The Augmented Spherical Wave Package

Hands on Session II

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Electronic Structure in a Nutshell

Outline

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Outline

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Main Programs and Shell Scripts I

mnmpr.x $\Longrightarrow$ mnmpr.run

machine parameters

mnsym.x $\Longrightarrow$ mnsym.run

symmetry check of the crystal structure

mnhlp.x

fully commented shell script $\hat{=}$ mnsym.x with HELP=T

mnscl.x $\Longrightarrow$ mnscl.run

setup of supercells

Main Programs and Shell Scripts II

mnpac.x $\Longrightarrow$ **mnpac.run**

optimal interstitial sites and atomic sphere radii

mnscf.x $\Longrightarrow$ **mnscf.run**

self-consistent field calculation
partial charges, magn. moments, partial DOS, total energies . . .

mnbnd.x $\Longrightarrow$ **mnbnd.run**

band structure

mndos.x $\Longrightarrow$ **mnscf.run**

partial DOS $\hat{=}$ mnscf.x with SAVDOS=T, QUIT=BND

Main Programs and Shell Scripts III

mnall.x $\Longrightarrow$ mnscf.run, mnbnd.run

self-consistent field calculation
+ band structure
+ DOS, COOP, Fermi surface

mnopt.x $\Longrightarrow$ mnscf.run

optical spectra $\hat{=}$ mnscf.x with SAVOPT=T, QUIT=BND

Main Programs and Shell Scripts IV

upctr

updates values of specific tokens in CTRL

upshl

updates shell scripts mn*.x

monic

monitores progress of convergence
(*susan* in elder versions)

o2log

removes information of intermediate iterations from output files

Plot Programs and Shell Scripts I

plstr.x	$\Longrightarrow$ plstr.run
crystal structure	RasMol

plxcr.x	
crystal structure	XCrysDen

Plot Programs and Shell Scripts II

plbnd.x	$\Longrightarrow$ plbnd.run
(weighted) band structure	gnuplot, LaTeX

pldos.x	$\Longrightarrow$ pldos.run
(partial) densities of states (DOS)	gnuplot, LaTeX

plcop.x	$\Longrightarrow$ plcop.run
(partial) crystal orbital overlap pop. (COOP)	gnuplot, LaTeX

Plot Programs and Shell Scripts III

plfrm.x	
Fermi surface	XCrysDen

plopt.x	$\Longrightarrow$ plopt.run
optical spectra	gnuplot, LaTeX

plrho.x	$\Longrightarrow$ plrho.run
electron density, Laplacian, and potential	gnuplot

Outline

Data files I

README

general information

INSTALL

installation guide

COPYRIGHT

copyright information

LICENCE

licence information

Data files II

CTRL $\Longrightarrow$ main and only input file for all main programs

contains information about, inter alia

- crystal structure
- constituing atoms (type and positions)
- symmetry lines
- options and control parameters
  - non-relativistic $\leftrightarrow$ scalar-relativistic
  - spin-degenerate $\leftrightarrow$ spin-polarized
  - Brillouin-zone sampling scheme and number of **k**-points
  - LDA/GGA-parametrization

all other files are automatically created and deleted

Data files III

CALL, CBAK

backup copies of CTRL

CNEW

updated copy of CTRL as created by mnpac.run

Data files IV

HELP

full list of categories and tokens
generated by setting HELP=T and running any of the main programs

SPCGRP

full list of space groups and generators
generated by setting HELP=T and running any of the main programs

Data files V

Part of file HELP

```
category IO
  token HELP= of cast logical
        Switch to print HELP file
  token SHOW= of cast logical
        Switch to echo CTRL file to output
  token VERBOS= of cast integer
        Verbosity level for printing of output
  token CLEAN= of cast logical
        Switch to shrink atomic files after convergence
  token WRITE= of cast character
        Name of file to which a copy of CTRL file is written
  token EXTENS= of cast character
        Default extension for all files besides CTRL file
```

Data files VI

Beginning of file SPCGRP

```
SPCGRP-file for ASW-2.3


Lat PG  SG O SG-Symbol  Generators

tri  1   1   P1         E
tri  2   2   P-1        I
 sm  3   3   P2         R2Y
 sm  3   3   P121       R2Y
 sm  3   4   P2_1       R2Y:T(0,1/2,0)
 sm  3   4   P12_11     R2Y:T(0,1/2,0)
 cm  3   5   C2         R2Y
 cm  3   5   A2         R2Y
 cm  3   5   I2         R2Y
 cm  3   5   C121       R2Y
 cm  3   5   A121       R2Y
 cm  3   5   I121       R2Y
```

Data files VII

atomic files $\Longrightarrow$ named after entries in CTRL

all information about an atom
(e.g. atomic number, electron density, potential)

outsym, outscf, outbnd, outdos, . . .

output files from main programs

MIX $\Longrightarrow$ unformatted

contains information needed for convergence acceleration

EIGE, EIGV, EIGVC, EIGVO $\Longrightarrow$ unformatted

temporary files used for the Brillouin zone integration and the Fermi surface

Data files VIII

STRU, STRX

crystal structure information

FREE

electron density, Laplacian, and potential of overlapping free atoms

RHO

electron density, Laplacian, and potential

Data files IX

BNDE

band structure ($E(\mathbf{k})$)

BNDV $\Longrightarrow$ unformatted

eigenvectors

DOS $\Longrightarrow$ unformatted

partial densities of states

COOP $\Longrightarrow$ unformatted

crystal orbital overlap population

Data files X

FERM

Fermi surface

OPT $\Longrightarrow$ unformatted

optical conductivity

bnd.tex, dos.tex, coop.tex, opt.tex

LaTeX files produced by the plot programs

bnd.ps, dos.ps, coop.ps, opt.ps, rho.ps, blk.ps

postscript files produced by the plot programs and gnuplot

Outline

Preparing for the Application

Create a directory tree

- create e.g. /home/user/appl/fes2 (iron pyrite)
- create e.g. /home/user/appl/fes2/nm (spin-deg. calcs.)

A minimum CTRL file

```
HEADER   FeS2 sc
VERSION  ASW-2.3
STRUC    ALAT=10.23476
CLASS    ATOM=FE Z=26
         ATOM=S  Z=16
SITE     CARTP=T
         ATOM=FE POS= 0.000000  0.000000  0.000000
         ATOM=S  POS= 0.384840  0.384840  0.384840
SYMGRP   GENPOS=T SGSYM=Pa-3
```

Preparing for the Application

Create a directory tree

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STRUC    ALAT=10.23476
CLASS    ATOM=FE Z=26
         ATOM=S  Z=16
SITE     CARTP=T
         ATOM=FE POS= 0.000000  0.000000  0.000000
         ATOM=S  POS= 0.384840  0.384840  0.384840
SYMGRP   GENPOS=T SGSYM=Pa-3
```

A Standard CTRL File I

```
HEADER  FeS2 sc
        data by E. D. Stevens, M. L. DeLucia, and P. Coppens,
        Inorg. Chem. 19, 813 (1980).
VERSION ASW-2.3
IO      HELP=F SHOW=T VERBOS=30 CLEAN=T
OPTIONS REL=T OVLCHK=T
STRUC   ALAT=10.23476 CNTR=P
CLASS   ATOM=FE Z=26 R=3.27603001 LMXL=2 CONF=4 4 3 4
                QVAL= 2.0  0.0  6.0  0.0
        ATOM=S  Z=16 R=2.43362229 LMXL=2 CONF=3 3 3 4
                QVAL= 2.0  4.0  0.0  0.0
SITE    CARTP=T
        ATOM=FE POS= 0.00000  0.00000  0.00000
        ATOM=FE POS= 0.00000 -0.50000 -0.50000
        ATOM=FE POS=-0.50000  0.00000 -0.50000
        ATOM=FE POS=-0.50000  0.50000  0.00000
...
```

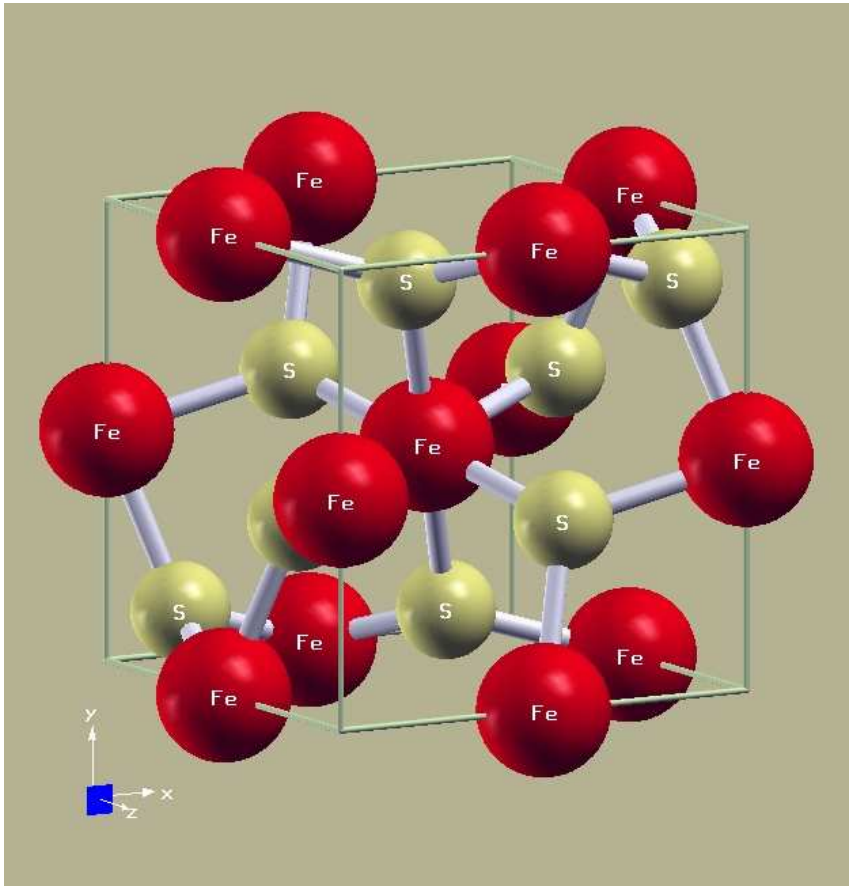
A Standard CTRL File II

