Computational Materials Science

Introduction

Volker Eyert

Institut für Physik, Universität Augsburg

Electronic Structure in a Nutshell

Organization of the Course

	Mon	Tue	Wed	Thu
General	Comp. Mat. Science	DFT Basics	DFT Basics	LDA Introduct.
ASW Method	Introduction History Background	Standard ASW	Full. Pot. ASW	Miscell.
ASW Program	Installation Cu, Be	Distribution Data Files FeS_2	CTRL File CrO_2	Miscell.

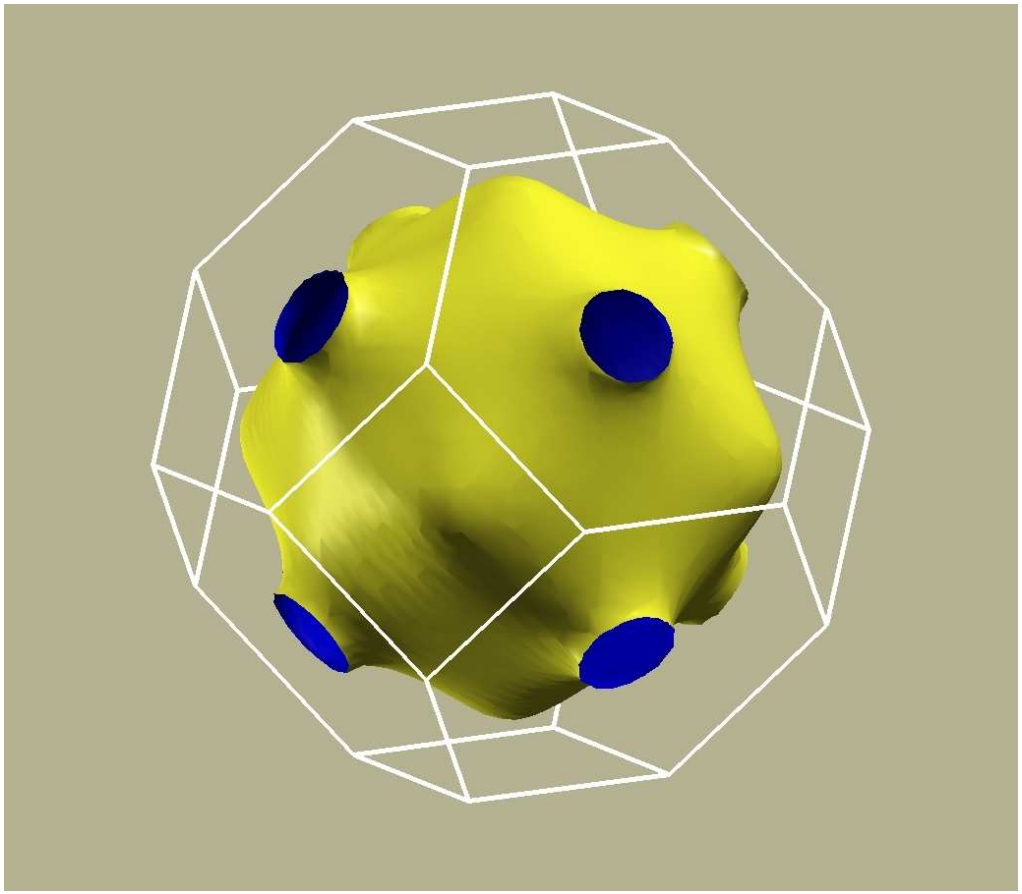
Outline

Outline

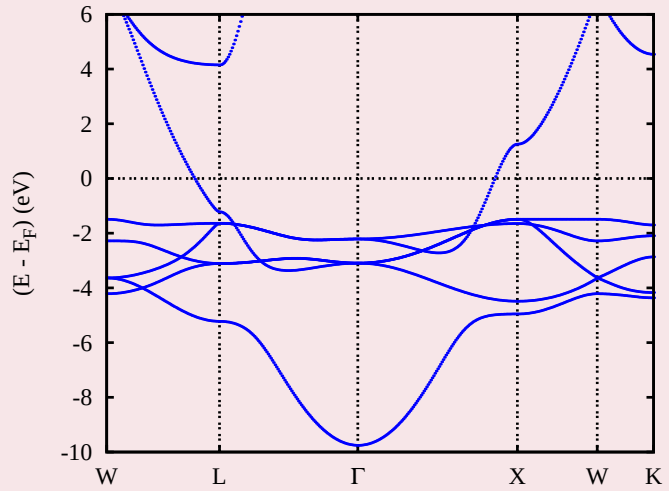
Outline

Outline

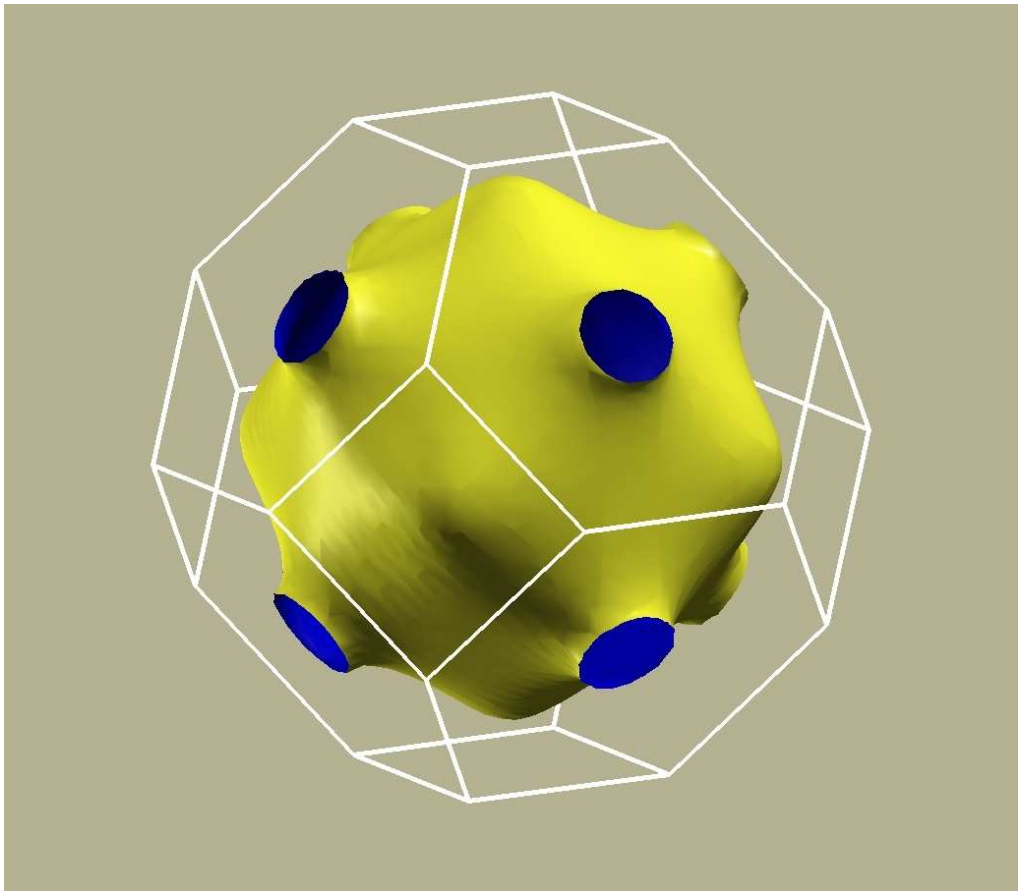
What Are We Aiming At?



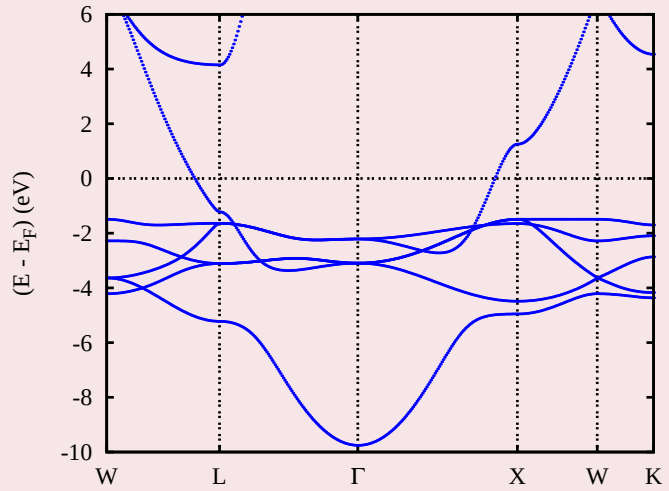
- Interpretation of Experiments,
- Understanding, and
- Prediction of Materials Properties



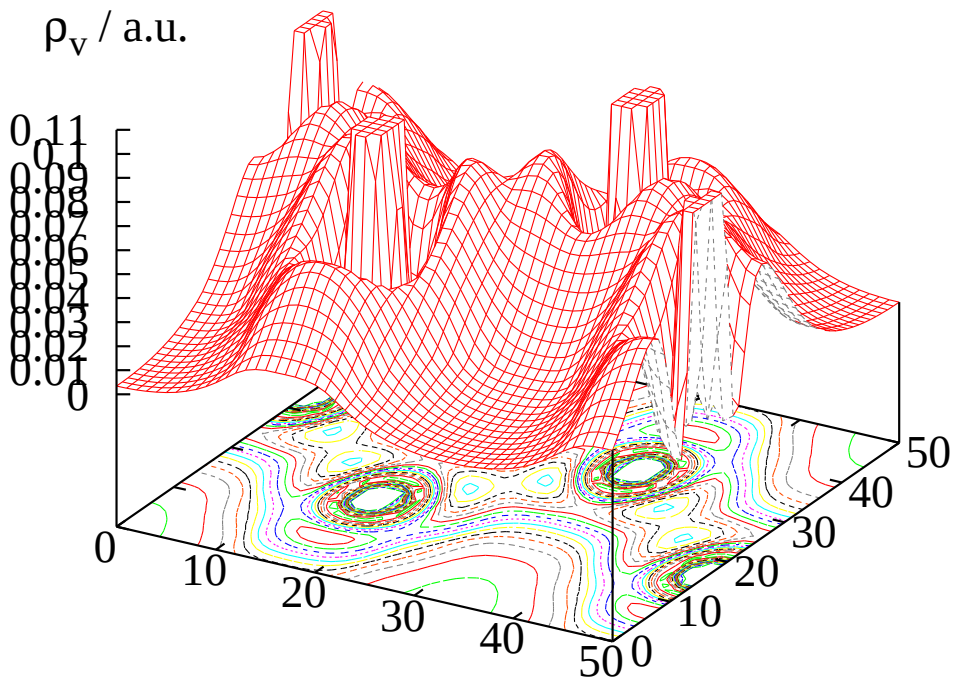
What Are We Aiming At?



