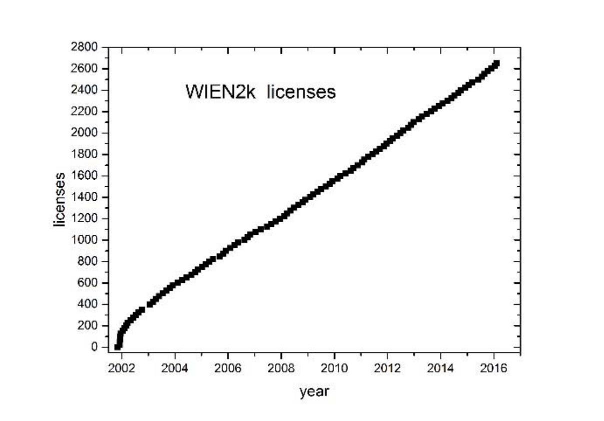
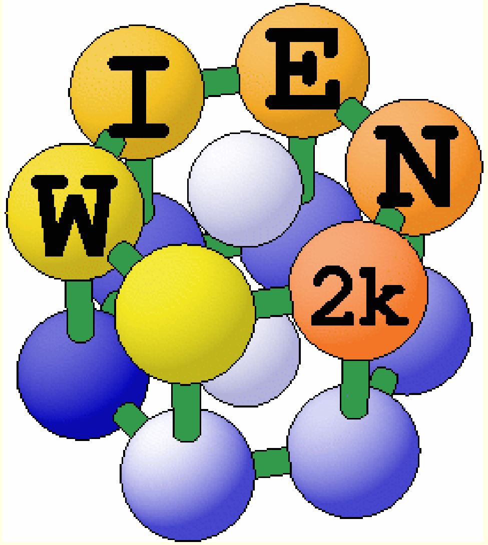
WIEN2k software package





WIEN97: ~500 users
WIEN2k: ~3000 users

**An Augmented Plane Wave Plus Local Orbital
Program for Calculating Crystal Properties**

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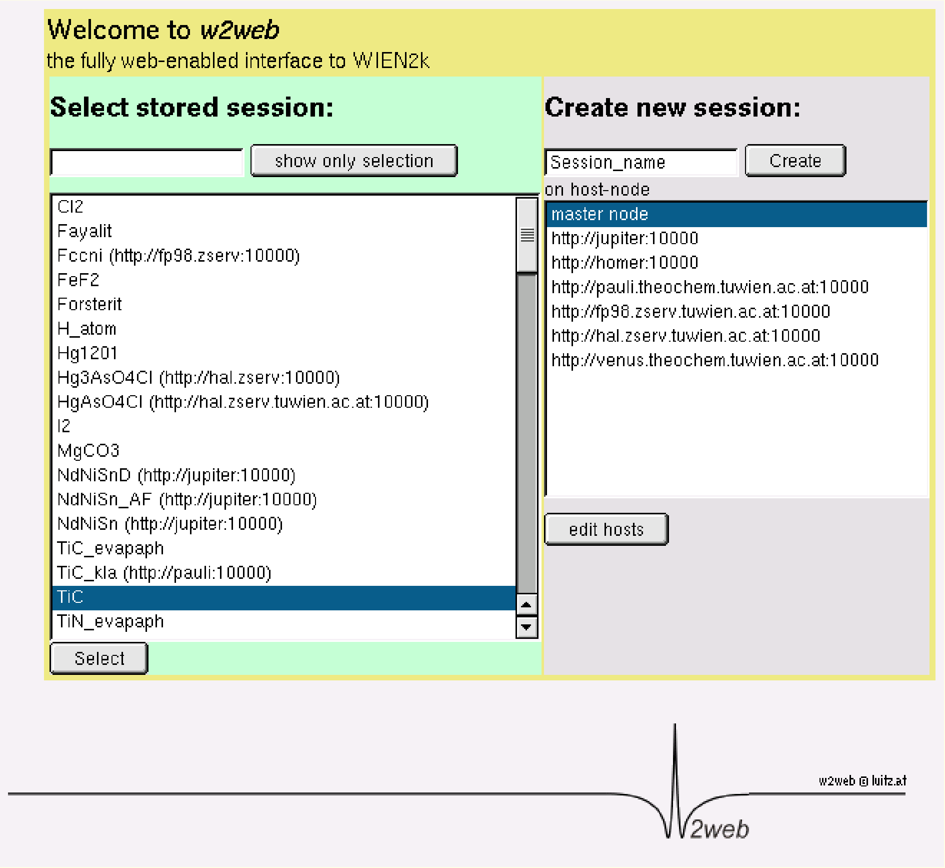
http://www.wien2k.at

General remarks on WIEN2k

- WIEN2k consists of many independent F90 programs, which are linked together via C-shell scripts.
- Each „case“ runs in his own directory   ./case
- The „master input“ is called   case.struct
- Initialize a calculation: init_lapw
- Run scf-cycle: run_lapw (runsp_lapw)
- You can run WIEN2k using any www-browser and the w2web interface, but also at the command line in an xterm.
- Input/output/scf files have endings as the corresponding programs:
  - *case.output1…lapw1; case.in2…lapw2; case.scf0…lapw0*
- Inputs are generated using STRUCTGEN(w2web) and init_lapw

w2web: the web-based GUI of WIEN2k

- Based on www
  - *WIEN2k can be managed remotely via w2web*
- Important steps:
  - *start w2web on all your hosts*
    - login to the desired host (ssh)
    - w2web (at first startup you will be asked for username/password, port-number, (master-)hostname. creates ~/.w2web directory)
  - *use your browser and connect to the (master) host:portnumber*
    - firefox http://fp98.zserv:10000
  - *create a new session on the desired host (or select an old one)*


Welcome to *w2web*

the fully web-enabled interface to WIEN2k

Select stored session:

Cl2
Fayalit
Fccni (http://fp98.zserv:10000)
FeF2
Forsterit
H_atom
Hg1201
Hg3AsO4Cl (http://hal.zserv:10000)
HgAsO4Cl (http://hal.zserv.tuwien.ac.at:10000)
I2
MgCO3
NdNiSnD (http://jupiter:10000)
NdNiSn_AF (http://jupiter:10000)
NdNiSn (http://jupiter:10000)
TiC_evapaph
TiC_kla (http://pauli:10000)
TiC
TiN_evapaph

Create new session:

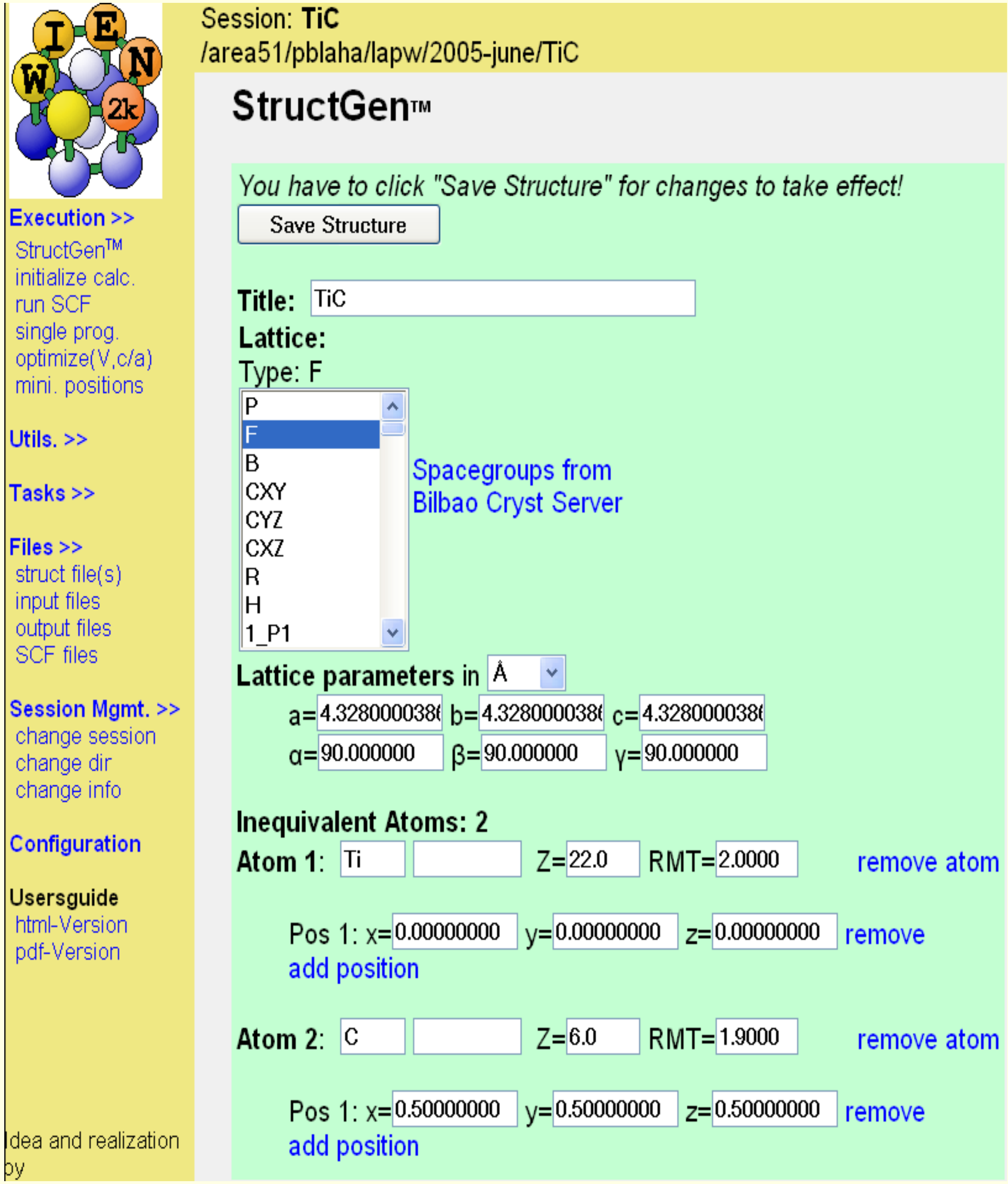
Session_name

on host-node

master node
http://jupiter:10000
http://homer:10000
http://pauli.theochem.tuwien.ac.at:10000
http://fp98.zserv.tuwien.ac.at:10000
http://hal.zserv.tuwien.ac.at:10000
http://venus.theochem.tuwien.ac.at:10000

w2web GUI (graphical user interface)

- Structure generator
  - *spacegroup selection*
  - *import cif or xyz file*
- step by step initialization
  - *symmetry detection*
  - *automatic input generation*
- SCF calculations
  - *Magnetism (spin-polarization)*
  - *Spin-orbit coupling*
  - *Forces (automatic geometry optimization)*
- Guided Tasks
  - *Energy band structure*
  - *DOS*
  - *Electron density*
  - *X-ray spectra*
  - *Optics*



Session: **TiC**
/area51/pblaha/lapw/2005-june/TiC

StructGen™

You have to click "Save Structure" for changes to take effect!

Title: TiC
Lattice:
Type: F

Lattice parameters in Å
a=4.3280000038 b=4.3280000038 c=4.3280000038
α=90.000000 β=90.000000 γ=90.000000

Inequivalent Atoms: 2

Atom 1: Ti Z=22.0 RMT=2.0000
Pos 1: x=0.00000000 y=0.00000000 z=0.00000000

Atom 2: C Z=6.0 RMT=1.9000
Pos 1: x=0.50000000 y=0.50000000 z=0.50000000

Spacegroup $P4_2/mnm$

Structure given by:

spacegroup

lattice parameter

positions of atoms

(basis)

Rutile TiO_2:

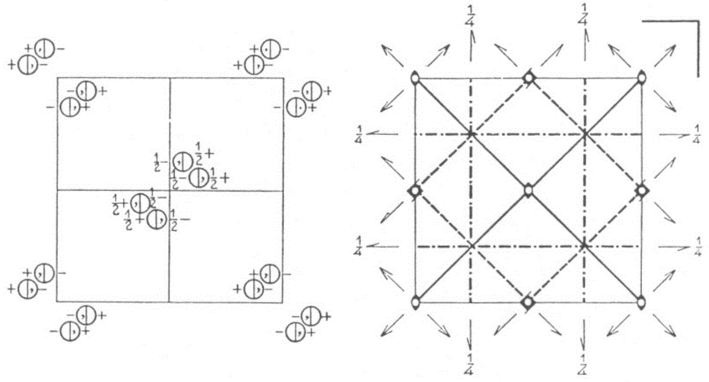
$P4_2/mnm$ (136)

a=8.68, c=5.59 bohr

Ti: (0,0,0)

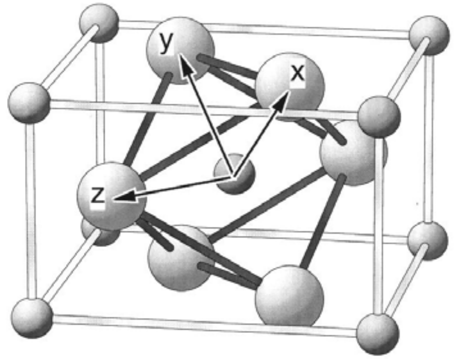
O: (0.304,0.304,0)

$P4_2/mnm$ D^{14}_{4h} No. 136 $P\,4_2/m\;2_1/n\;2/m$ $4/m\,m\,m$ Tetragonal



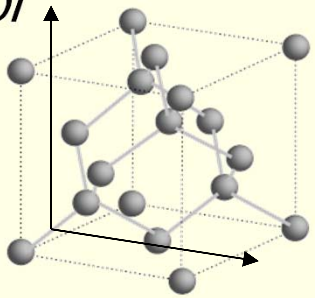
Origin at centre (mmm)

Number of positions, Wyckoff notation, and point symmetry			Co-ordinates of equivalent positions	Conditions limiting possible reflections
				General:
16	k	1	x,y,z; $\bar{x},\bar{y},z$; $\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z$; $\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}+z$; $x,y,\bar{z}$; $\bar{x},\bar{y},\bar{z}$; $\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}-z$; $\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z$; y,x,z; $\bar{y},\bar{x},z$; $\frac{1}{2}+y,\frac{1}{2}-x,\frac{1}{2}+z$; $\frac{1}{2}-y,\frac{1}{2}+x,\frac{1}{2}+z$; $y,x,\bar{z}$; $\bar{y},\bar{x},\bar{z}$; $\frac{1}{2}+y,\frac{1}{2}-x,\frac{1}{2}-z$; $\frac{1}{2}-y,\frac{1}{2}+x,\frac{1}{2}-z$.	hkl: No conditions $hk0$: No conditions $0kl$: $k+l=2n$ hhl: No conditions
				Special: as above, plus
8	j	m	x,x,z; $\bar{x},\bar{x},z$; $\frac{1}{2}+x,\frac{1}{2}-x,\frac{1}{2}+z$; $\frac{1}{2}-x,\frac{1}{2}+x,\frac{1}{2}+z$; $x,x,\bar{z}$; $\bar{x},\bar{x},\bar{z}$; $\frac{1}{2}+x,\frac{1}{2}-x,\frac{1}{2}-z$; $\frac{1}{2}-x,\frac{1}{2}+x,\frac{1}{2}-z$.	no extra conditions
8	i	m	$x,y,0$; $\bar{x},\bar{y},0$; $\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}$; $\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}$; $y,x,0$; $\bar{y},\bar{x},0$; $\frac{1}{2}+y,\frac{1}{2}-x,\frac{1}{2}$; $\frac{1}{2}-y,\frac{1}{2}+x,\frac{1}{2}$.	
8	h	2	$0,\frac{1}{2},z$; $0,\frac{1}{2},\bar{z}$; $0,\frac{1}{2},\frac{1}{2}+z$; $0,\frac{1}{2},\frac{1}{2}-z$; $\frac{1}{2},0,z$; $\frac{1}{2},0,\bar{z}$; $\frac{1}{2},0,\frac{1}{2}+z$; $\frac{1}{2},0,\frac{1}{2}-z$.	hkl: $h+k=2n$; $l=2n$
4	g	mm	$x,\bar{x},0$; $\bar{x},x,0$; $\frac{1}{2}+x,\frac{1}{2}+x,\frac{1}{2}$; $\frac{1}{2}-x,\frac{1}{2}-x,\frac{1}{2}$.	
4	f	mm	$x,x,0$; $\bar{x},\bar{x},0$; $\frac{1}{2}+x,\frac{1}{2}-x,\frac{1}{2}$; $\frac{1}{2}-x,\frac{1}{2}+x,\frac{1}{2}$.	
4	e	mm	$0,0,z$; $0,0,\bar{z}$; $\frac{1}{2},\frac{1}{2},\frac{1}{2}+z$; $\frac{1}{2},\frac{1}{2},\frac{1}{2}-z$.	
4	d	$\bar{4}$	$0,\frac{1}{2},\frac{1}{4}$; $\frac{1}{2},0,\frac{1}{4}$; $0,\frac{1}{2},\frac{3}{4}$; $\frac{1}{2},0,\frac{3}{4}$.	
4	c	$2/m$	$0,\frac{1}{2},0$; $\frac{1}{2},0,0$; $0,\frac{1}{2},\frac{1}{2}$; $\frac{1}{2},0,\frac{1}{2}$.	
2	b	mmm	$0,0,\frac{1}{2}$; $\frac{1}{2},\frac{1}{2},0$.	
2	a	mmm	$0,0,0$; $\frac{1}{2},\frac{1}{2},\frac{1}{2}$.	