```
          ATOM=S   POS= 0.38484  0.38484  0.38484
          ATOM=S   POS= 0.11516 -0.38484 -0.11516
          ATOM=S   POS=-0.38484 -0.38484 -0.38484
          ATOM=S   POS=-0.11516  0.38484  0.11516
          ATOM=S   POS=-0.11516  0.11516 -0.38484
          ATOM=S   POS=-0.38484 -0.11516  0.11516
          ATOM=S   POS= 0.11516 -0.11516  0.38484
          ATOM=S   POS= 0.38484  0.11516 -0.11516
SYMGRP
ENVEL     EKAP=-0.015
BZSMP     NKBAB=6 BZINT=LTM EMIN=-1.0 EMAX=1.5 NDOS=2500
          NORD=3 WIDTH=0.01 SAVDOS=F SAVCOOP=F SAVFERM=F
CHARGE    NETA=2 EETA=-1.0 -3.0 SAVRHO=T
CONTROL   START= QUIT= FREE=F NITBND=99 CNVG=1.0D-08 CNVGET=1.0D-08
          NITATM=50 CNVGQA=1.0D-10
MIXING    NMIXB=5 BETAB=0.5 INCBB=T NMIXA=5 BETAA=0.5
...
```

A Standard CTRL File III

```
SYMLIN   NPAN=6 NPTS=400 ORBWGT=F CARTE=F
         LABEL=R ENDPT= 0.5  0.5  0.5
         LABEL=g ENDPT= 0.0  0.0  0.0
         LABEL=X ENDPT= 0.5  0.0  0.0
         LABEL=M ENDPT= 0.5  0.5  0.0
         LABEL=R ENDPT= 0.5  0.5  0.5
         LABEL=X ENDPT= 0.0  0.5  0.0
         LABEL=M ENDPT= 0.5  0.5  0.0
PLOT     CARTV=T
         ORIGIN= 0.5  0.0  0.0
         RPLOT1= 1.0  0.0  0.0
         RPLOT2= 0.0  1.0  0.0
         RPLOT3= 0.0  0.0  1.0
         NPDIV1=100 NPDIV2=100
```

Plotting the Crystal Structure



Pyrite

- $Pa\bar{3}$ (T_h^6)
- NaCl structure sublattices occupied by
  - iron
  - sulfur pairs
- sulfur pairs $\parallel \langle 111 \rangle$ axes
- rotated FeS_6 octahedra

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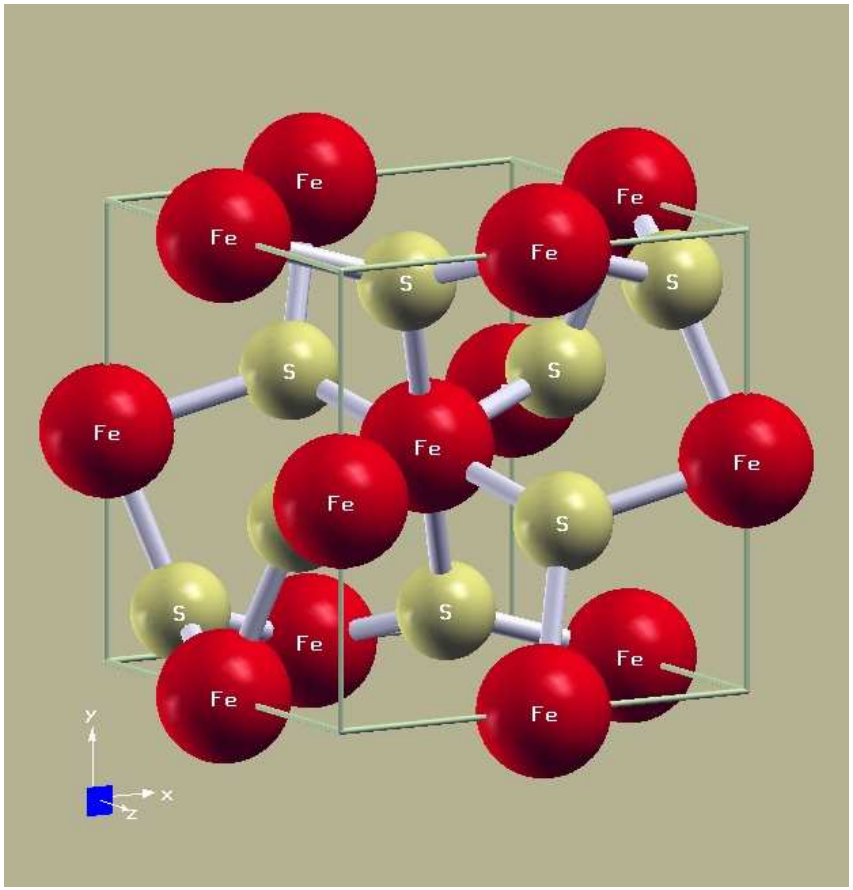
Plotting the Crystal Structure



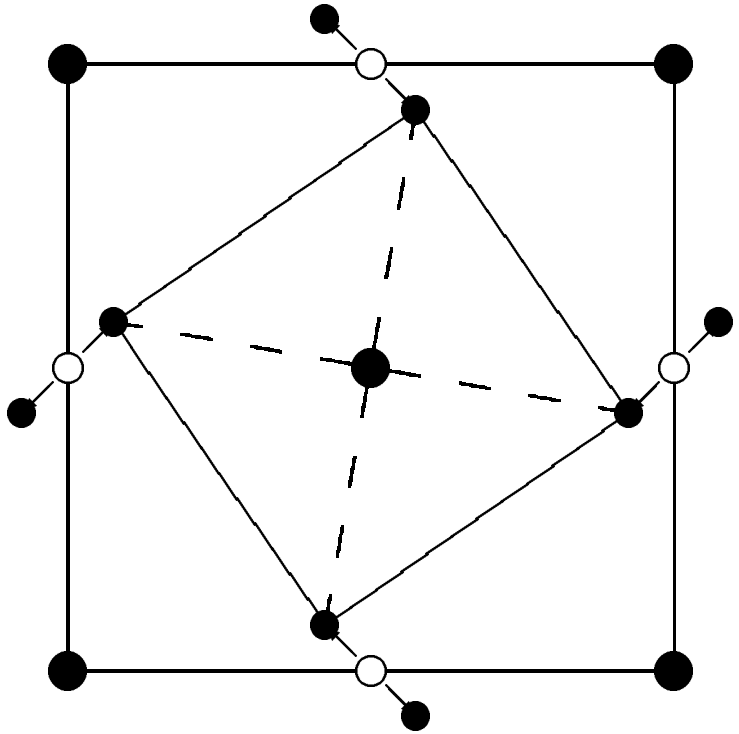
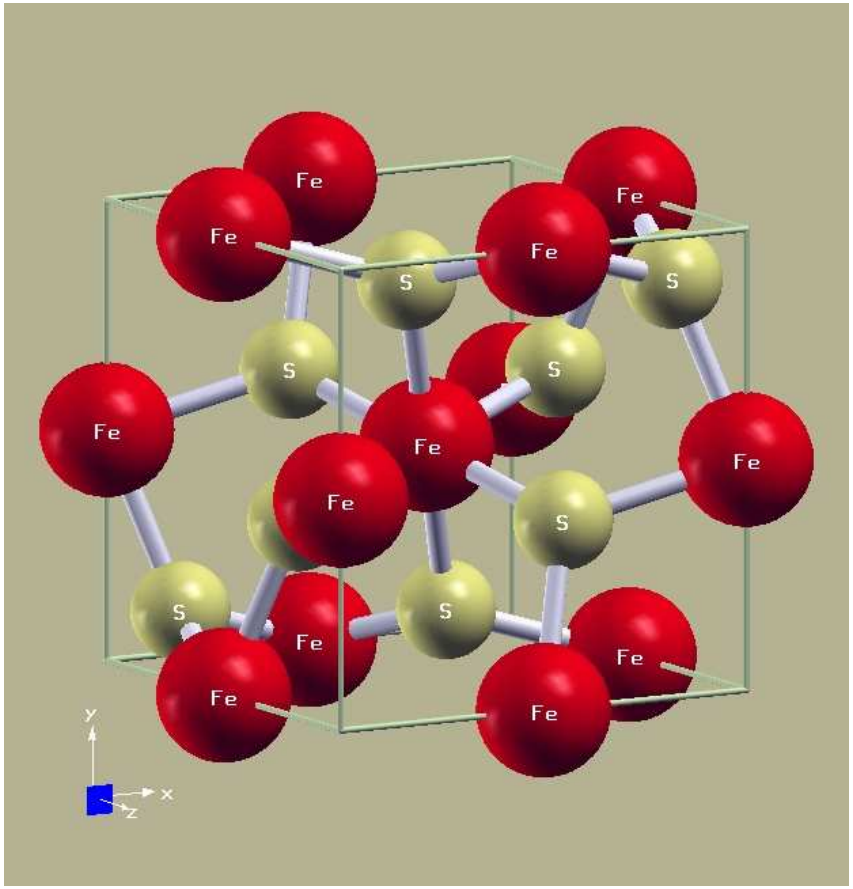


Figure: 2D analogon

Plotting the Crystal Structure



Pyrite

- open crystal structure
- space filling with only Fe and S spheres
  $\Longrightarrow$ large sphere overlaps

Checking the Atomic Sphere Overlap

From the output of mnsym.x

```
Check overlap of atomic spheres for OVLCHK=T:

...

ib jb cl1  cl2    tau(jb)-tau(ib)   dist  sumrs   ovlp  */dist  */r1   */r2
 1  6 FE   S    -1.18  3.94  1.18   4.28   5.71   1.43   0.33   0.44   0.59 !!!
 1  8 FE   S     1.18 -3.94 -1.18   4.28   5.71   1.43   0.33   0.44   0.59 !!!
 1  9 FE   S     1.18 -1.18  3.94   4.28   5.71   1.43   0.33   0.44   0.59 !!!
 1 10 FE   S     3.94  1.18 -1.18   4.28   5.71   1.43   0.33   0.44   0.59 !!!
 1 11 FE   S    -1.18  1.18 -3.94   4.28   5.71   1.43   0.33   0.44   0.59 !!!
 1 12 FE   S    -3.94 -1.18  1.18   4.28   5.71   1.43   0.33   0.44   0.59 !!!