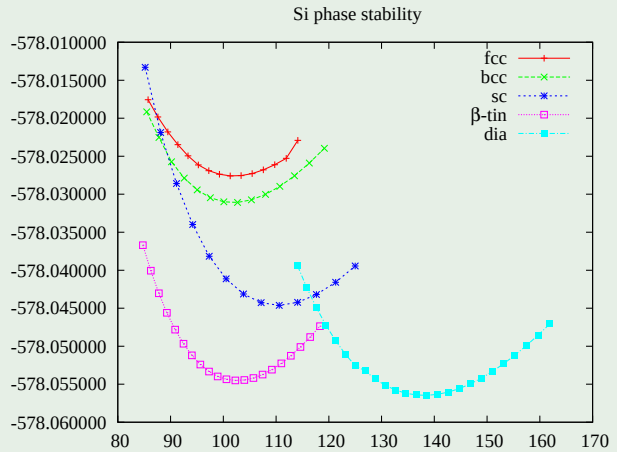
- Interpretation of Experiments,
- Understanding, and
- Prediction of Materials Properties



What Are We Aiming At?



- Interpretation of Experiments,
- Understanding, and
- Prediction of Materials Properties



Outline

Structural and Mechanical Properties

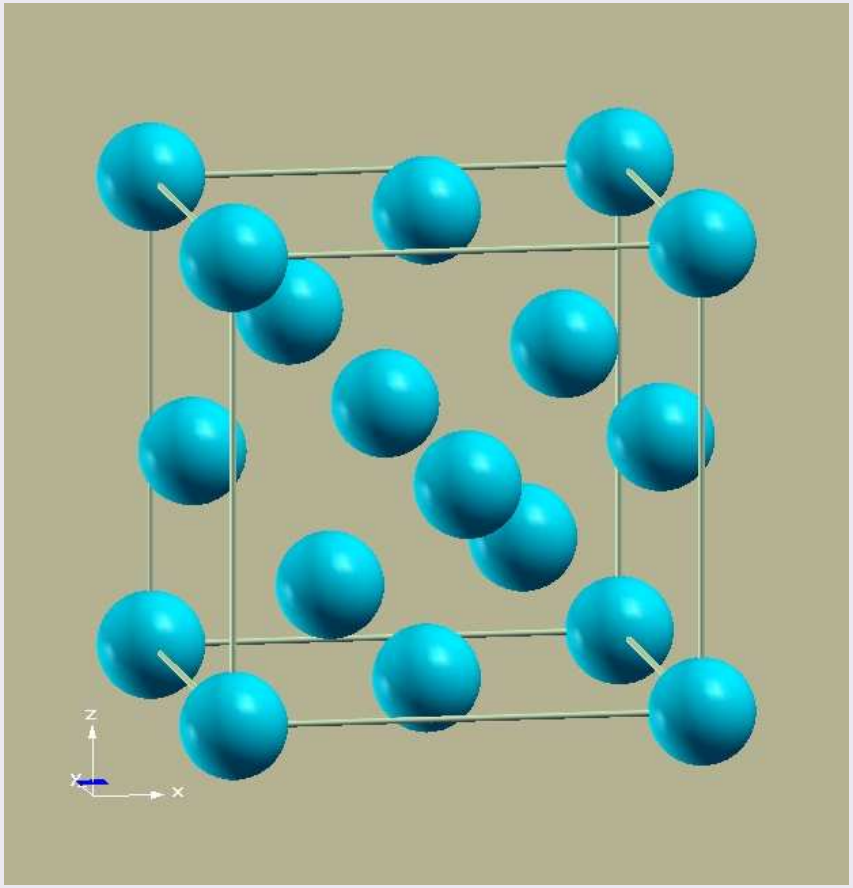
Structural

- geometries of molecules
- crystal structures
- electron densities
- defect structures
- interface structures
- surface structures
- adsorption

Structural and Mechanical Properties

Structural

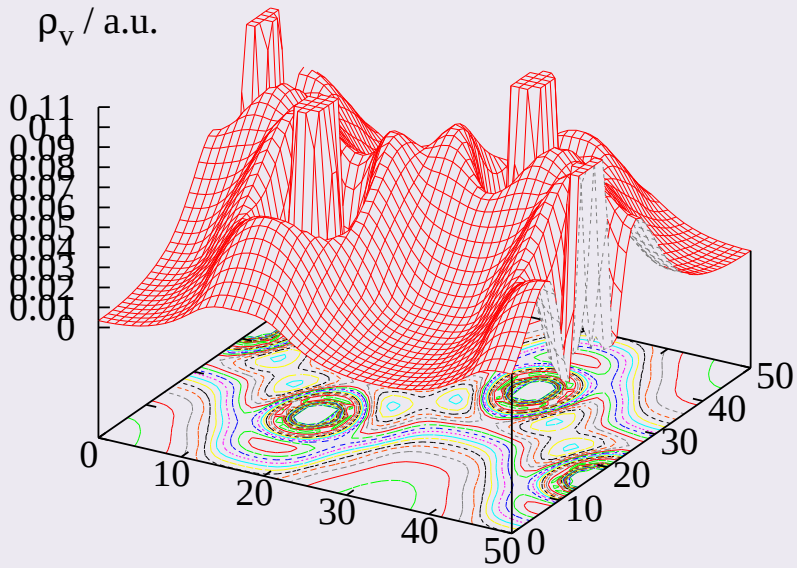
- geometries of molecules
- crystal structures
- electron densities
- defect structures
- interface structures
- surface structures
- adsorption



Structural and Mechanical Properties

Structural

- geometries of molecules
- crystal structures
- electron densities
- defect structures
- interface structures
- surface structures
- adsorption



INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

Structural and Mechanical Properties

Structural

- geometries of molecules
- crystal structures
- electron densities
- defect structures
- interface structures
- surface structures
- adsorption

Structural and Mechanical Properties

Structural

- geometries of molecules
- crystal structures
- electron densities
- defect structures
- interface structures
- surface structures
- adsorption

Structural and Mechanical Properties

Structural

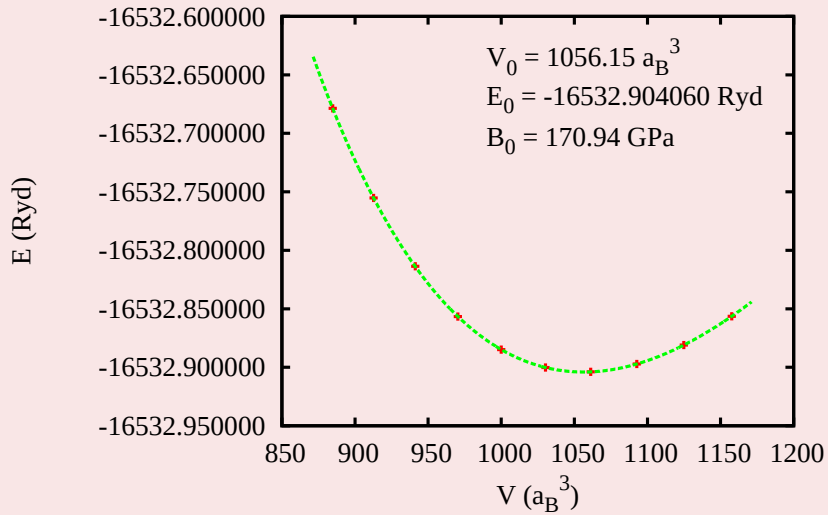
- geometries of molecules
- crystal structures
- electron densities
- defect structures
- interface structures
- surface structures
- adsorption

Structural and Mechanical Properties

Structural

- geometries of molecules
- crystal structures
- electron densities
- defect structures
- interface structures
- surface structures
- adsorption

Structural and Mechanical Properties



Mechanical

- compressibility
- elastic moduli
- thermal expansion
- vibrational properties
- hardness

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

Structural and Mechanical Properties

Mechanical

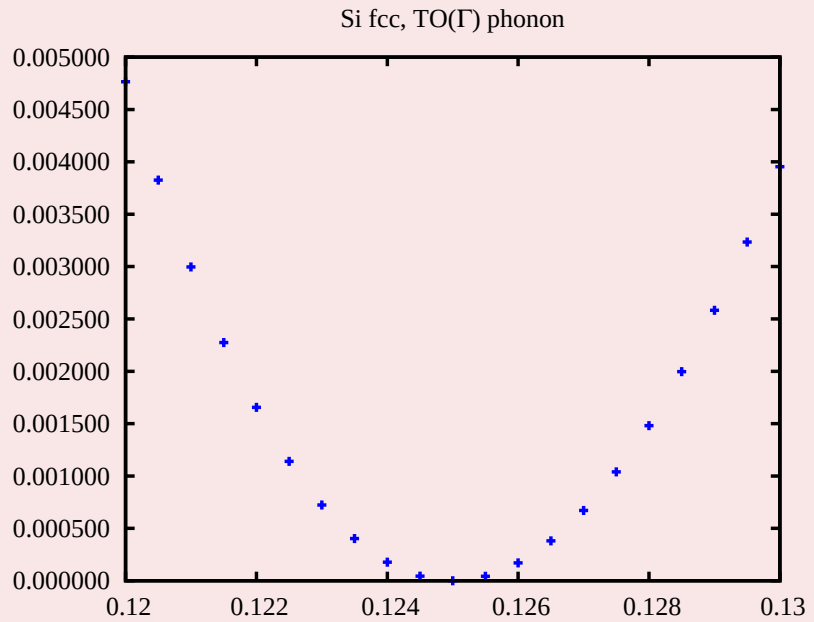
- compressibility
- elastic moduli
- thermal expansion
- vibrational properties
- hardness

Structural and Mechanical Properties

Mechanical

- compressibility
- elastic moduli
- thermal expansion
- vibrational properties
- hardness

Structural and Mechanical Properties



Mechanical

- compressibility
- elastic moduli
- thermal expansion
- vibrational properties
- hardness

Structural and Mechanical Properties

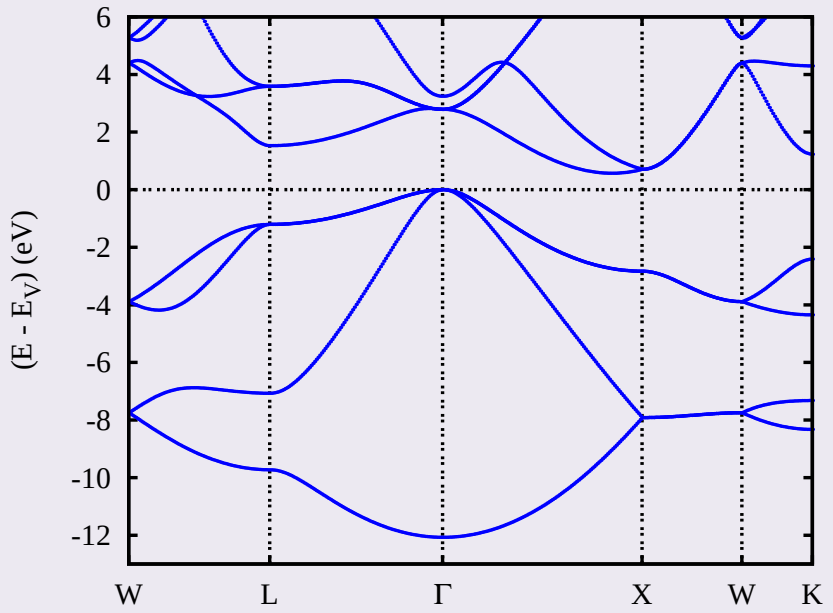
Mechanical

- compressibility
- elastic moduli
- thermal expansion
- vibrational properties
- hardness

