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FPLO: Full-Potential Local-Orbital Approach to the Electronic Structure of Solids and Molecules

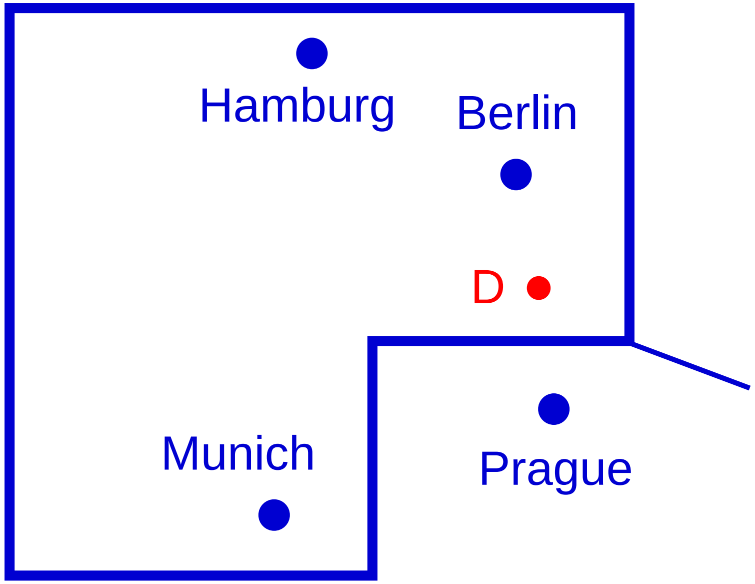
1. Introduction: Why yet another DFT solver?
2. Linear combination of local orbitals (LCLO) equations and core-valence transformation
3. Optimum local basis: strategies
4. Performance and application
5. Summary and licence

Psi-k Training Graduate School
Bristol, March 25 to March 31, 2007

Dresden: founded in 1206; flooded in 2002

500.000 inhabitants, 7.000+ in microelectronics (AMD, Qimonda)

50.000 at University, 3 Max-Planck-Institutes, 3 Leibniz-Institutes, several (10?) Fraunhofer-Institutes



IFW: Solid State and Materials Res.

≈ 400 employees, 65 staff scientists

ITF: Theoretical Solid State Physics

Group Numerical Solid State Physics and Simulations with

8 senior scientists, 1 IT lady,
3 postdocs, 3 PhD students,
4 students, guests

≈ 200 CPUs

1. Introduction: Why yet another DFT solver?

There are nine and sixty ways of constructing tribal lays,
And-every-single-one-of-them-is-right.
(R. Kipling)

Headline to the chapter "Electronic states"
in Ziman's textbook *Principles of the Theory of Solids*

Task:

$$\hat{H}\psi = \epsilon\psi \qquad \text{single particle, e.g. Kohn} - \text{Sham}$$

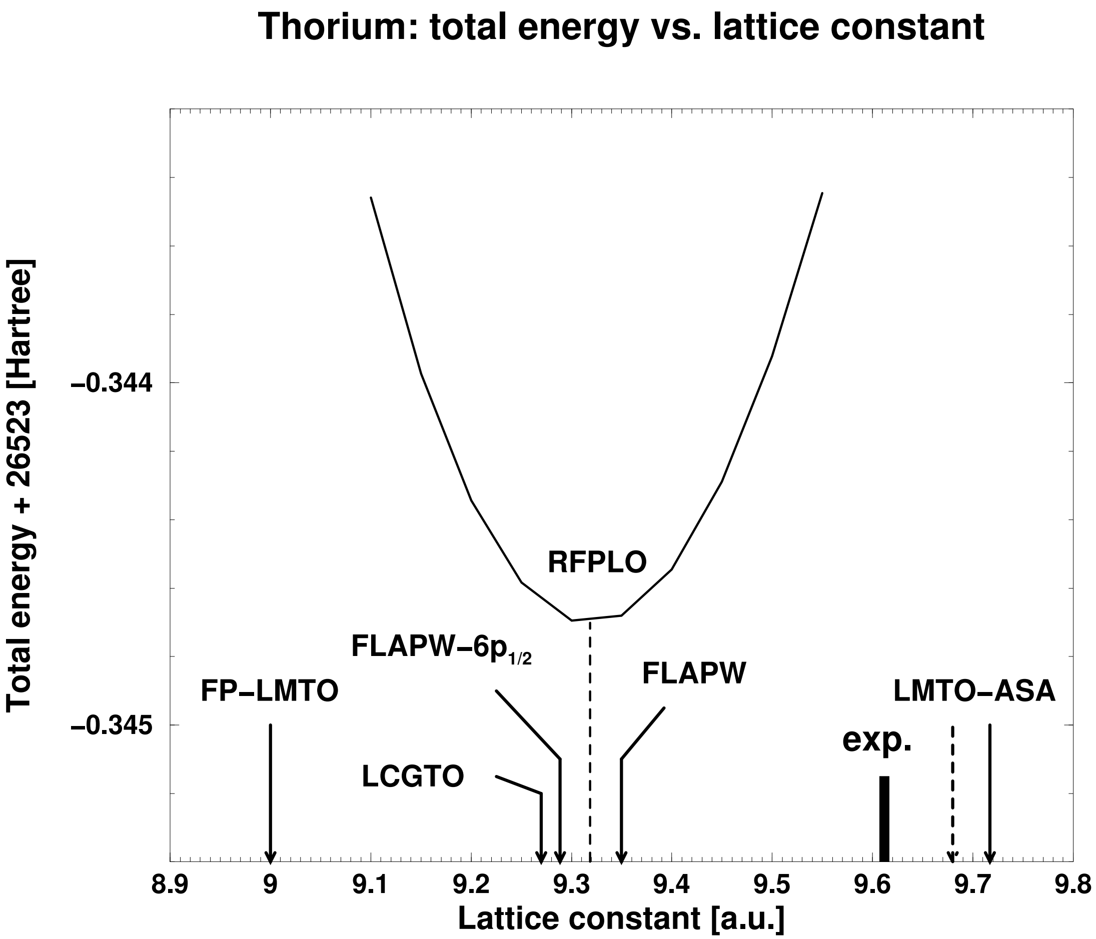
Existing solvers:

FLAPW/APW+lo, (FP-)LMTO, (screened) KKR, PP-PW,
...

1. Introduction: Why yet another DFT solver?

method	advantages	disadvantages
FLAPW/APW+lo	accuracy	only periodic structures, only ordered structures (no CPA)
LMTO, ASW	speed, flexibility	little accuracy, no high-lying states
FP-LMTO	accuracy (?)	only periodic structures
(screened) KKR	flexibility (structures), CPA, transport, high-ϵ states	performance vs. accuracy
PP-PW	simplicity, no Pulay forces	restricted accuracy (heavy atoms), only periodic, ordered structures
FPLO	accuracy, speed, flexibility (0D-3D), CPA	no high-ϵ states

1. Introduction: Why yet another DFT solver?



State of the art, 2001:
Lattice constants obtained by different full-potential methods differ by 3.5% (figure).

2007 (estimate): 0.5%

This corresponds to a considerably improved total energy stability, as

$$V = V_0 \left(1 - \frac{1}{B_0} \frac{d\Delta E^{\rm num}}{dV} + \ldots \right)$$

Only with such a stability we can address the improvement of DFT approximations.

Specified task: Kohn-Sham equations with periodic potential

$$\begin{aligned}
(-\frac{\Delta}{2} + V_{\mathrm{ext}} + V_{\mathrm{Hartree}} + V_{\mathrm{xc}})\psi_{\mathbf{k}n}(\mathbf{r}) &= \psi_{\mathbf{k}n}(\mathbf{r})\epsilon_{\mathbf{k}n} \\
\rho(\mathbf{r}) &= \sum_{\mathbf{k}n}^{\mathrm{occ}} |\psi_{\mathbf{k}n}(\mathbf{r})|^2 \\
V_{\mathrm{Hartree}}(\mathbf{r}) &= \int d^3r' \rho(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'| \\
V_{\mathrm{xc}}(\mathbf{r}) &= \delta E_{\mathrm{xc}}[\rho]/\delta\rho
\end{aligned}$$

“Kohn-Sham-equations”, a set of non-linear integro-differential equations, to be solved by iteration, intuition, and precise numerics.

“Total energy”: $E[V_{\mathrm{ext}}]$, can be evaluated from ρ, V_{Hartree}, V_{xc}, and $\epsilon_{\mathbf{k}n}$.

“LDA”, “GGA”: particular approximations for $E_{\mathrm{xc}}[\rho]$.

“LSDA”: $\rho \longrightarrow \rho_{ss'}$; $V_{\mathrm{xc}} \longrightarrow V_{\mathrm{xc}} + \mathbf{B}_{\mathrm{xc}}\,\hat{\sigma}$.

2. LCLO equations and core-valence transformation

Focus now on the solution of $\hat{H}\psi = \epsilon\psi$.