Structure generator

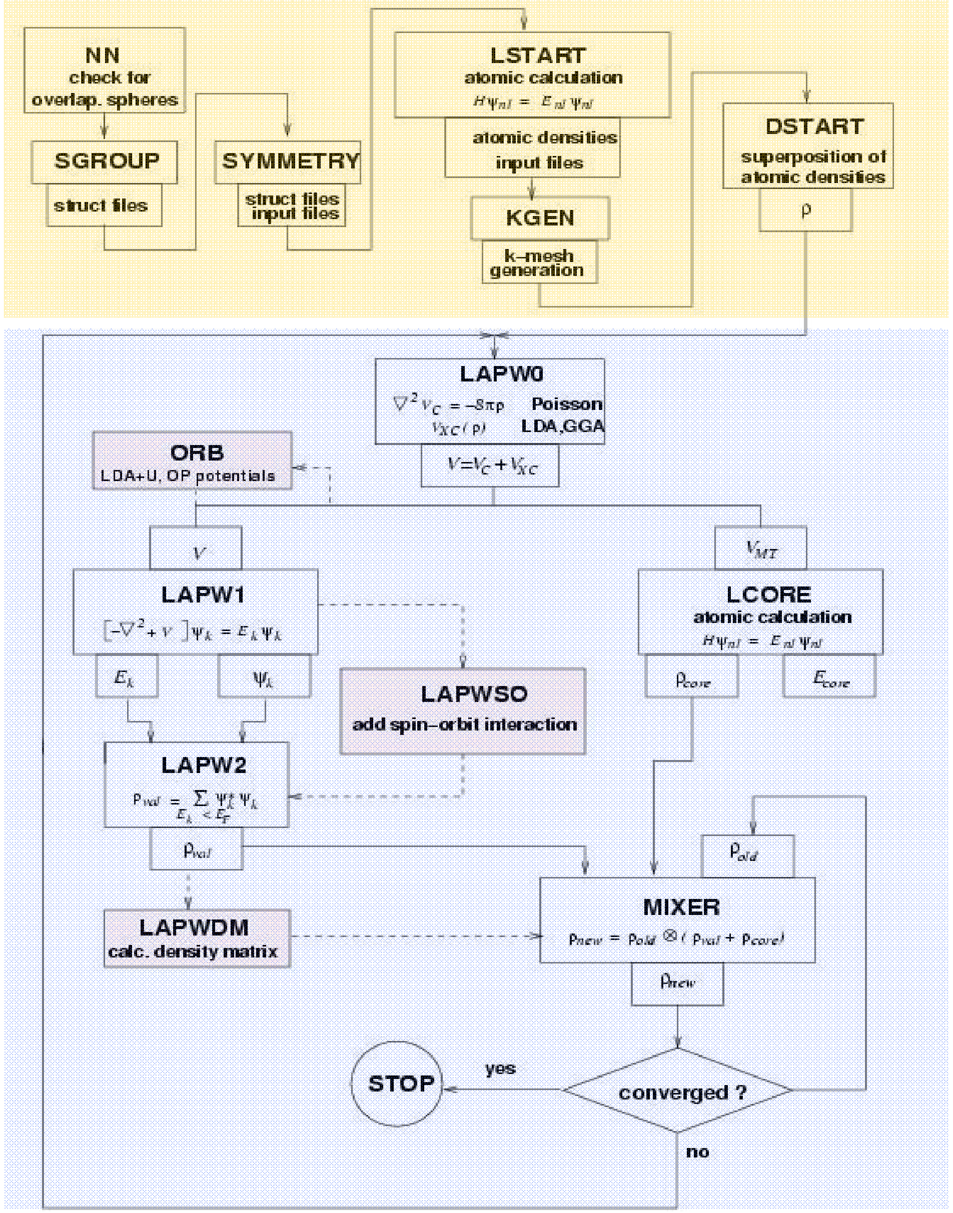
- Specify:
  - *Number of nonequivalent atoms*
  - *lattice type (P, F, B, H, CXY, CXZ, CYZ) or spacegroup symbol*
    - if existing, you must use a SG-setting with inversion symmetry:
      - Si: ±(1/8,1/8,1/8), not (0,0,0)+(1/4,1/4,1/4)!
  - *lattice parameters a,b,c (in Å or bohr)*
  - *name of atoms (Si) and fractional coordinates (position)*
    - as numbers (0.123); fractions (1/3); simple expressions (x-1/2,…)
    - in fcc (bcc) specify just one atom, not the others in (1/2,1/2,0; …)



- „save structure "
  - *updates automatically Z, r0, equivalent positions*
- „set RMT and continue": (specify proper "reduction" of NN-distances)
  - *non-overlapping „as large as possible" (saves time, may require L^{vns}=6(8))*
  - *RMT for sp (d) - elements 10-20 % smaller than for d (f) elements*
  - *largest spheres not more than 50 % larger than smallest sphere*
  - *Exception: H in C-H or O-H bonds: RMT~0.6 bohr (RKMAX~3-4)*
  - *Do not change RMT in a „series" of calculations, RMT equal for same atoms*
- „save structure – save+cleanup"

Program structure of WIEN2k

- init_lapw
  - *step-by-step or batch initialization*
  - *symmetry detection (F, I, C-centering, inversion)*
  - *input generation with recommended defaults*
  - *quality (and computing time) depends on **k-mesh** and **R.Kmax** (determines #PW)*
- run_lapw
  - *scf-cycle*
  - *optional with SO and/or LDA+U*
  - *different convergence criteria (energy, charge, forces)*
- save_lapw tic_gga_100k_rk7_vol0
  - *cp case.struct and clmsum files,*
  - *mv case.scf file*
  - *rm case.broyd* files*


NN
check for overlap. spheres
SGROUP
struct files
SYMMETRY
struct files input files
LSTART
atomic calculation
$H\psi_{nl} = E_{nl}\psi_{nl}$
atomic densities input files
KGEN
k-mesh generation
DSTART
superposition of atomic densities
ρ
LAPW0
$\nabla^2 V_C = -8\pi\rho$ Poisson
$V_{XC}(\rho)$ LDA,GGA
$V=V_C+V_{XC}$
ORB
LDA+U, OP potentials
V
V_{MT}
LAPW1
$[-\nabla^2+V]\psi_k = E_k\psi_k$
E_k
ψ_k
LCORE
atomic calculation
$H\psi_{nl} = E_{nl}\psi_{nl}$
ρ_{core}
E_{core}
LAPWSO
add spin-orbit interaction
LAPW2
$\rho_{val} = \sum_{E_k < E_F} \psi_k^* \psi_k$
ρ_{val}
ρ_{old}
LAPWDM
calc. density matrix
MIXER
$\rho_{new} = \rho_{old} \otimes (\rho_{val} + \rho_{core})$
ρ_{new}
STOP
yes
converged ?
no

RKMAX

- The convergence criterion in APW is the product of R_{MT}.Kmax

$$\Psi = \sum_{K_n}^{KMAX} c_{K_n} \; e^{iK_n r}$$

- http://www.wien2k.at/reg_user/faq/rkmax.html
- medium quality convergence for **smallest** atom:

Rkmax	Element
3.0	H
4.5	Li
5.0	Be, B, Si
5.5	C, P
6.0	N, S
6.5	O, Cl, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Al
7.0	F
7.5	Sc-Cr, Ga-Br, Y-Mo
8.0	Mn-Zn, Ru-Cd, In-I, La, Ce, Hf-Re
8.5	Os-At, Pr-Lu, Ac-Lr

- basis set scales with $RKmax^3$
- cputime scales with $N_{PW}{}^3$

- increasing Rkmax by 10 %

  ⟹ doubles cputime

START with **SMALL** Rkmax (relaxation), **increase / test** later

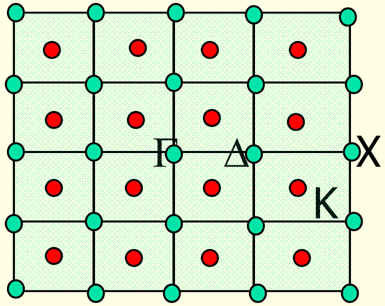
BZ integration, “FERMI”-methods

- Replace the “integral” of the BZ by a finite summation on a mesh of “k-points”

$$\rho(r) = \sum_{n}^{E_n<E_F} \int \psi_{k,n}^{*}\, \psi_{k,n}\, d^3k \quad = \quad \sum_{k,n} w_{k,n}\, \psi_k^{*} \psi_k$$

- weights $w_{k,n}$ depend on k and bandindex n (occupation)
  - *for full “bands” the weight is given by “symmetry”*
    - w(Γ)=1, w(x)=2, w(Δ)=4, w(k)=8

    ⇨ shifted “Monkhorst-Pack” mesh



  - *for partially filled bands (metals) one must find the Fermi-energy (integration up to NE) and determine the weights for each state $E_{k,n}$*
    - linear tetrahedron method (TETRA, eval=999)
    - linear tetrahedron method + “Bloechl” corrections (TETRA)
    - “broadening methods”
      - gauss-broadening (GAUSS 0.002)
      - temperature broadening (TEMP/TEMPS 0.002)
  - *broadening useful to damp scf oszillations, but dangerous (magnetic moment)*

k-mesh generation

- x kgen (generates k-mesh and reduces to irreducible wedge using symmetry)
  - *automatically "adds inversion"*
    - time inversion holds and E(k) = E(-k)
    - except in magnetic spin-orbit calculations (`x -so kgen`; uses case.ksym file)
    - `x -fbz kgen` (generates „full mesh" in BZ)
  - *always "shift" the mesh for scf-cycle*
    - gaps often at Γ ! (might not be in your mesh)
  - *small unit cells and metals require large k-mesh (1000-100000)*
  - *large unit cells and insulators need only 1-10 k-points*
  - *use at first a fairly **coarse** mesh for scf/relaxations*
  - *continue **later** with **finer** mesh*
    - mesh was good if nothing changes and scf terminates after few (3) iterations
  - *use even finer meshes for DOS, spectra, optics,…*

Program execution:

- All programs are executed via the „master“ shell-script x_lapw

  x lapw2 –up –orb

- This generates a „def“ file: lapw2.def

```
5,'tin.in2c',         'old',    'formatted'
6,'tin.output2up',    'unknown','formatted'
8,'tin.clmvalup',     'unknown','formatted'
10,'./tin.vectorup','unknown','unformatted'
```

- and executes: lapw2c lapw2.def
- All WIEN2k-shell scripts have long and short names:
  - *x_lapw; runsp_lapw, runfsm_lapw → x; runsp; runfsm*
- All scripts have a „help“ switch „-h“, which explains flags and options (without actually execution)

  x –h *x lapw1 -h*

scf-cycle

- run_lapw [options] (for nonmagnetic cases)

-ec 0.0001	*convergence of total energy (Ry)*
-cc 0.0001	*convergence of charge distance (e^-)*
-fc 1.0	*convergence of forces (mRy/bohr)*
-it (-it1,-it2 , -noHinv)	*iterative diagonalization (large speedup)*
-p	*parallel calculation (needs .machines file)*
-so	*add spin-orbit (only after „init_so")*

- *Spacegroups without inversion use automatically lapw1c, lapw2c (case.in1c,in2c)*

- case.scf: master output file, contains history of the scf-cycle
  - *most information is stored with some „labels" (grep :label case.scf)*
    - :ENE :DIS :FER :GAP :CTO001 :NTO001 :QTL001
    - `:FOR002:    2.ATOM     19.470     0.000     0.000     19.470`
    - `:FGL002:    2.ATOM     13.767     13.767     0.000  total forces`
    - :LAT :VOL :POSxxx

Getting help

- *_lapw –h „help switch" of all WIEN2k-scripts
- help_lapw:
  - *opens usersguide.pdf; Use ^f keyword to search for an item („index")*
- html-version of the UG: ($WIENROOT/SRC_usersguide/usersguide.html)
- http://www.wien2k.at/reg_user
  - *FAQ page with answers to common questions*
  - *Update information: When you think the program has an error, please check newest version*
  - *Textbook section: DFT and the family of LAPW methods by S.Cottenier*
  - *Mailing-list:*
    - subscribe to the list (always use the same email)
    - full text search of the „digest" (your questions may have been answered before)
    - posting questions: Provide sufficient information, locate your problem (case.dayfile, *.error, case.scf, case.outputX).
    - „My calculation crashed. Please help." This will most likely not be answered.

most common problems

- „QTL-B“ value too large - STOP (or :WARN): “ghostbands”
  - *identify for which **eigenvalue**, **atom** and ℓ it happens, check E_F (case.scf2, case.output2)*
  - *identify the corresponding linearization energies in case.scf1*
  - *change the corresponding linearization energy in case.in1*
    - compare and check with :EPL and :EPH lines in case.scf2
    - default E-parameters are adapted automatically but may need changes for
      - surfaces, molecules (negative EF) or heavy elements (EF often larger than 1.0)
    - add a local orbital (or adjust its energy)
  - *if QTL-B occurs for an atom with large RMT, reduce RMT*
    - this may happen for larger RKMAX („numerical linear dependency“)
- scf-cycle diverges (grep :DIS case.scf):
  - *check structure (most likely a wrong structure caused divergence);*
  - *check E-parameters (see above), check :NEC01 (correct number of e^-)*
  - *rm *.broyd* case.scf; x dstart*

case.in1

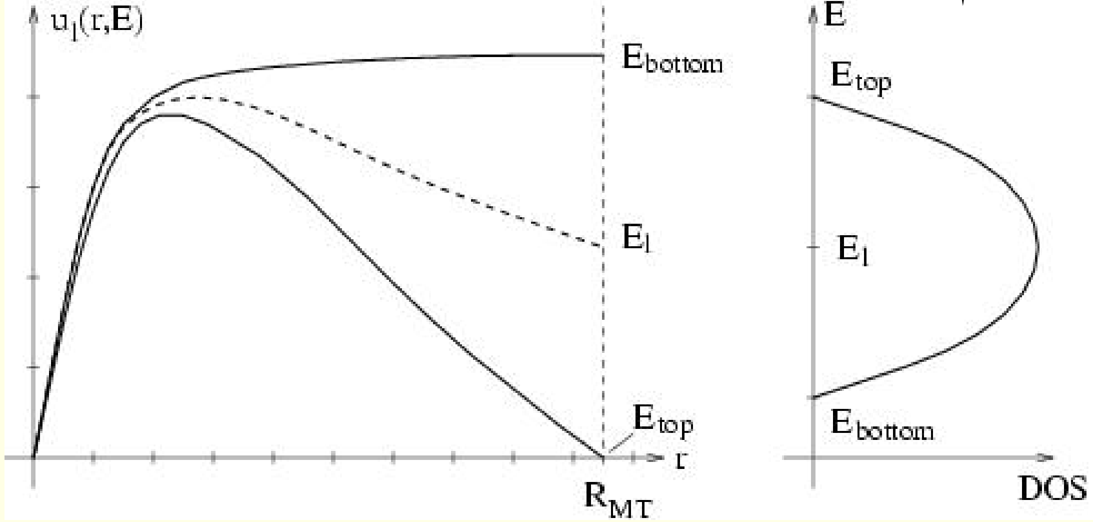
set E_l to E_F-0.2 Ry

```
WFFIL    EF=0.634                       (WFPRI, SUPWF)
  7.00   10   4          (R-MT*K-MAX; MAX L IN WF, V-NMT
  0.30     5   0        global E-param with N other, napw
 0      0.30       0.000 CONT 1         Es
 0     -3.72       0.005 STOP 1         Es-LO with search
 1     -2.07       0.010 CONT 1         Ep    with search
 1      0.30       0.000 CONT 1         Ep-LO
 2      0.30       0.010 CONT 1         0/1…LAPW/APW+lo
K-VECTORS FROM UNIT:4  -7.0  1.5  16  emin/emax; nband
```

$$\Psi = \sum_{K_n}^{KMAX} c_{K_n} \; e^{iK_n r}$$

$$\Phi_{K_n} = \sum_{l}^{l\,\max} A_{lm} u_l(E_l, r) Y_{lm}$$

$$H_{n,m}^{NS} = \left\langle \Phi_l \middle| V_{LM}^{NS} \middle| \Phi_{l'} \right\rangle$$

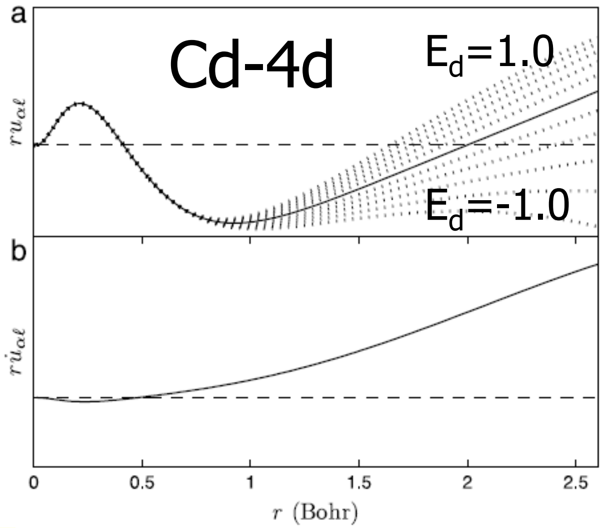


HDLOs: case.in1

- f (d) wavefunctions have a large E-dependency in cases with large RMT
- For high precision calculations

extend the basis set with a HDLO

(high derivative LO):