Electronic, Optical and Magnetic Properties

Electronic

- band structure
  - metal
  - semiconductor
  - insulator
- band gap
- band offsets
- density distributions
- polarizabilities
- ionization energies
- electron affinities
- electrostatic potential



INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

Electronic, Optical and Magnetic Properties

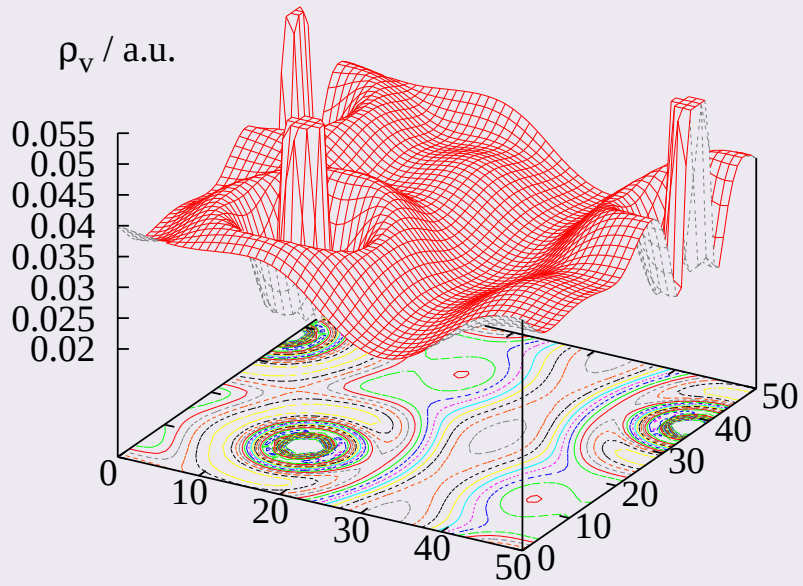
Electronic

- band structure
- band gap
- band offsets
- density distributions
- polarizabilities
- ionization energies
- electron affinities
- electrostatic potential
- work functions

Electronic, Optical and Magnetic Properties

Electronic

- band structure
- band gap
- band offsets
- density distributions
  - electrical moments
  - electric field gradients
- polarizabilities
- ionization energies
- electron affinities
- electrostatic potential
- work functions



INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

Electronic, Optical and Magnetic Properties

Electronic

- band structure
- band gap
- band offsets
- density distributions
- polarizabilities
- ionization energies
- electron affinities
- electrostatic potential
- work functions

Electronic, Optical and Magnetic Properties

Electronic

- band structure
- band gap
- band offsets
- density distributions
- polarizabilities
- ionization energies
- electron affinities
- electrostatic potential
- work functions

Electronic, Optical and Magnetic Properties

Electronic

- band structure
- band gap
- band offsets
- density distributions
- polarizabilities
- ionization energies
- electron affinities
- electrostatic potential
- work functions

Electronic, Optical and Magnetic Properties

Electronic

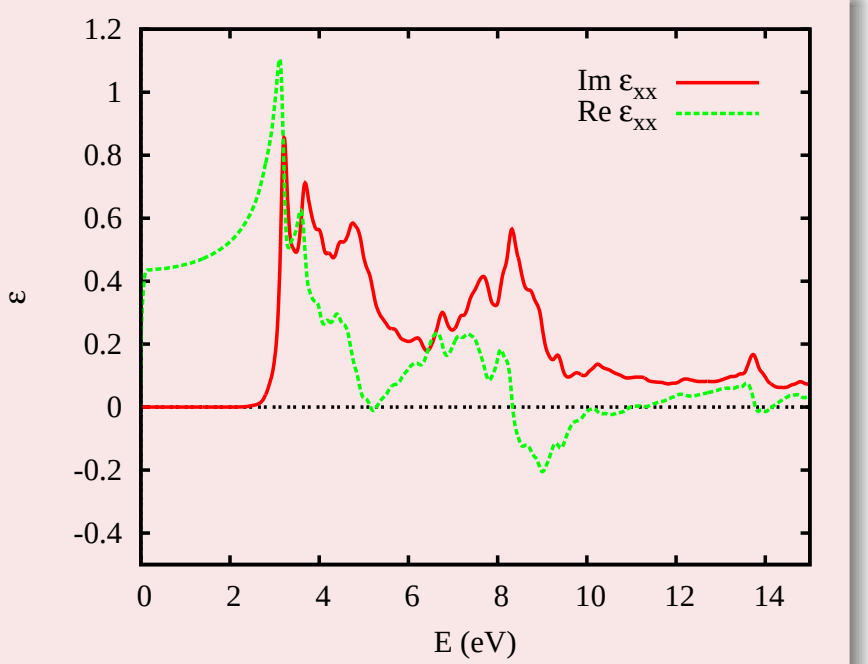
- band structure
- band gap
- band offsets
- density distributions
- polarizabilities
- ionization energies
- electron affinities
- electrostatic potential
- work functions

Electronic, Optical and Magnetic Properties

Electronic

- band structure
- band gap
- band offsets
- density distributions
- polarizabilities
- ionization energies
- electron affinities
- electrostatic potential
- work functions

Electronic, Optical and Magnetic Properties



Optical

- optical spectra
- magneto-optical properties
- dielectric response
- luminescence
- fluorescence

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

Electronic, Optical and Magnetic Properties

Optical

- optical spectra
- magneto-optical properties
- dielectric response
- luminescence
- fluorescence

Electronic, Optical and Magnetic Properties

Optical

- optical spectra
- magneto-optical properties
- dielectric response
- luminescence
- fluorescence

Electronic, Optical and Magnetic Properties

Optical

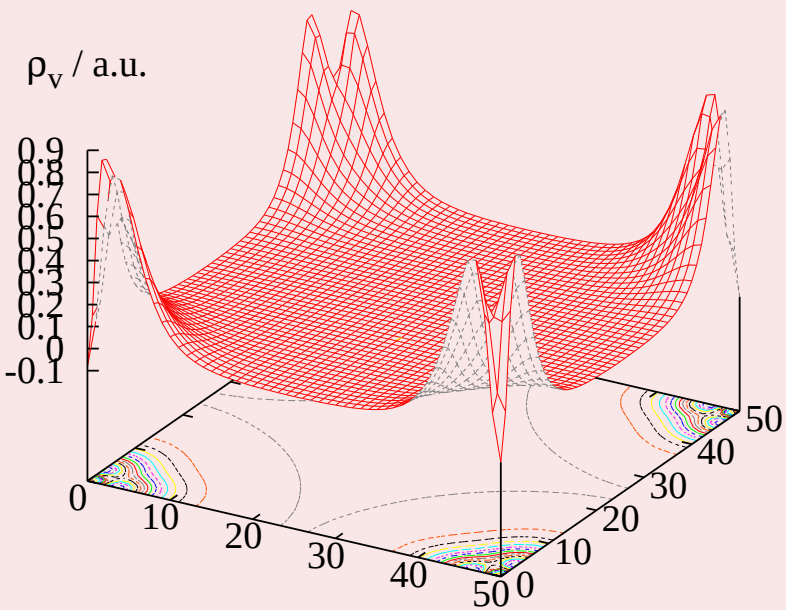
- optical spectra
- magneto-optical properties
- dielectric response
- luminescence
- fluorescence

Electronic, Optical and Magnetic Properties

Optical

- optical spectra
- magneto-optical properties
- dielectric response
- luminescence
- fluorescence

Electronic, Optical and Magnetic Properties



Magnetic

- spin-density distribution
- magnetic moments
- NMR chemical shifts

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

Electronic, Optical and Magnetic Properties

Magnetic

- spin-density distribution
- magnetic moments
- NMR chemical shifts

Electronic, Optical and Magnetic Properties

Magnetic

- spin-density distribution
- magnetic moments
- NMR chemical shifts

Transport, Chemical, and Thermodynamic Properties

Transport

- electrical conductivity
- thermal conductivity
- diffusion constants
- permeability

Thermodynamic

- binding energies
- phase transitions
- phase diagrams

Chemical

- catalytic properties
- corrosion
- surface reactivity
- photochemical properties

Transport, Chemical, and Thermodynamic Properties

Transport

- electrical conductivity
- thermal conductivity
- diffusion constants
- permeability

Thermodynamic

- binding energies
- phase transitions
- phase diagrams

Chemical

- catalytic properties
- corrosion
- surface reactivity
- photochemical properties

Transport, Chemical, and Thermodynamic Properties

Transport

- electrical conductivity
- thermal conductivity
- diffusion constants
- permeability

Thermodynamic

- binding energies
- phase transitions
- phase diagrams

Chemical

- catalytic properties
- corrosion
- surface reactivity
- photochemical properties

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

Transport, Chemical, and Thermodynamic Properties

Transport

- electrical conductivity
- thermal conductivity
- diffusion constants
- permeability

Thermodynamic

- binding energies
- phase transitions
- phase diagrams

Chemical

- catalytic properties
- corrosion
- surface reactivity
- photochemical properties

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

Transport, Chemical, and Thermodynamic Properties

Transport

- electrical conductivity
- thermal conductivity
- diffusion constants
- permeability

Chemical

- catalytic properties
- corrosion
- surface reactivity
- photochemical properties

Thermodynamic

- binding energies
- phase transitions
- phase diagrams

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

Transport, Chemical, and Thermodynamic Properties

Transport

- electrical conductivity
- thermal conductivity
- diffusion constants
- permeability

Chemical

- catalytic properties
- corrosion
- surface reactivity
- photochemical properties

Thermodynamic

- binding energies
- phase transitions
- phase diagrams

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

Transport, Chemical, and Thermodynamic Properties

Transport

- electrical conductivity
- thermal conductivity
- diffusion constants
- permeability

Chemical

- catalytic properties
- corrosion
- surface reactivity
- photochemical properties

Thermodynamic

- binding energies
- phase transitions
- phase diagrams

Transport, Chemical, and Thermodynamic Properties

Transport

- electrical conductivity
- thermal conductivity
- diffusion constants
- permeability

Chemical

- catalytic properties
- corrosion
- surface reactivity
- photochemical properties

Thermodynamic

- binding energies
- phase transitions
- phase diagrams

Transport, Chemical, and Thermodynamic Properties

Transport

- electrical conductivity
- thermal conductivity
- diffusion constants
- permeability

Chemical

- catalytic properties
- corrosion
- surface reactivity
- photochemical properties

Thermodynamic

- binding energies
- phase transitions
- phase diagrams

Transport, Chemical, and Thermodynamic Properties

Transport

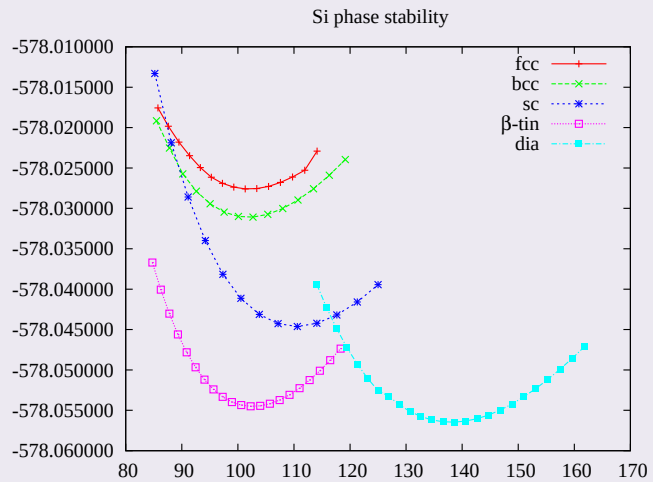
- electrical conductivity
- thermal conductivity
- diffusion constants
- permeability