Blochs ansatz for his states $\psi_{\mathbf{k}n}(\mathbf{r})$,

$$\psi_{\mathbf{k}n}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}\mathbf{s}L} C_{L\mathbf{s},\mathbf{k}n}\ \phi_{\mathbf{s}L}(\mathbf{r} - \mathbf{R} - \mathbf{s})\ e^{i\mathbf{k}(\mathbf{R}+\mathbf{s})}\ .$$

Basis states $\phi_{\mathbf{s}L} = \langle \hat{\mathbf{r}} | \mathbf{R}\mathbf{s}L \rangle$: local overlapping orbitals at sites s in the cell at $\mathbf{R}$

Quantum numbers: $L = \{\nu, l, m\}$

Secular equation for a nonorthogonal basis:

$$\sum_{\mathbf{R}\mathbf{s}L} \hat{H}\ |\mathbf{R}\mathbf{s}L\rangle\ e^{i\mathbf{k}(\mathbf{R}+\mathbf{s})}\ C_{L\mathbf{s},\mathbf{k}n} = \sum_{\mathbf{R}\mathbf{s}L} |\mathbf{R}\mathbf{s}L\rangle\ e^{i\mathbf{k}(\mathbf{R}+\mathbf{s})}\ C_{L\mathbf{s},\mathbf{k}n}\ \epsilon$$

2. LCLO equations and core-valence transformation

Solution of the secular equation:

$$\begin{aligned}
\sum_{\mathbf{R}\mathbf{s}L} \hat{H}\,|\mathbf{R}\mathbf{s}L\rangle\; e^{i\mathbf{k}(\mathbf{R}+\mathbf{s})}\; C_{L\mathbf{s},\mathbf{k}n} &= \sum_{\mathbf{R}\mathbf{s}L} |\mathbf{R}\mathbf{s}L\rangle\; e^{i\mathbf{k}(\mathbf{R}+\mathbf{s})}\; C_{L\mathbf{s},\mathbf{k}n}\;\epsilon \\
\sum_{\mathbf{R}\mathbf{s}L} \langle \mathbf{0}\mathbf{s}'L'|\hat{H}|\mathbf{R}\mathbf{s}L\rangle\; e^{i\mathbf{k}(\mathbf{R}+\mathbf{s}-\mathbf{s}')}\; C_{L\mathbf{s},\mathbf{k}n} &= \sum_{\mathbf{R}\mathbf{s}L} \langle \mathbf{0}\mathbf{s}'L'|\mathbf{R}\mathbf{s}L\rangle\; e^{i\mathbf{k}(\mathbf{R}+\mathbf{s}-\mathbf{s}')}\; C_{L\mathbf{s},\mathbf{k}n}\;\epsilon
\end{aligned}$$

This yields the matrix eigenvalue problem

$$HC = SC\epsilon$$

with

$$\begin{aligned}
H_{\mathbf{s}'L',\mathbf{s}L} &= \sum_{\mathbf{R}} \langle \mathbf{0}\mathbf{s}'L'|\hat{H}|\mathbf{R}\mathbf{s}L\rangle\; e^{i\mathbf{k}(\mathbf{R}+\mathbf{s}-\mathbf{s}')}, \\
S_{\mathbf{s}'L',\mathbf{s}L} &= \sum_{\mathbf{R}} \langle \mathbf{0}\mathbf{s}'L'|\mathbf{R}\mathbf{s}L\rangle\; e^{i\mathbf{k}(\mathbf{R}+\mathbf{s}-\mathbf{s}')}.
\end{aligned}$$

2. LCLO equations and core-valence transformation

To reduce the rank of the matrices, basis states are divided into the valence states $\phi_{\mathbf{s}L_v}$ and the core states $\phi_{\mathbf{s}L_c}$. The latter are defined by

$$\langle \mathbf{R}'\mathbf{s}'L'_c|\mathbf{R}\mathbf{s}L_c\rangle = \delta_{cc'}\delta_{\mathbf{R}\mathbf{R}'}\delta_{\mathbf{s}\mathbf{s}'}$$

and can be removed from the basis by an exact transformation (A. Ernst, PhD thesis, TU Dresden, 1997). Let

$$S = \begin{pmatrix} 1 & S_{cv} \\ S_{vc} & S_{vv} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ S_{vc} & S^L_{vv} \end{pmatrix} \begin{pmatrix} 1 & S_{cv} \\ 0 & S^R_{vv} \end{pmatrix} = S^L S^R,$$

$$S^L_{vv} S^R_{vv} = S_{vv} - S_{vc}S_{cv} \; .$$

By definition of the core states,

$$H = \begin{pmatrix} \epsilon_c 1 & \epsilon_c S_{cv} \\ S_{vc}\epsilon_c & H_{vv} \end{pmatrix}, \quad \epsilon_c = \mathrm{diag}(\cdots, \epsilon_{\mathbf{s}L_c}, \cdots).$$

2. LCLO equations and core-valence transformation

Re-writing the secular equation,

$$(S^L)^{-1}H(S^R)^{-1}(S^RC) = (S^RC)\ \epsilon$$

leads to the reduced problem

$$\tilde{H}_{vv}\tilde{C}_{vv} = \tilde{C}_{vv}\ \epsilon_v\ ,$$

$$\tilde{H}_{vv} = (S^L_{vv})^{-1}(H_{vv} - S_{vc}H_{cc}S_{cv})(S^R_{vv})^{-1}$$

$$C = \begin{pmatrix} 1 & -S_{cv}(S^R_{vv})^{-1}\tilde{C}_{vv} \\ & \\ 0 & (S^R_{vv})^{-1}\tilde{C}_{vv} \end{pmatrix}\ .$$

This exact transformation allows to keep all electrons in the calculation, while the effort is reduced to the solution of the valence state problem.

Problem: incompatibility of ϕ_ν and ϕ_c in the scalar relativistic approximation.

3. Optimum local basis: strategies to define the $\phi_{\mathbf{s}L}$

The ancestor: LCAO

Linear **C**ombination of **A**tomic **O**rbitals (Bloch, Slater & Koster, Callaway, ...)

The descendants:

Optimized LCAO (Dresden code, H. Eschrig, 1975-2000)

Optimized minimum local basis, implemented in FPLO-2 (2002) ... FPLO-5 (2005)

Adjusted fixed local basis, implemented in DMol (B. Delley, PSI Villingen) and in FPLO-6 (K. Koepernik, IFW Dresden, 2007)

3. Optimum local basis: strategies to define the $\phi_{\mathrm{s}L}$

Solve the Kohn-Sham equations for a spherical atom (ion) and obtain the density:

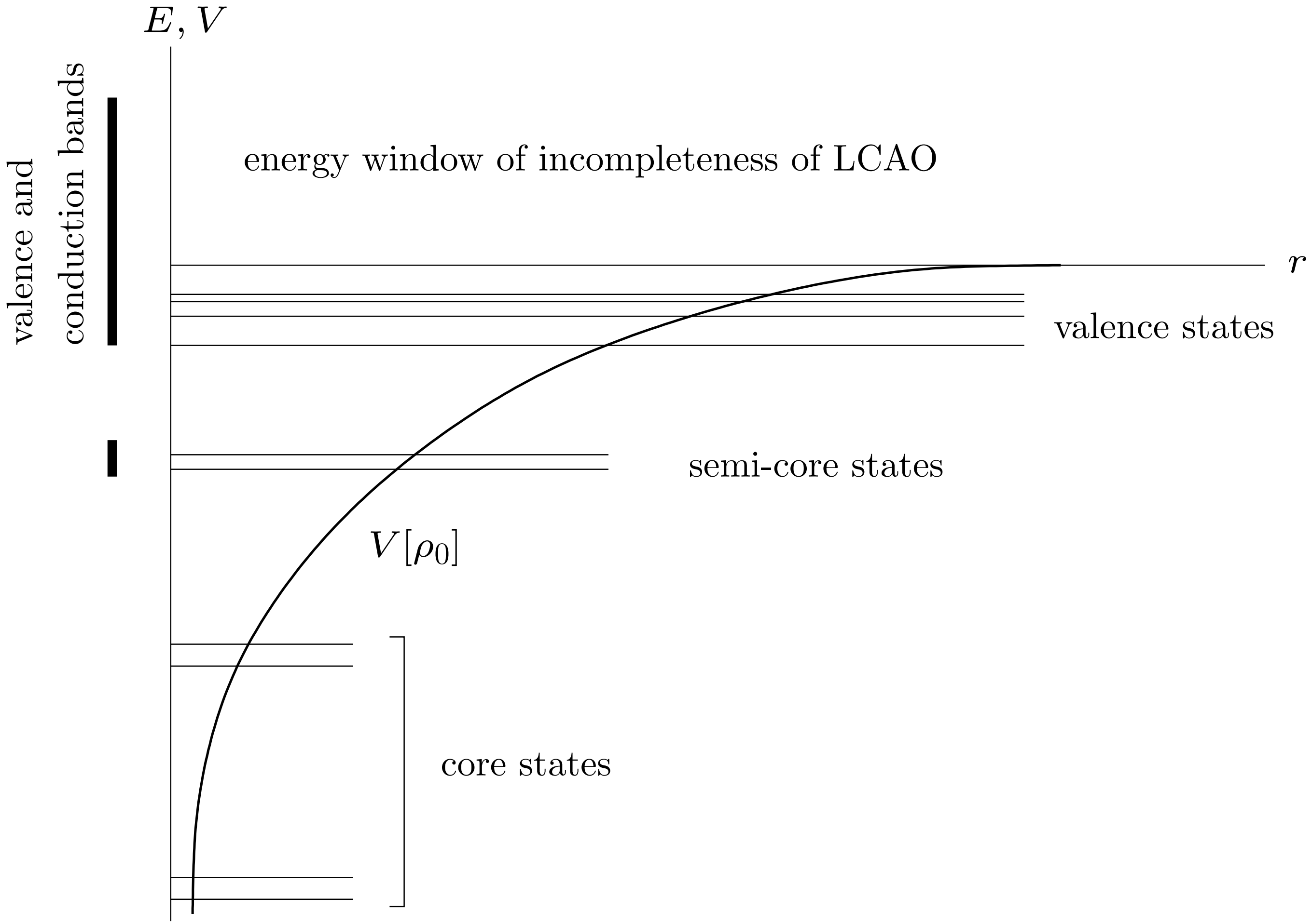
$$\rho_0(r) = \sum_{i=1}^{N} |\phi_i(r)|^2, \qquad \phi_i : \text{ radial orbital functions}$$