...

ib jb cl1  cl2    tau(jb)-tau(ib)   dist  sumrs   ovlp  */dist  */r1   */r2
 5  2 S    FE    3.94 -1.18 -1.18   4.28   5.71   1.43   0.33   0.59   0.44 !!!
 5  3 S    FE   -1.18  3.94 -1.18   4.28   5.71   1.43   0.33   0.59   0.44 !!!
 5  4 S    FE   -1.18 -1.18  3.94   4.28   5.71   1.43   0.33   0.59   0.44 !!!
 5  7 S    S    -2.36 -2.36 -2.36   4.08   4.87   0.78   0.19   0.32   0.32 !
                           in atomic units

The overlap limits are not fulfilled!
```

Running the Packing Routine: mnpac.x

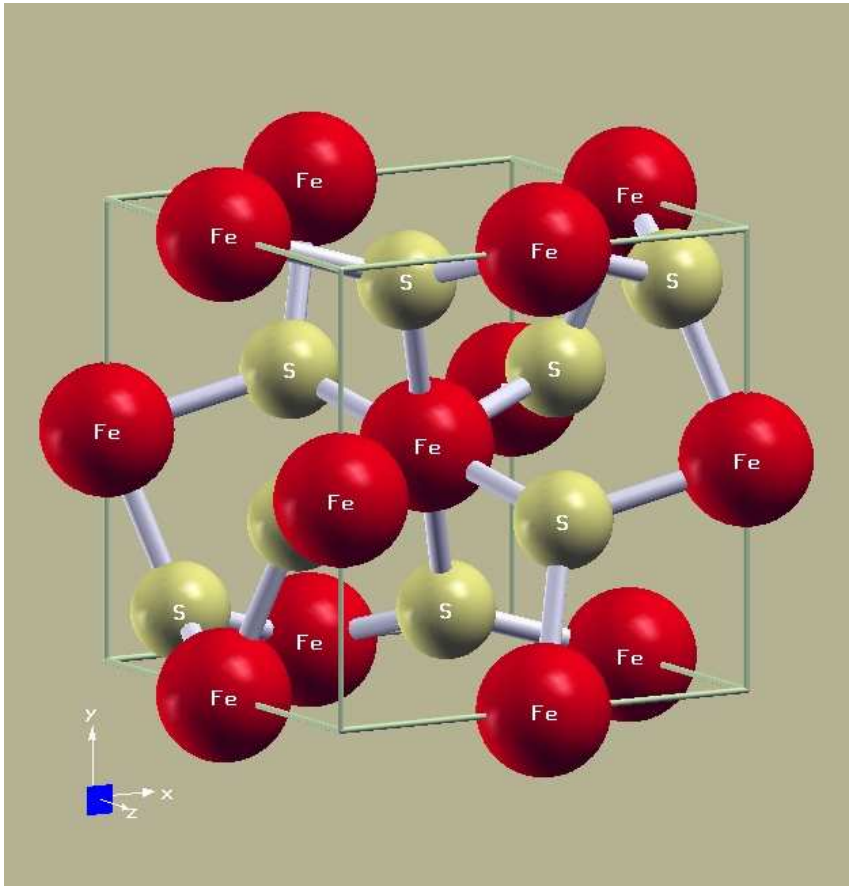
Fill Large Voids of Open Structures

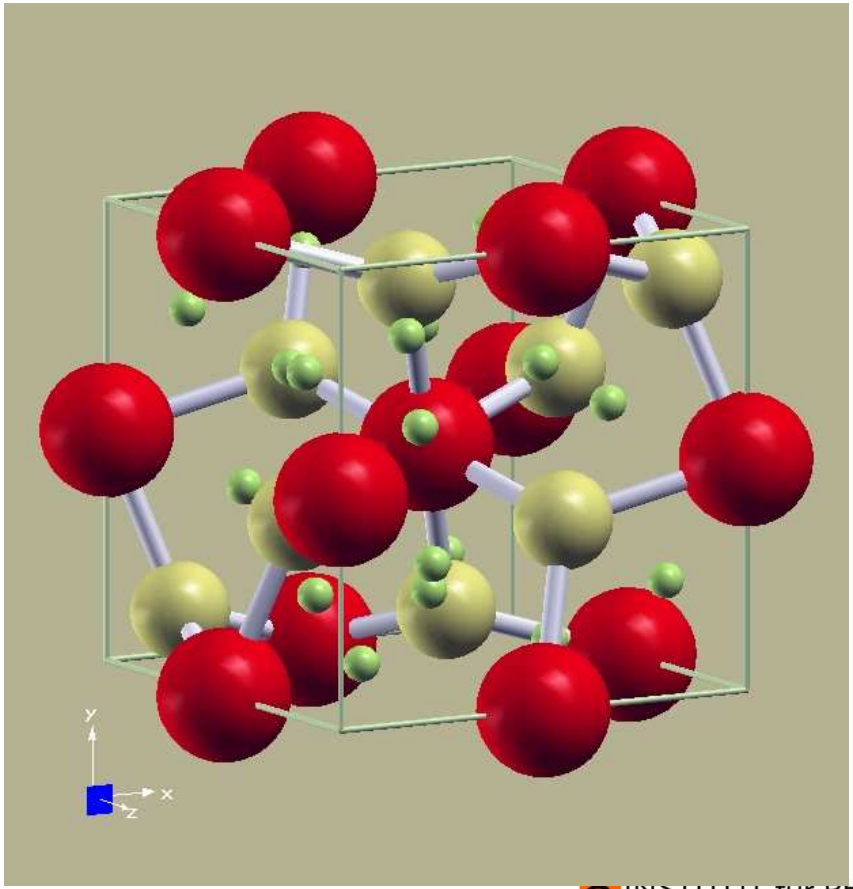
- check space filling within the allowed overlaps
- find positions for empty spheres
- determine the maximally allowed sphere radii
- repeat until complete space filling is achieved
- write result to file CNEW

Completing the Space Filling

```
Space can be filled to  62.9% without empty spheres.
Space can be filled to  75.7% with   1 empty sphere class(es).
Space can be filled to 104.0% with   2 empty sphere class(es).
```

Filling Space





The Updated CTRL File I

Category CLASS

```
CLASS   ATOM=FE Z=26 R=2.40019794 LMXL=2 CONF=4 4 3 4
                QVAL= 2.0  0.0  6.0  0.0
        ATOM=S  Z=16 R=2.31735801 LMXL=2 CONF=3 3 3 4
                QVAL= 2.0  4.0  0.0  0.0
        ATOM=E1 Z= 0 R=1.57781865 LMXL=1 CONF=1 2 3
                QVAL= 0.0  0.0  0.0
        ATOM=E2 Z= 0 R=1.42640878 LMXL=1 CONF=1 2 3
                QVAL= 0.0  0.0  0.0
```

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The Updated CTRL File II

Category SITE