Chemical

- catalytic properties
- corrosion
- surface reactivity
- photochemical properties

Thermodynamic

- binding energies
- phase transitions
- phase diagrams



Transport, Chemical, and Thermodynamic Properties

Transport

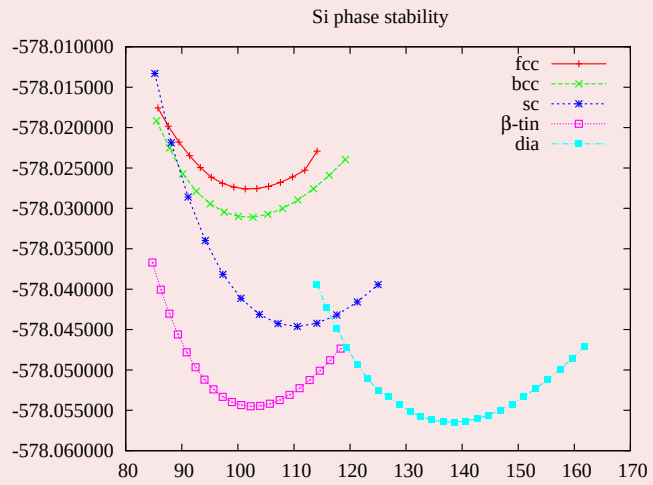
- electrical conductivity
- thermal conductivity
- diffusion constants
- permeability

Chemical

- catalytic properties
- corrosion
- surface reactivity
- photochemical properties

Thermodynamic

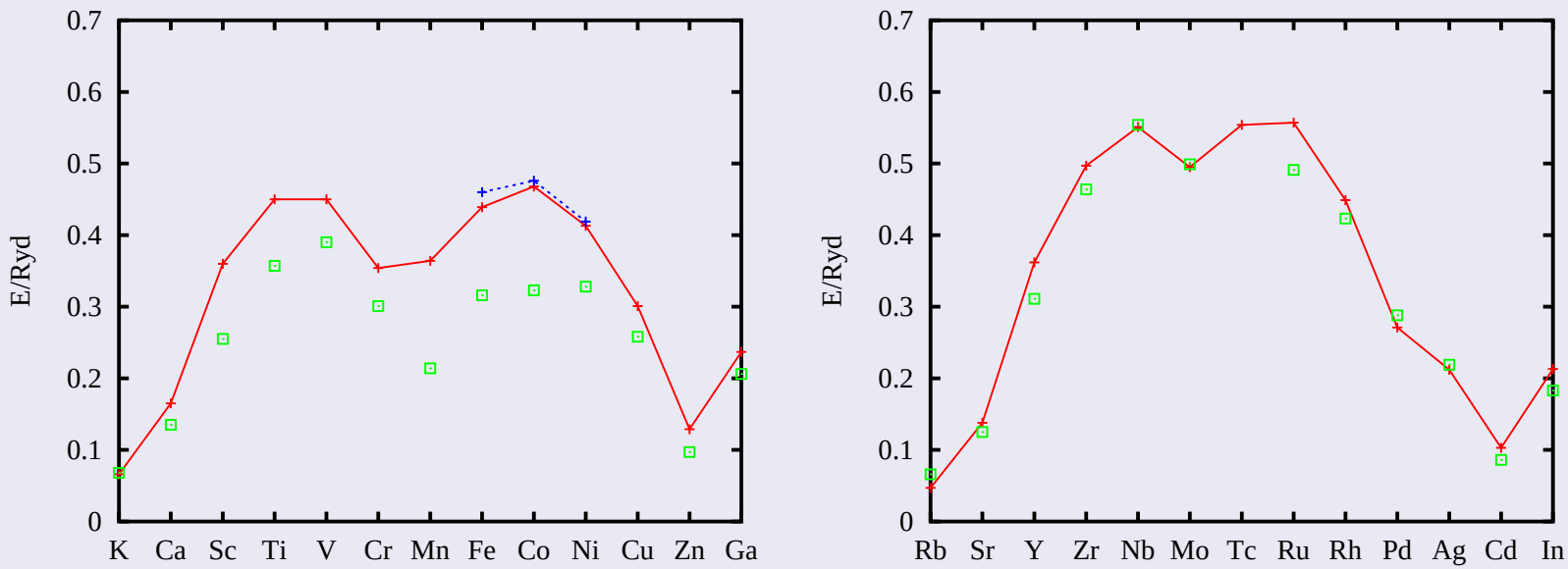
- binding energies
- phase transitions
- phase diagrams