$$N = Z : \text{ atom}, \qquad N < Z : \text{ ion.}$$

Spherical atom (ion) Kohn-Sham potential:

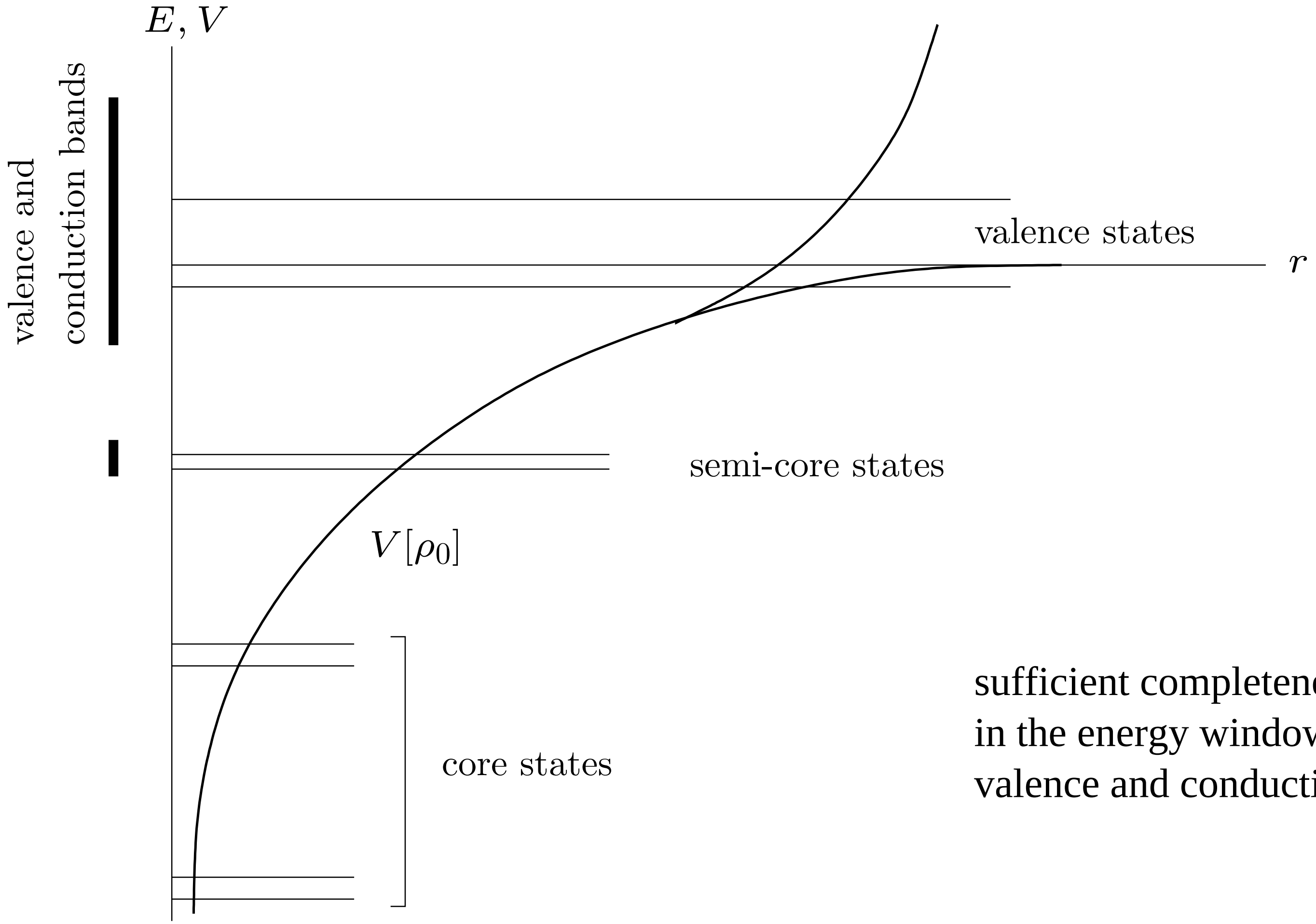
$$\begin{aligned} V[\rho_0] &= V_{\mathrm{ext}} + \quad V_{\mathrm{Hartree}} \quad + V_{\mathrm{xc}} \\ &= -\frac{Z}{r} + \int d^3r' \frac{\rho_0(r')}{|\boldsymbol{r} - \boldsymbol{r}'|} + V_{\mathsf{xc}}(\rho_0(r)) \end{aligned}$$

Linear combination of atomic orbitals (Callaway)



Optimized minimum basis (OLCAO ... FPLO5)

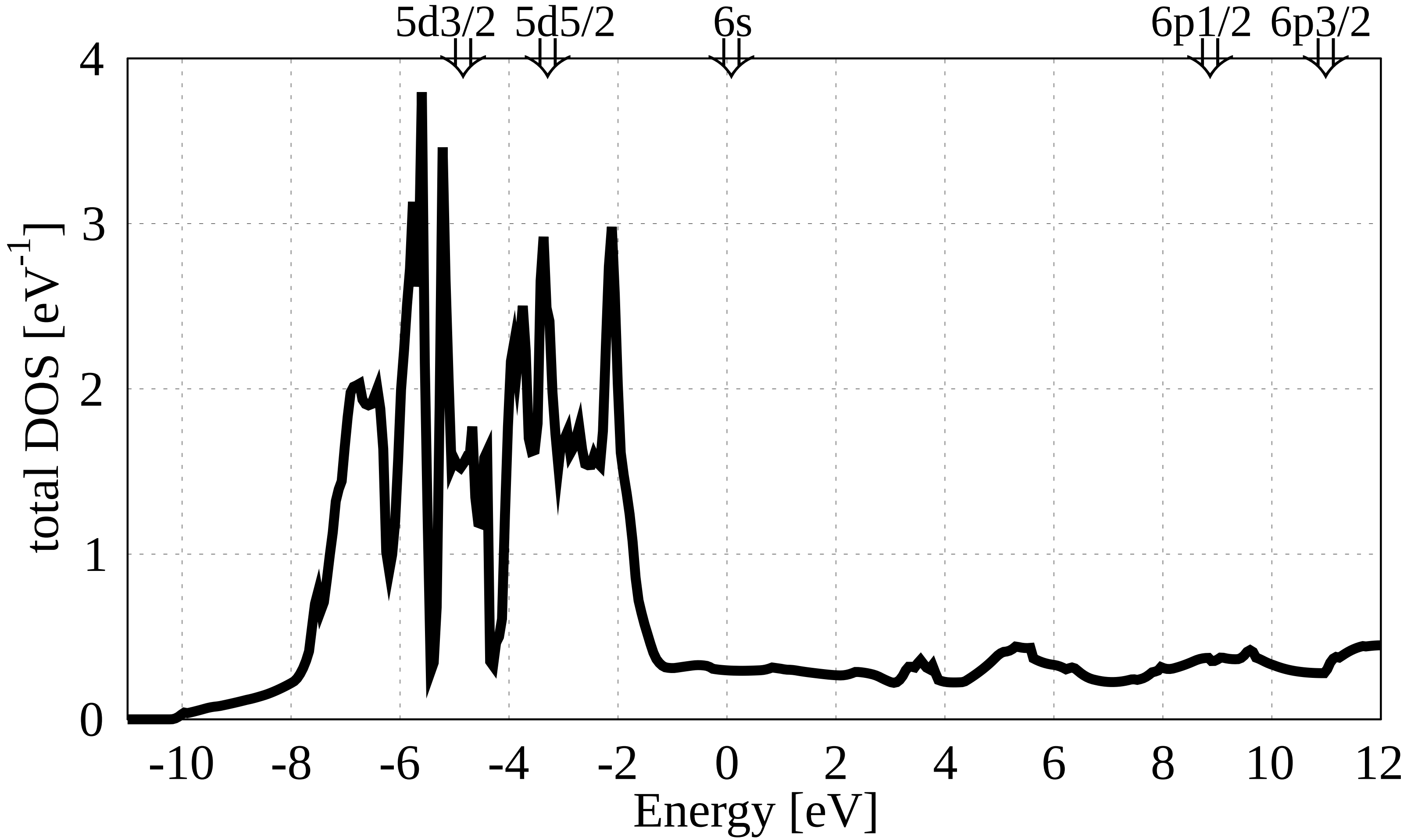
$$V_0(r) = V[\rho_0] + \left(\frac{r}{r_i}\right)^n, \quad r_i: \text{ optimization parameter, } n = 4 \text{ or } 5.$$



