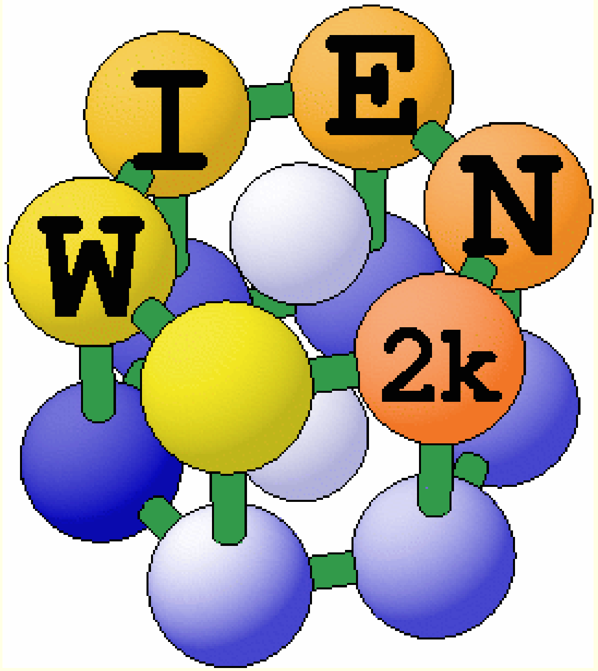
WIEN2k software package



WIEN97: ~500 users
WIEN2k: ~960 users

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

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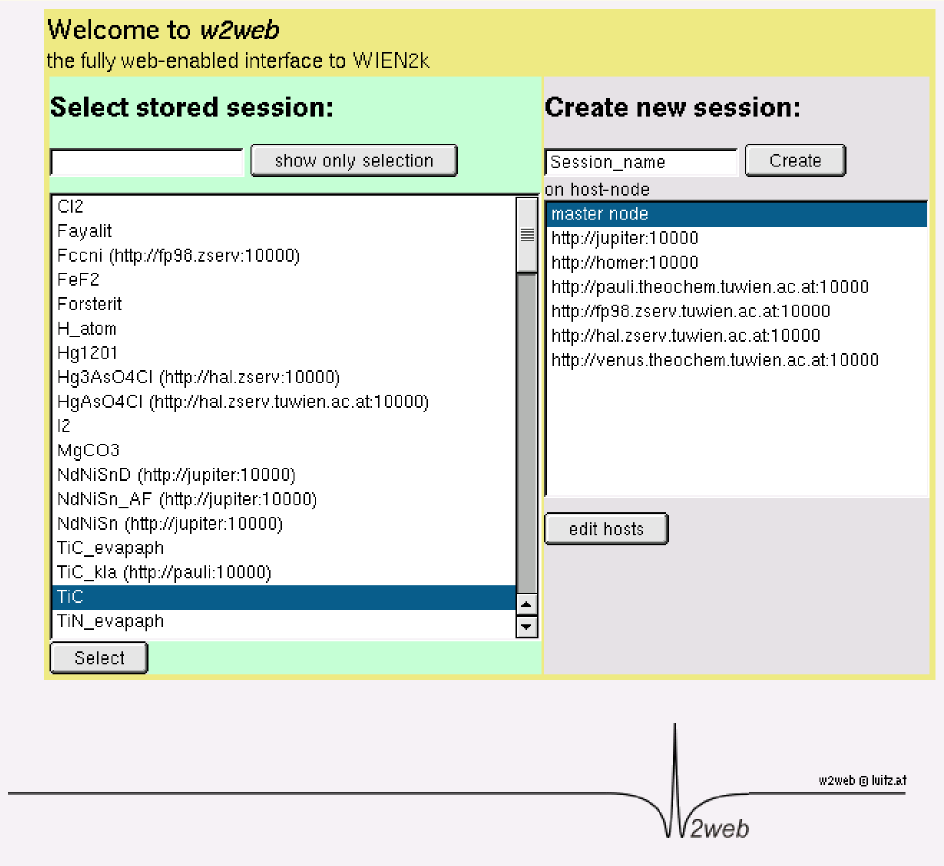
http://www.wien2k.at

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 of 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*
    - mozilla 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:

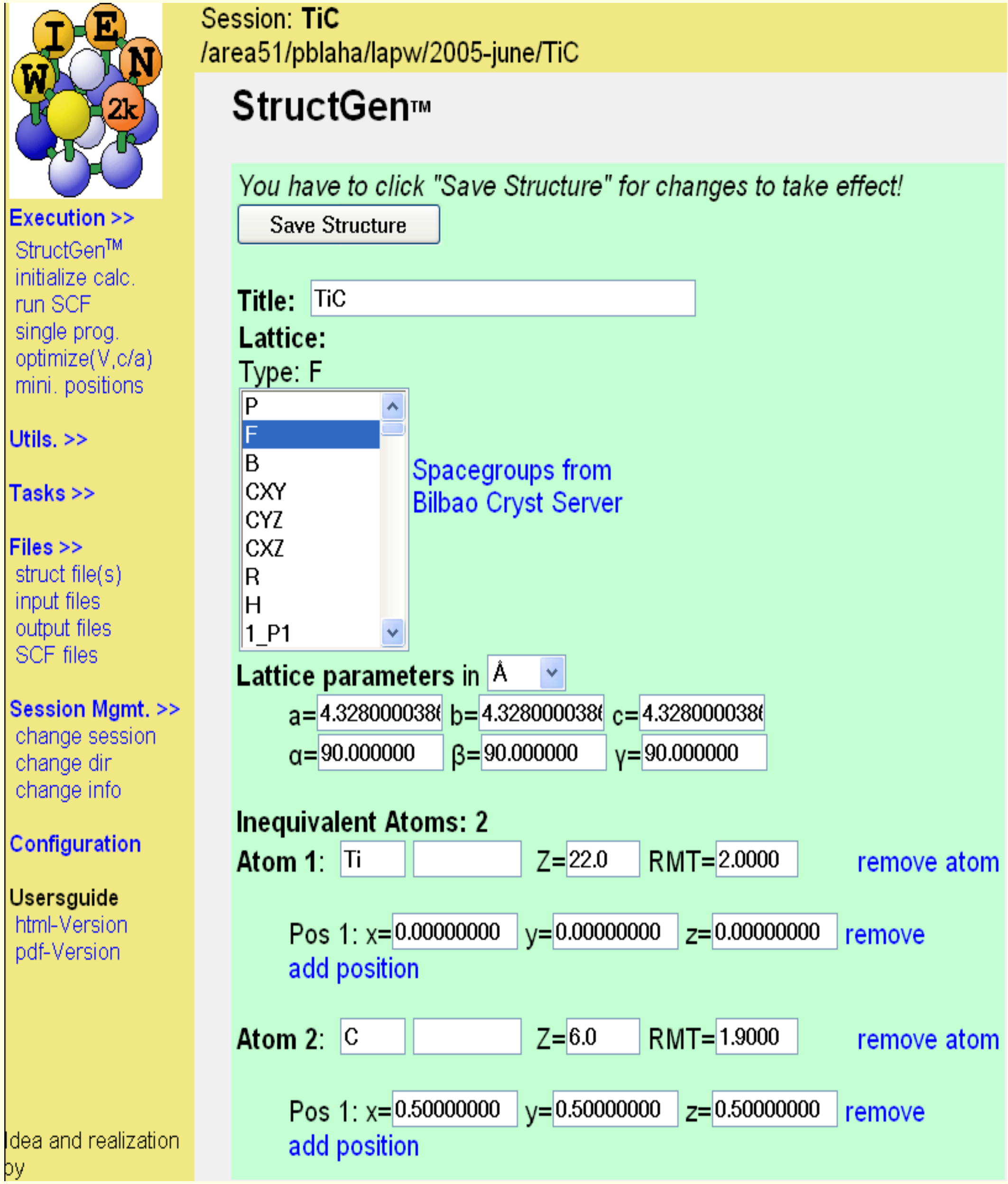
Session_name

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 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!

Save Structure

Title: TiC

Lattice:

Type: F

Lattice parameters in Å

a=4.328000038 b=4.328000038 c=4.328000038

α=90.000000 β=90.000000 γ=90.000000

Inequivalent Atoms: 2

Atom 1: Ti Z=22.0 RMT=2.0000 remove atom

Pos 1: x=0.00000000 y=0.00000000 z=0.00000000 remove

add position

Atom 2: C Z=6.0 RMT=1.9000 remove atom

Pos 1: x=0.50000000 y=0.50000000 z=0.50000000 remove

add position

Spacegroup $P4_2$/mnm

Structure given by:

spacegroup

lattice parameter

positions of atoms

(basis)