Calculated Electronic Properties of Metals

Cohesive Energies

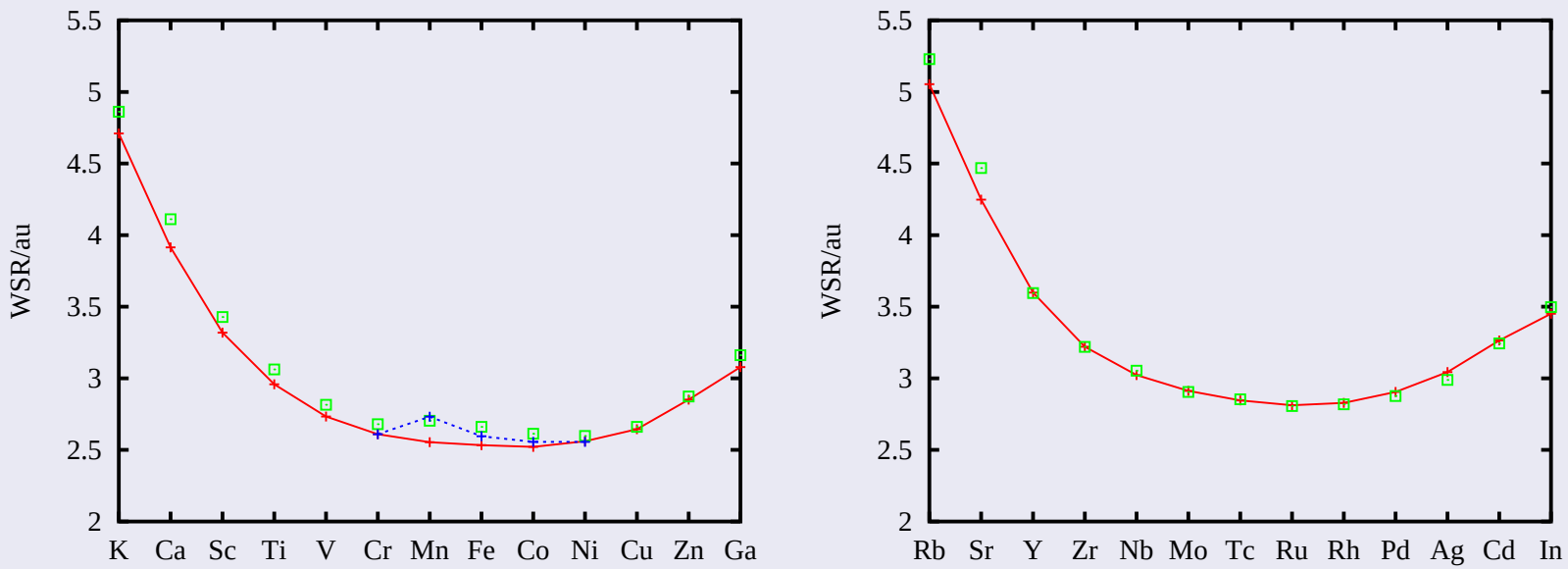
Moruzzi, Janak, Williams, 1978



Calculated Electronic Properties of Metals

Wigner-Seitz Radii

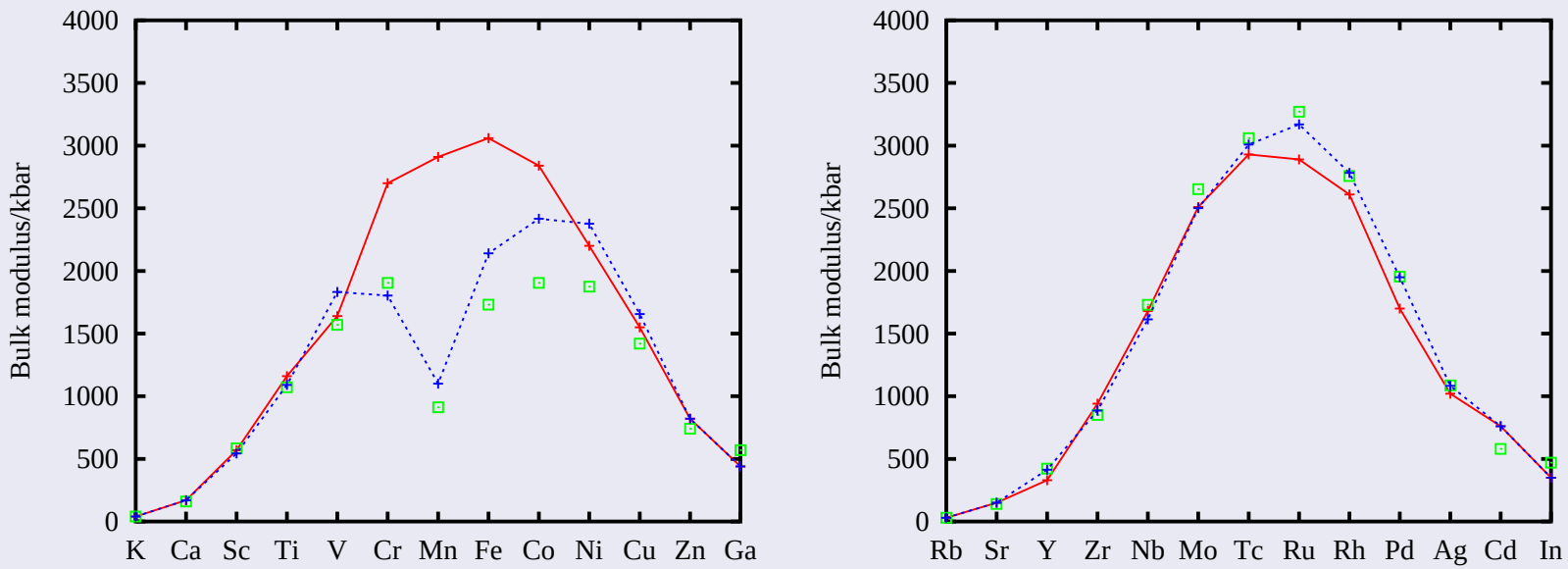
Moruzzi, Janak, Williams, 1978



Calculated Electronic Properties of Metals

Bulk Moduli

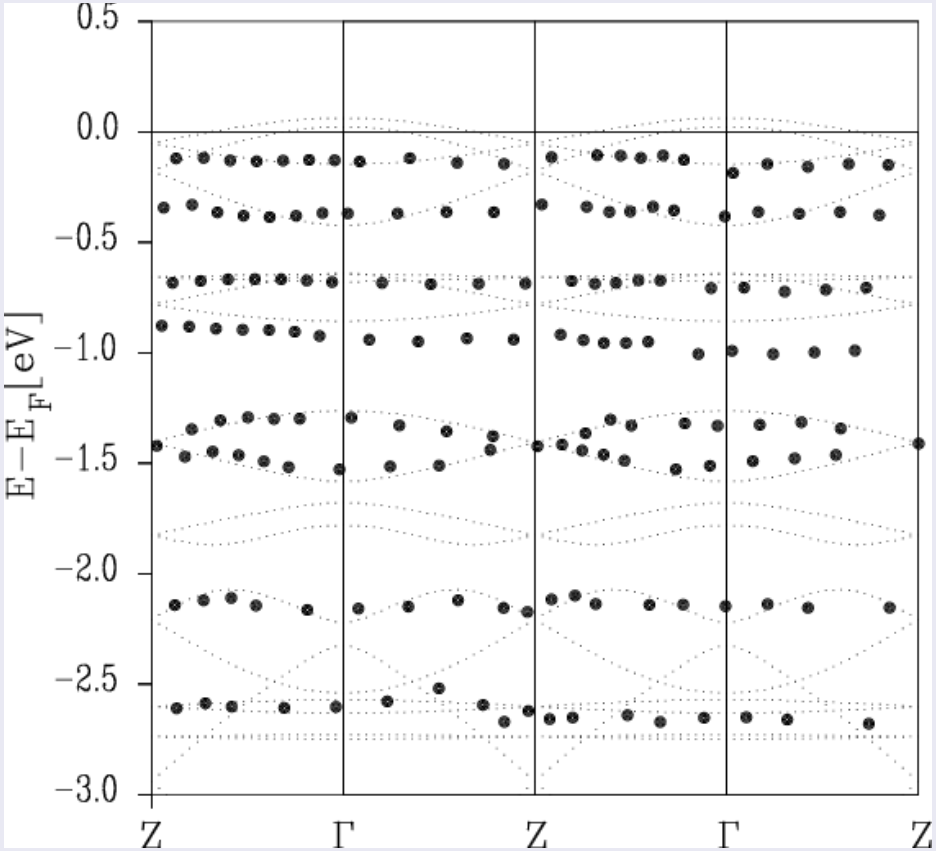
Moruzzi, Janak, Williams, 1978



Calculated Electronic Properties

ARPES Data and Calculated Band Structure of Td-WTe_2

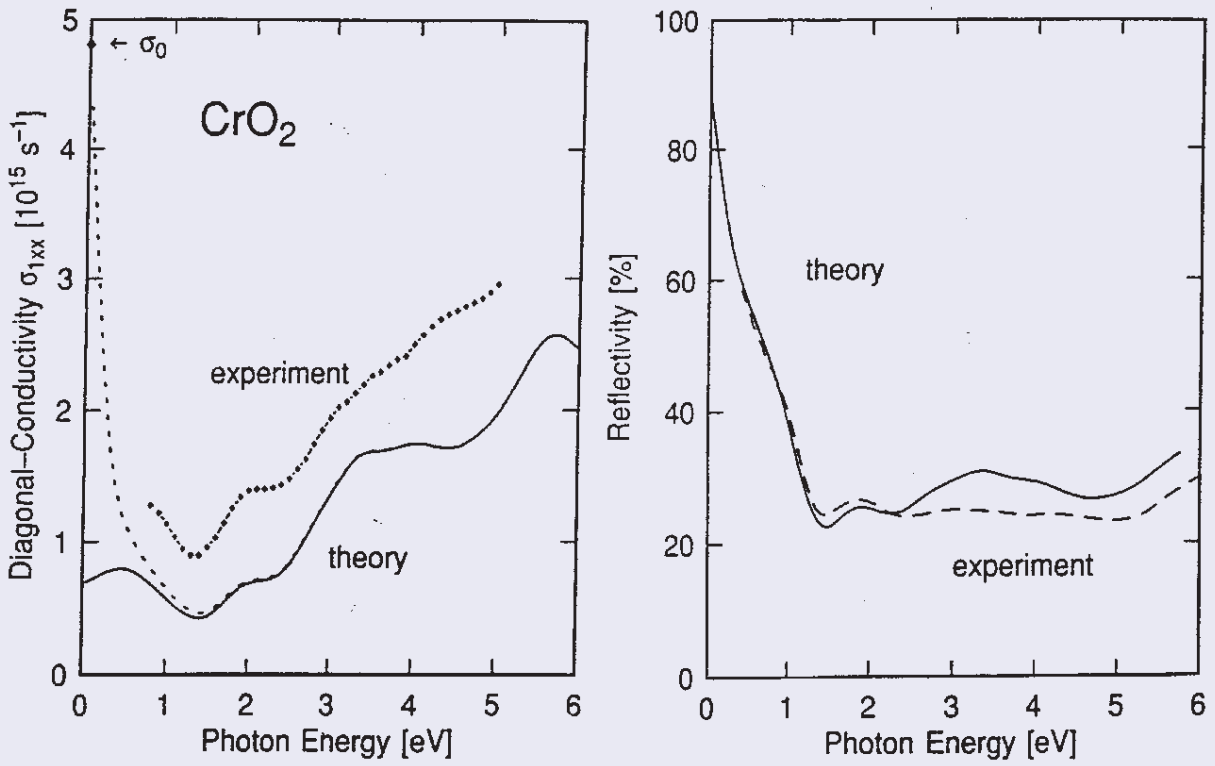
Augustin *et al.*, 2000



Calculated Optical Properties

Diagonal-Conductivity and Normal Incidence Reflectivity of CrO_2

Brändle *et al.*, 1993



Calculated Electronic Properties

Experimental and Calculated Fermi Surface of Cu and $TiTe_2$

Straub *et al.*, 1997

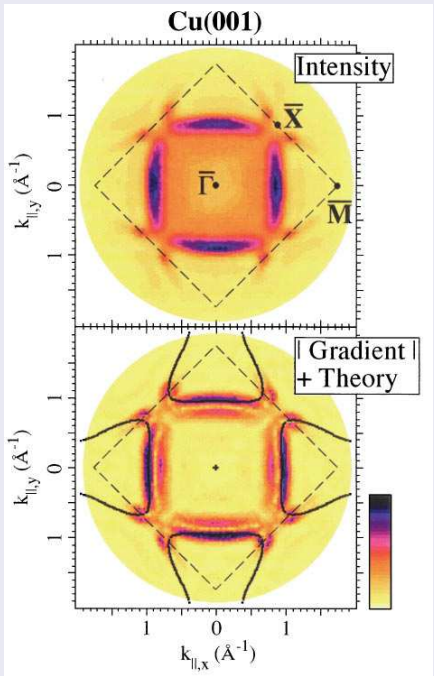


FIG. 3. (Color) Top: Fermi-level intensity map of Cu(001). The surface Brillouin zone is indicated. Bottom: Modulus of the gradient ($|\nabla_{\mathbf{k}} w(\mathbf{k})|$) of the intensity map, together with the theoretical FS contour (black line).

continuous penetration of a lifetime broadened peak into a typically Gaussian energy window, given by the instrumental response function.

This is illustrated on Cu(001) as an example. Figure 3 shows that the position of the intensity maximum along the Γ-M direction of the surface BZ *does not coincide* with an independent determination of the Fermi vector from the measured dispersion of the sp band (Fig. 4), as obtained from energy distribution curves on the same surface. Rather, it

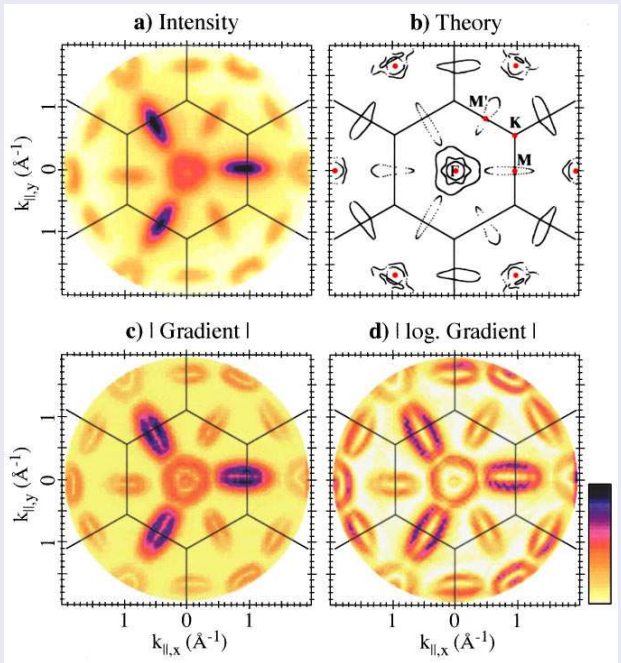
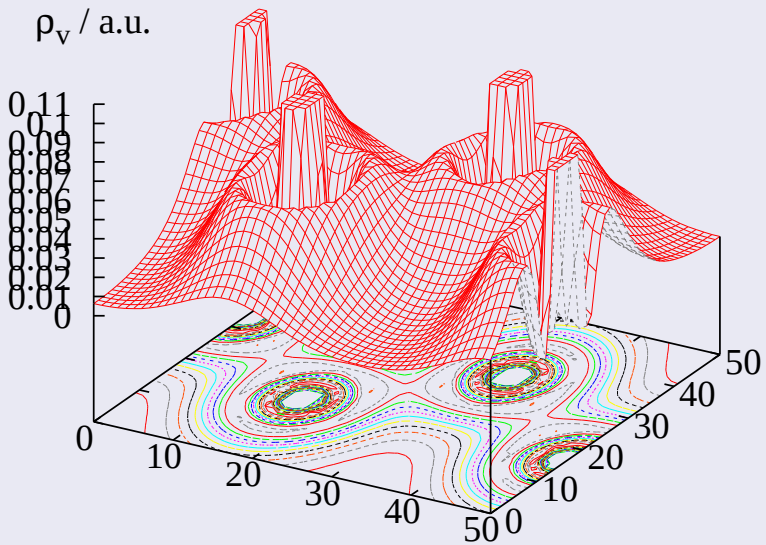


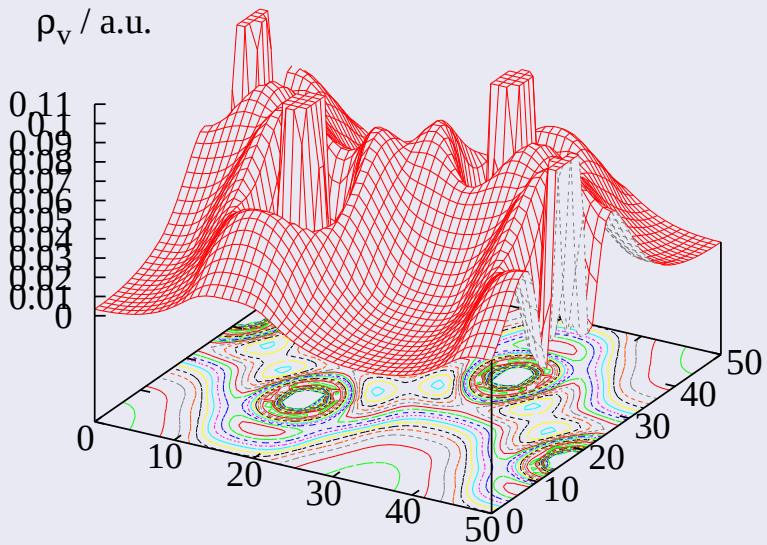
FIG. 1. (Color) (a) Photoemission intensity map $w(\mathbf{k})$ for excitations from the Fermi level of $TiTe_2$ ($h\nu$=21.2 eV). The Brillouin zone is indicated. (b) Corresponding Fermi-surface contours obtained from an ASW band calculation. (c) Modulus of the two-dimensional gradient $|\nabla_{\mathbf{k}} w(\mathbf{k})|$ of the map in (a). (d) Modulus of the logarithmic gradient $|\nabla_{\mathbf{k}} \ln w(\mathbf{k})|$

nent features are the ''cigar-shaped'' intensity maxima centered at the M points, which originate from the Ti 3d band. The observed intensity pattern reflects the threefold symmetry of the crystal structure that requires a distinction between M and M' points.[7] Though the electronic band structure itself does not deviate much from sixfold symmetry in the hexagonal 1T structure,[7] the optical transition matrix element spot at the Γ point. Note that we can also access parts of the second BZ (in the periodic zone scheme). The identification of the intensity maxima becomes possible by comparison to conventional band mapping results[7] and to a corresponding FS cut derived from our ASW calculations [Fig. 1(b)]. Apparently, the overall shape of the measured intensity map is already in good agreement with the calculated FS topology.