sufficient completeness
in the energy window of
valence and conduction bands

Optimized minimum basis, example: Au

Positions of the local state energies:



Optimized minimum local basis

The price of the minimum basis is that the basis orbitals must be well adjusted to the self-consistent potential. Therefore, in a calculation for a solid the basis must be recalculated in every self-consistency cycle.

The chance of this strategy is that an automatic basis optimization (r_i) can be incorporated into the self-consistency cycle by applying a Hellmann-Feynman type approach. (The total energy is optimized with respect to the (r_i).)

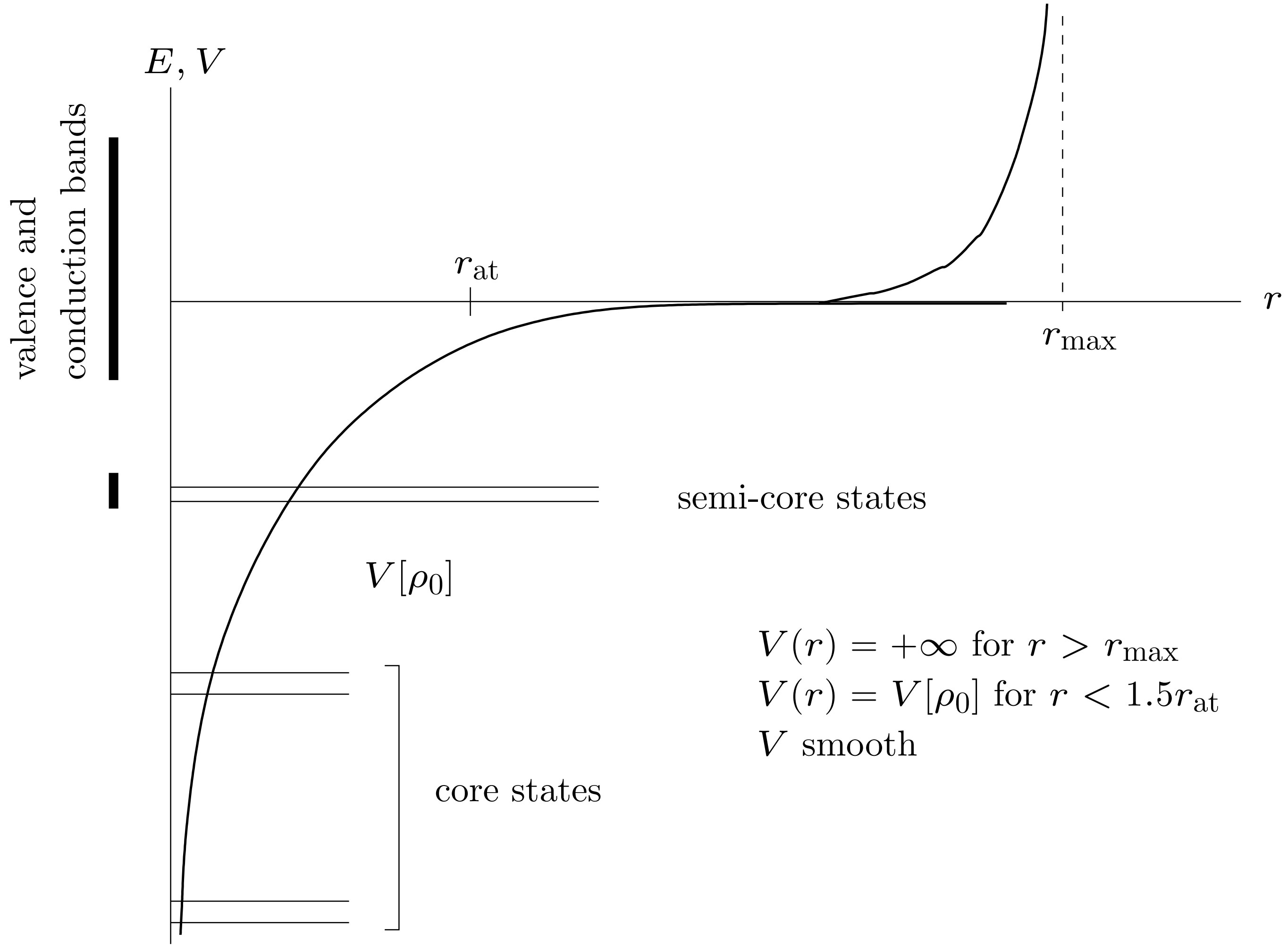
This way, a very high accuracy of total energies and densities is achieved (in most cases comparable with FLAPW-WIEN2k). For the first time ever, two independent all-electron schemes provided the same total energies, $\Delta E/E \approx 10^{-6} \ldots 10^{-7}$, for a number of close-packed structures.

However, the optimization is not suited for the calculations of forces.

Adjusted fixed basis (FPLO6)

$$V_0(r) = V[\rho_0] + \left(\frac{r}{\alpha_0 r_{\mathsf{max}}}\right)^{n_0} + \Theta(r_{\mathsf{max}} - r), \quad \alpha_0 = 0.7\ldots0.8,\ n_0 = 14\ldots18$$

$r_{\mathsf{max}} = \ldots 8 \ldots 12\ \mathsf{a}_0$



$V(r) = +\infty$ for $r > r_{\mathrm{max}}$
$V(r) = V[\rho_0]$ for $r < 1.5 r_{\mathrm{at}}$
V smooth

Adjusted fixed basis (FPLO6)

(Construction approved in the package DMol; courtesy of Bernhard Delley)

Self-consistent calculation of neutral quasi-atomic states and potential:

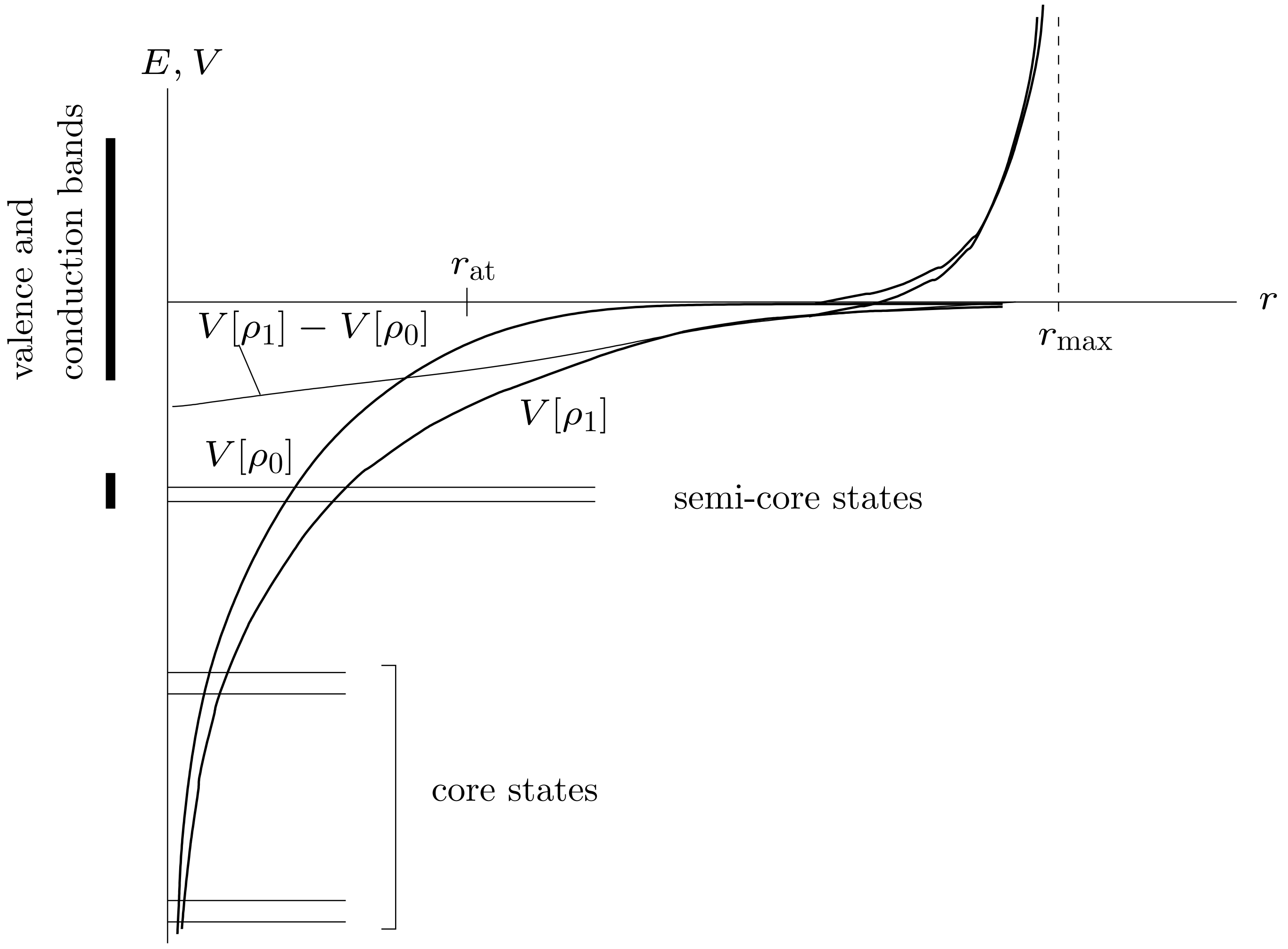
$$\phi_i, \qquad \rho_0 = \sum_{i=1}^{Z} |\phi_i|^2, \qquad V_0(r) = V[\rho_0] + \left(\frac{r}{\alpha_0 r_{\text{max}}}\right)^{n_0} + \Theta(r_{\text{max}} - r)$$

Then, an ionic potential is constructed with $N = Z - Q$, $Q = 0 \ldots 6 \leq Z$,

$$\rho_1 = \sum_{i=1}^{N} |\phi_i|^2, \qquad V_1(r) = V[\rho_1] + \left(\frac{r}{\alpha_1 r_{\text{max}}}\right)^{n_1} + \Theta(r_{\text{max}} - r)$$

α_1 and n_1 may be chosen slightly smaller than α_0 and n_0.

Adjusted fixed basis (FPLO6)



Adjusted fixed basis (FPLO6)

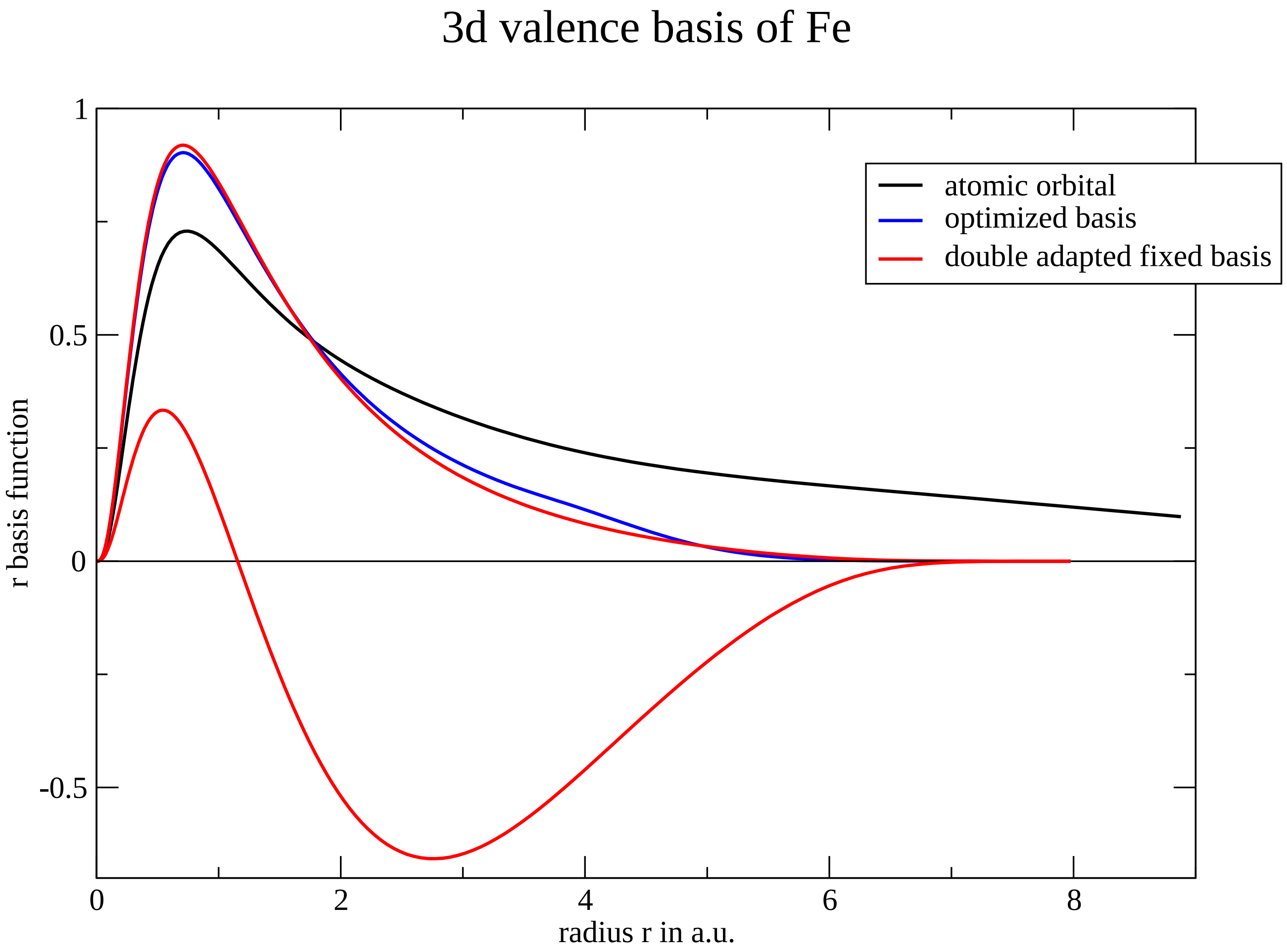
Construction of the fixed basis (numerical on an inhomogeneous radial grid) by minimization of dimer and close-package bonding energies with respect to Q.

$$V_k \rightarrow \hat{H}_k, \qquad \hat{H}_k \phi_i = \phi_i \epsilon_i$$

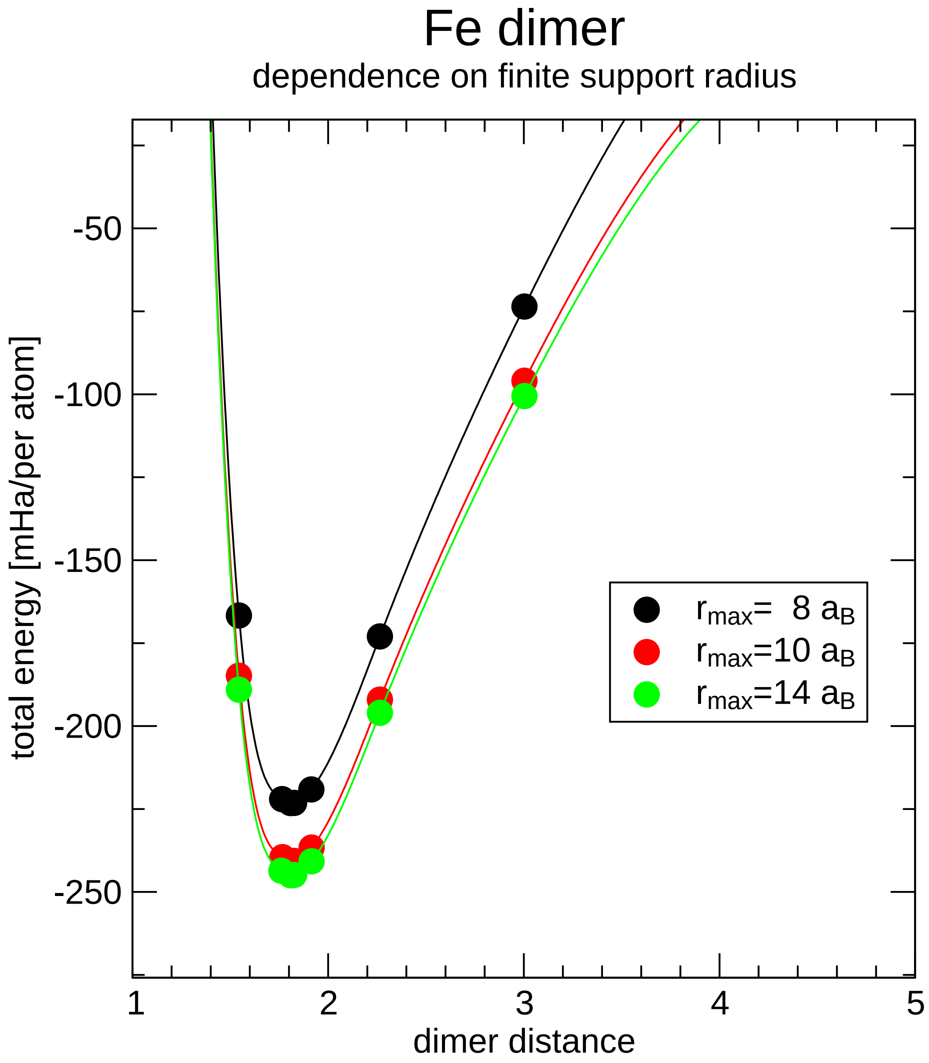
occupied, no overlap	core states:	$\phi_{\nu l}$ from V_0
occupied, overlap	semi-core states:	$\phi_{\nu l}$ from V_0
partly occupied	valence states:	$\phi_{\nu l}$ from V_0
empty	doubled valence state:	$\phi_{\nu+1,l}$ from V_1
empty	polarization states:	$\phi_{\nu l}$ from V_1

