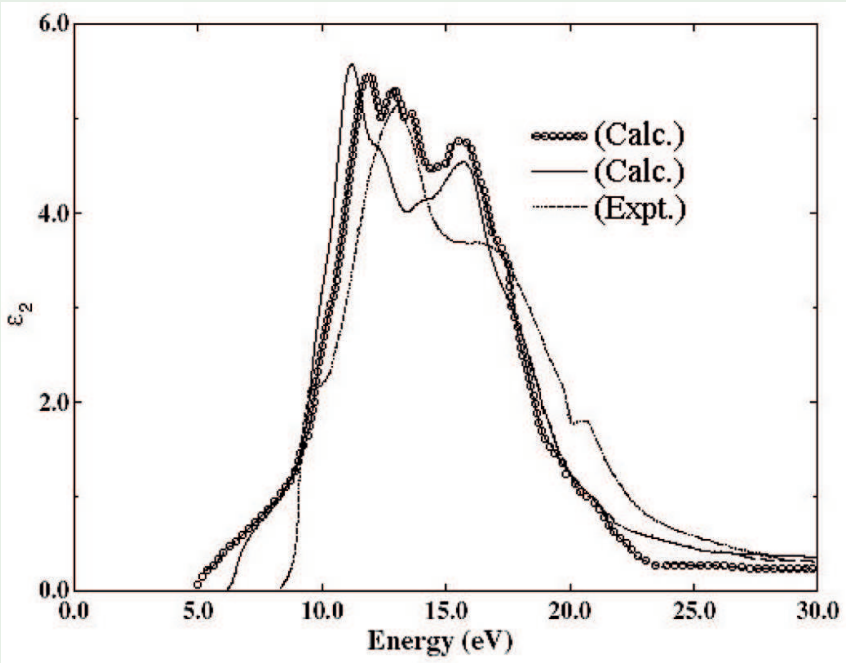
0.378	NCPP	Zeng and Holzwarth '94
0.377	FPLO	Opahle *et al.* '99
0.378	CRYSTAL98	Muscat *et al.* '02
0.382	CASTEP	Muscat *et al.* '02
0.382	FPASW	present work
0.386	exp.	Finklea *et al.* '76
0.386	exp.	Will *et al.* '84
0.385	exp.	Stevens *et al.* '91