Calculated Electronic Properties

Calculated Electron Density of Si

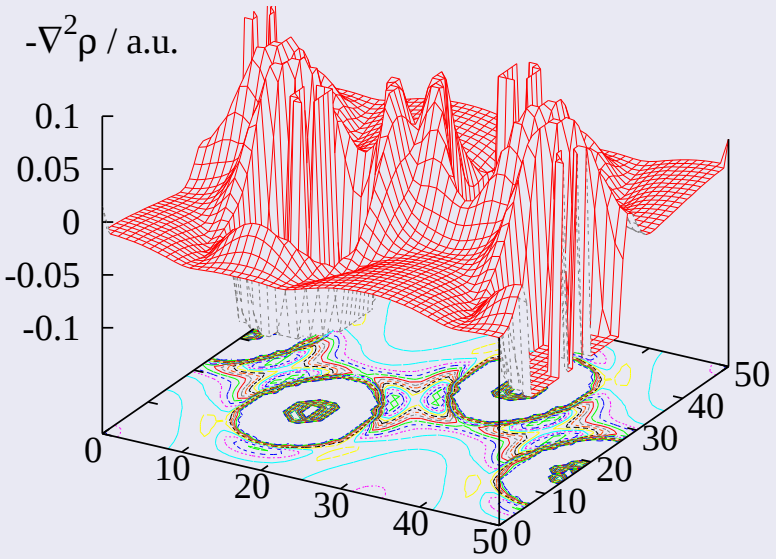


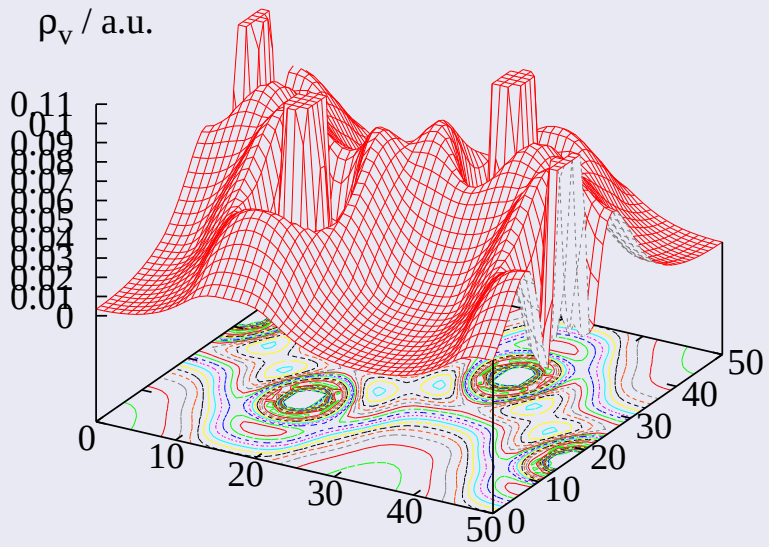


INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

Calculated Electronic Properties

Calculated Electron Density of Si

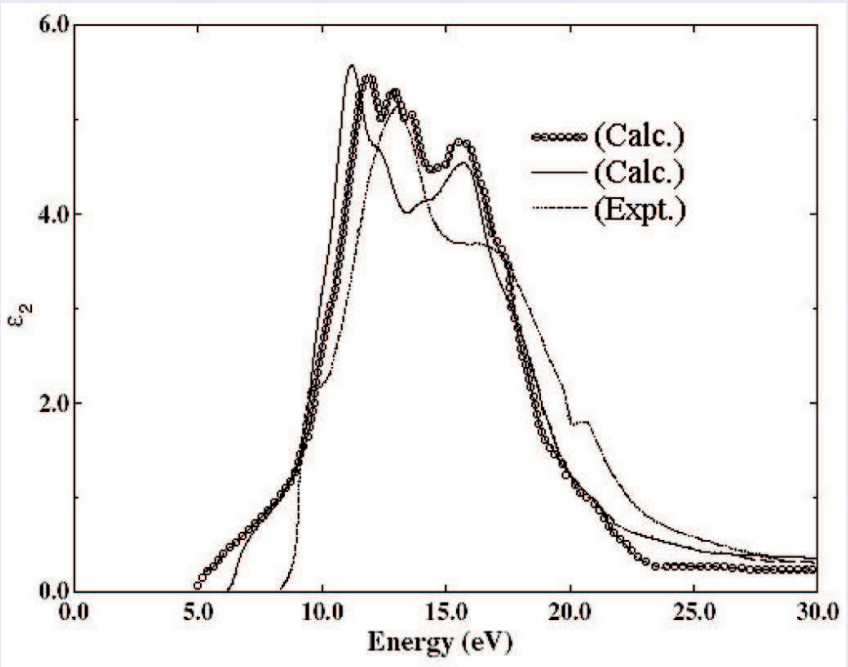




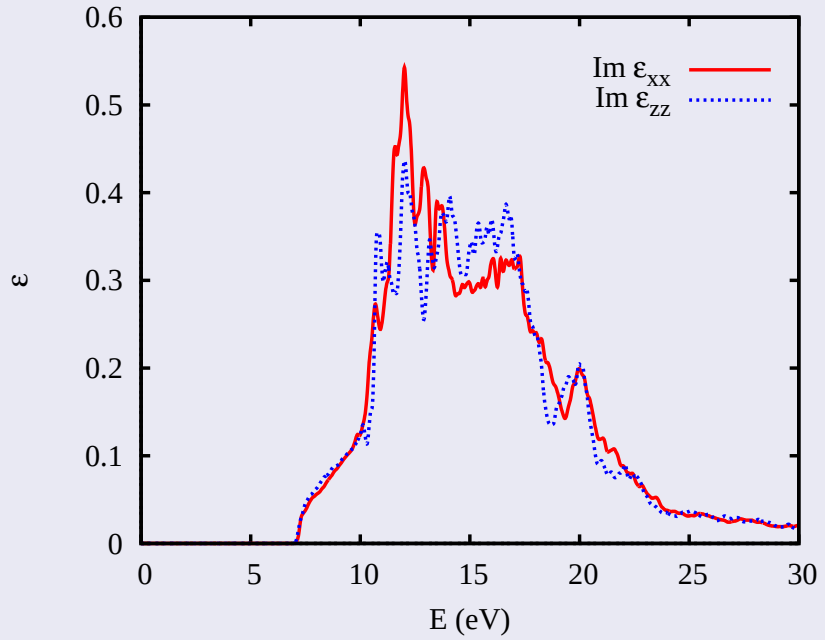
Calculated Optical Properties

Dielectric Function of Al_2O_3

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



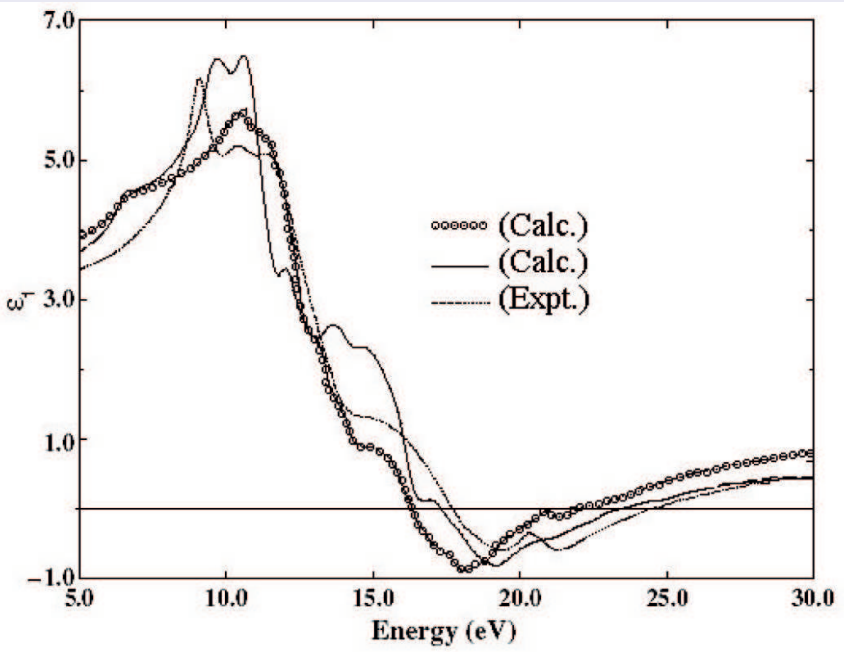
present work



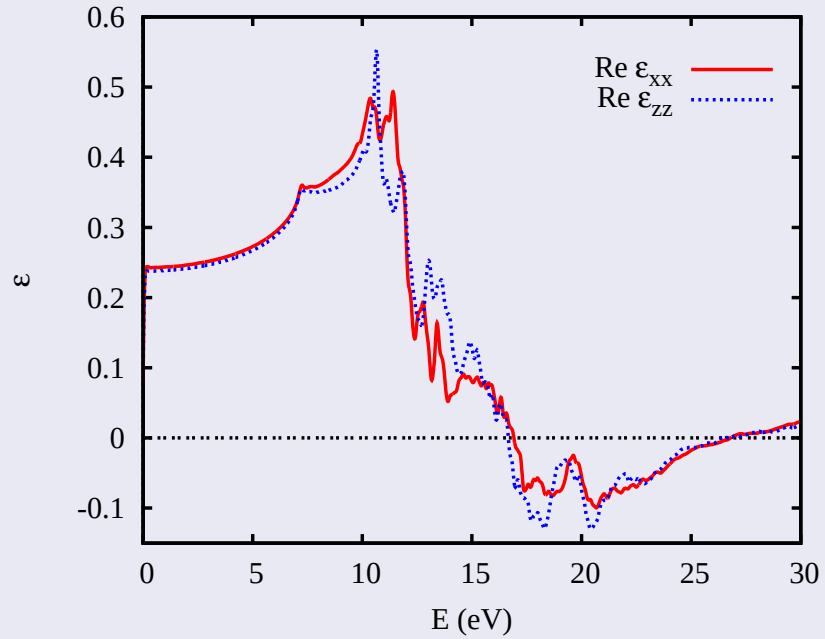
Calculated Optical Properties

Dielectric Function of Al_2O_3

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



present work



Outline

Theoretical Foundation

Newton's 2nd Law

$$\mathbf{F} = -\nabla E = m\mathbf{a}$$

Schrödinger's Equation

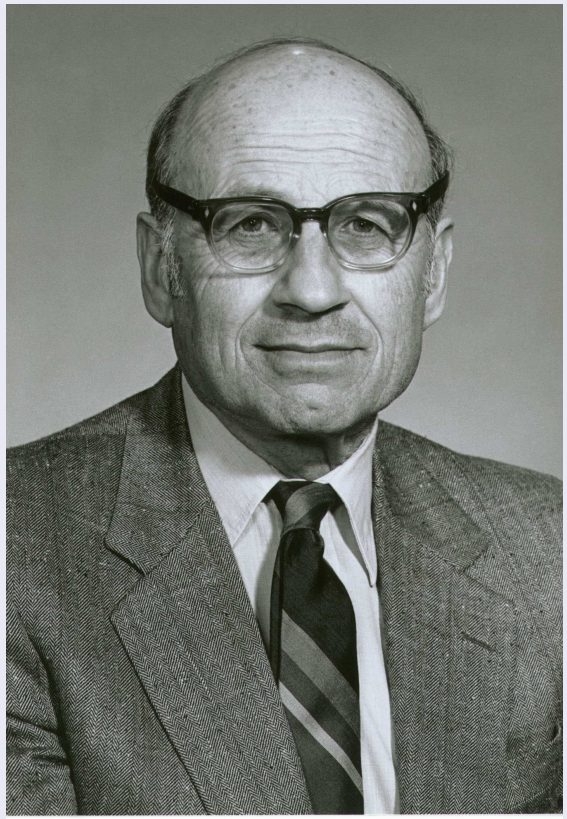
$$\mathcal{H}\psi = \mathcal{E}\psi$$

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

Foundation of Density Functional Theory 1964/1965

Pierre C. Hohenberg

Walter Kohn



Lu Jeu Sham

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

Density Functional Theory I

Guidelines $\Longrightarrow$ to remember

- theory for the ground state
  - no excitations (!)
- electron density as the central variable
  - no need for the many-body wave function
  - many-body wave function and potential from the density
- variational principle with respect to the electron density
  - minimization of total energy
- many-body problem $\Longleftrightarrow$ single-particle problem
  - exact mapping

Density Functional Theory I

Guidelines $\Longrightarrow$ to remember

- theory for the ground state
  - no excitations (!)
- electron density as the central variable
  - no need for the many-body wave function
  - many-body wave function and potential from the density
- variational principle with respect to the electron density
  - minimization of total energy
- many-body problem $\Longleftrightarrow$ single-particle problem
  - exact mapping

Density Functional Theory I

Guidelines $\Longrightarrow$ to remember

- theory for the ground state
  - no excitations (!)
- electron density as the central variable
  - no need for the many-body wave function
  - many-body wave function and potential from the density
- variational principle with respect to the electron density
  - minimization of total energy
- many-body problem $\Longleftrightarrow$ single-particle problem
  - exact mapping

Density Functional Theory I

Guidelines $\Longrightarrow$ to remember

- theory for the ground state
  - no excitations (!)
- electron density as the central variable
  - no need for the many-body wave function
  - many-body wave function and potential from the density
- variational principle with respect to the electron density
  - minimization of total energy
- many-body problem $\Longleftrightarrow$ single-particle problem
  - exact mapping

Density Functional Theory II

Many-Body $\Longleftrightarrow$ Single-Particle

Exact Mapping

- many-body problem
  - real, unsolvable (!!!)
  - density ρ_{mb}
- single-particle problem
  - fictitious, solvable (???)
  - density $\rho_{sp} \stackrel{!}{=} \rho_{mb}$
  - effective single-particle potential

$$v_{eff,\sigma}(\mathbf{r}) = v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc,\sigma}(\mathbf{r})$$

  - single-particle equations: Kohn-Sham equations

$$\left[-\nabla^2 + v_{eff,\sigma}(\mathbf{r}) - \varepsilon_\sigma\right] \psi_\sigma(\mathbf{r}) = 0$$

Density Functional Theory II

Many-Body $\Longleftrightarrow$ Single-Particle

Exact Mapping

- many-body problem
  - real, unsolvable (!!!)
  - density ρ_{mb}
- single-particle problem
  - fictitious, solvable (???)
  - density $\rho_{sp} \stackrel{!}{=} \rho_{mb}$
  - effective single-particle potential

$$v_{eff,\sigma}(\mathbf{r}) = v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc,\sigma}(\mathbf{r})$$

  - single-particle equations: Kohn-Sham equations

$$\left[-\nabla^2 + v_{eff,\sigma}(\mathbf{r}) - \varepsilon_\sigma\right]\psi_\sigma(\mathbf{r}) = 0$$

Density Functional Theory II

Many-Body $\Longleftrightarrow$ Single-Particle

Exact Mapping

- many-body problem
  - real, unsolvable (!!!)
  - density ρ_{mb}
- single-particle problem
  - fictitious, solvable (???)
  - density $\rho_{sp} \stackrel{!}{=} \rho_{mb}$
  - effective single-particle potential

$$v_{eff,\sigma}(\mathbf{r}) = v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc,\sigma}(\mathbf{r})$$

  - single-particle equations: Kohn-Sham equations