	core	semi-core	valence	polarization	rank of matrix
Al:	(1s)	(2s,2p)	(3s,4s,3p,4p)	(3d)	17
Fe:	(1s,2s,2p)	(3s,3p)	(3d,4d,4s,5s)	(4p)	19

Example: Radial basis functions for Fe

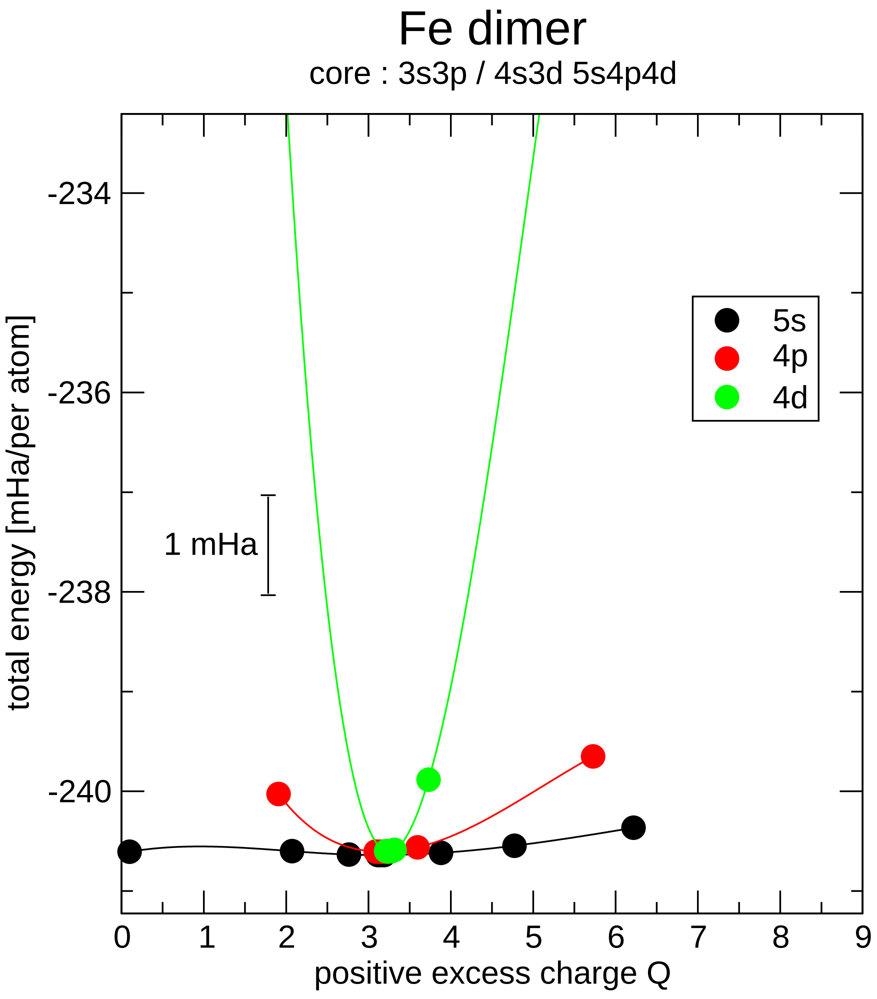


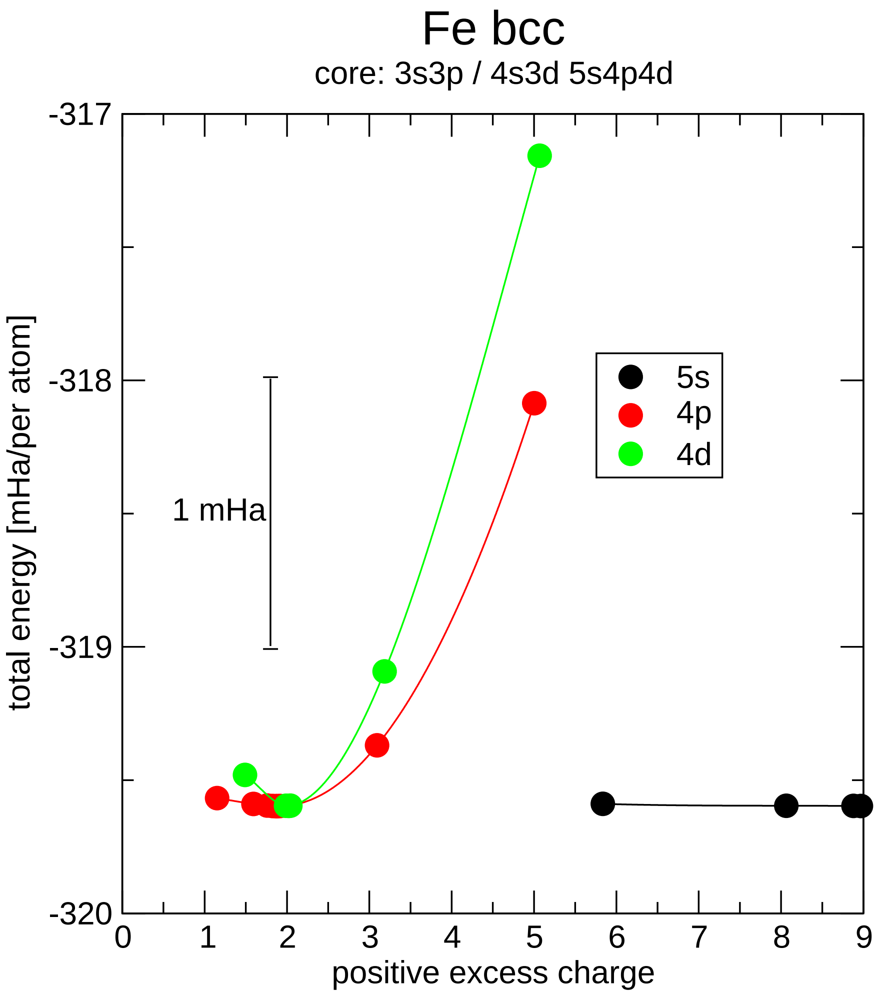
Dependence of total energies on the finite support radius



The total energies are shifted by a constant. Thus, a moderate compression of the atomic states has no influence on forces and on calculated geometries.

Dependence of total energies on the optimization charges





Dimers and close packed systems can be treated with the same basis set.