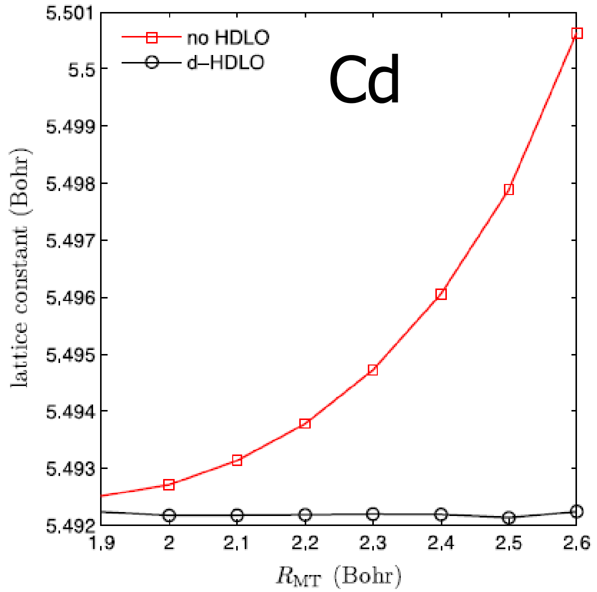
$$\Phi_{K_n} = \sum_l A_{lm}(K_n)u_l(E_l,r)Y_{lm}$$ APW

$$\phi_{l,atom} = (A_{lm}u_{lm} + B_{lm}\dot{u}_l)Y_{lm}$$ lo

$$\phi_{l,atom} = (A_{lm}u_{lm} + C_{lm}\ddot{u}_l)Y_{lm}$$ HDLO

- `2 0.30   0.010 CONT 1` APW+lo
- `2 0.30   0.010 CONT 2` HDLO

- F.Karsai et al., CPC 220, 230(2017)



case.klist, case.in2

```
GAMMA          0    0    0   40   1.0   IX, IY, IZ, IDIV, WEIGHT
               1    0    0   40   6.0
...
X             40    0    0   40   3.0
END
```

case.in2:

```
TOT                            (TOT,FOR,QTL,EFG,FERMI)
-9.0 16.0     0.50 0.05         EMIN, NE,  ESEPARMIN, ESEPAR0
TETRA    0.000                 (GAUSS,ROOT,TEMP,TETRA,ALL    eval)
 0 0  4 0  4 4  6 0  6 4
 0 0  4 0  4 4  6 0  6 4
 14.          GMAX(for small H set it to 20-24)
FILE          FILE/NOFILE  write recprlist
```

$$\rho(r)=\sum_{\boxed{LM}}\rho_{LM}(r)Y_{LM}(\hat{r}) \qquad\qquad \rho(r)=\sum_{G}^{\boxed{GMAX}}\rho_G e^{iGr}$$

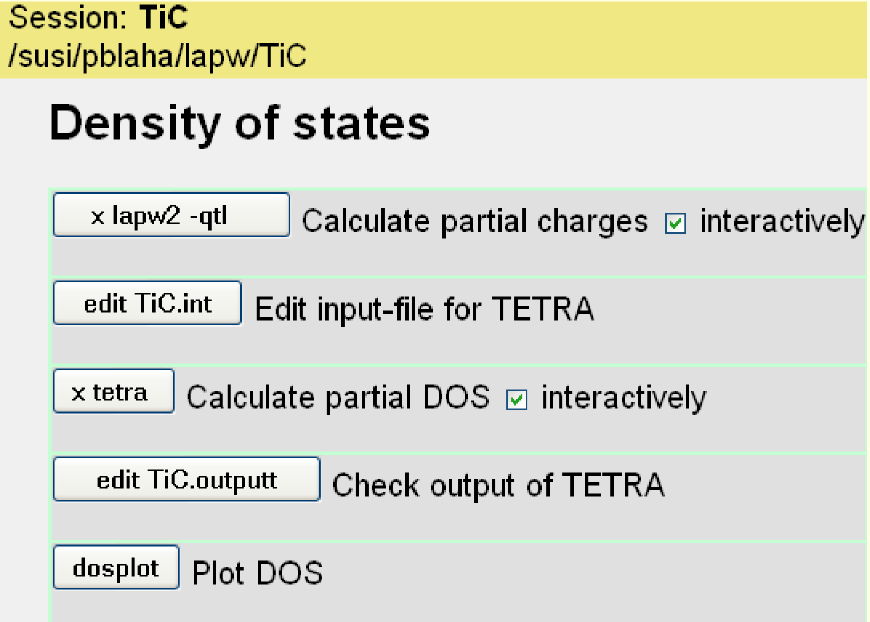
Properties with WIEN2k - I

- Energy bands
  - *classification of irreducible representations*
  - *´character-plot´ (emphasize a certain band-character)*
- Density of states
  - *including partial DOS with l and m- character (eg. p_x , p_y , p_z)*
- Electron density, potential
  - *total-, valence-, difference-, spin-densities, ρ of selected states*
  - *1-D, 2D- and 3D-plots (Xcrysden)*
  - *X-ray structure factors*
  - *Bader´s atom-in-molecule analysis, critical-points, atomic basins and charges ($\nabla\rho.\vec{n} = 0$)*
  - *spin+orbital magnetic moments (spin-orbit / LDA+U)*
- Hyperfine parameters
  - *hyperfine fields (contact + dipolar + orbital contribution)*
  - *Isomer shift*
  - *Electric field gradients*

partial charges “qtl” + DOS

- be sure to have case.vector on a dense tetrahedral mesh after a scf calculation
  - *eventually:*
    - x kgen
    - edit case.in1 (larger Emax)
    - x lapw1
- x lapw2 –qtl

  $\Psi_n{*}\Psi_n = 1 = q_{out} + \sum_t^{at} \sum_l q_{t,l}$
- case.outputt
  - *integrated DOS*
- case.dos1ev (3ev)
  - *text-file for plotting*
  - *E-zero at E_F*



Session: **TiC**
/susi/pblaha/lapw/TiC

Density of states

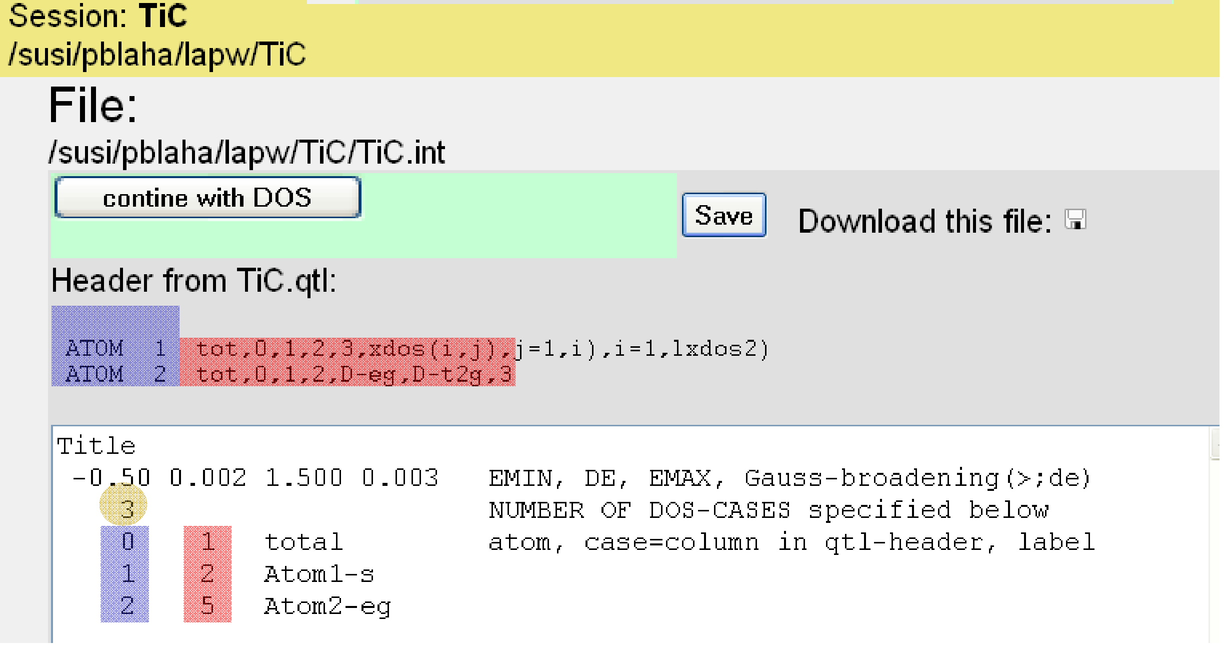
Calculate partial charges ☑ interactively

Edit input-file for TETRA

Calculate partial DOS ☑ interactively

Check output of TETRA

Plot DOS



Session: **TiC**
/susi/pblaha/lapw/TiC

File:
/susi/pblaha/lapw/TiC/TiC.int

Download this file:

Header from TiC.qtl:

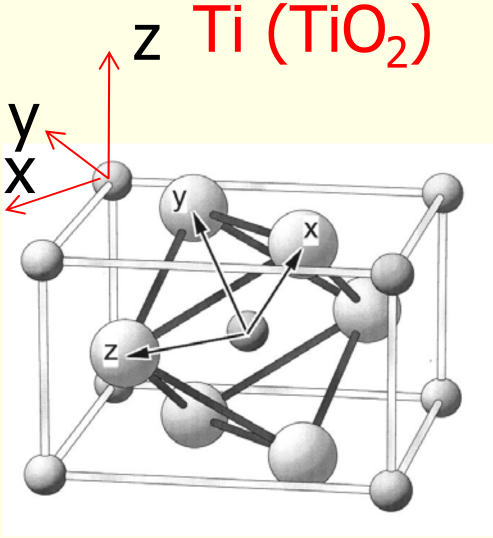
```
 ATOM  1  tot,0,1,2,3,xdos(i,j),j=1,i),i=1,lxdos2)
 ATOM  2  tot,0,1,2,D-eg,D-t2g,3
```

```
Title
 -0.50 0.002 1.500 0.003    EMIN, DE, EMAX, Gauss-broadening(>;de)
    3                       NUMBER OF DOS-CASES specified below
    0    1    total         atom, case=column in qtl-header, label
    1    2    Atom1-s
    2    5    Atom2-eg
```

partial charges:

- local rotation matrix:
  - *transfers z (y) into highest symmetry*
  - *reduces terms in LM series*
  - *"chemical" interpretation*
    - p_x is different from p_y

$$\begin{pmatrix} 1/\sqrt{2} & 1/\sqrt{2} & 0 \\ -1/\sqrt{2} & 1/\sqrt{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$



Ti (TiO_2)

  - *see case.struct and case.outputs*

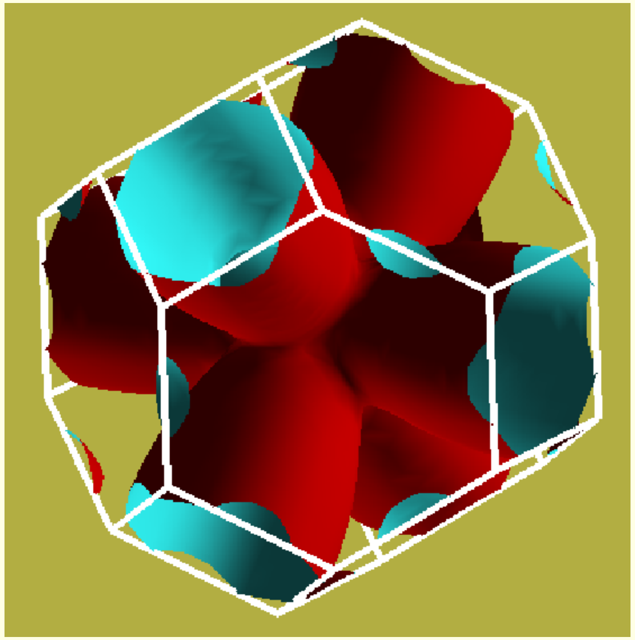
- x qtl (instead of x lapw2 -qtl)
  - ***f**-orbitals*
  - *qtls for **different coordinate system** (eg."octahedral" in TiO_2)*
  - *relativistic basis (**$p_{1/2}$-$p_{3/2}$** or **$d_{3/2}$-$d_{5/2}$** splitting in so calculation)*
  - *for angular dependend TELNES (ISPLIT 88, 99)*

Properties with WIEN2k - II

- Total energy and forces
  - *optimization of internal coordinates, (MD, BROYDEN)*
  - *cell parameter only via E_{tot} (no stress tensor)*
  - *elastic constants for cubic, hexagonal, and tetragonal cells*
  - *Phonons via supercells*
    - interface to PHONON (K.Parlinski) – bands, DOS, thermodynamics, neutrons
    - interface to PHONOPY (A. Togo)
      - http://www.wien2k.at/reg_user/unsupported
- Spectroscopy
  - *core level shifts*
  - *X-ray emission, absorption, electron-energy-loss (with core holes)*
    - core-valence/conduction bands including matrix elements and angular dep.
  - *optical properties (dielectric function in RPA approximation, JDOS including momentum matrix elements and Kramers-Kronig)*
- fermi surface: 2D, 3D (using XcrysDen)

Fermi surfaces

- **`xcrysden --wien_fermisurface tin.struct`**
  - choose a good k-mesh (eg. 10000 points)
  - plot the FS for all bands which cross E_F and compare to band structure



- *for 2D plots there is also a WIEN2k-tool „fsgen" (see UG)*
- *SKEAF (www.wien2k.at/reg_users/unsupported): quantum oszillations*

Properties with WIEN2k - II

- Total energy and forces
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- fermi surface: 2D, 3D (using XcrysDen)

Cohesive energy

$$E_{A_x B_y}^{cohes.} = E^{crystal} - xE_A^{atom} - yE_B^{atom}$$

- $E^{crystal}$: scalar-relativistic valence (or approx. SO)

- E^{atom} : LSTART: fully-relativistic➔ inconsistent description

  ➔ for heavier elements (2nd row):

  supercell with one atom in a ~30 bohr **distorted** FCC box (identical RMT, equivalent RKmax, 1 k-point, spinpolarized)

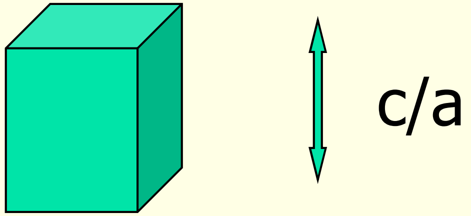
Structural optimizations:

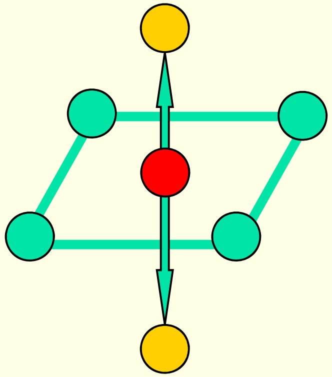
- Lattice parameters, volume, c/a ratio only via total energies:
  - *x optimize: creates a series of "struct" files + script "optimize.job"*
    - select volume or c/a, …
    - select number of cases and desired changes in volume (in % of V_0)
  - *edit optimize.job*
    - adapt to your need: change / uncomment various lines, eg.:
      - select different convergence parameters, parallelization, more iterations (-i 40)
      - modify "save_lapw" line (with more specific names)
      - replace "run_lapw" by "runsp_lapw" or add options (-min –fc 1 –orb)
  - *execute optimize.job*
  - *plot (analyse) the results*

  - *combinations of volume and c/a are possible: 2Doptimize*
    - "x optimize" always uses case_initial.struct (if present)
    - do a "volume" optimization to create case_vol_xx.struct files
    - copy the respective case_vol_xx.struct file to case_initial.struct
    - x optimize with "c/a" for this particular volume and proceed as above.