```
SITE    CARTP=T
...
        ATOM=E1 POS= 0.305462 -0.194538 -0.305462
        ATOM=E1 POS=-0.305462  0.194538  0.305462
        ATOM=E1 POS=-0.194538 -0.305462  0.305462
        ATOM=E1 POS= 0.194538  0.305462 -0.305462
        ATOM=E1 POS=-0.305462  0.305462 -0.194538
        ATOM=E1 POS= 0.305462 -0.305462  0.194538
        ATOM=E1 POS= 0.194538  0.194538  0.194538
        ATOM=E1 POS=-0.194538 -0.194538 -0.194538
        ATOM=E2 POS=-0.302589  0.062226 -0.134569
        ATOM=E2 POS= 0.302589 -0.062226  0.134569
        ATOM=E2 POS= 0.197411  0.437774  0.134569
        ATOM=E2 POS=-0.197411 -0.437774 -0.134569
        ATOM=E2 POS= 0.302589 -0.437774 -0.365431
        ATOM=E2 POS=-0.302589  0.437774  0.365431
...
```

Running the Main Programs

Complete set of calculations: mnall.x

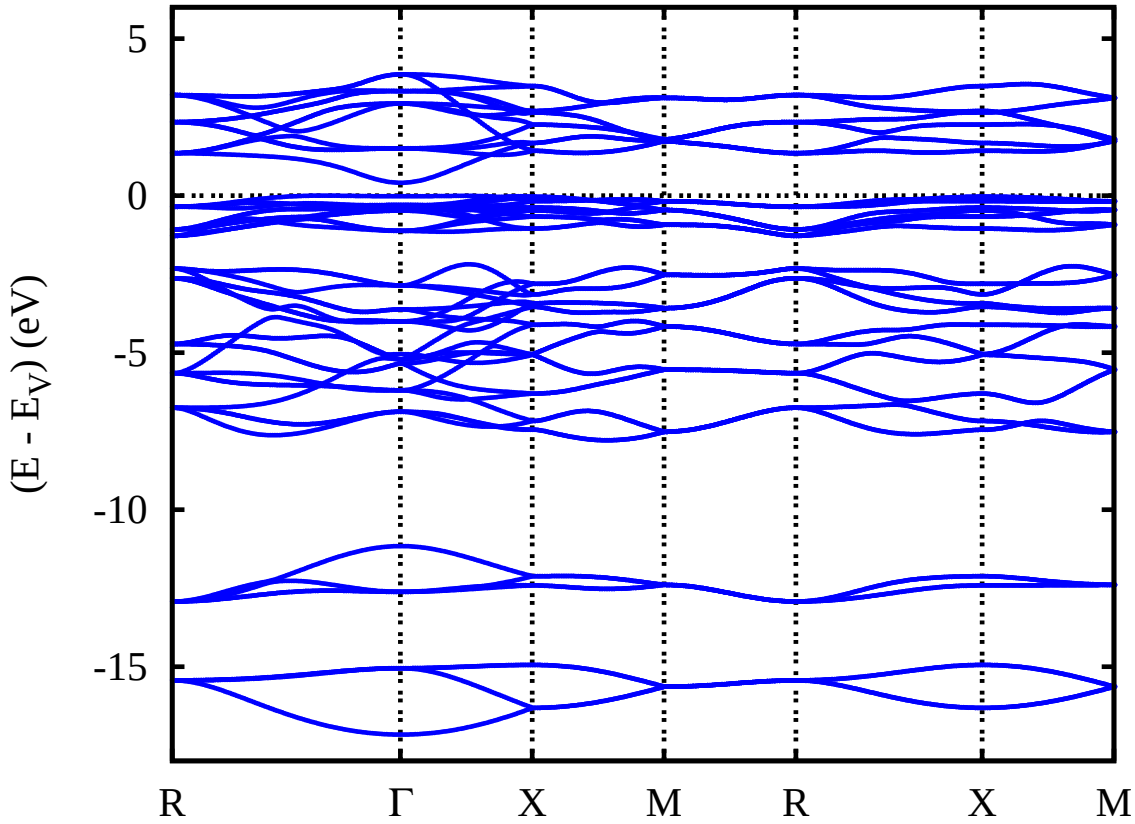
scf-cycle + band structure + DOS, COOP, Fermi surface

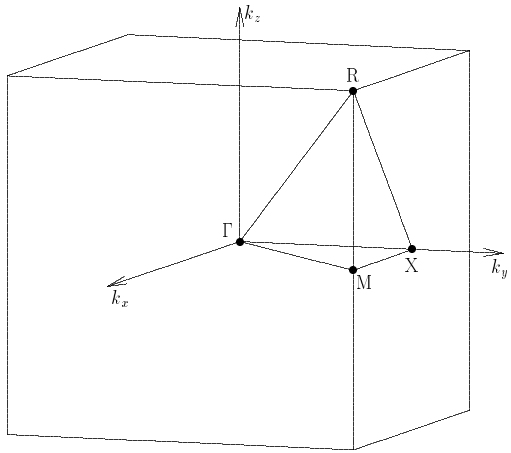
Summary Generated by Shell Script monic