Rutile TiO_2:

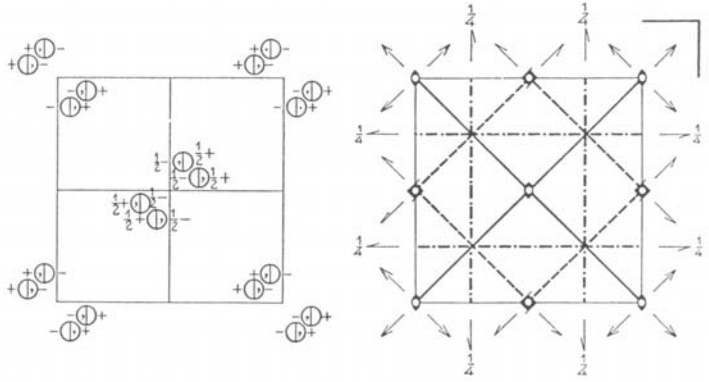
$P4_2$/mnm (136)

a=8.68, c=5.59 bohr

Ti: (0,0,0)

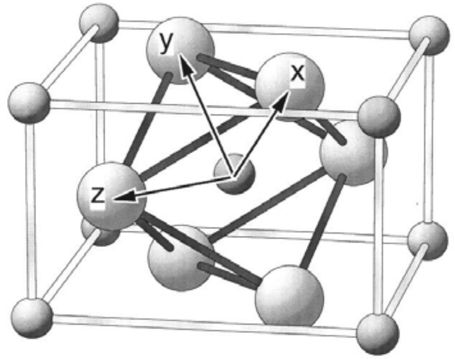
O: (0.304,0.304,0)

$P4_2/mnm$ D_{4h}^{14} 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
16	*k*	1	x,y,z; $x,y,\bar{z}$; y,x,z; $y,x,\bar{z}$;	$\bar{x},\bar{y},z$; $\bar{x},\bar{y},\bar{z}$; $\bar{y},\bar{x},z$; $\bar{y},\bar{x},\bar{z}$;	$\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z$; $\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}-z$; $\frac{1}{2}+y,\frac{1}{2}-x,\frac{1}{2}+z$; $\frac{1}{2}+y,\frac{1}{2}-x,\frac{1}{2}-z$;	$\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}+z$; $\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z$; $\frac{1}{2}-y,\frac{1}{2}+x,\frac{1}{2}+z$; $\frac{1}{2}-y,\frac{1}{2}+x,\frac{1}{2}-z$.	General: *hkl*: No conditions *hk*0: No conditions 0*kl*: $k+l=2n$ *hhl*: No conditions
8	*j*	*m*	x,x,z; $x,x,\bar{z}$;	$\bar{x},\bar{x},z$; $\bar{x},\bar{x},\bar{z}$;	$\frac{1}{2}+x,\frac{1}{2}-x,\frac{1}{2}+z$; $\frac{1}{2}+x,\frac{1}{2}-x,\frac{1}{2}-z$;	$\frac{1}{2}-x,\frac{1}{2}+x,\frac{1}{2}+z$; $\frac{1}{2}-x,\frac{1}{2}+x,\frac{1}{2}-z$.	Special: as above, plus no extra conditions
8	*i*	*m*	$x,y,0$; $y,x,0$;	$\bar{x},\bar{y},0$; $\bar{y},\bar{x},0$;	$\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}$; $\frac{1}{2}+y,\frac{1}{2}-x,\frac{1}{2}$;	$\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}$; $\frac{1}{2}-y,\frac{1}{2}+x,\frac{1}{2}$.	
8	*h*	2	$0,\frac{1}{2},z$; $\frac{1}{2},0,z$;	$0,\frac{1}{2},\bar{z}$; $\frac{1}{2},0,\bar{z}$;	$0,\frac{1}{2},\frac{1}{2}+z$; $\frac{1}{2},0,\frac{1}{2}+z$;	$0,\frac{1}{2},\frac{1}{2}-z$; $\frac{1}{2},0,\frac{1}{2}-z$.	*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*	$0,0,0$;	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$.			