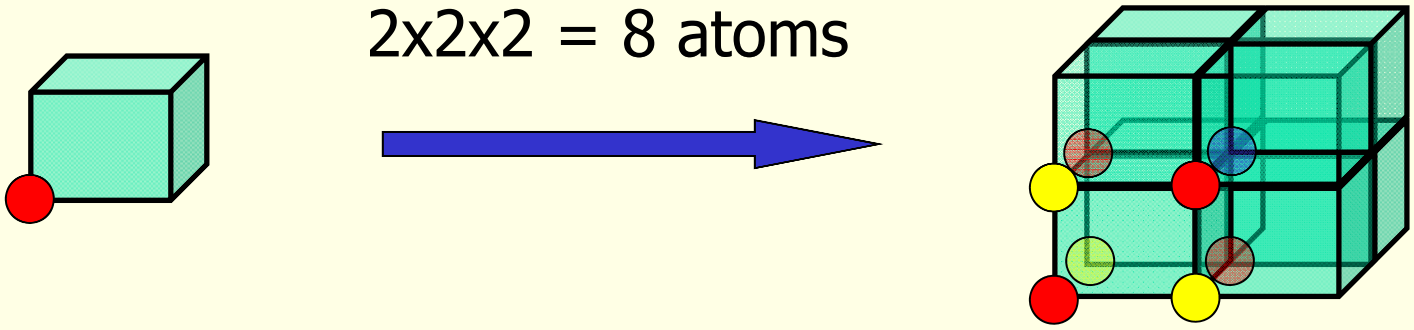
Symmetry:

- WIEN „preserves" symmetry:
  - *c/a optimization of „cubic" TiC:*
    - change c lattice parameter in TiC.struct (tetragonal distortion, #sym.op=0)
    - init_lapw
    - change c back to cubic
    - x optimize …
  - *„Jahn-Teller" distortion:*
    - when you start with a perfect octahedra, you will never get any distortion
    - ➔start with slightly distorted positions





Supercells (impurities, vacancies, alloys)

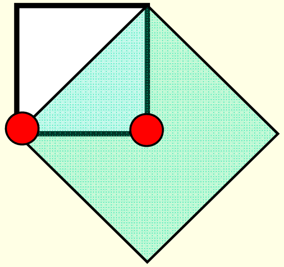


2x2x2 = 8 atoms

(0,0,0)	P→ 8 atoms	(0,0,0)	(.5,0,0) (0,.5,0) (0,0,.5)	(.5,.5,0) (.5,0,.5) (0,.5,.5)	(.5,.5,.5)
	B→ 4 atoms	yes	yes	no	no
	F→ 2 atoms	yes	no	no	yes

4x4x4 supercells: P (64), B (32), F (16) atoms

$\sqrt{2}x\sqrt{2}$ supercells (1 → 2 atoms)

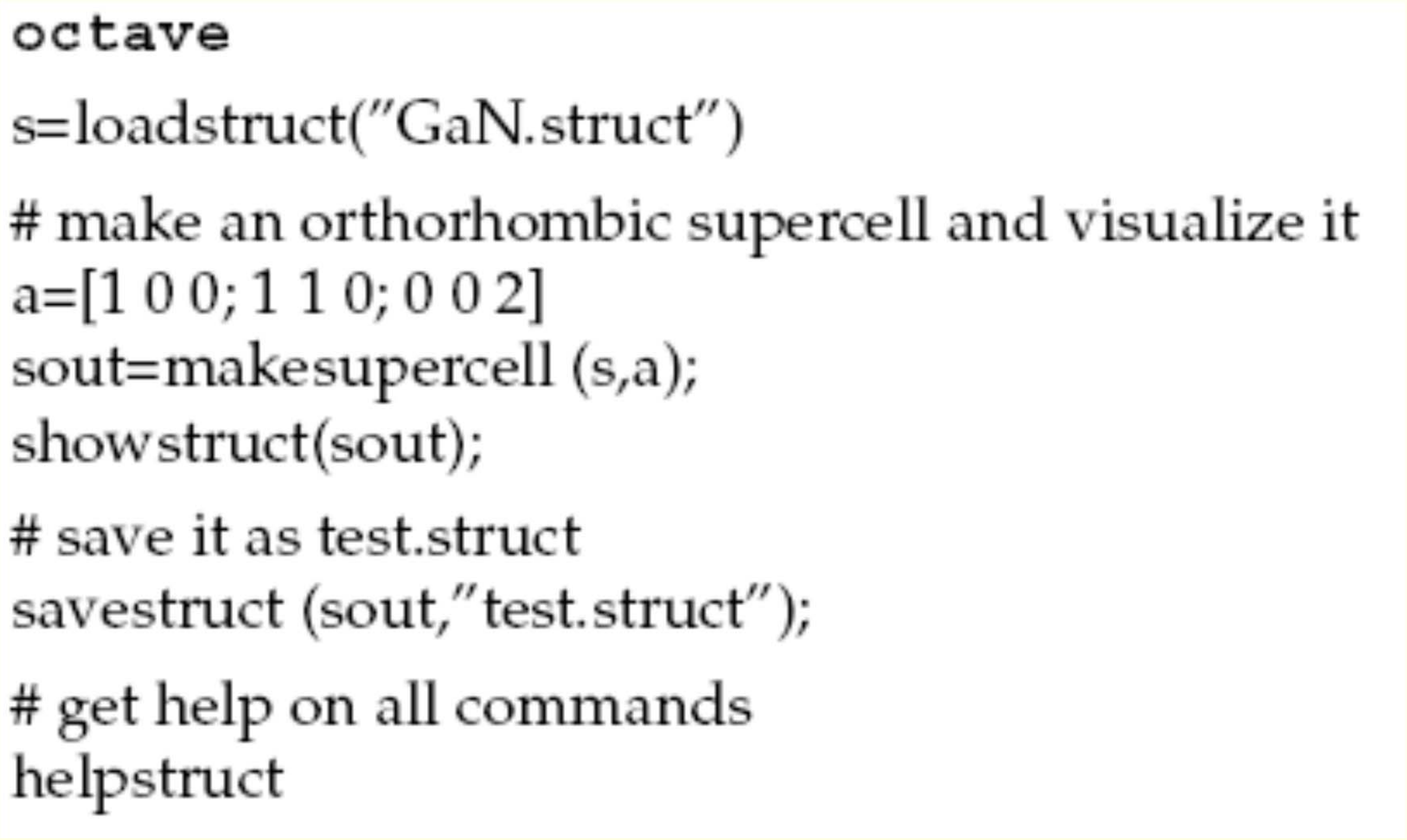


Supercells

- Program „supercell“:
  - *start with „small“ struct file*
  - *specify number of repetitions in x,y,z (only integers, e.g. 2x2x1)*
  - *specify P, B or F lattice*
  - *add „vacuum“ for surface slabs (only (001) indexed surfaces)*
  - *shift all atoms in cell*
- You must break symmetry !!! (otherwise sgroup will restore your original struct file)
  - *replace (impurities, vacancies) or*
  - *displace (phonons) or*
  - *label at least 1 atom (core-holes, specific magnetic order; change "Fe" to "Fe1"; this tells the symmetry-programs that Fe1 is NOT a Fe atom!!)*
- „supercell“ works only along unit-cell axes!!!

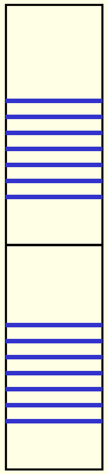
Structeditor (by R.Laskowski)

- requires octave (matlab) and xcrysden (visualization)
- allows complex operations on struct-files



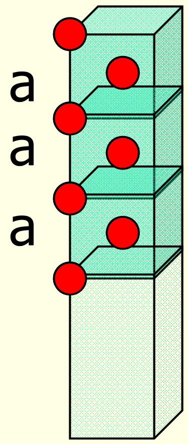
```
octave
s=loadstruct(”GaN.struct”)
# make an orthorhombic supercell and visualize it
a=[1 0 0; 1 1 0; 0 0 2]
sout=makesupercell (s,a);
showstruct(sout);
# save it as test.struct
savestruct (sout,”test.struct”);
# get help on all commands
helpstruct
```

Surfaces



- 2D-slabs with finite number of layers with „vacuum“ in 3^rd dimension

bcc (001) 7 layers:



(0 0 6z)
(.5 .5 5z)
(0 0 4z)
(.5 .5 3z)
(0 0 2z)
(.5 .5 z)
(0 0 0)

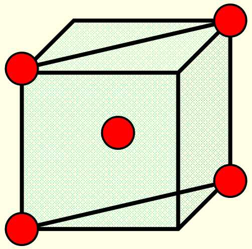
shift to
➔
inversion

(.5 .5 +/-3z)
(0 0 +/-2z)
(.5 .5 +/-z)
(0 0 0)

with lattice parameters:
a, a, c=(3a+15-20bohr vacuum)

z= a/2c

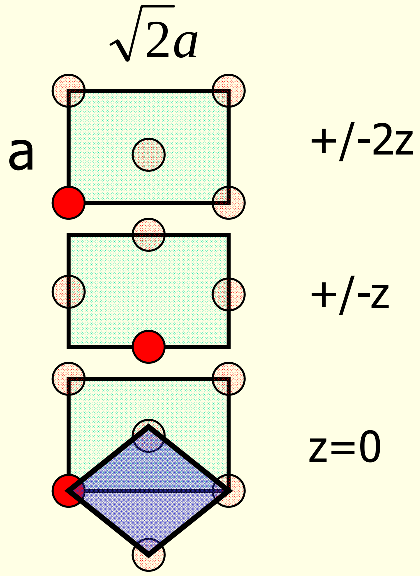
bcc (110):



orthorhombic CXY-lattice: a, $\sqrt{2}a$, c

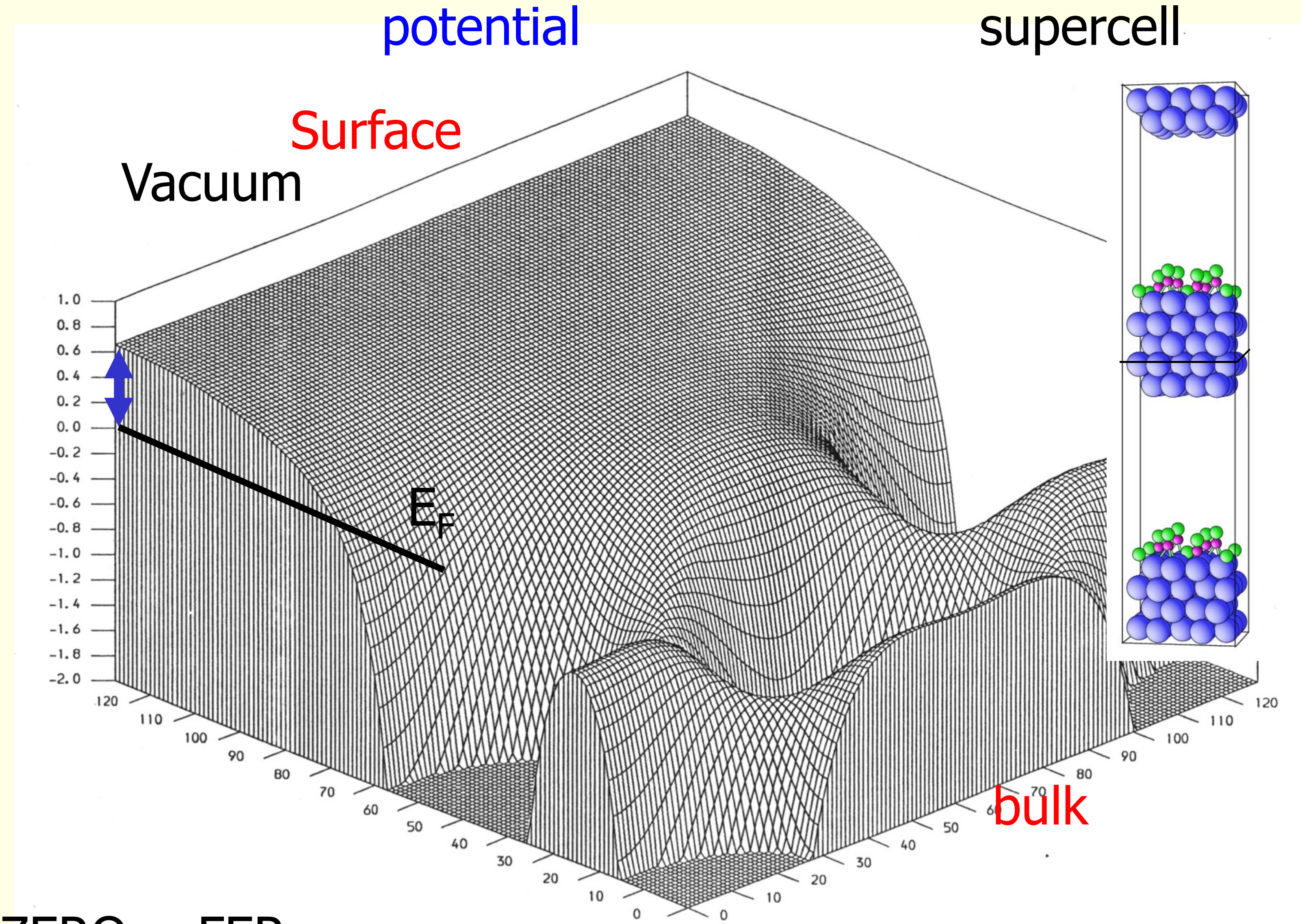
(0 0 0)
(0 .5 +/-z)
(0 0 +/-2z)

z=a/$\sqrt{2}a$ c



Work function

Work function



WF= :VZERO - :FER (check convergence with vacuum)

Total energies and atomic forces

(Yu et al.; Kohler et al.)

- Total Energy:
  - *Electrostatic energy*
  - *Kinetic energy*
  - *XC-energy*

$$U[\rho] = \tfrac{1}{2}\int d^3\vec{r}\;\rho(\vec{r})V_{es}(\vec{r}) + \tfrac{1}{2}\sum\nolimits_{\alpha} Z_{\alpha}V_{es}^{\alpha}(\vec{r})$$

$$T[\rho] = \sum\nolimits_{i} n_i\varepsilon_i - \int d^3\vec{r}\;\rho(\vec{r})V_{eff}(\vec{r})$$

$$E_{xc}[\rho] = \int d^3\vec{r}\;\rho(\vec{r})\varepsilon_{xc}(\vec{r})$$

- Force on atom α:

$$\vec{F}^{\alpha} = \frac{-dE_{tot}}{d\vec{R}_{\alpha}} = F_{HF}^{\alpha} + F_{core}^{\alpha} + F_{val}^{\alpha}$$

  - *Hellmann-Feynman-force*
  - *Pulay corrections*
    - Core
    - Valence
- expensive, contains a summation of matrix elements over all occupied states

$$F_{HF}^{\alpha} = Z_{\alpha}\sum_{m=-1}^{1}\lim_{r_{\alpha}\to 0}\frac{V_{1m}^{es}(r_{\alpha})}{r_{\alpha}}\nabla_{\alpha}\left[r_{\alpha}Y_{1m}(\hat{r})\right]$$

$$F_{core}^{\alpha} = -\int \rho_{core}(r)\nabla_{\alpha}V_{eff}(r)\,d\vec{r}$$

$$F_{val}^{\alpha} = \int_{\alpha} V_{eff}(r)\nabla_{\alpha}\rho_{val}(r)\,d\vec{r} + \sum_{k,i} n_i \sum_{K,K'} c_i^{*}(K')c_i(K)\times$$

$$\left[(K^2-\varepsilon_i)\oint \phi_{K'}^{*}(r)\phi_K(r)\,dS_{\alpha} - i(K-K')\left\langle \phi_{K'}\middle|H-\varepsilon_i\middle|\phi_K\right\rangle_{\alpha}\right]$$

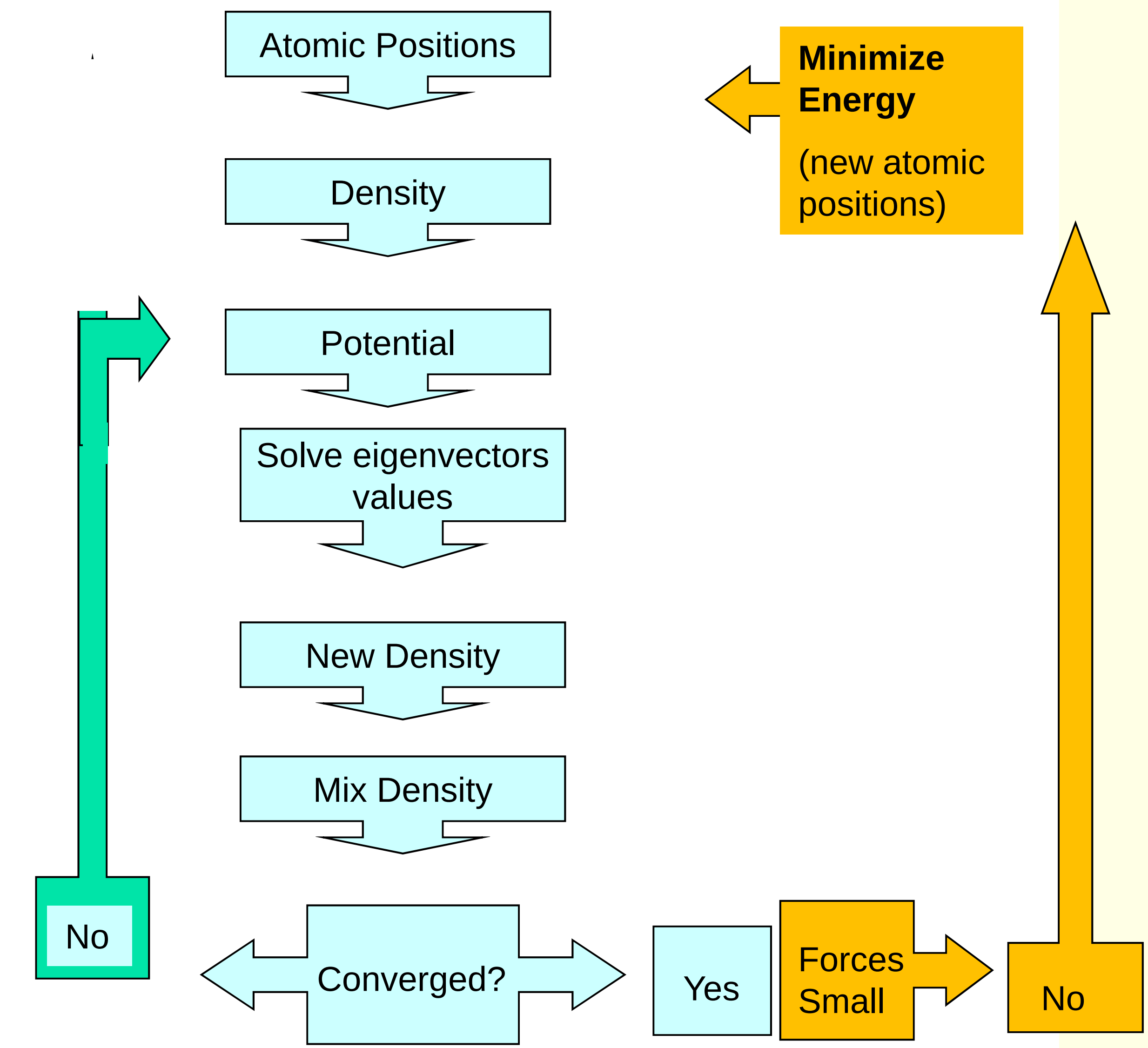
Optimization of internal parameters using "forces"