$$\left[-\nabla^2 + v_{eff,\sigma}(\mathbf{r}) - \varepsilon_\sigma\right] \psi_\sigma(\mathbf{r}) = 0$$

DFT Implementations I

Kohn-Sham Equation

$$\left[-\nabla^2 + v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc,\sigma}(\mathbf{r}) - \varepsilon_\sigma(\mathbf{k}) \right] \psi_\sigma(\mathbf{k}, \mathbf{r}) = 0$$

DFT Implementations I

Kohn-Sham Equation

$$\left[-\nabla^2 + v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc,\sigma}(\mathbf{r}) - \varepsilon_\sigma(\mathbf{k}) \right] \psi_\sigma(\mathbf{k},\mathbf{r}) = 0$$

Kinetic Energy

- non-relativistic
- scalar-relativistic
- fully relativistic

DFT Implementations I

Kohn-Sham Equation

$$\left[-\nabla^2 + v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc,\sigma}(\mathbf{r}) - \varepsilon_\sigma(\mathbf{k}) \right] \psi_\sigma(\mathbf{k}, \mathbf{r}) = 0$$

External Potential (Ions)

- non-periodic
- periodic

DFT Implementations I

Kohn-Sham Equation

$$\left[-\nabla^2 + v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc,\sigma}(\mathbf{r}) - \varepsilon_\sigma(\mathbf{k}) \right] \psi_\sigma(\mathbf{k},\mathbf{r}) = 0$$

Effective Potential

- all-electron muffin-tin
- all-electron full potential
- all-electron PAW
- pseudopotential

DFT Implementations I

Kohn-Sham Equation

$$\left[-\nabla^2 + v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc,\sigma}(\mathbf{r}) - \varepsilon_\sigma(\mathbf{k}) \right] \psi_\sigma(\mathbf{k},\mathbf{r}) = 0$$

Exchange-Correlation Potential

- non-spin-polarized
- spin-polarized

DFT Implementations I

Kohn-Sham Equation

$$\left[-\nabla^2 + v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc,\sigma}(\mathbf{r}) - \varepsilon_\sigma(\mathbf{k}) \right] \psi_\sigma(\mathbf{k},\mathbf{r}) = 0$$

Exchange-Correlation Potential

- local-density approximation (LDA)
- generalized gradient approximation (GGA)
- beyond LDA/GGA

DFT Implementations I

Kohn-Sham Equation

$$\left[-\nabla^2 + v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc,\sigma}(\mathbf{r}) - \varepsilon_\sigma(\mathbf{k}) \right] \psi_\sigma(\mathbf{k},\mathbf{r}) = 0$$

Exchange-Correlation Potential

- local-density approximation (LDA)
- generalized gradient approximation (GGA)
- beyond LDA/GGA
  - self-interaction correction (SIC)
  - LDA+U, LDA+DMFT

DFT Implementations I

Kohn-Sham Equation

$$\left[-\nabla^2 + v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc,\sigma}(\mathbf{r}) - \varepsilon_\sigma(\mathbf{k}) \right] \psi_\sigma(\mathbf{k},\mathbf{r}) = 0$$

Exchange-Correlation Potential

- local-density approximation (LDA)
- generalized gradient approximation (GGA)
- beyond LDA/GGA
  - optimized effective potential (OEP)
  - exact exchange (EXX)
  - screened exchange (sX)

DFT Implementations I

Kohn-Sham Equation

$$\left[-\nabla^2 + v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc,\sigma}(\mathbf{r}) - \varepsilon_\sigma(\mathbf{k}) \right] \psi_\sigma(\mathbf{k},\mathbf{r}) = 0$$

Exchange-Correlation Potential

- local-density approximation (LDA)
- generalized gradient approximation (GGA)
- beyond LDA/GGA, beyond DFT
  - model GW
  - GW
  - time-dependent DFT (TDDFT)

DFT Implementations I

Kohn-Sham Equation

$$\left[-\nabla^2 + v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc,\sigma}(\mathbf{r}) - \varepsilon_\sigma(\mathbf{k}) \right] \psi_\sigma(\mathbf{k},\mathbf{r}) = 0$$

Wave Function, Expanded in

- atomic orbitals
- plane waves
- augmented plane waves
- augmented spherical waves
- fully numerical functions

DFT Implementations I

Kohn-Sham Equation

$$\left[-\nabla^2 + v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc,\sigma}(\mathbf{r}) - \varepsilon_\sigma(\mathbf{k}) \right] \psi_\sigma(\mathbf{k},\mathbf{r}) = 0$$

Wave Function, Expanded in

- atomic orbitals
  - Gaussians (GTO)
  - Slater-type (STO)
  - numerical (DMol, Siesta)
- plane waves
- augmented plane waves
- augmented spherical waves
- fully numerical functions

DFT Implementations I

Kohn-Sham Equation

$$\left[-\nabla^2 + v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc,\sigma}(\mathbf{r}) - \varepsilon_\sigma(\mathbf{k}) \right] \psi_\sigma(\mathbf{k},\mathbf{r}) = 0$$

Wave Function, Expanded in

- atomic orbitals
- plane waves
- augmented plane waves
- augmented spherical waves
- fully numerical functions

DFT Implementations I

Kohn-Sham Equation

$$\left[-\nabla^2 + v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc,\sigma}(\mathbf{r}) - \varepsilon_\sigma(\mathbf{k}) \right] \psi_\sigma(\mathbf{k},\mathbf{r}) = 0$$