```
ASW-2.3, program MNSCF started on asterix at Fri, 19 Jan 2007, 15:19:46.
Calculation converged after  11 iteration(s).
                      Start of Iteration   11
    76 irreducible k-points generated from    1331 ( 11, 11, 11).
          Fermi energy - MTZ =     0.830903 Ryd.
The system is a semiconductor:
           Indirect band gap =     0.030102 Ryd =     0.409559 eV
Mean-square residual:                   0.757648D-21
Total free atom energies     : -16526.992322 Ryd
Total variational energy     : -16532.902747 Ryd
Cohesive energy              :      5.910426 Ryd
 qdiff =       0.00000000  <        0.00000001
 ediff =       0.00000001  <        0.00000001
ASW-2.3, program MNSCF ended on asterix at Fri, 19 Jan 2007, 15:54:18.
```

Running the Plot Programs I

Band Structure: plbnd.x/plbnd.run





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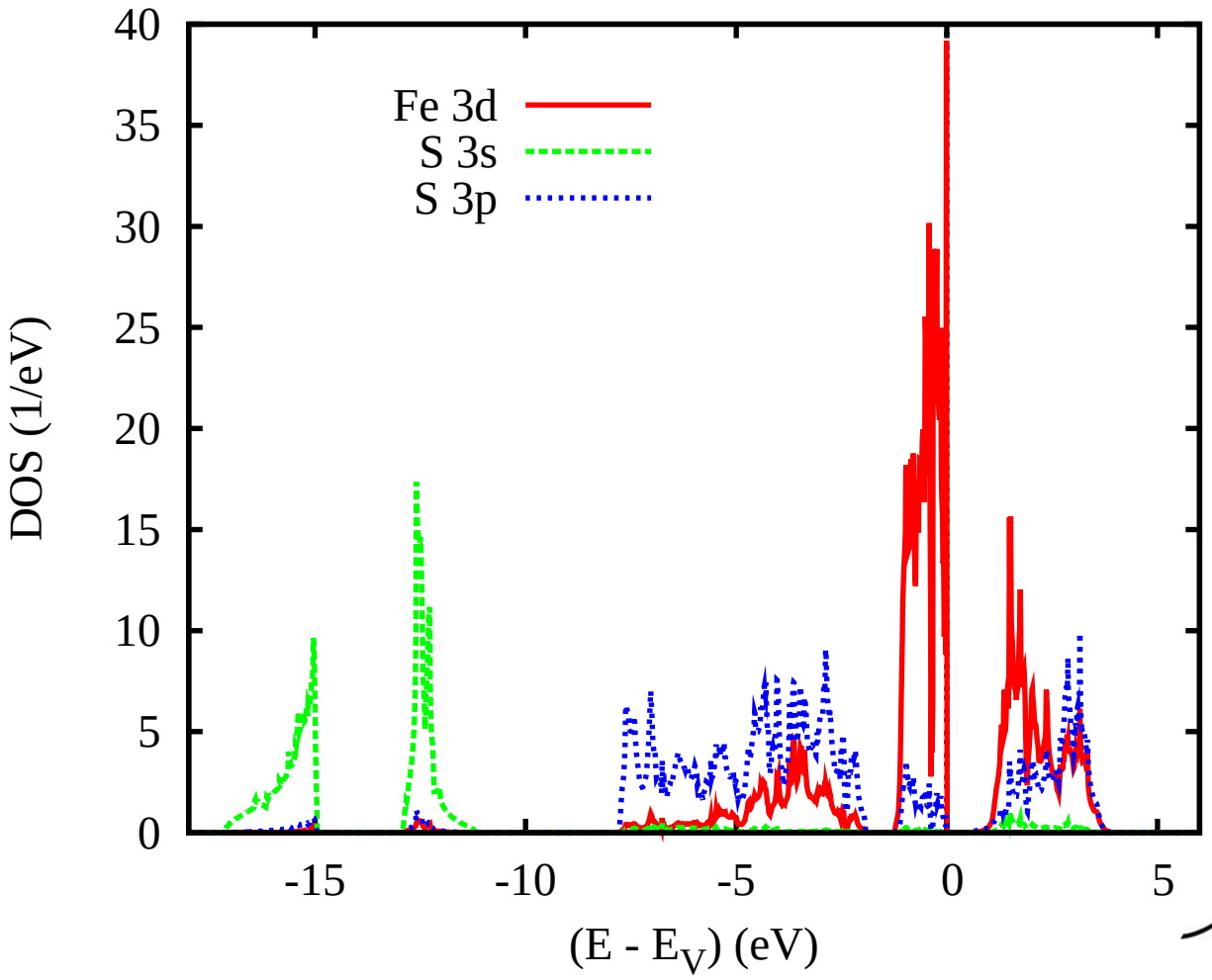
Running the Plot Programs II

Densities of States: pldos.x/pldos.run



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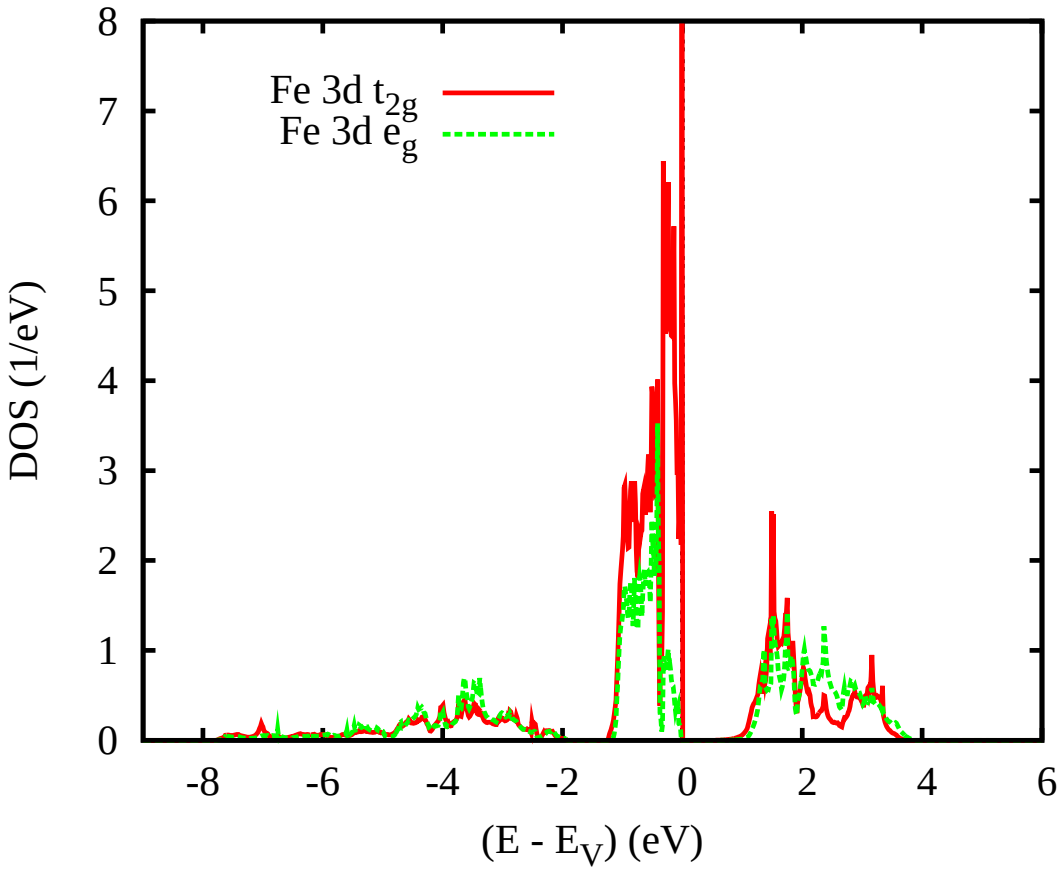