- Forces only for "free" structural parameters:
  - *NaCl: (0,0,0), (0.5,0.5,0.5) : all positions fixed by symmetry*
  - *TiO_2: Ti (0,0,0), O (u,u,0): one free parameter (u,x,y,z)*
- Forces are only calculated when using "-fc":
  - *run_lapw –fc 1.0   (mRy/bohr)*
    - grep :fgl002 case.scf

200.	partial	
-130.	partial	
140.	partial	
135	partial	only $F_{HF} + F_{core}$
120	partial	
122	partial	forces converging
121	partial	→ changes "TOT" to "FOR" in case.in2
-12.3	**total**	$F_{HF} + F_{core} + F_{val}$, only this last number is correct

- Forces are useful for
  - *structural optimization (of internal parameters)*
  - *phonons*

Structure optimization (atomic positions)



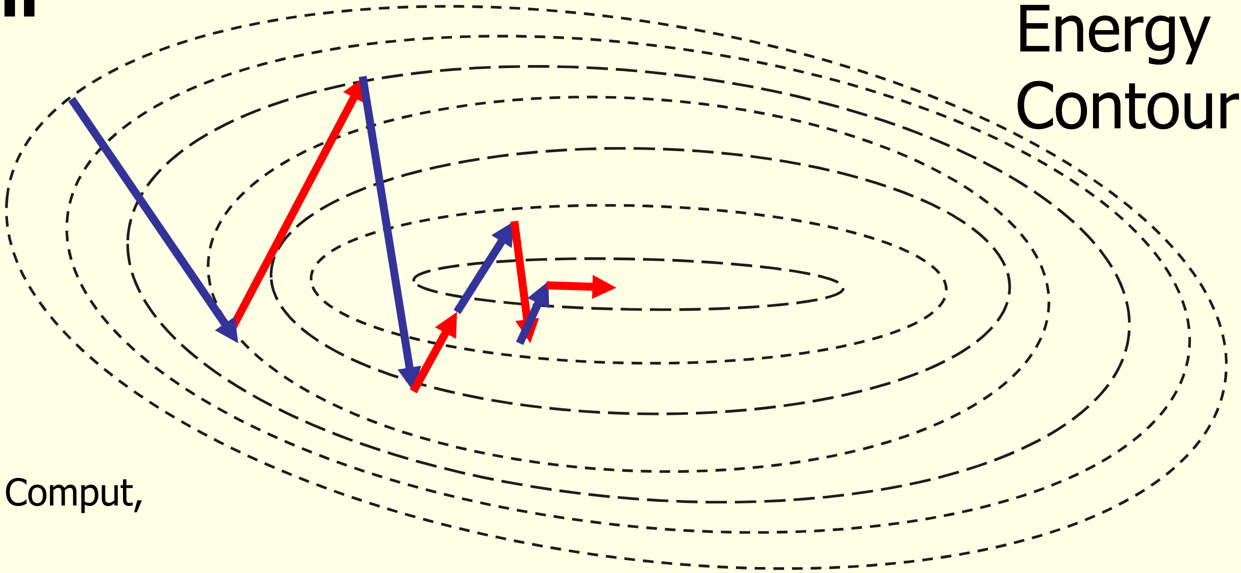
Traditional way:

- Inner loop: obtain fixed-point for given atom positions
- Outer loop: optimize atomic positions

Traditional algorithm:

- Calculate SCF mapping, time T_0
- Broyden expansion for fixed-point problem, self-consistent density, N_{SCF} iterations
- BFGS is most common for optimizing the atomic positions (Energy), N_{BFGS}
- Time scales as $\mathbf{N_{SCF}*N_{BFGS}*T_0}$

each step is a **full** scf calculation producing **accurate** forces



L.D.Marks: J. Chem. Theory Comput, DOI: 10.1021/ct4001685

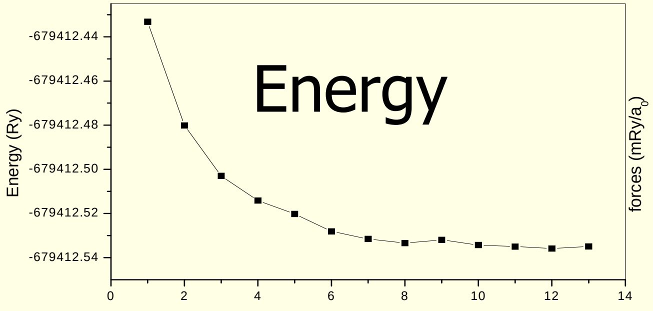
Structural optimization of internal parameters using “PORT”

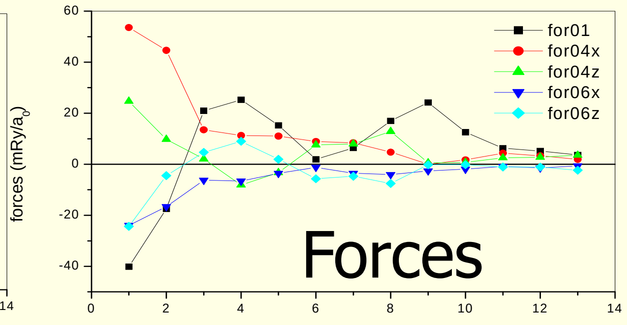
- /home/pblaha/tio2> min_lapw [-p -it -sp] [-j “run -fc 1 -p -it”] [-NI]
  - *performs scf-cycle for fixed positions*
  - *get forces and move atoms along forces (building an approximate Hessian) and writing a new case.struct file*
  - *extrapolate density (case.clmsum)*
  - *perform next scf cycle and loop until forces are below „tolf"*
  - *CONTROL FILES:*
    - .minstop   stop after next structure change
- tio2.inM (generated automatically by “pairhess” at first call of min_lapw)
    - PORT 2.0   #(NEW1, NOSE, MOLD, **tolf** (a4,f5.2))
    - 0.0 1.0 1.0 1.0   # Atom1 (0 will **constrain** a coordinate)
    - 1.0 1.0 1.0 1.0   # Atom2 (NEW1: 1,2,3:delta_i, 4:eta (1=MOLD, damping))
- **monitor minimization in file   case.scf_mini**
  - *contains **last** iteration of each **geometry** step*
  - *each step N is saved as case_N.scf (overwritten with next min_lapw !)*
    - grep :ENE case.scf_mini
    - grep :FGLxxx case.scf_mini   (:POSxxx)

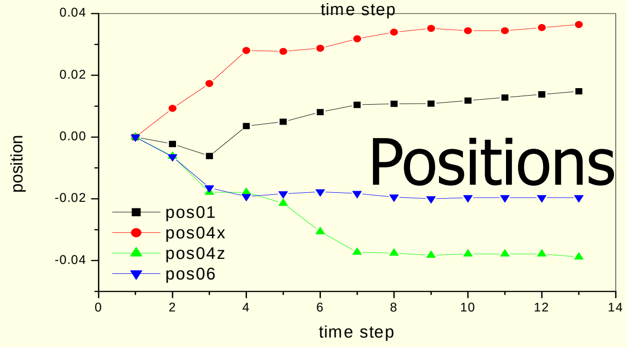
Optimization of atomic posistions (E-minimization via forces)

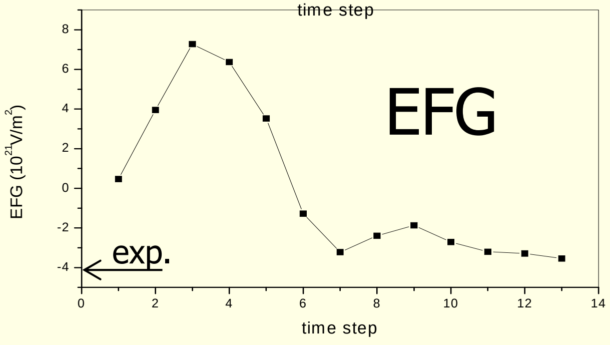
- damped Newton mechanics scheme (NEW1: with variable step)
- quite efficient quasi-Newton (PORT) scheme
  - minimizes E (using forces as gradients and construct approx. Hessian)
  - If minimizations gets stuck or oscillates: (because E and F_i are inconsistent):
    - touch .minstop; min –nohess   (or rm case.tmpM .min_hess)
    - improve scf-convergence (-ec), Rkmax, k-mesh, …
    - change to NEW1 scheme

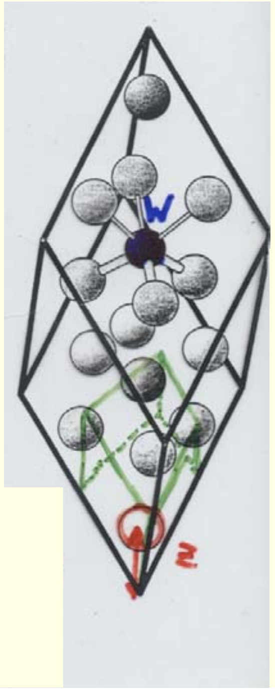
W impurity in Bi (2x2x2 supercell: $Bi_{15}W$)





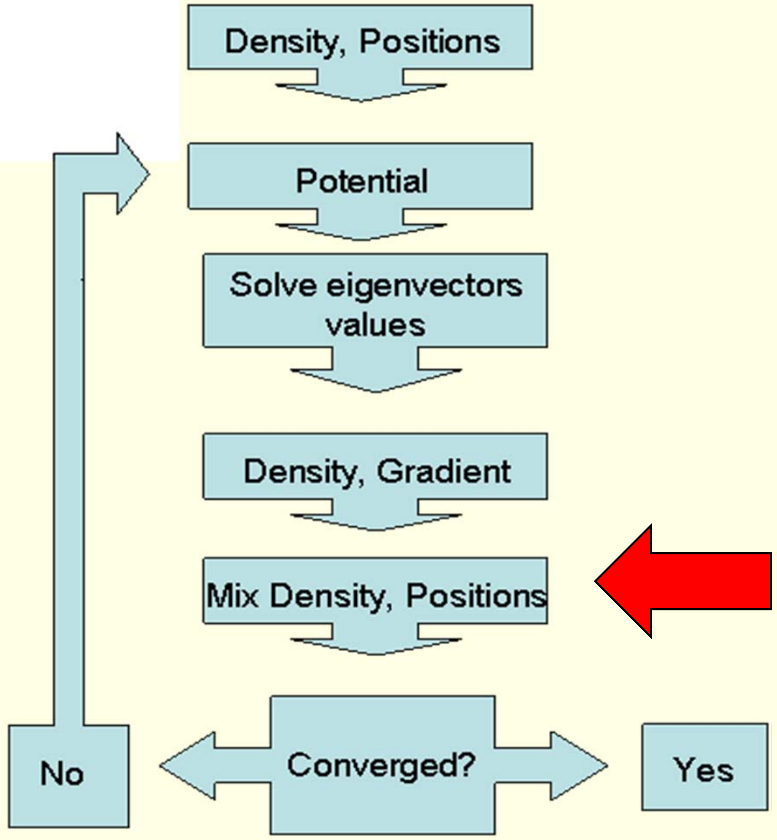






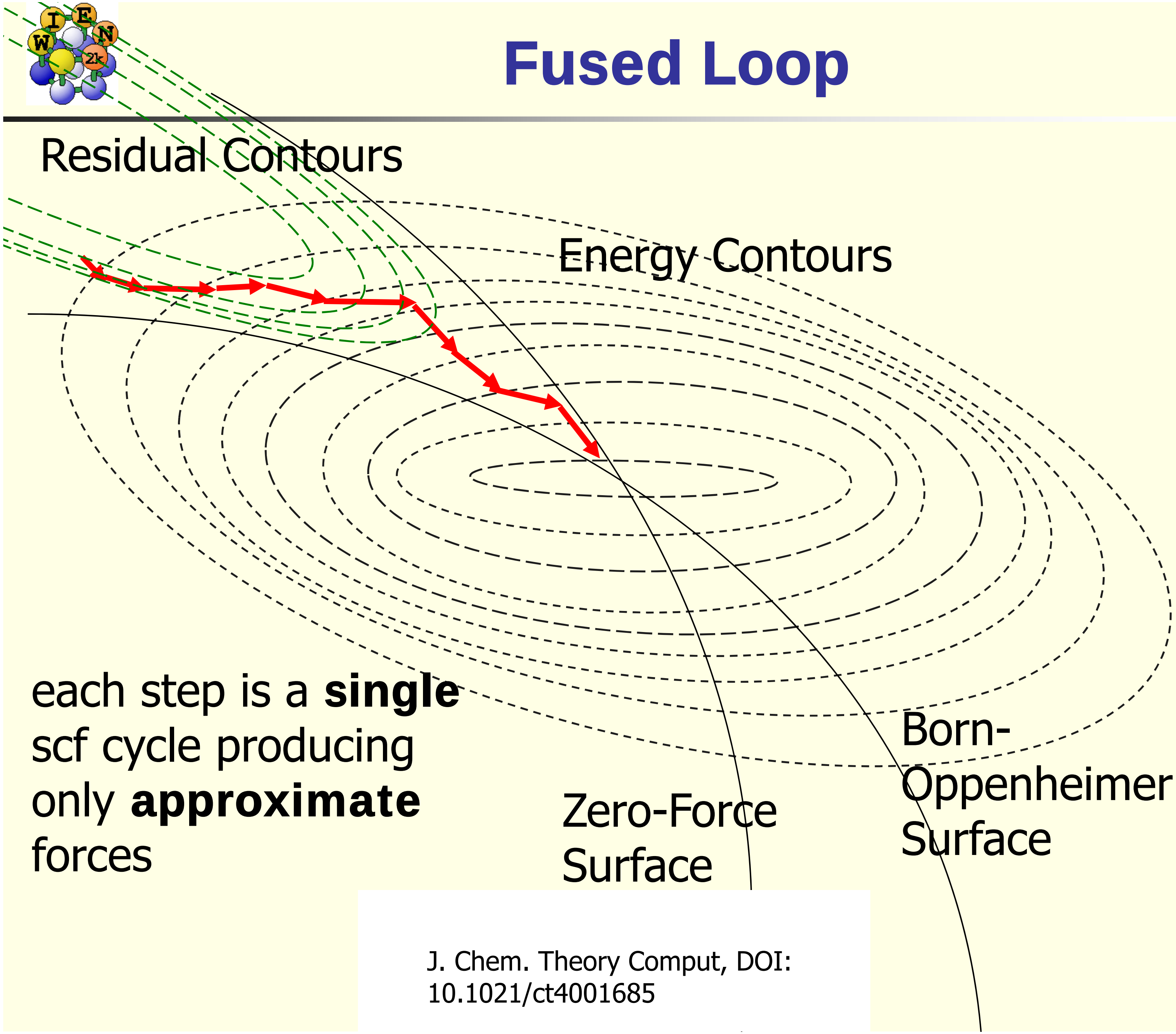
Alternative method: **Fused Loop**

- Treat the **density** and **atomic positions** ***all*** at the same time.
- No restrictions to “special” cases, general algorithm has to work for insulators, metals, semiconductors, surfaces, defects, hybrids….
- Few to no user adjustable parameters



L.D. Marks, J. Chem. Theory Comput, DOI: 10.1021/ct4001685

Fused Loop



each step is a **single** scf cycle producing only **approximate** forces

J. Chem. Theory Comput, DOI: 10.1021/ct4001685

Broyden Fixed-Point Methods

- Solve *$(\rho(r,x)-F(\rho(r,x)),G)=0$*
- $s_k = (\rho,x)_{k+1} - (\rho,x)_k ; y_k = (F(\rho,x),G)_{k+1} - (F(\rho,x),G)_k$
- Broyden's "Good Method"

$$B_{k+1} = B_k + \frac{(y_k - B_k s_k)s_k^T}{s_k^T s_k} \qquad H_{k+1} = H_k + \frac{(s_k - H_k y_k)s_k^T}{s_k^T y_k}$$

- Broyden's "Bad Method"

$$H_{k+1} = H_k + \frac{(s_k - H_k y_k)y_k^T}{y_k^T y_k}$$

C.G. Broyden, A Class of Methods for Solving Nonlinear Simultaneous Equations, Mathematics of Computation, 19 (1965) 577-593.