Wave Function, Expanded in

- atomic orbitals
- plane waves
- augmented plane waves
  - augmented plane waves (APW)
  - linear augmented plane waves (LAPW)
  - full-potential linear augmented plane waves (FLAPW)
- augmented spherical waves
- fully numerical functions

DFT Implementations I

Kohn-Sham Equation

$$\left[-\nabla^2 + v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc,\sigma}(\mathbf{r}) - \varepsilon_\sigma(\mathbf{k}) \right] \psi_\sigma(\mathbf{k},\mathbf{r}) = 0$$

Wave Function, Expanded in

- atomic orbitals
- plane waves
- augmented plane waves
- augmented spherical waves
  - Korringa Kohn Rostoker (KKR)
  - linear muffin-tin orbital (LMTO)
  - augmented spherical wave (ASW)
- fully numerical functions

DFT Implementations I

Kohn-Sham Equation

$$\left[-\nabla^2 + v_{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc,\sigma}(\mathbf{r}) - \varepsilon_\sigma(\mathbf{k}) \right] \psi_\sigma(\mathbf{k},\mathbf{r}) = 0$$

Wave Function, Expanded in

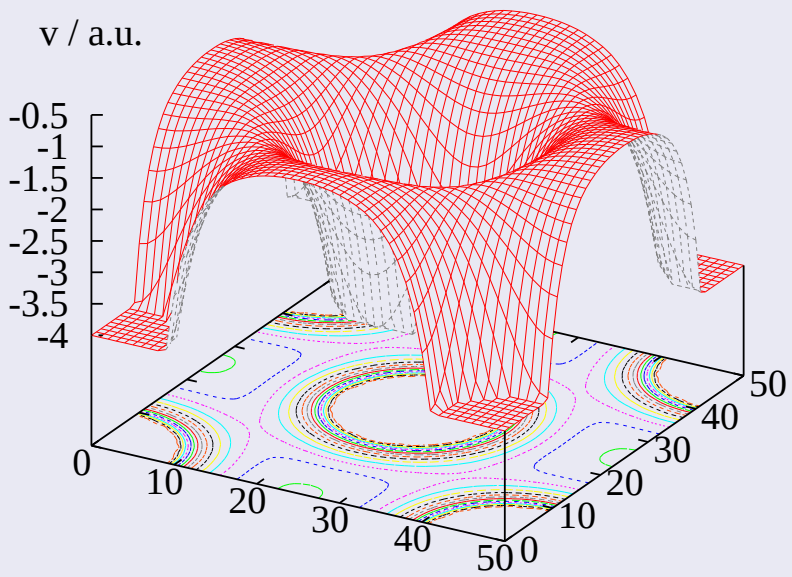
- atomic orbitals
- plane waves
- augmented plane waves
- augmented spherical waves
- fully numerical functions

courtesy of E. Wimmer

DFT Implementations II

Potentials and Partial Waves

Full Potential



Full Potential

- spherical symmetric near nuclei
- flat outside the atomic cores

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

DFT Implementations II

Potentials and Partial Waves

John C. Slater

Full Potential

- spherical symmetric near nuclei
- flat outside the atomic cores

Muffin-Tin Approximation

- approximate the potential

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

DFT Implementations II

Potentials and Partial Waves

John C. Slater

Muffin-Tin Approximation

distinguish:

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

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

DFT Implementations II

Potentials and Partial Waves

Muffin-Tin Potential

Muffin-Tin Approximation

distinguish:

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

INSTITUT für PHYSIK
UNIVERSITÄT AUGSBURG

DFT Implementations II

Potentials and Partial Waves

Muffin-Tin Potential

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“)

DFT Implementations III

Plane Waves $\Longleftrightarrow$ Spherical Waves

Augmented Plane Waves

- require periodic cell
- good for solids and surfaces
- good for metals, semiconductors, and insulators
- not recommended for rare earth and actinides
- inefficient for open structures
- systematic but slow convergence of basis set
- matrix elements easy to calculate
- easy to implement

DFT Implementations III

Plane Waves $\Longleftrightarrow$ Spherical Waves

Augmented Plane Waves

- require periodic cell
- good for solids and surfaces
- good for metals, semiconductors, and insulators
- not recommended for rare earth and actinides
- inefficient for open structures
- systematic but slow convergence of basis set
- matrix elements easy to calculate
- easy to implement

DFT Implementations III

Plane Waves $\Longleftrightarrow$ Spherical Waves

Augmented Plane Waves

- require periodic cell
- good for solids and surfaces
- good for metals, semiconductors, and insulators
- not recommended for rare earth and actinides
- inefficient for open structures
- systematic but slow convergence of basis set
- matrix elements easy to calculate
- easy to implement

DFT Implementations III

Plane Waves $\Longleftrightarrow$ Spherical Waves

Augmented Plane Waves

- require periodic cell
- good for solids and surfaces
- good for metals, semiconductors, and insulators
- not recommended for rare earth and actinides
- inefficient for open structures
- systematic but slow convergence of basis set
- matrix elements easy to calculate
- easy to implement

DFT Implementations III

Plane Waves $\Longleftrightarrow$ Spherical Waves

Augmented Plane Waves

- require periodic cell
- good for solids and surfaces
- good for metals, semiconductors, and insulators
- not recommended for rare earth and actinides
- inefficient for open structures
- systematic but slow convergence of basis set
- matrix elements easy to calculate
- easy to implement

DFT Implementations III

Plane Waves $\Longleftrightarrow$ Spherical Waves

Augmented Plane Waves

- require periodic cell
- good for solids and surfaces
- good for metals, semiconductors, and insulators
- not recommended for rare earth and actinides
- inefficient for open structures
- systematic but slow convergence of basis set
- matrix elements easy to calculate
- easy to implement

DFT Implementations III

Plane Waves $\Longleftrightarrow$ Spherical Waves

Augmented Plane Waves

- require periodic cell
- good for solids and surfaces
- good for metals, semiconductors, and insulators
- not recommended for rare earth and actinides
- inefficient for open structures
- systematic but slow convergence of basis set
- matrix elements easy to calculate
- easy to implement

DFT Implementations III

Plane Waves $\Longleftrightarrow$ Spherical Waves

Augmented Plane Waves

- require periodic cell
- good for solids and surfaces
- good for metals, semiconductors, and insulators
- not recommended for rare earth and actinides
- inefficient for open structures
- systematic but slow convergence of basis set
- matrix elements easy to calculate
- easy to implement

DFT Implementations IV

Plane Waves $\Longleftrightarrow$ Spherical Waves

Augmented Spherical Waves

- do not require periodic cell
- good for solids and surfaces
- good for metals, semiconductors, and insulators
- good for all atoms including transition metals, rare earth, and actinides
- still efficient for open structures
- minimal basis set
- computationally efficient
- difficult to implement

DFT Implementations IV

Plane Waves $\Longleftrightarrow$ Spherical Waves

Augmented Spherical Waves

- do not require periodic cell
- good for solids and surfaces
- good for metals, semiconductors, and insulators
- good for all atoms including transition metals, rare earth, and actinides
- still efficient for open structures
- minimal basis set
- computationally efficient
- difficult to implement

DFT Implementations IV

Plane Waves $\Longleftrightarrow$ Spherical Waves

Augmented Spherical Waves

- do not require periodic cell
- good for solids and surfaces
- good for metals, semiconductors, and insulators
- good for all atoms including transition metals, rare earth, and actinides
- still efficient for open structures
- minimal basis set
- computationally efficient
- difficult to implement

DFT Implementations IV

Plane Waves $\Longleftrightarrow$ Spherical Waves

Augmented Spherical Waves

- do not require periodic cell
- good for solids and surfaces
- good for metals, semiconductors, and insulators
- good for all atoms including transition metals, rare earth, and actinides
- still efficient for open structures
- minimal basis set
- computationally efficient
- difficult to implement

DFT Implementations IV

Plane Waves $\Longleftrightarrow$ Spherical Waves

Augmented Spherical Waves

- do not require periodic cell
- good for solids and surfaces
- good for metals, semiconductors, and insulators
- good for all atoms including transition metals, rare earth, and actinides
- still efficient for open structures
- minimal basis set
- computationally efficient
- difficult to implement

DFT Implementations IV

Plane Waves $\Longleftrightarrow$ Spherical Waves

Augmented Spherical Waves

- do not require periodic cell
- good for solids and surfaces
- good for metals, semiconductors, and insulators
- good for all atoms including transition metals, rare earth, and actinides
- still efficient for open structures
- minimal basis set
- computationally efficient
- difficult to implement

DFT Implementations IV

Plane Waves $\Longleftrightarrow$ Spherical Waves

Augmented Spherical Waves

- do not require periodic cell
- good for solids and surfaces
- good for metals, semiconductors, and insulators
- good for all atoms including transition metals, rare earth, and actinides
- still efficient for open structures
- minimal basis set
- computationally efficient
- difficult to implement

DFT Implementations IV

Plane Waves $\Longleftrightarrow$ Spherical Waves

Augmented Spherical Waves

- do not require periodic cell
- good for solids and surfaces
- good for metals, semiconductors, and insulators
- good for all atoms including transition metals, rare earth, and actinides
- still efficient for open structures
- minimal basis set
- computationally efficient
- difficult to implement

Summary

Density Functional Theory . . .

- allows for an accurate determination of a still growing number of materials properties
- is a ground state theory
- is in principle exact
- has given rise to a large variety of implementations

Summary

Density Functional Theory . . .

- allows for an accurate determination of a still growing number of materials properties
- is a ground state theory
- is in principle exact
- has given rise to a large variety of implementations

Summary

Density Functional Theory . . .

- allows for an accurate determination of a still growing number of materials properties
- is a ground state theory
- is in principle exact
- has given rise to a large variety of implementations

Summary

Density Functional Theory . . .

- allows for an accurate determination of a still growing number of materials properties
- is a ground state theory
- is in principle exact
- has given rise to a large variety of implementations

Further Reading I


P. Hohenberg and W. Kohn
Inhomogeneous Electron Gas
Phys. Rev. **136**, B864 (1964)


W. Kohn and L. J. Sham
Quantum Density Oscillations in an Inhomogeneous Electron Gas
Phys. Rev. **140**, A1133 (1965)


W. Kohn
An Essay on Condensed Matter Physics in the Twentieth Century
Rev. Mod. Phys. **71**, S59 (1999)

Further Reading II

- R. M. Dreizler and E. K. U. Gross
  Density Functional Theory (Springer, Berlin, 1990)
- R. G. Parr and W. Yang
  Density-Functional Theory of Atoms and Molecules (Oxford University Press, Oxford, 1989)
- H. Eschrig
  The Fundamentals of Density-Functional Theory (Edition am Gutenbergplatz, Leipzig 2003)

Further Reading III


J. Kübler and V. Eyert
Electronic structure calculations
in: *Electronic and Magnetic Properties of Metals and Ceramics*
ed by K. H. J. Buschow (VCH, Weinheim, 1992), pp. 1-145
Volume 3A of *Materials Science and Technology*


E. Wimmer
Prediction of Materials Properties
in: *Encyclopedia of Computational Chemistry*
ed by P. von Ragué-Schleyer (Wiley, New York, 1998)