Running the Plot Programs III

Partial Densities of States: pldos.x/pldos.run



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)

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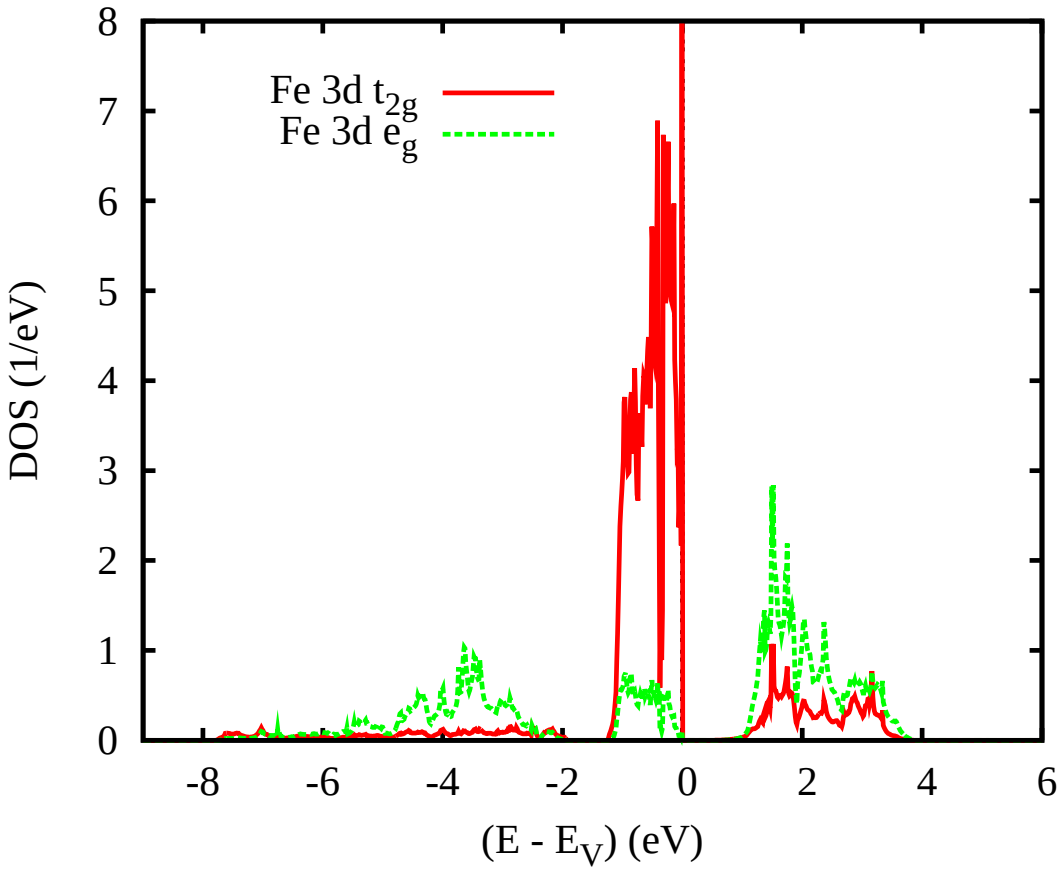
Running the Plot Programs III

Partial Densities of States: pldos.x/pldos.run



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)

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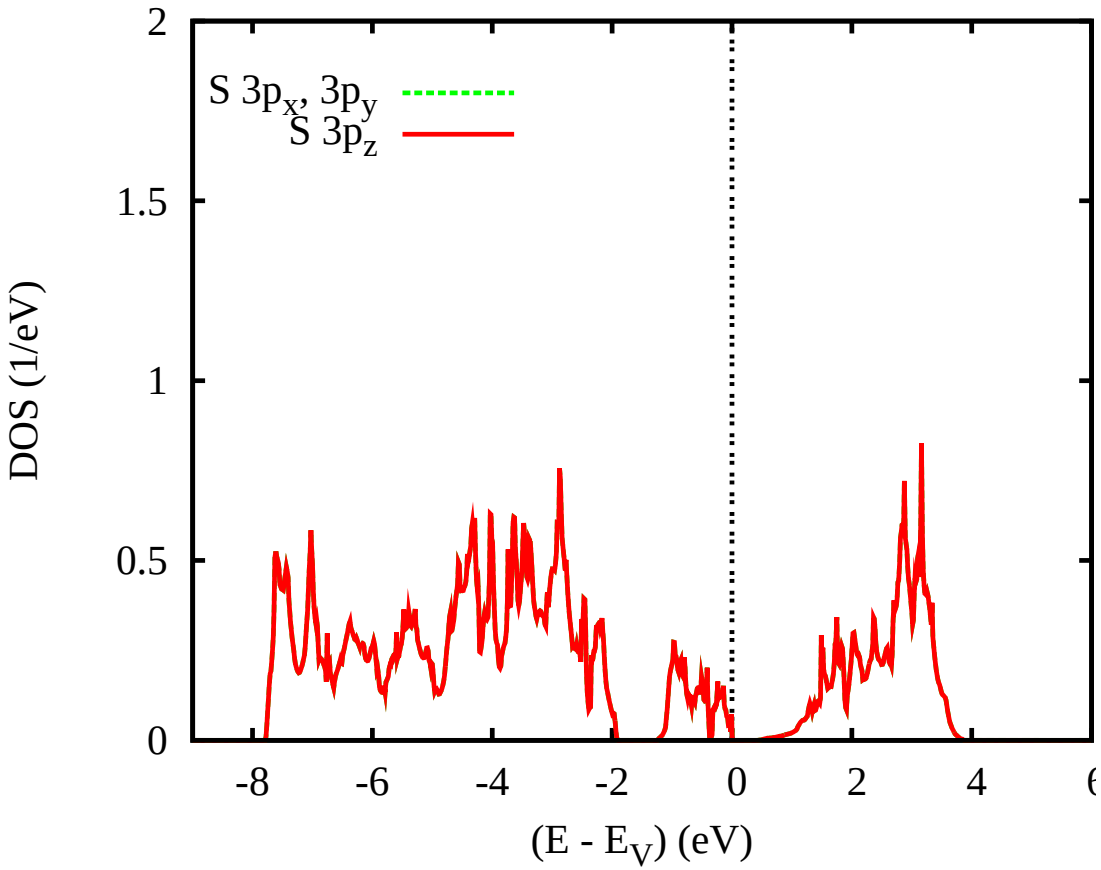
Running the Plot Programs IV

Partial Densities of States: pldos.x/pldos.run



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)

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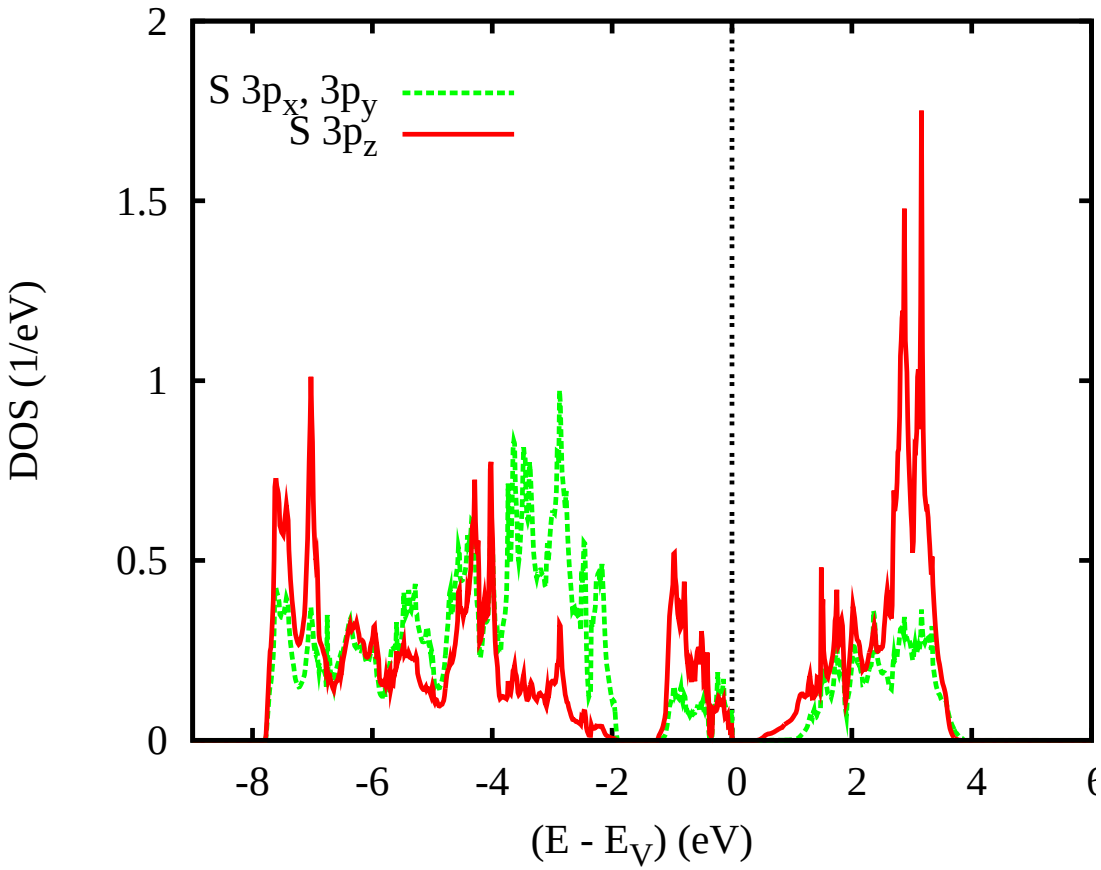
Running the Plot Programs IV

Partial Densities of States: pldos.x/pldos.run



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)

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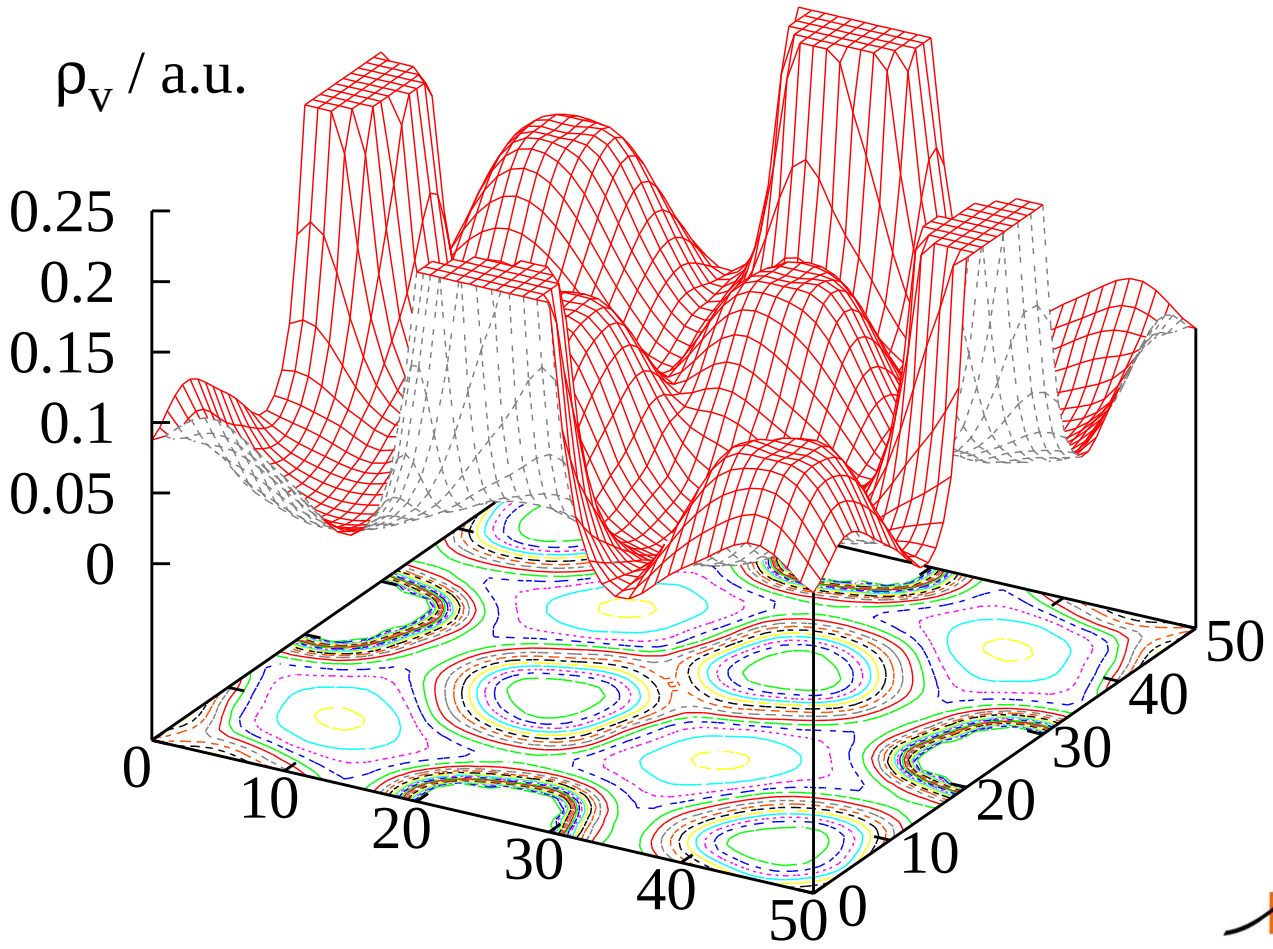
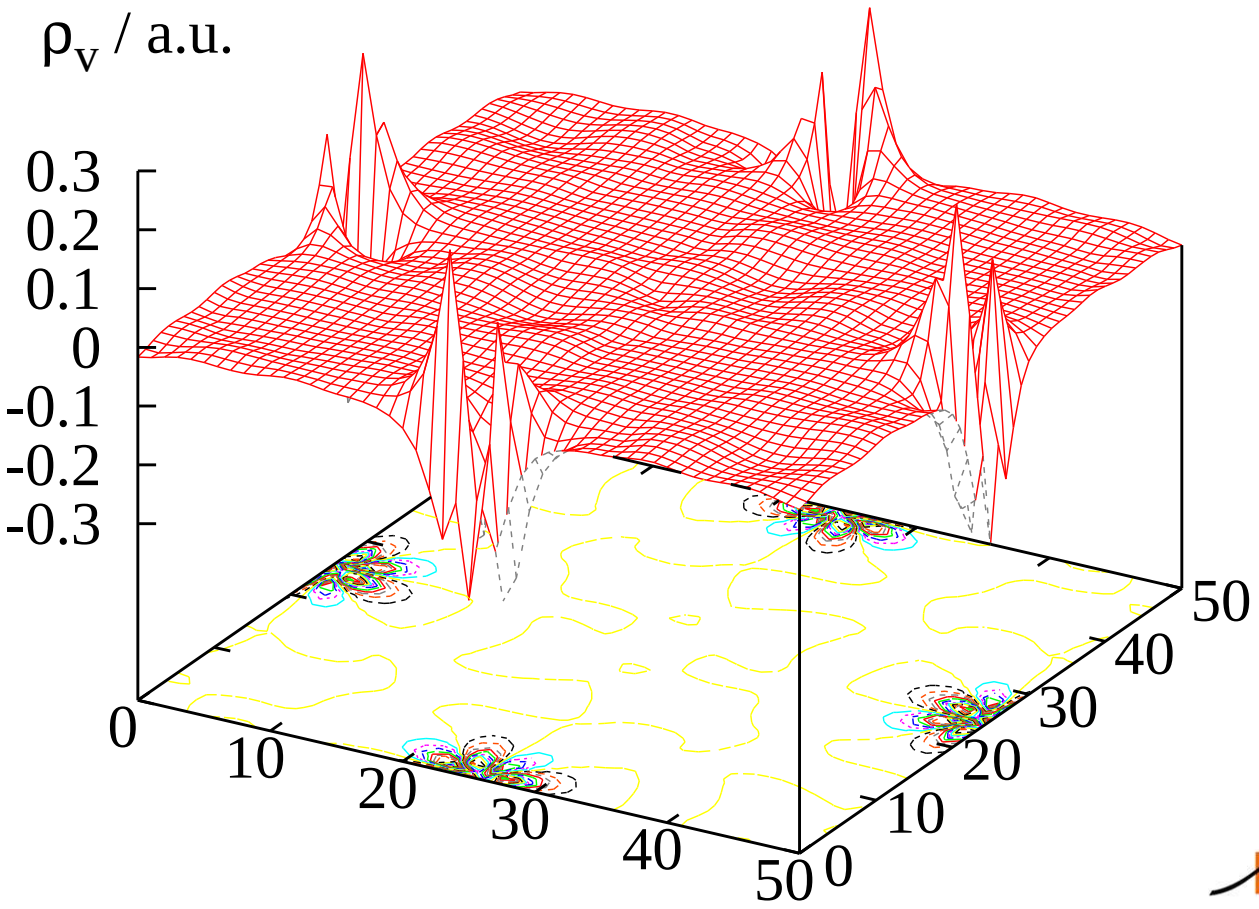
Running the Plot Programs V

Valence Electron Density: plrho.x/plrho.run