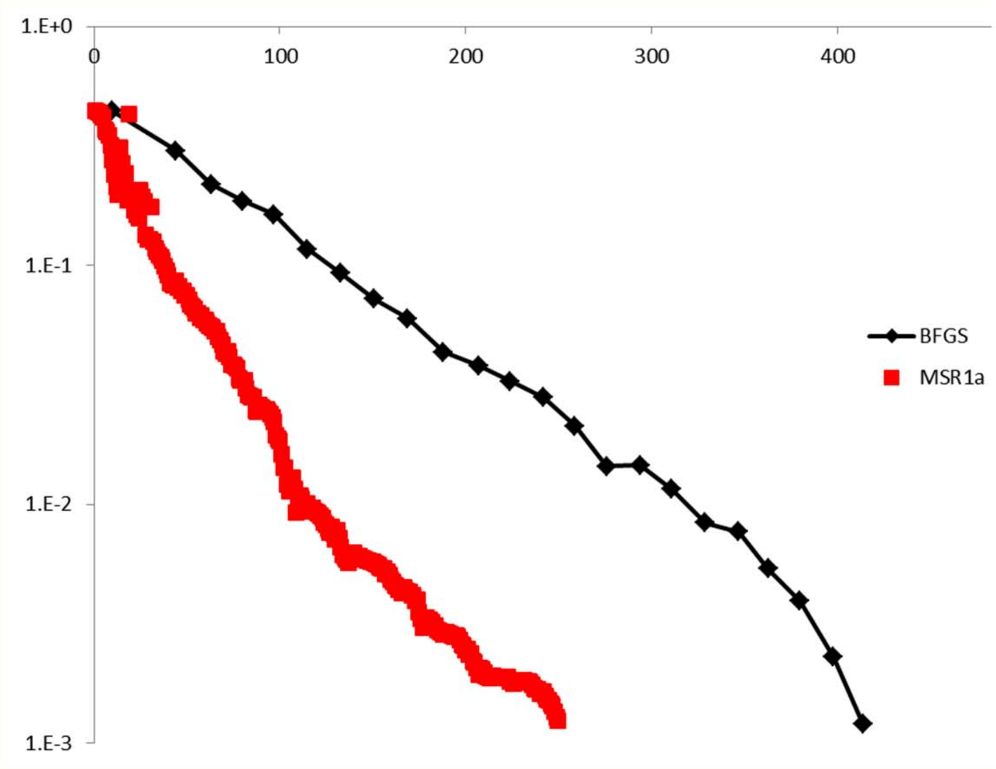
- Generalizable to multisecant method (better,

L.D.Marks: J. Chem. Theory Comput, DOI: 10.1021/ct4001685

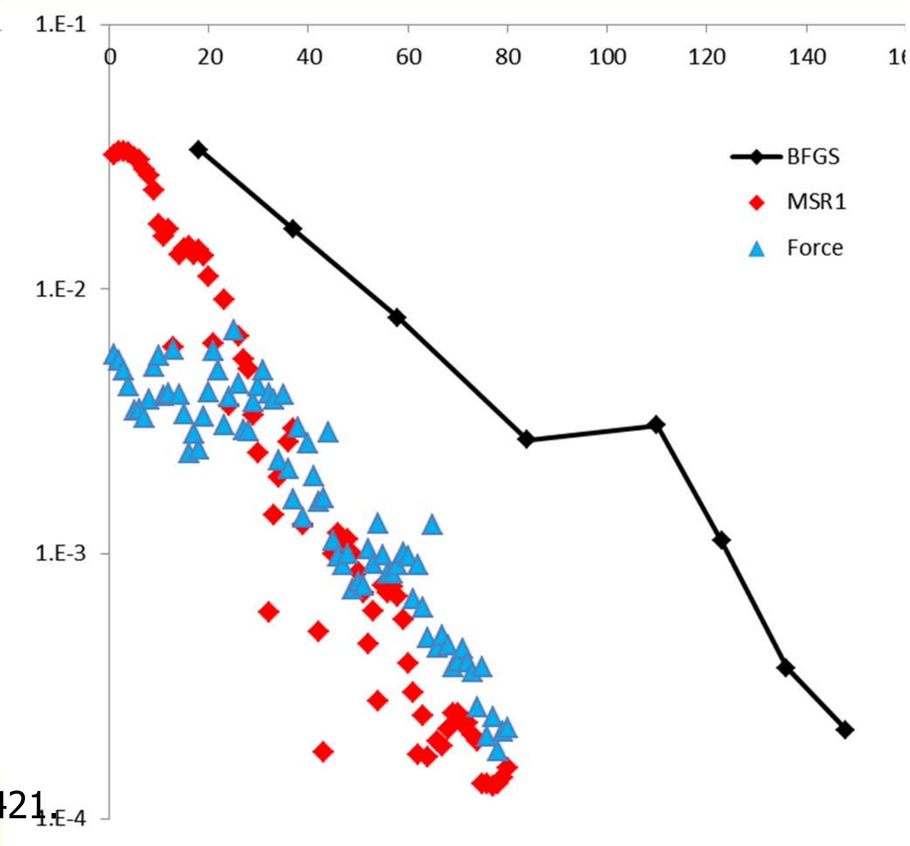
Comparison of the 2 methods

Larger Problems:

52 atoms, MgO (111)+H_2O 108 atoms AlFe



J. Ciston, A. Subramanian, L.D. Marks, PRB, 79 (2009) 085421



Lyudmila V. Dobysheva (2011)

J. Chem. Theory Comput, DOI: 10.1021/ct4001685

Structural optimization of internal parameters using “**MSR1a**”

- run_lapw **–min** -fc 1.0 -cc 0.001 -ec 0.0001 [-it -noHinv -p]
- modifies case.inm and sets „**MSR1a**“

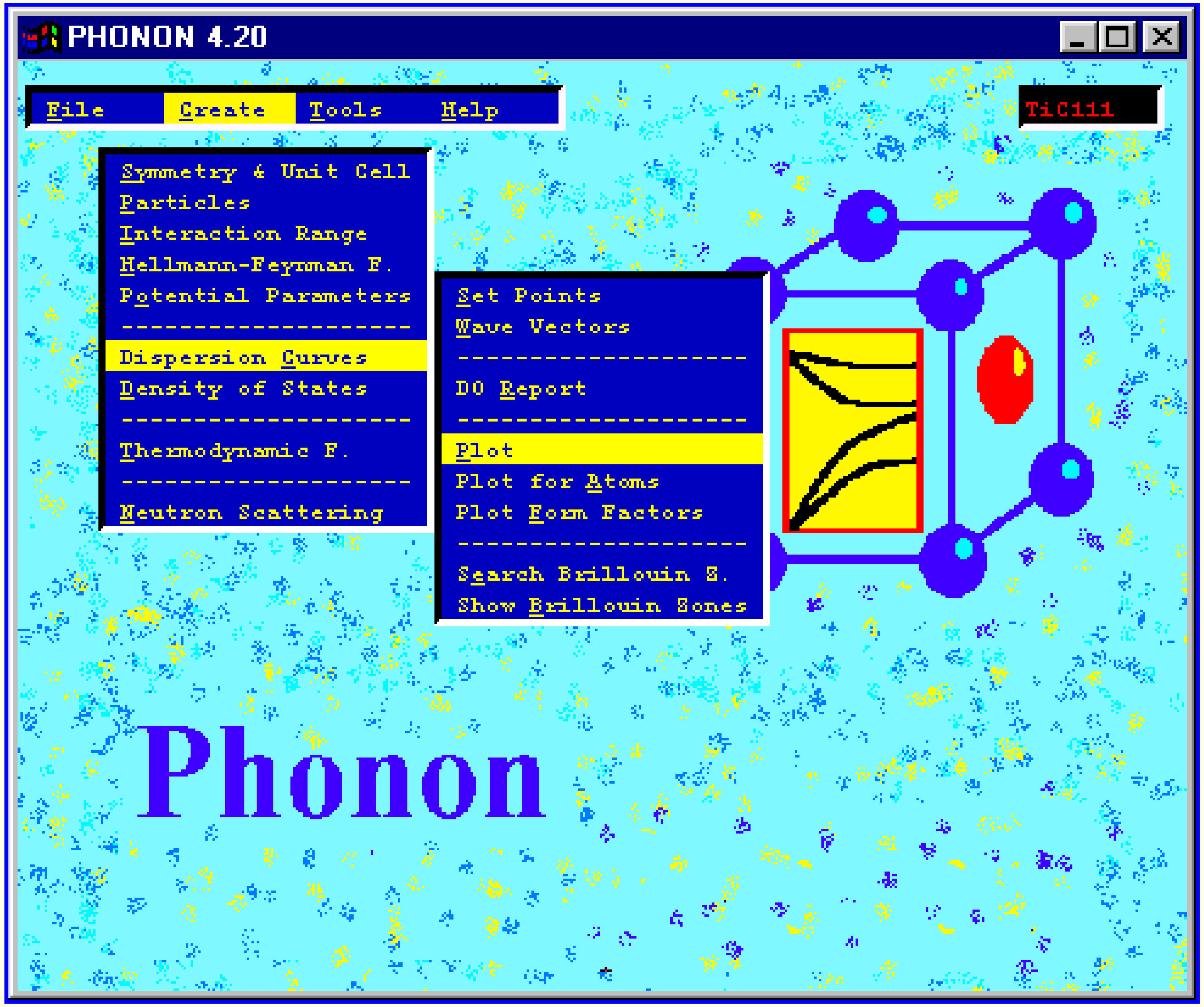
- This runs ONE big scf-calculations optimizing the density and the positions (forces towards zero) simultaneously (may need hundreds of iterations).

- Monitor: :ENE and :FR (av. and max forces, movements)

- it continues until all :FR quantities are below „tolf“ (case.inM) and switches then automatically to MSR1 for a final charge optimization (with fixed positions).

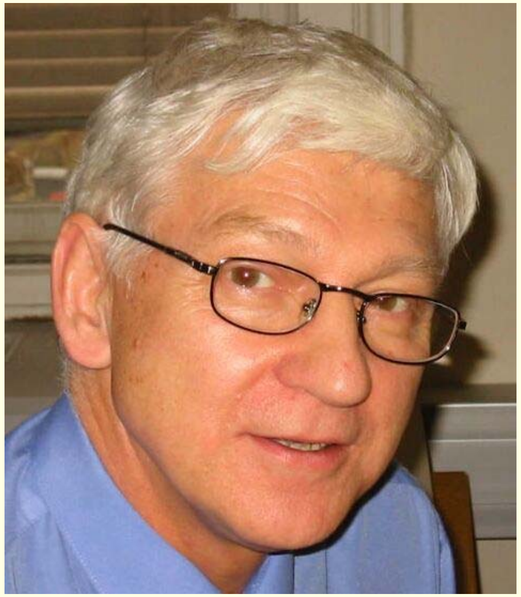
- quite efficient, **recommended** method, still under development by L.Marks (Northwestern Univ).

Calculations of Phonons: The Direct Method



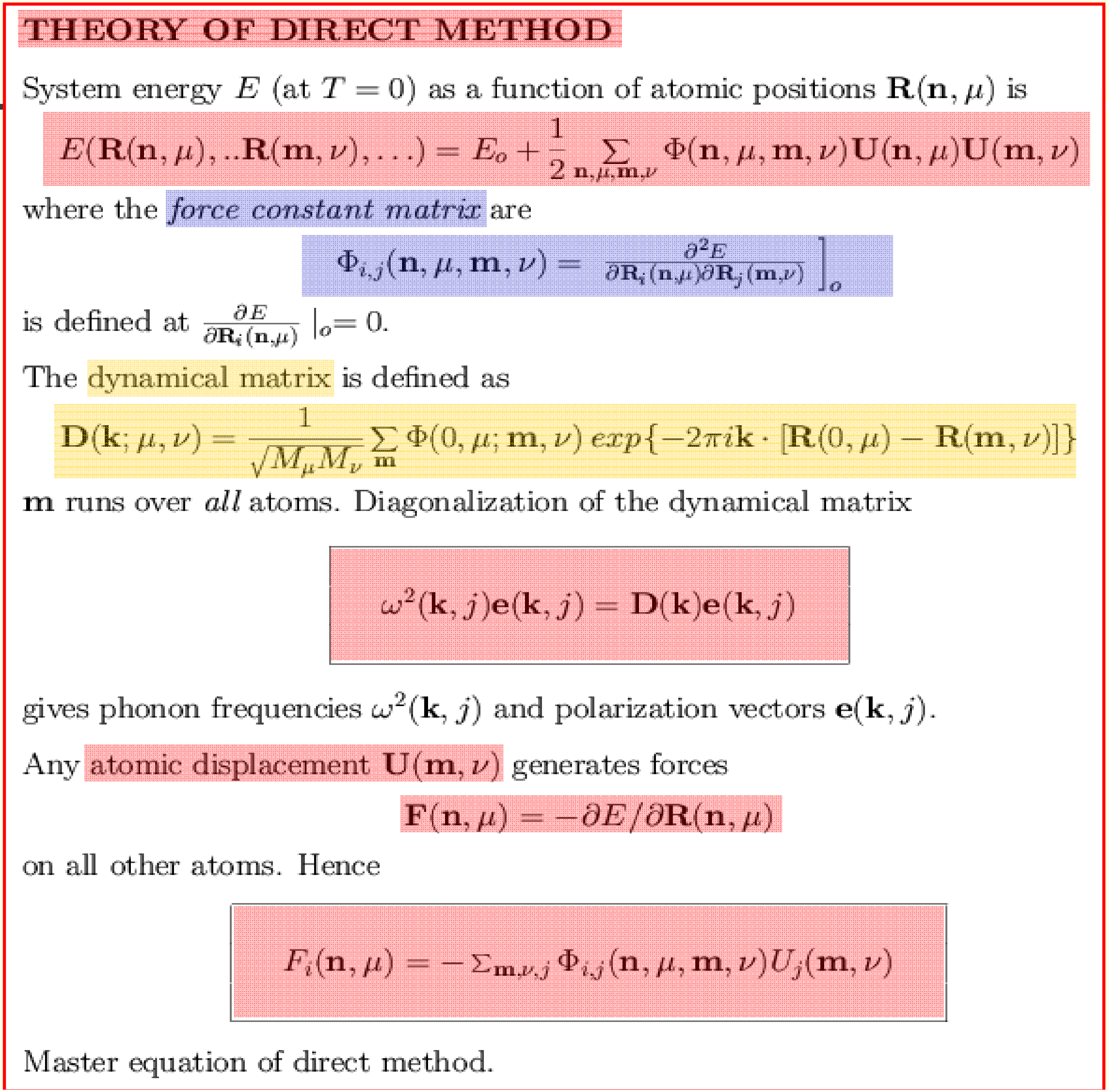
WIEN2k + Phonon

Copyright by K.Parlinski



http://wolf.ifj.edu.pl/phonon/

alternatively use A.Togo`s **PHONOPY** code
(see www.wien2k.at/unsupported)



THEORY OF DIRECT METHOD

System energy E (at $T=0$) as a function of atomic positions $\mathbf{R}(\mathbf{n},\mu)$ is

$$E(\mathbf{R}(\mathbf{n},\mu),..\mathbf{R}(\mathbf{m},\nu),\ldots) = E_o + \frac{1}{2}\sum_{\mathbf{n},\mu,\mathbf{m},\nu}\Phi(\mathbf{n},\mu,\mathbf{m},\nu)\mathbf{U}(\mathbf{n},\mu)\mathbf{U}(\mathbf{m},\nu)$$

where the *force constant matrix* are

$$\Phi_{i,j}(\mathbf{n},\mu,\mathbf{m},\nu) = \left.\frac{\partial^2 E}{\partial\mathbf{R}_i(\mathbf{n},\mu)\partial\mathbf{R}_j(\mathbf{m},\nu)}\right]_o$$

is defined at $\frac{\partial E}{\partial\mathbf{R}_i(\mathbf{n},\mu)}\,|_o = 0$.

The dynamical matrix is defined as

$$\mathbf{D}(\mathbf{k};\mu,\nu) = \frac{1}{\sqrt{M_\mu M_\nu}}\sum_{\mathbf{m}}\Phi(0,\mu;\mathbf{m},\nu)\,exp\{-2\pi i\mathbf{k}\cdot[\mathbf{R}(0,\mu)-\mathbf{R}(\mathbf{m},\nu)]\}$$

$\mathbf{m}$ runs over *all* atoms. Diagonalization of the dynamical matrix

$$\boxed{\omega^2(\mathbf{k},j)\mathbf{e}(\mathbf{k},j) = \mathbf{D}(\mathbf{k})\mathbf{e}(\mathbf{k},j)}$$

gives phonon frequencies $\omega^2(\mathbf{k},j)$ and polarization vectors $\mathbf{e}(\mathbf{k},j)$.