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

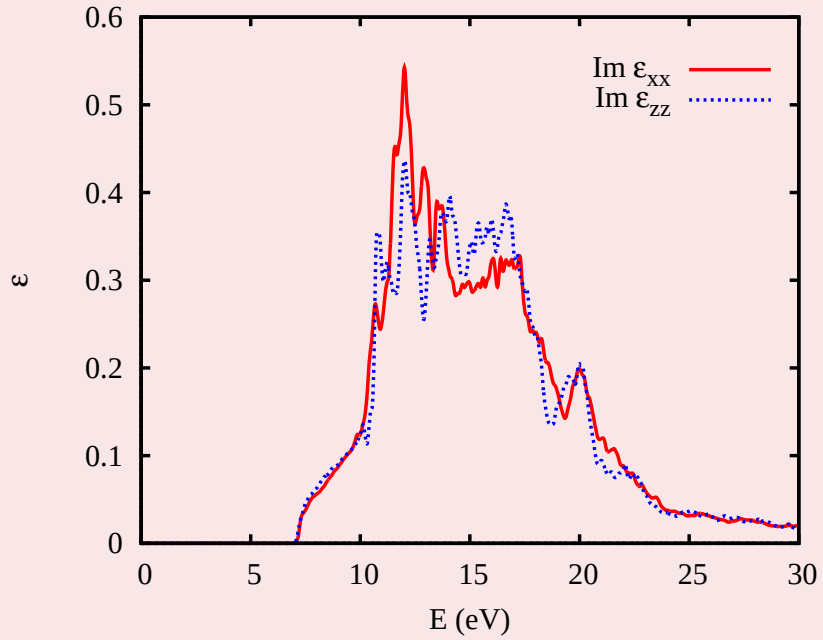
Dielectric Functions of Corundum

Imaginary Part

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



FPASW

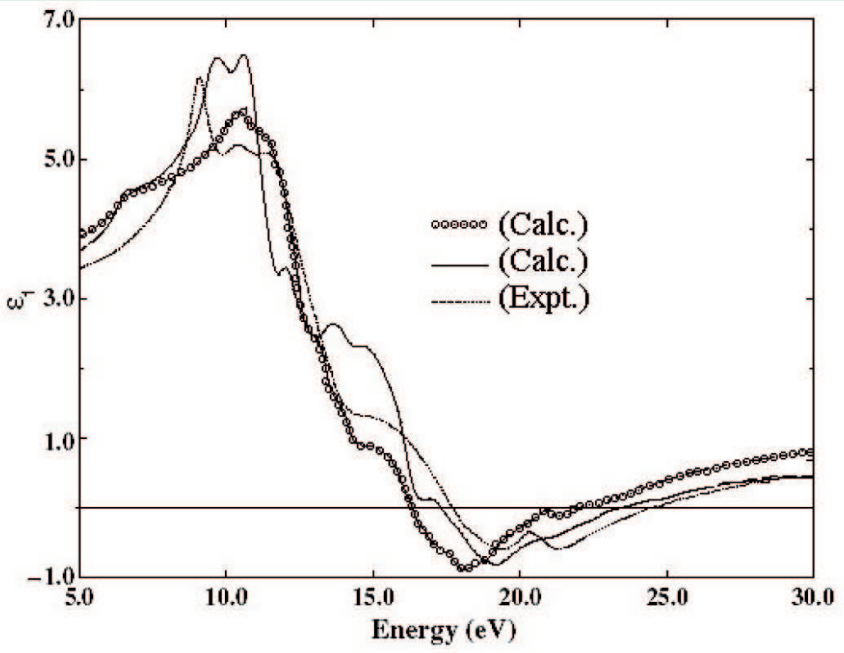


INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

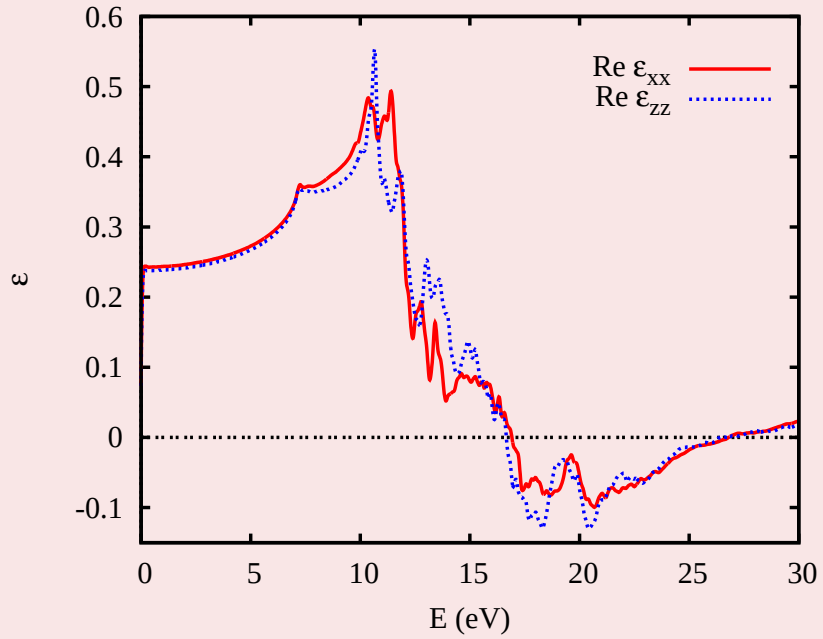
Dielectric Functions of Corundum

Real Part

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



FPASW



INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

Summary

Full-Potential ASW Method

- ASA Geometry used for Basis Functions
- MT Geometry used for Density and Potential
- $\mathcal{O}$(ASA) Speed
- Encouraging Results

Outlook

- Additional Tests
- Implementation of
  - ELF, ELI
  - Topological Analysis, AIM
- Exact Exchange Interaction (at $\mathcal{O}$(ASA) speed???)