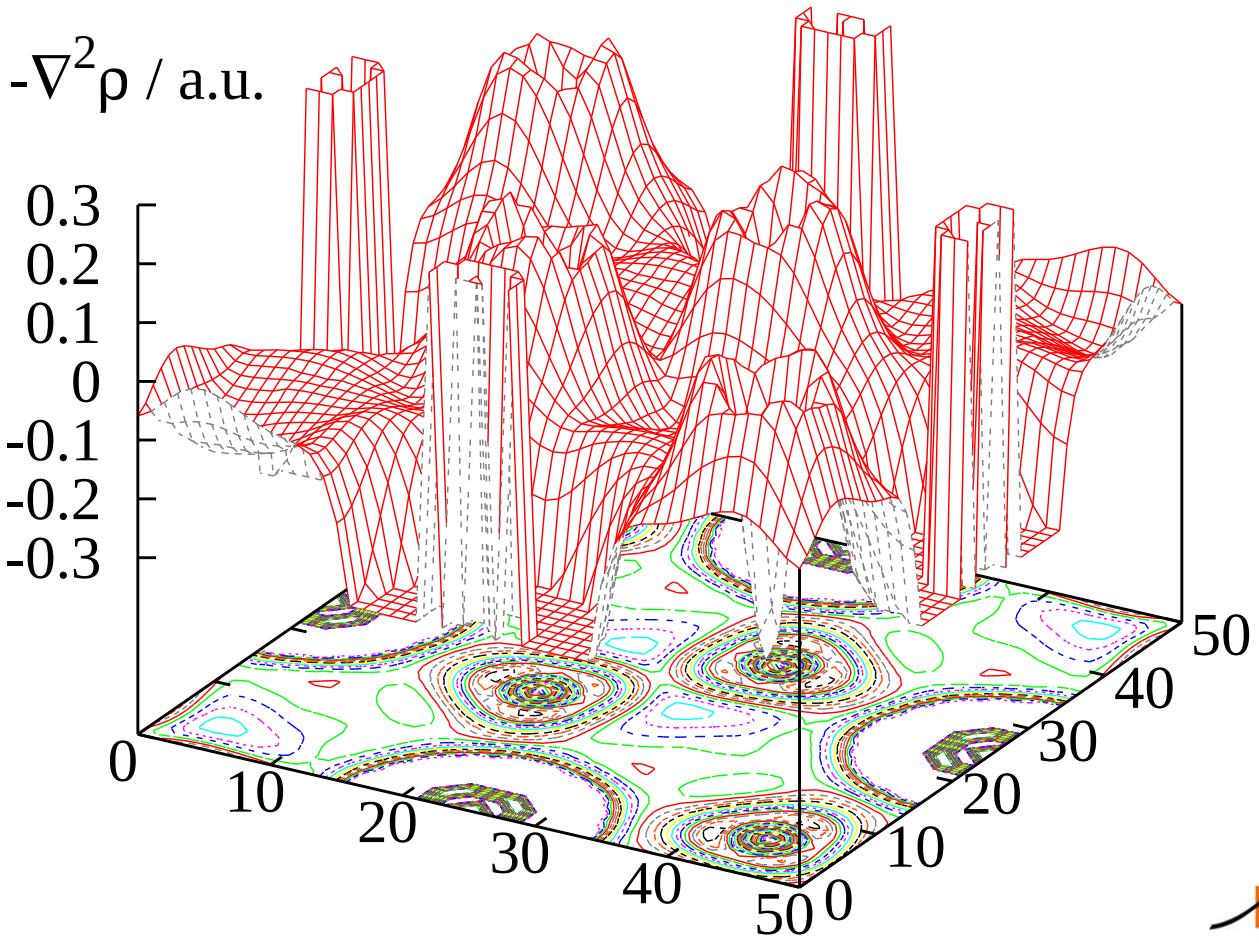
Running the Plot Programs VI

Difference Valence Electron Density: plrho.x/plrho.run



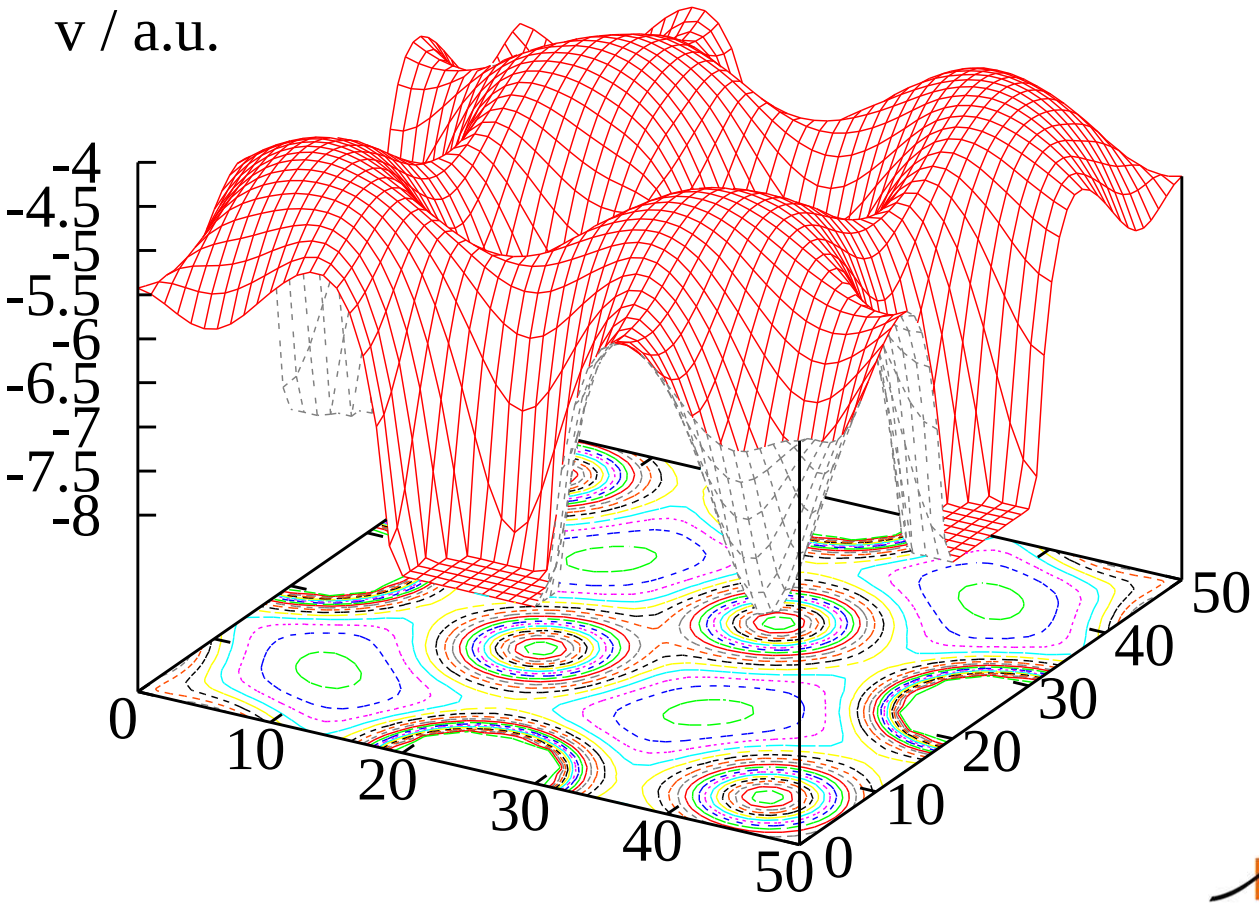
Running the Plot Programs VII

Laplacian of Electron Density: plrho.x/plrho.run



Running the Plot Programs VIII

Potential: plrho.x/plrho.run



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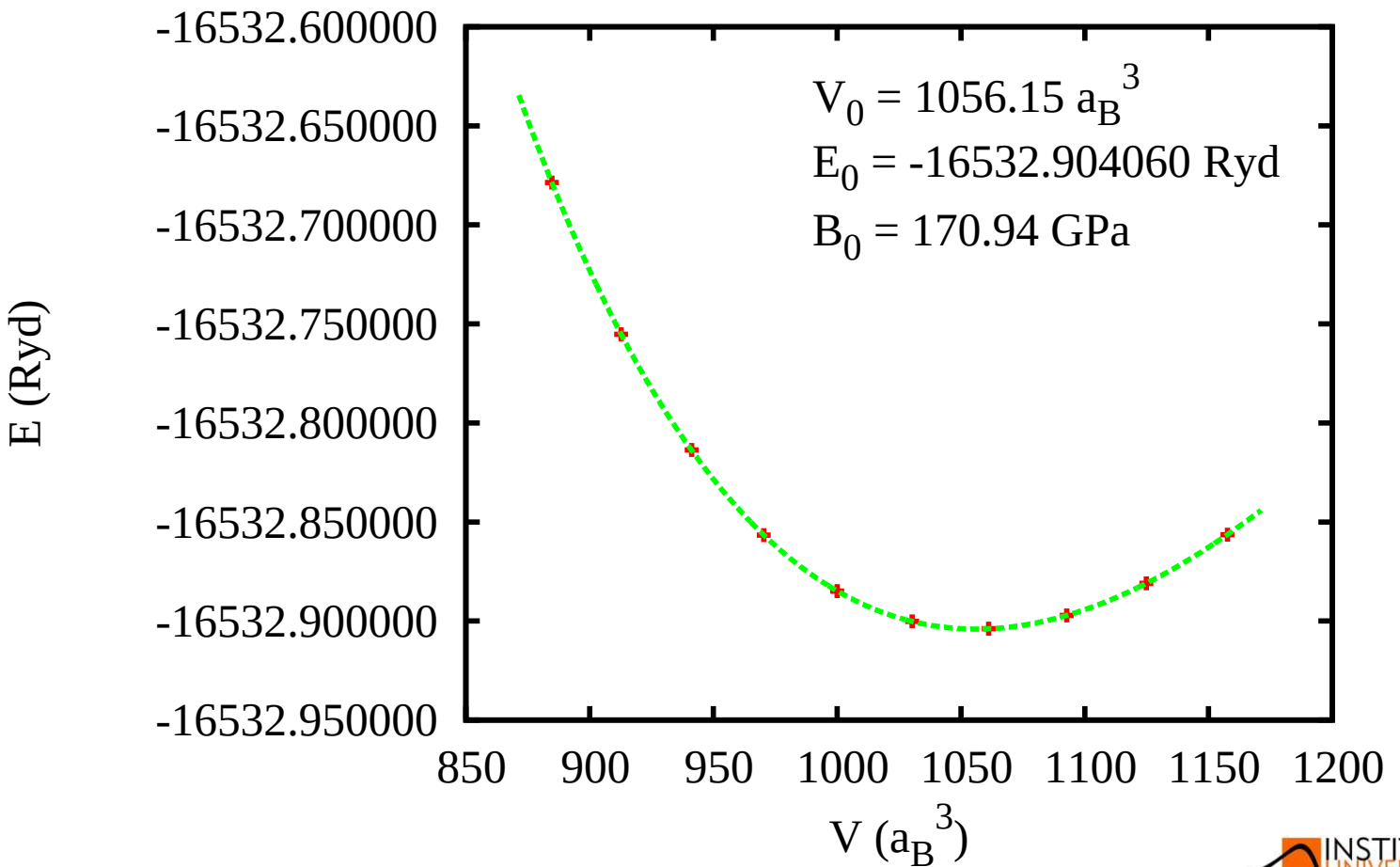
Optimizing the Lattice Constant I

Bulk Modulus: plblk.x/plblk.run



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Optimizing the Lattice Constant II

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
10.23	exp.	Finklea *et al.* '76
10.22	exp.	Will *et al.* '84
10.23	exp.	Stevens *et al.* '91

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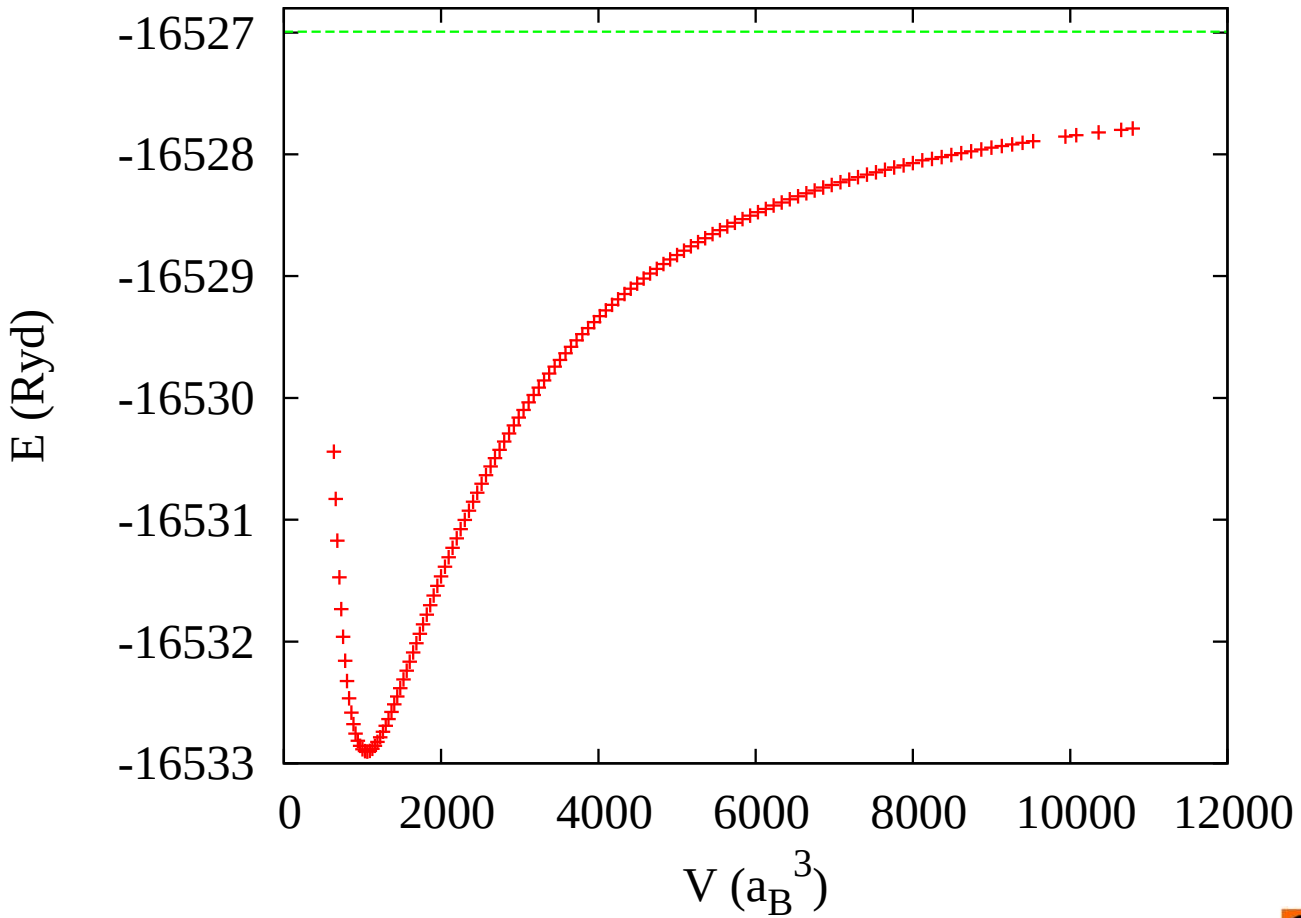
Optimizing the Lattice Constant III

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
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

From Atoms to Solids



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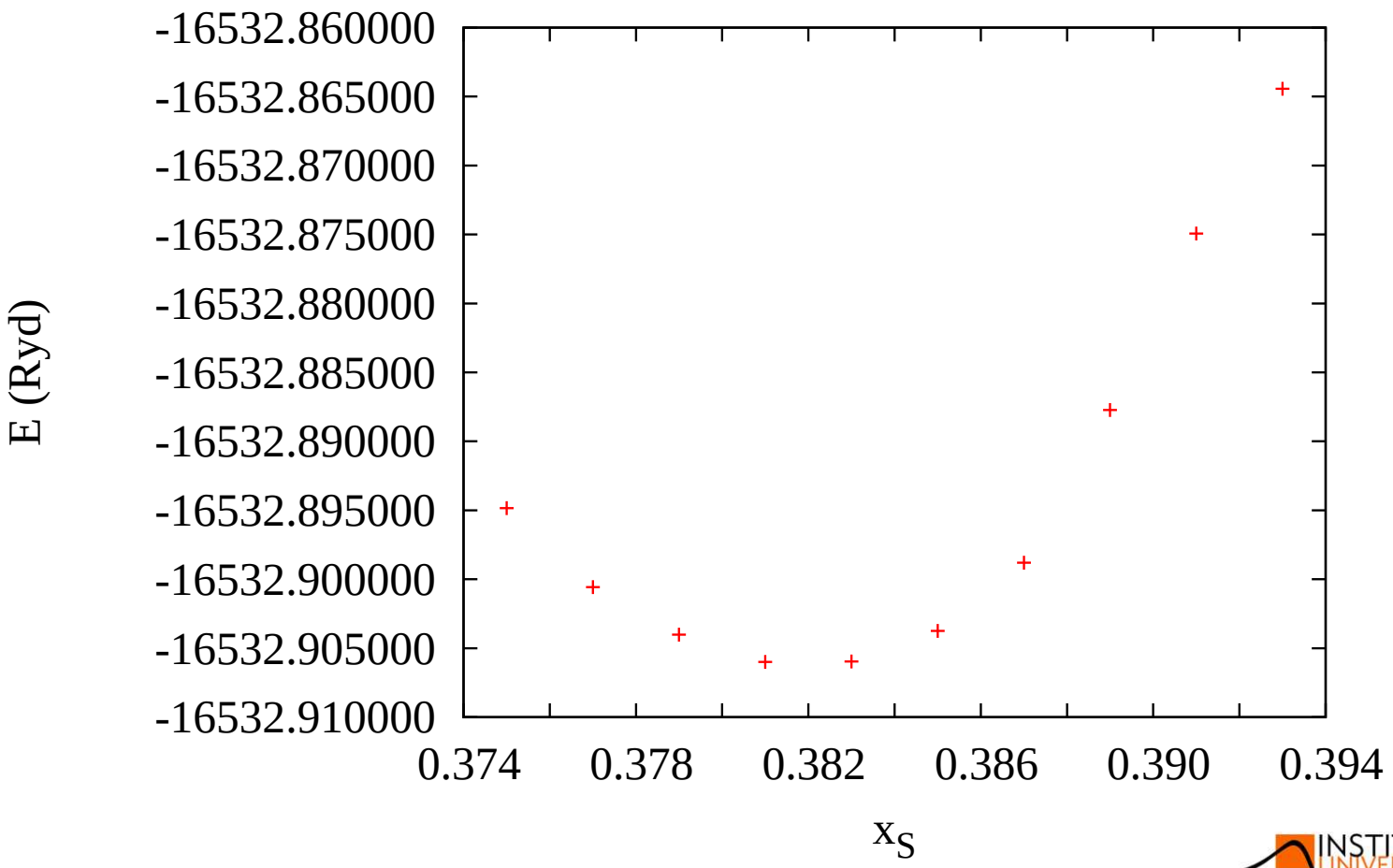
Optimizing the Sulfur Position I

Frozen Phonon Calculation



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Optimizing the Sulfur Position II

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
0.386	exp.	Finklea *et al.* '76
0.386	exp.	Will *et al.* '84
0.385	exp.	Stevens *et al.* '91

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Summary

Sphere Geometry Optimization (SGO)

- sphere packing (mnpac.run)

Complete set of calculations: mnall.x

- self-consistent field calculation
- band structure, DOS, COOP, FS

Analyze results

- check output (use monic or edit)
- use rotated reference frames for plotting weighted band structures and partial DOS

Further Reading I

V. Eyert
The Augmented Spherical Wave Method — An Extended User Guide.

V. Eyert, K.-H. Höck, S. Fiechter, and H. Tributsch
Electronic structure of FeS_2: The crucial role of electron-lattice interaction
Phys. Rev. B **57**, 6350 (1998)

V. Eyert
Basic notions and applications of the augmented spherical wave method
Int. J. Quantum Chem. **77**, 1007 (2000)