Any atomic displacement $\mathbf{U}(\mathbf{m},\nu)$ generates forces

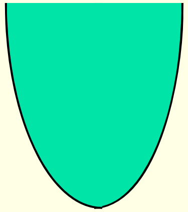
$$\mathbf{F}(\mathbf{n},\mu) = -\partial E/\partial\mathbf{R}(\mathbf{n},\mu)$$

on all other atoms. Hence

$$\boxed{F_i(\mathbf{n},\mu) = -\Sigma_{\mathbf{m},\nu,j}\,\Phi_{i,j}(\mathbf{n},\mu,\mathbf{m},\nu)U_j(\mathbf{m},\nu)}$$

Master equation of direct method.

$$V = \frac{1}{2}kx^2$$



n,m: cells

μ,ν: atoms

CUMMULANT FORCE CONSTANTS

Displace an atom by $\mathbf{U}(\mathbf{m},\nu)$

$$F_i(\mathbf{n},\mu) = -\sum_{\mathbf{L}} \Phi_{i,j}(\mathbf{n},\mu,\mathbf{m}+\mathbf{L}),\nu) U_j(\mathbf{m},\nu)$$

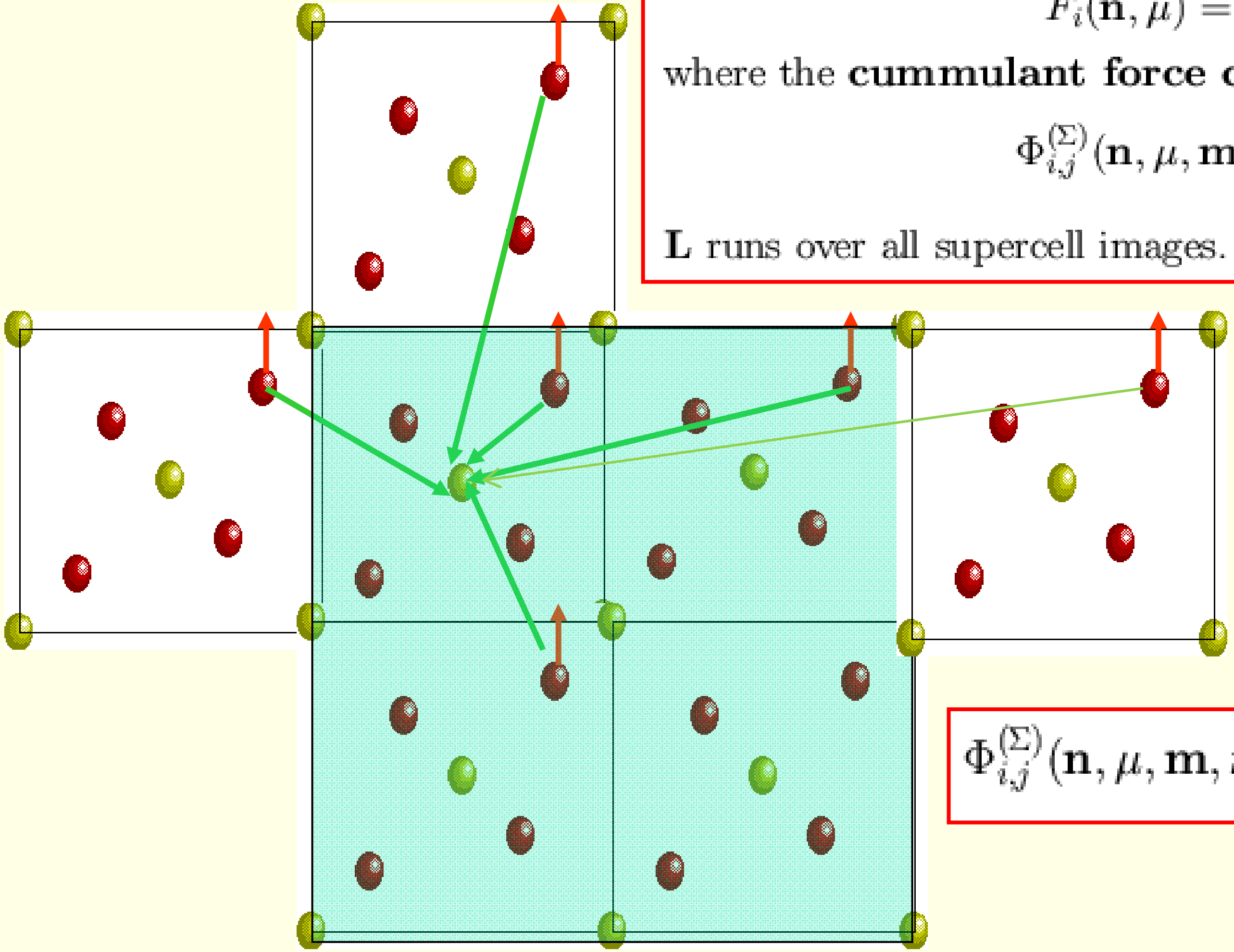
$\mathbf{L} = (L_a, L_b, L_c)$ are the indices of supercell lattice constants.
or

$$F_i(\mathbf{n},\mu) = -\Phi^{(\Sigma)}_{i,j}(\mathbf{n},\mu,\mathbf{m},\nu) U_j(\mathbf{m},\nu)$$

where the **cummulant force constant** is

$$\Phi^{(\Sigma)}_{i,j}(\mathbf{n},\mu,\mathbf{m},\nu) = \sum_{\mathbf{L}} \Phi_{i,j}(\mathbf{n},\mu,\mathbf{m}+\mathbf{L},\nu)$$

L runs over all supercell images.



$$\boxed{\Phi^{(\Sigma)}_{i,j}(\mathbf{n},\mu,\mathbf{m},\nu) = \sum_{\mathbf{L}} \Phi_{i,j}(\mathbf{n},\mu,\mathbf{m}+\mathbf{L},\nu)}$$

Supercell dynamical matrix. Exact wave vectors.

Conventional dynamical matrix:

$$\mathbf{D}(\mathbf{k};\mu,\nu) = \frac{1}{\sqrt{M_\mu M_\nu}} \sum_{\mathbf{m}} \Phi(0,\mu;\mathbf{m},\nu)\, exp\{-2\pi i\mathbf{k}\cdot[\mathbf{R}(0,\mu)-\mathbf{R}(\mathbf{m},\nu)]\}$$

Supercell dynamical matrix:

$$\mathbf{D}^{(SC)}(\mathbf{k};\mu,\nu) = \frac{1}{\sqrt{M_\mu M_\nu}} \sum_{\mathbf{m}\in SC} \Phi^{(SC)}(0,\mu;\mathbf{m},\nu)\, exp\{-2\pi i\mathbf{k}\cdot[\mathbf{R}(0,\mu)-\mathbf{R}(\mathbf{m},\nu)]\}$$

These two matrices are equal if

$$\mathbf{D}^{(SC)}(\mathbf{k};\mu,\nu) = \mathbf{D}(\mathbf{k};\mu,\nu)$$

- **interaction range** is confined **to interior** of supercell (supercell is big enough)
- wave vector is **commensurate with the supercell** and fulfils the condition (independent of interaction range):

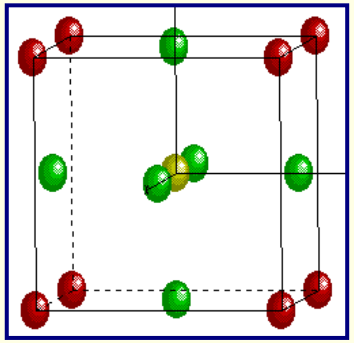
$$exp\{-2\pi i\mathbf{k}_s\cdot\mathbf{L}\} = 1$$

At wave vectors $\mathbf{k}_s$ the phonon frequencies are “exact”, provided the **supercell contains the complete list of neighbors.**

Wave vectors $\mathbf{k}_s$ are commensurate with the supercell size.

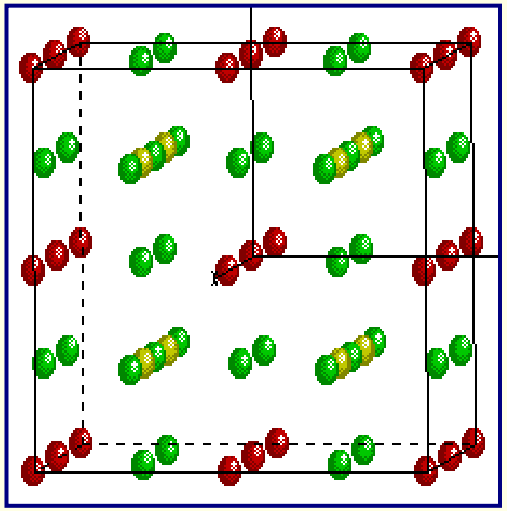
Exact wave vectors

1x1x1



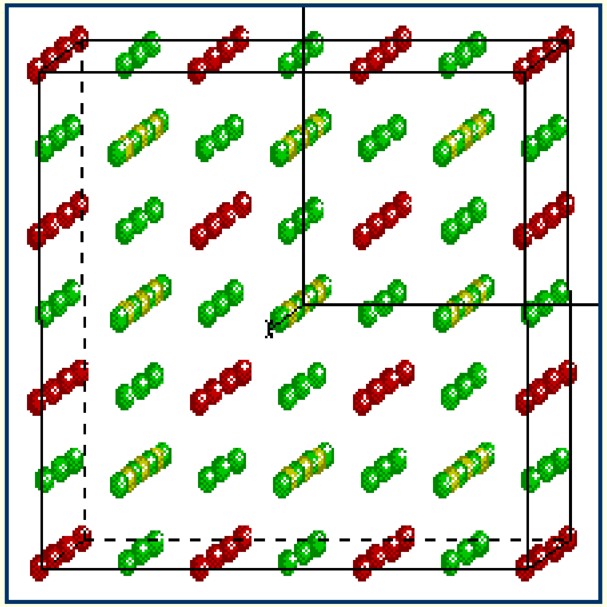
Exact: Γ

2x2x2

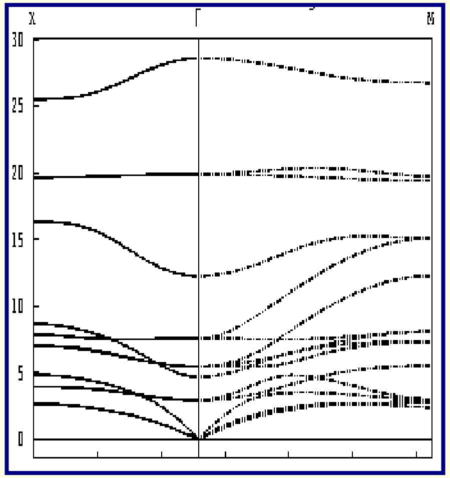


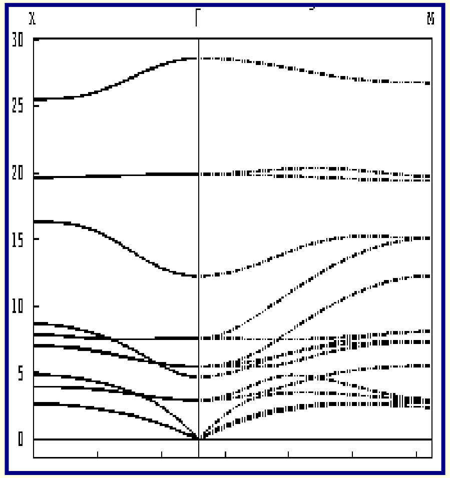
Exact: Γ, X, M, R

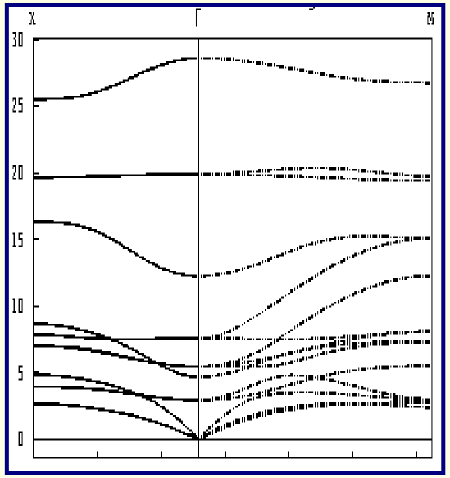
3x3x3



Exact: Γ X Γ M ↓ Γ ↓



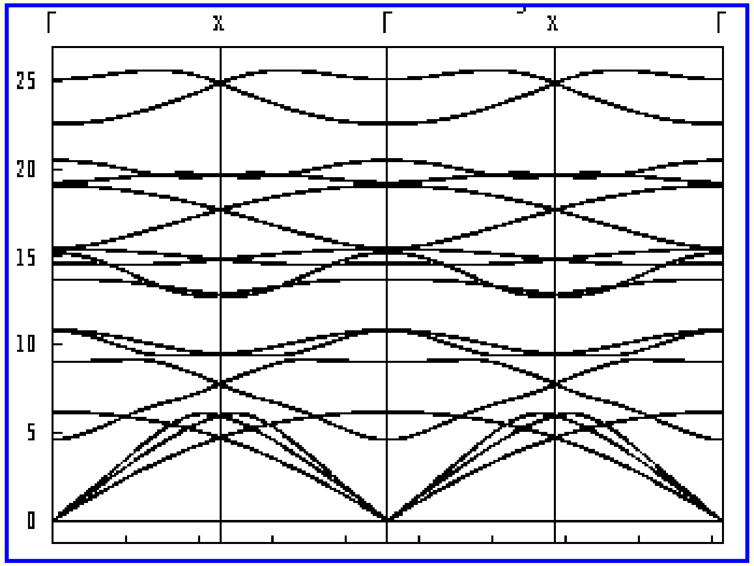




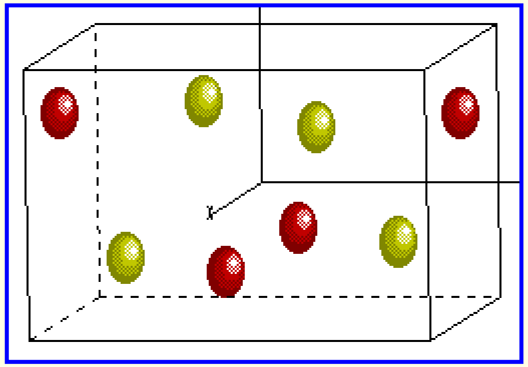
Phonon dispersions + density of states

Frequency

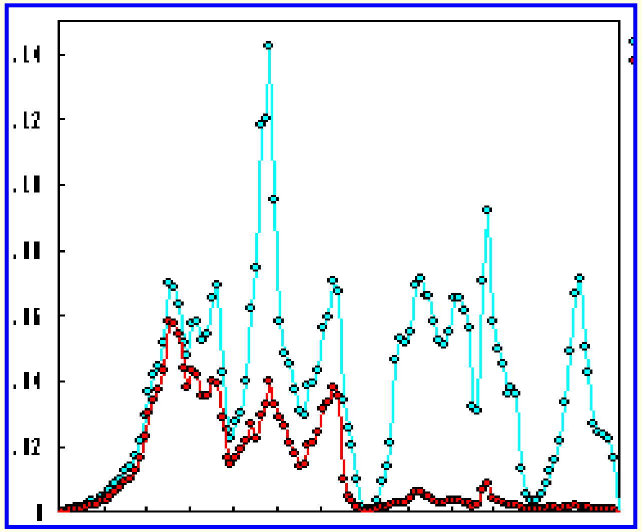
ω



GeO_2 P4_2/mnm

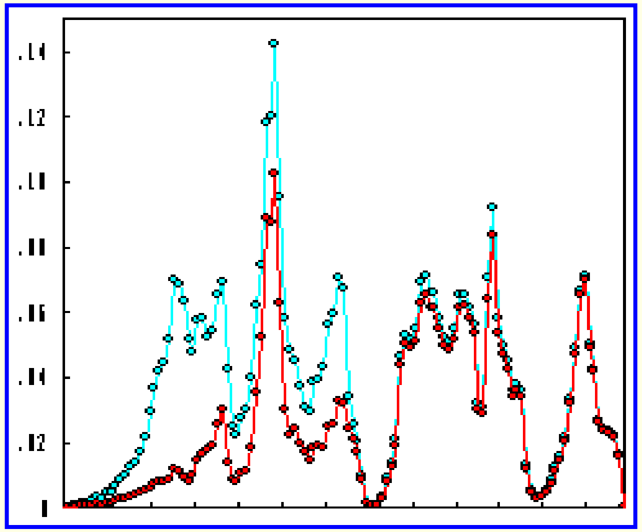


Total + Germanium



ω

Total + Oxygen



ω

Thermodynamic functions of phonon vibrations

Internal energy:

$$\boxed{E \quad = \frac{1}{2} r \int_0^\infty d\omega \, g(\omega) \, (\hbar\omega) \, coth \left(\frac{\hbar\omega}{2k_B T} \right)}$$

Free energy:

$$\boxed{F \quad = r k_B T \int_0^\infty d\omega \, g(\omega) \, ln \left[2sinh \left(\frac{\hbar\omega}{2k_B T} \right) \right]}$$

Entropy:

$$\boxed{S \; = \; r k_B \int_0^\infty d\omega \, g(\omega) \, \left\{ \left(\frac{\hbar\omega}{2k_B T} \right) \left[coth \left(\frac{\hbar\omega}{2k_B T} \right) \; - \; 1 \right] \; - \; ln \left[1 \; - \; exp \left(- \frac{\hbar\omega}{k_B T} \right) \right] \right\} (79)}$$

Heat capacity C$_v$:

$$\boxed{C \quad = r k_B \int_0^\infty d\omega \, g(\omega) \, \left(\frac{\hbar\omega}{k_B T} \right)^2 \frac{exp(\frac{\hbar\omega}{k_B T})}{\left[exp \left(\frac{\hbar\omega}{k_B T} \right) \; - \; 1 \right]^2}}$$