Summary

Full-Potential ASW Method

- ASA Geometry used for Basis Functions
- MT Geometry used for Density and Potential
- $\mathcal{O}$(ASA) Speed
- Encouraging Results

Outlook

- Additional Tests
- Implementation of
  - ELF, ELI
  - Topological Analysis, AIM
- Exact Exchange Interaction (at $\mathcal{O}$(ASA) speed???)

Summary

Full-Potential ASW Method

- ASA Geometry used for Basis Functions
- MT Geometry used for Density and Potential
- $\mathcal{O}$(ASA) Speed
- Encouraging Results

Outlook

- Additional Tests
- Implementation of
  - ELF, ELI
  - Topological Analysis, AIM
- Exact Exchange Interaction (at $\mathcal{O}$(ASA) speed???)

Summary

Full-Potential ASW Method

- ASA Geometry used for Basis Functions
- MT Geometry used for Density and Potential
- $\mathcal{O}$(ASA) Speed
- Encouraging Results

Outlook

- Additional Tests
- Implementation of
  - ELF, ELI
  - Topological Analysis, AIM
- Exact Exchange Interaction (at $\mathcal{O}$(ASA) speed???)

Summary

Full-Potential ASW Method

- ASA Geometry used for Basis Functions
- MT Geometry used for Density and Potential
- $\mathcal{O}$(ASA) Speed
- Encouraging Results

Outlook

- Additional Tests
- Implementation of
  - ELF, ELI
  - Topological Analysis, AIM
- Exact Exchange Interaction (at $\mathcal{O}$(ASA) speed???)

Summary

Full-Potential ASW Method

- ASA Geometry used for Basis Functions
- MT Geometry used for Density and Potential
- $\mathcal{O}$(ASA) Speed
- Encouraging Results

Outlook

- Additional Tests
- Implementation of
  - ELF, ELI
  - Topological Analysis, AIM
- Exact Exchange Interaction (at $\mathcal{O}$(ASA) speed???)

Summary

Full-Potential ASW Method

- ASA Geometry used for Basis Functions
- MT Geometry used for Density and Potential
- $\mathcal{O}$(ASA) Speed
- Encouraging Results

Outlook

- Additional Tests
- Implementation of
  - ELF, ELI
  - Topological Analysis, AIM
- Exact Exchange Interaction (at $\mathcal{O}$(ASA) speed???)

Summary

Full-Potential ASW Method

- ASA Geometry used for Basis Functions
- MT Geometry used for Density and Potential
- $\mathcal{O}$(ASA) Speed
- Encouraging Results

Outlook

- Additional Tests
- Implementation of
  - ELF, ELI
  - Topological Analysis, AIM
- Exact Exchange Interaction (at $\mathcal{O}$(ASA) speed???)

Summary

Full-Potential ASW Method

- ASA Geometry used for Basis Functions
- MT Geometry used for Density and Potential
- $\mathcal{O}$(ASA) Speed
- Encouraging Results

Outlook

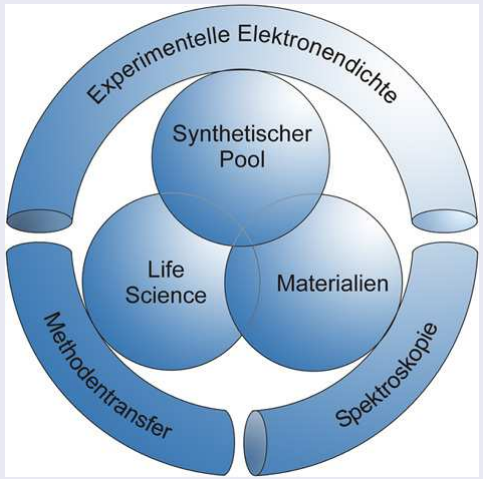
- Additional Tests
- Implementation of
  - ELF, ELI
  - Topological Analysis, AIM
- Exact Exchange Interaction (at $\mathcal{O}$(ASA) speed???)

Acknowlegments

SFB 484

Stuttgart
O. Andersen

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



Darmstadt
J. Sticht †

Darmstadt
P. C. Schmidt, M. Stephan

Paris
E. Wimmer

Vienna
W. Wolf

Stockholm
A. Mavromaras

IK RG

Acknowlegments

Oran

Thank You for Your Attention!