4. Performance

method	basis functions per atom	remark
PP-PW	> 500	considerable reduction by PAW
LAPW	> 100	
APW+lo	> 50	
FPLO	$10 \ldots 40$	interpretation in chemical terms
LMTO	$9 \ldots 16$	multiple basis for better accuracy

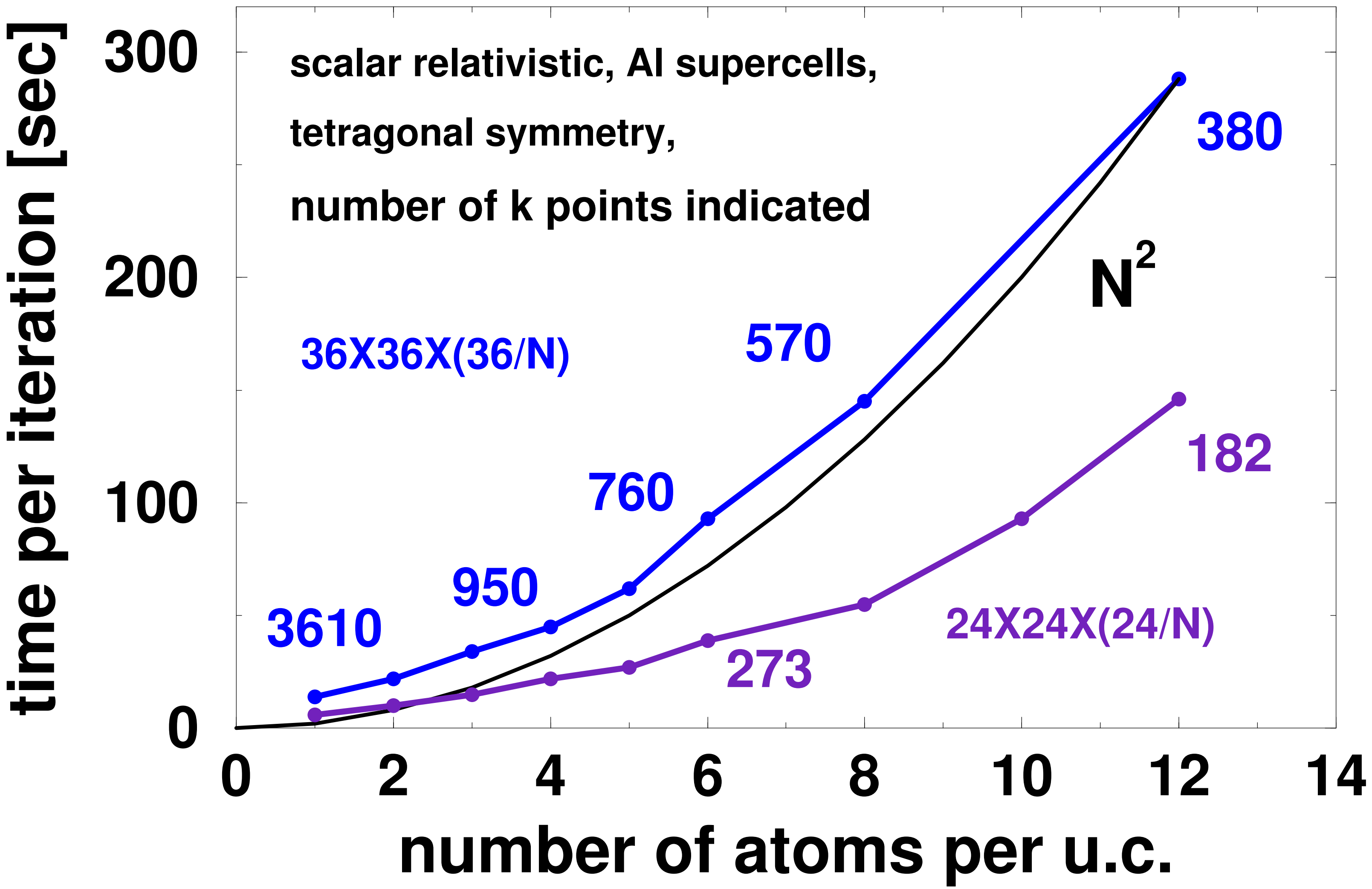
Note that the large-N scaling is with the third power of the matrix rank.

FPLO: no parallelization, except on shell level.

Performance check was carried out at my 5 years old laptop in the train from London to Bristol.

Performance of FPLO-6

single processor laptop from 2002



4. Performance: why do we need so many k points?

Converge the quantity you wish to calculate with respect to all parameters of the k-space integration.

If you once do this, you will avoid smearing techniques for **metallic** systems forever.

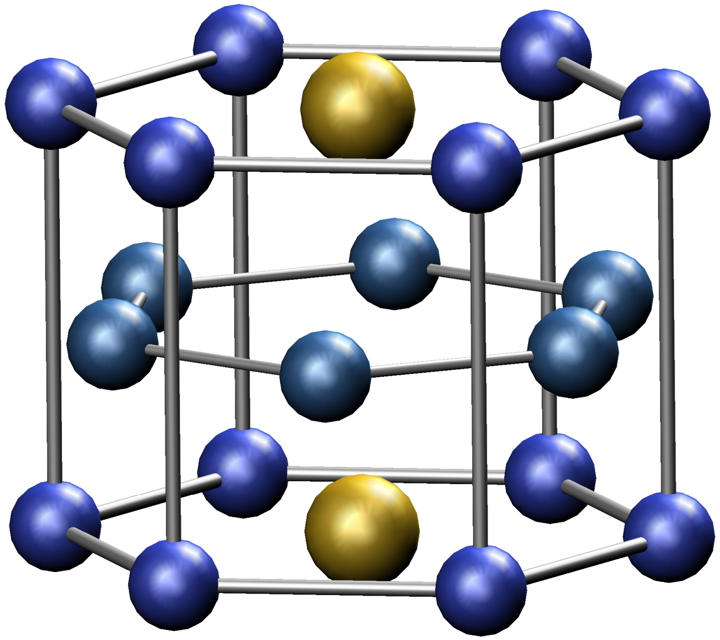
Tetrahedron method: only one convergence parameter.

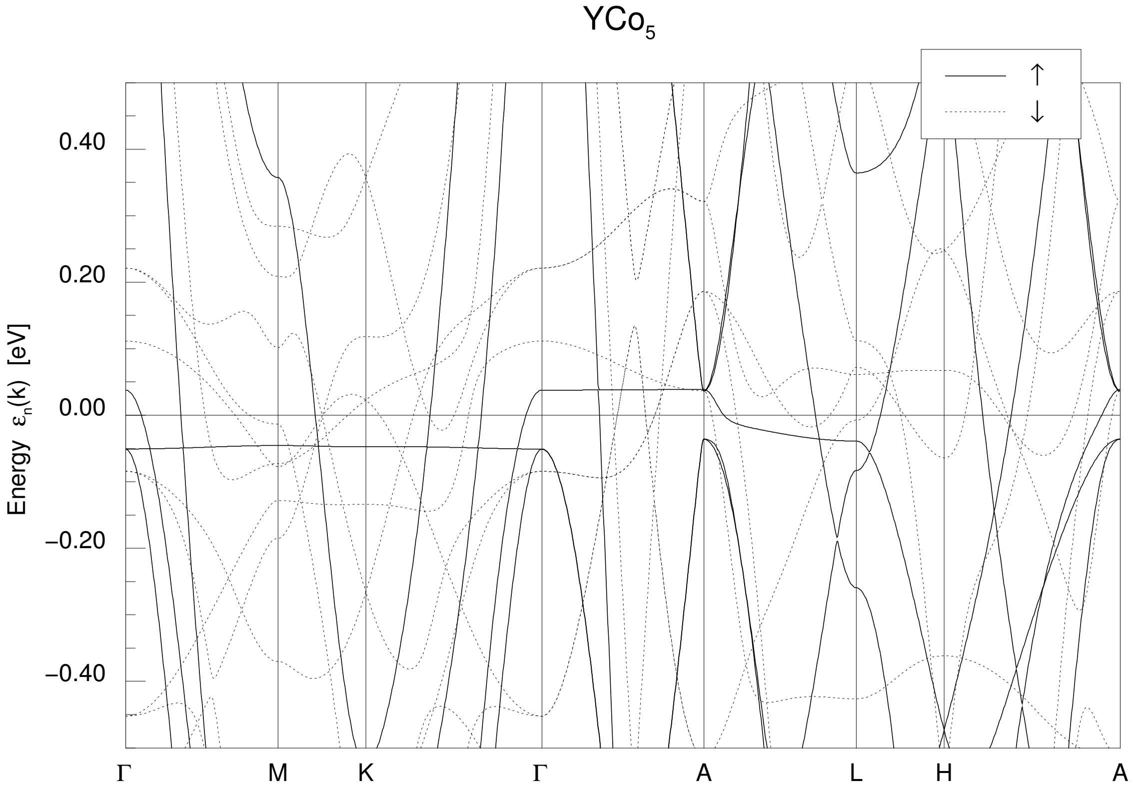
Examples will be given in the hands-on:

The spin moment of Ni changes by 5%, if you enhance the k-mesh density from 12^3 to 24^3 points in the full Brillouin zone.

The DOS of Al changes (at some energies) by 10%, if you enhance the k-mesh density from 24^3 to 48^3 points in the full Brillouin zone.