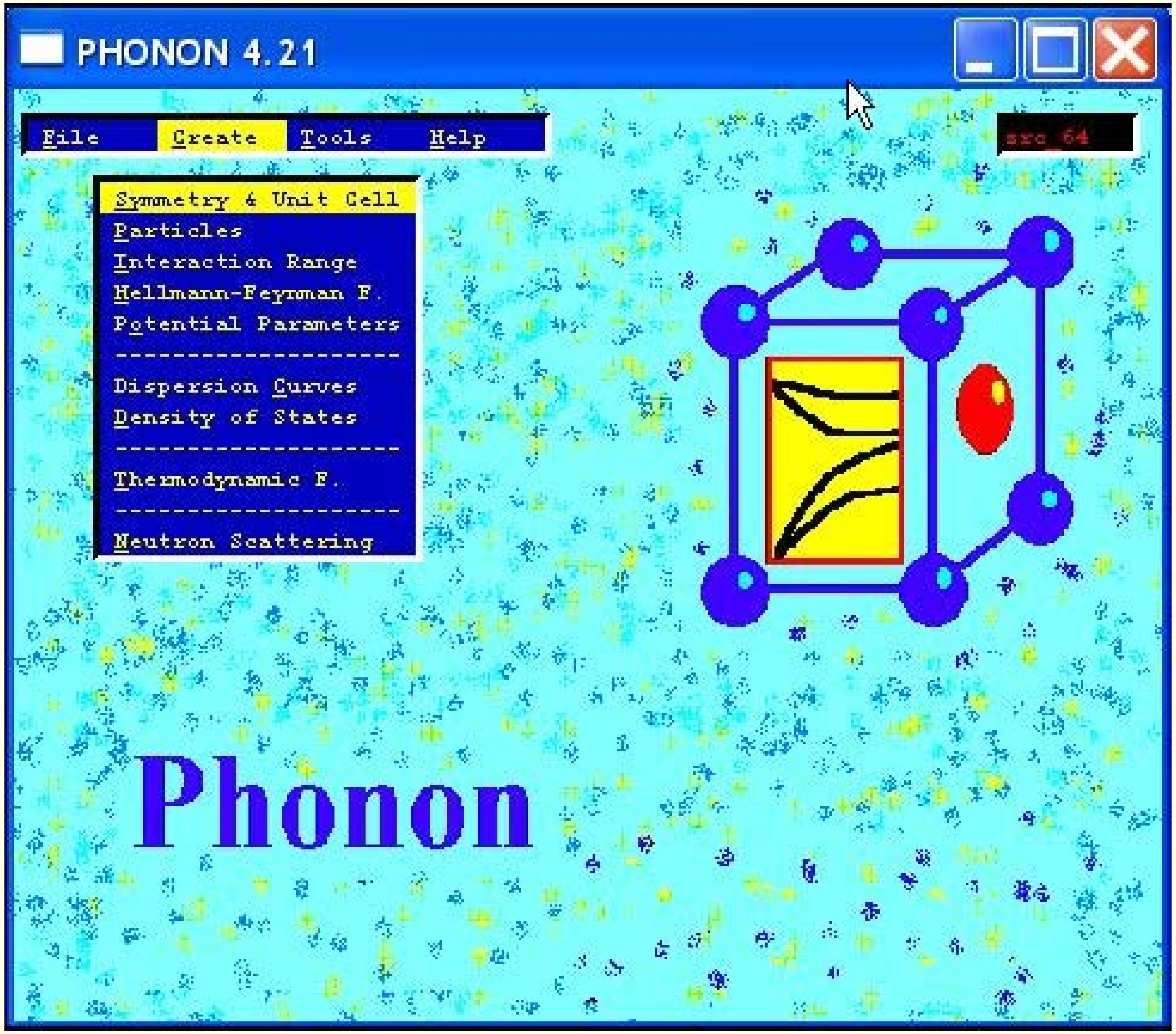
Thermal displacements:

$$\boxed{B_{ij}(\mu) = < U_i(\mu) U_j(\mu) >}$$

$$\boxed{B_{il}(\mu) = \frac{\hbar r}{2M_\mu} \int_0^\infty d\omega \, g_{il,\mu}(\omega) \, \frac{1}{\omega} coth \left(\frac{\hbar\omega}{2k_B T} \right)}$$

PHONON-I

- PHONON
  - *by K.Parlinski (Crakow)*
  - *Linux or MS-windows*
  - *uses a „direct" method to calculate Force-constants with the help of an ab initio program*
  - *with these Force-constants phonons at arbitrary k-points can be obtained*

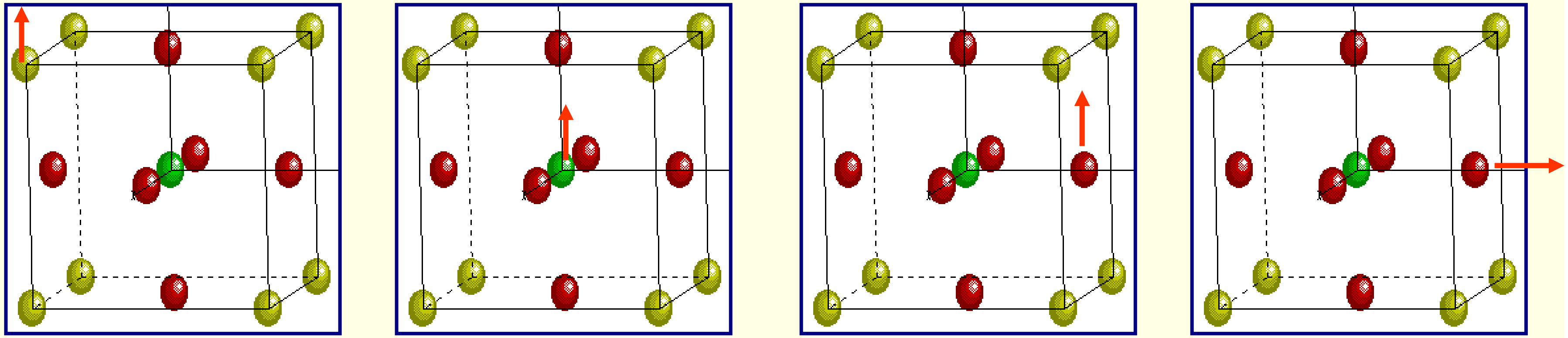


- Define your spacegroup
- Define all atoms

http://wolf.ifj.edu.pl/phonon/

Phonons:

- *selects symmetry adapted atomic displacements (4 displacements in cubic perovskites)*



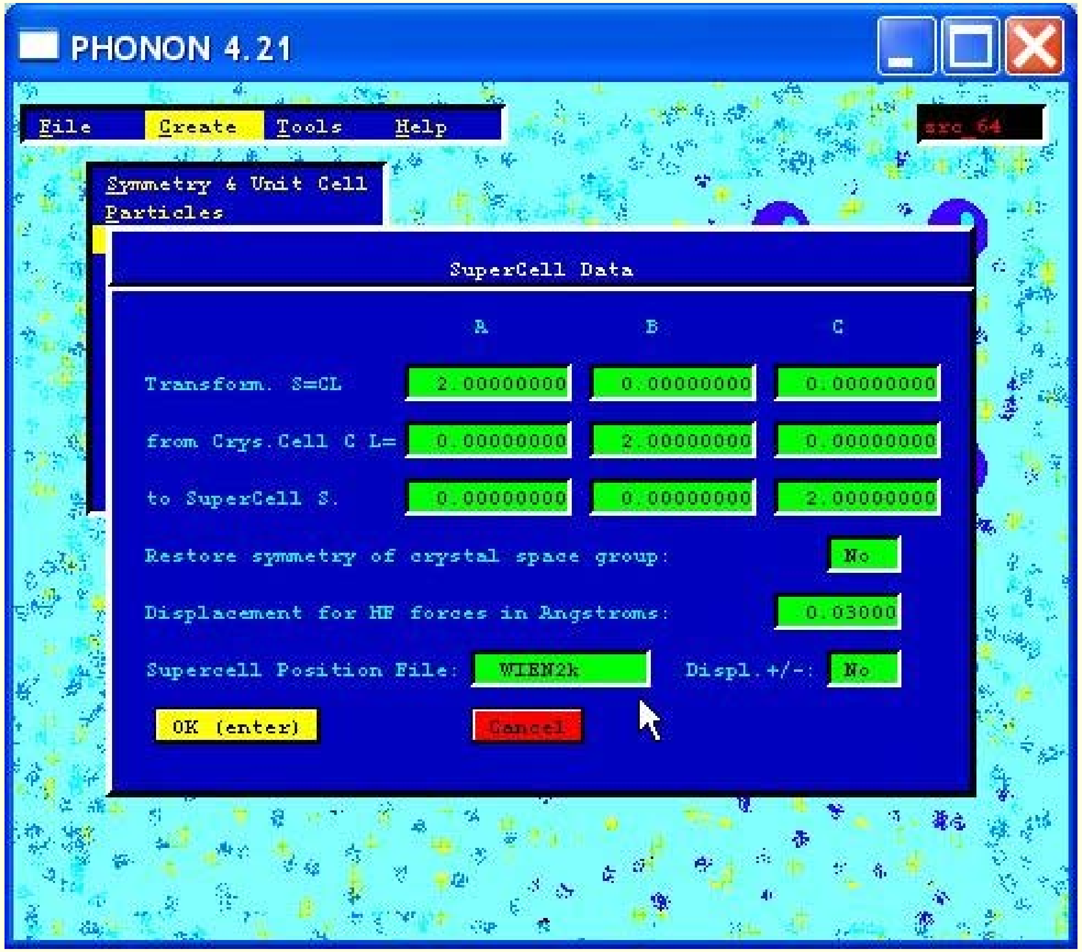
(Displacement pattern for cubic perovskite)

- *select a supercell: (eg. 2x2x2 atom P-type cell)*
- *calculate all forces for these displacements with high accuracy(WIEN2k)*

- *→ force constants between all atoms in the supercell*
- *→ dynamical matrix for arbitrary q-vectors*
- *→ phonon-dispersion ("bandstructure") using PHONON (K.Parlinski)*

PHONON-II

- Define an interaction range (supercell)
  - *create displacement file*
  - *transfer case.d45 to Unix*
- Calculate forces for all required displacements
  - *init_phonon_lapw*
    - for each displacement a case_XX.struct file is generated in an extra directory
    - runs nn and lets you define RMT values like:
      - 1.85 1-16



SuperCell Data

	A	B	C
Transform. S=CL	2.00000000	0.00000000	0.00000000
from Crys.Cell C L=	0.00000000	2.00000000	0.00000000
to SuperCell S.	0.00000000	0.00000000	2.00000000

Restore symmetry of crystal space group: No

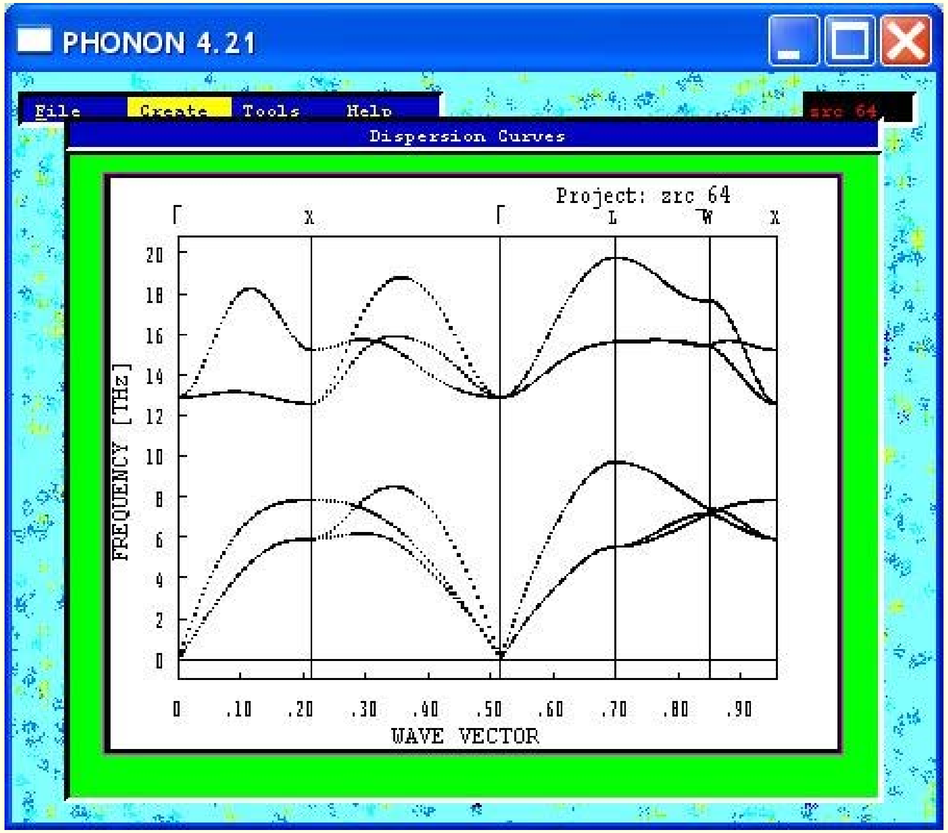
Displacement for HF forces in Angstroms: 0.03000

Supercell Position File: WIEN2k Displ.+/-: No

- init_lapw: either without symmetry (and then copies this setup to all case_XX)
  or with symmetry (must run init_lapw for all case_XX) (Do NOT use SGROUP)
- run_phonon: run_lapw –fc 0.1 –i 40 for each case_XX

PHONON-III

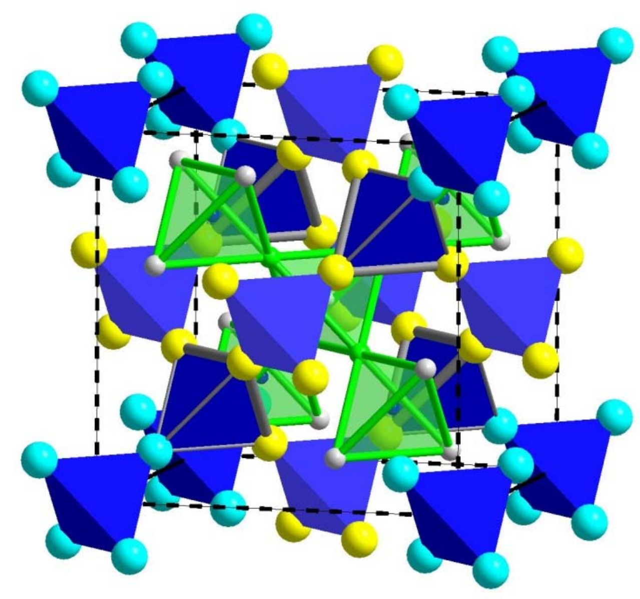
- analyze_phonon_lapw
  - *reads the forces of the scf runs*
  - *generates „Hellman-Feynman" file case.dat and a „symmetrized HF-file case.dsy (when you have displacements in both directions)*
    - check quality of forces:
    - sum F_x should be small (0)
    - abs(F_x) should be similar for +/- displacements
- transfer case.dat (dsy) to Windows
- Import HF files to PHONON
- Calculate force constants
- Calculate phonons, analyze phonons eigenmodes, thermodynamic functions

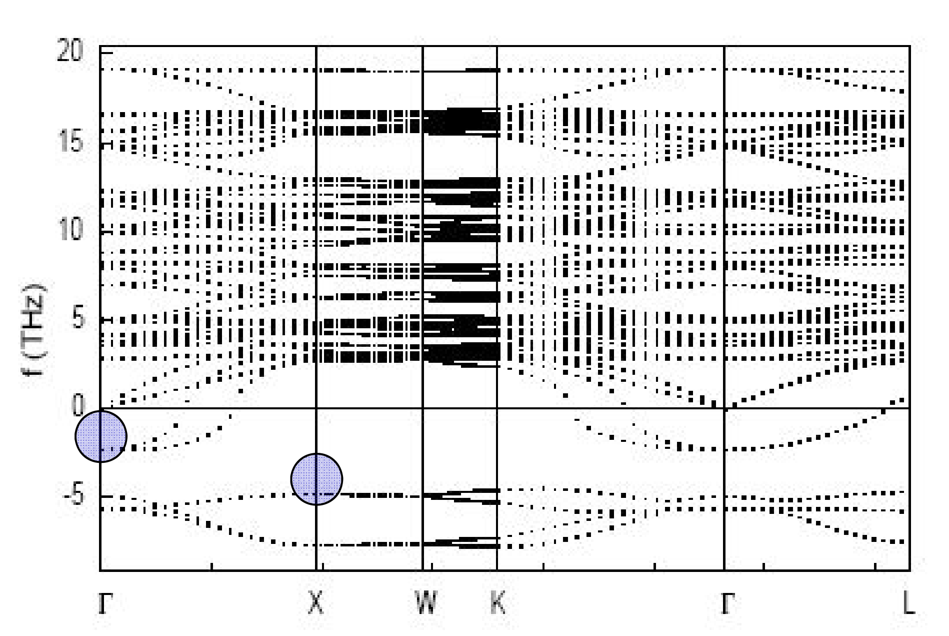


Applications:

- phonon frequencies (compare with IR, raman, neutrons)
- identify dynamically unstable structures, describe phase transitions, find more stable (low T) phases.
- free energies at T>0; quasiharmonic approximation

Pyrochlore structure of $Y_2Nb_2O_7$: strong phonon instabilities → phase transition




f (THz)
Γ
X
W
K
Γ
L