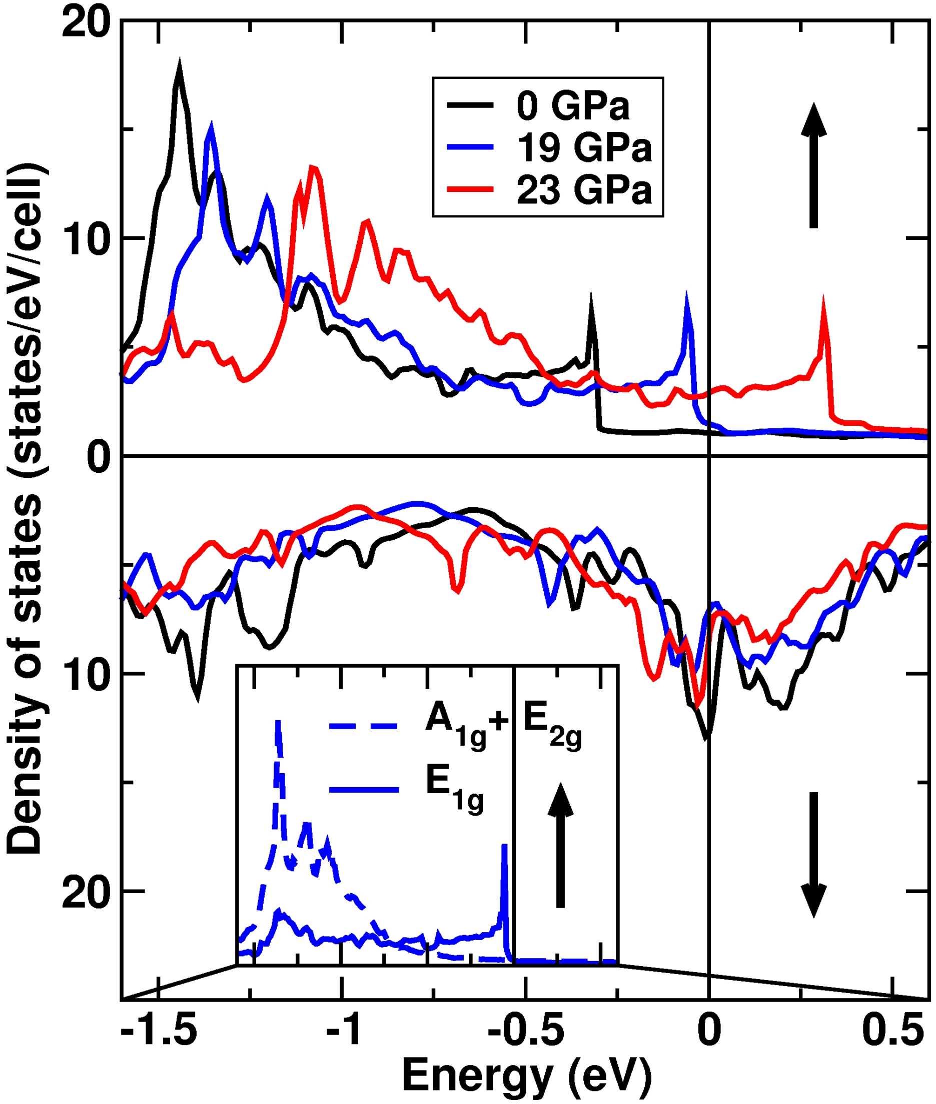
YCo_5 - Balls and Spaghetti





Ferromagnetic ground state

YCo_5 - pressure dependent DOS



A strong 1-D van-Hove-singularity is shifted through E_{F}.

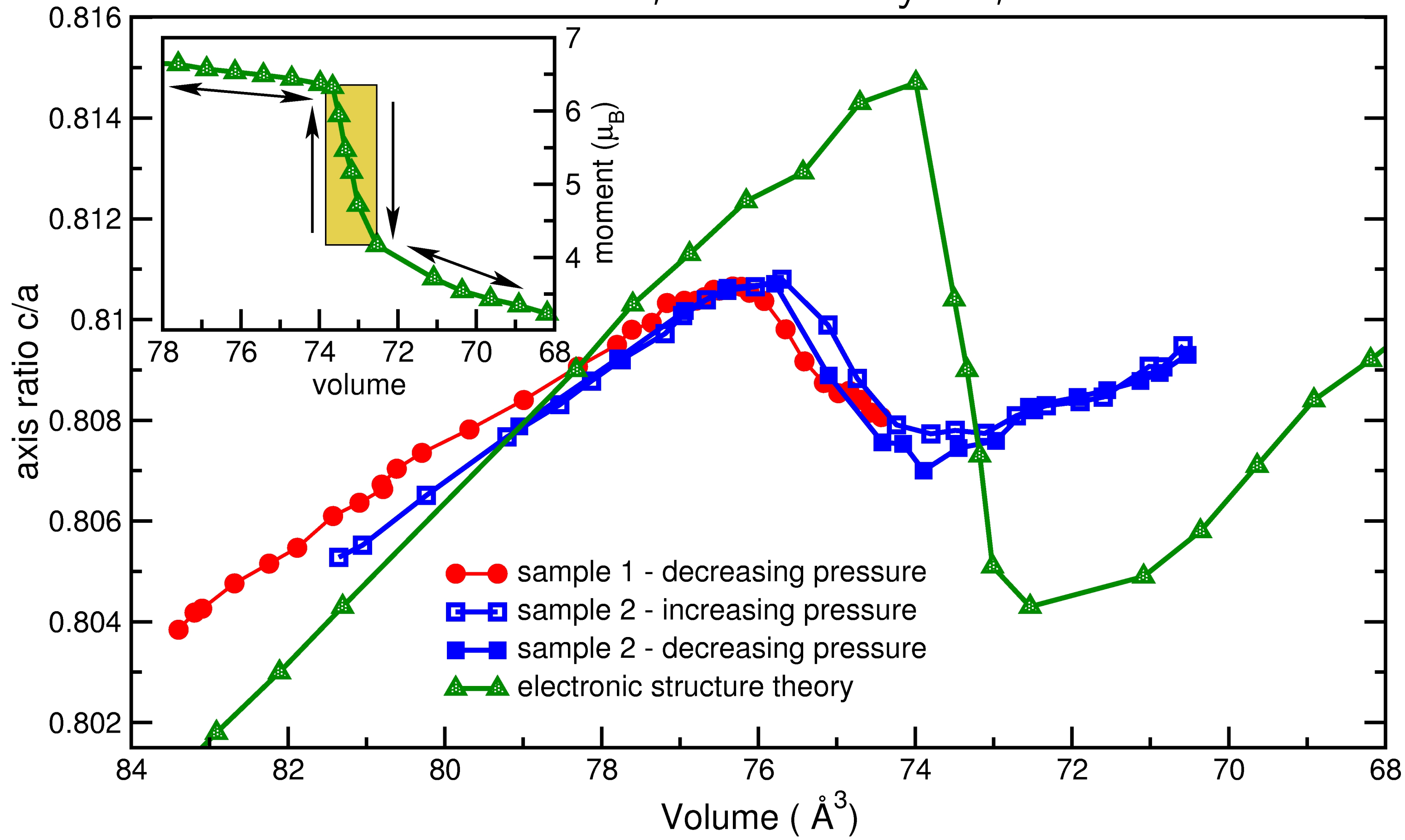
The DOS shift is facilitated by a concomitant reduction of the moment and the exchange split.

The large DOS yields a negative compressibility.

YCo_5 - Isostructural Phase Transition

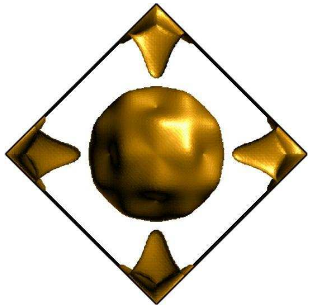
$\Delta V \approx 1.6\%$ at $p_c \approx 20$ GPa

H. Rosner *et al.*, Nature Physics, 2006



5. Summary http://www.FPLO.de/

- numerical atomic-like basis set, all-electron
- efficient: 10 (H) $\ldots 40$ (Actinides) local functions per atom
- relative stability 10^{-6} $^{(\ldots -8)}$ eV/atom, absolute accuracy about 0.1 eV/atom
- open core, LSDA+U (Igor Chaplygin, 2000)
- more features: (CPA; DLM); fat bands; Fermi surfaces and velocities; forces
- 4-component Dirac-Kohn-Sham, LSDA+OP (Ingo Opahle, 2001)
- cluster-version on the same footing as the periodic version
- 0D ... 3D periodicity (slabs and rods in test, Ferenc Tasnadi)
- spin spirals with continuous variation of spin direction (Wenxu Zhang, in prep.)
- handy user interface, good portability, 10^5 lines source code, 20 person years



Advertisements and licence

http://www.FPLO.de/

- annual hands-on workshops (Daresbury, March 25-31, 2007)
- annual user- and developer meetings (La Plata, November 12-17, 2007)

Licence:

- cover fee (400 Euro) for academic use
- source code is provided and can be modified, but not distributed
- citation requested
- mailing list (do not hesitate to read the 50 manual pages!)

Acknowledgments

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