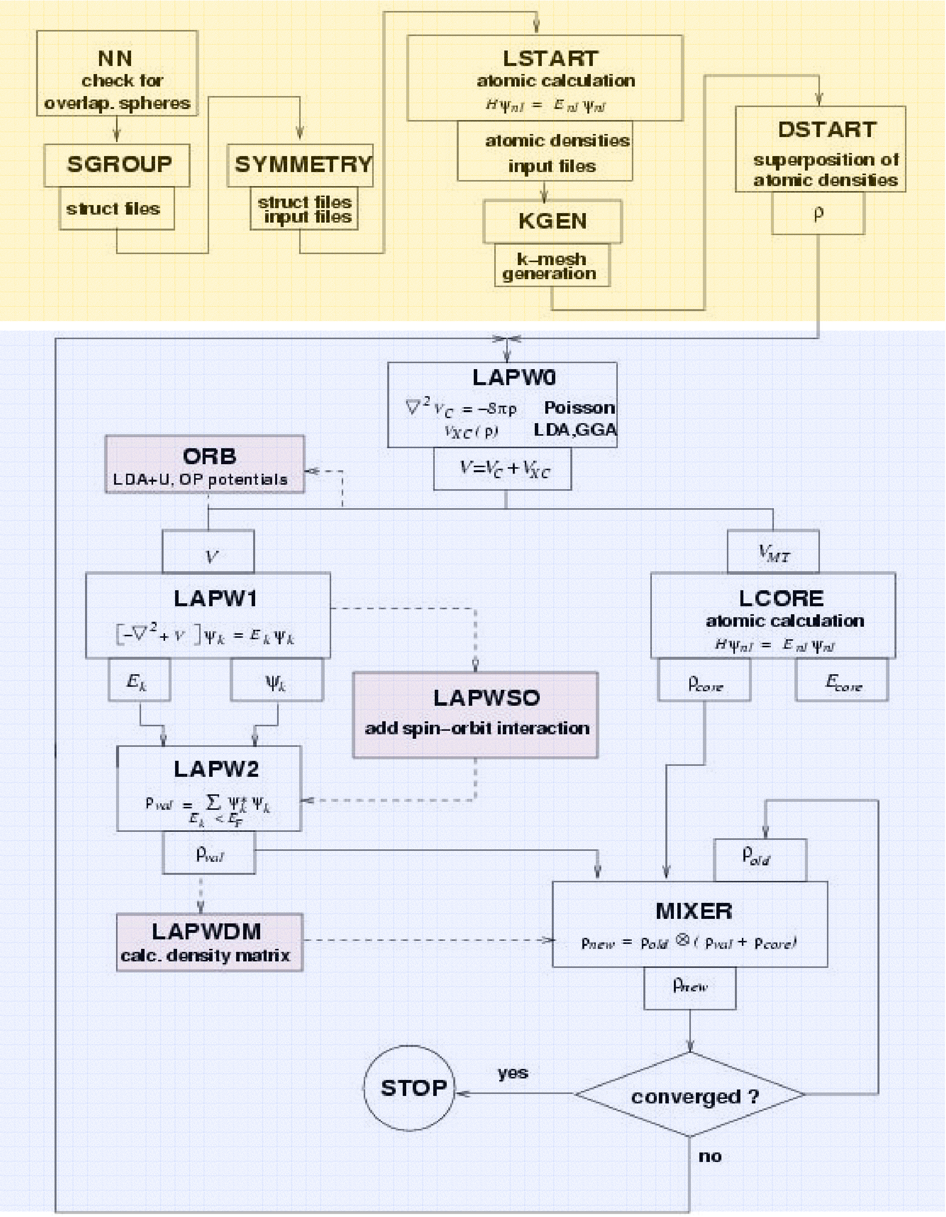


Structure generator

- 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 and generates case.inst*
- „set RMT and continue": (specify proper "reduction" of NN-distances)
  - *non-overlapping „as large as possible" (saves time), but not larger than 3 bohr*
  - *RMT for sp-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*
- „save structure – save+cleanup"

Program structure of WIEN2k

- init_lapw
  - *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*



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)*
  - *-p* *parallel calculation (needs .machines file)*
  - *-so* *add spin-orbit*
  - *Spacegroups without inversion use automatically lapw1c, lapw2c (case.in1c,in2c)*
  - *If scf-cycle diverges (grep :DIS case.scf): check struture; reduce mixing in case.inm; rm *.broyd* case.scf; x dstart*
- 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 :CTO001 :NTO001 :QTL001
    - :FOR002: 2.ATOM 19.470 0.000 0.000 19.470
    - :FGL002: 2.ATOM 13.767 13.767 0.000
    - :LAT :VOL :POSxxx

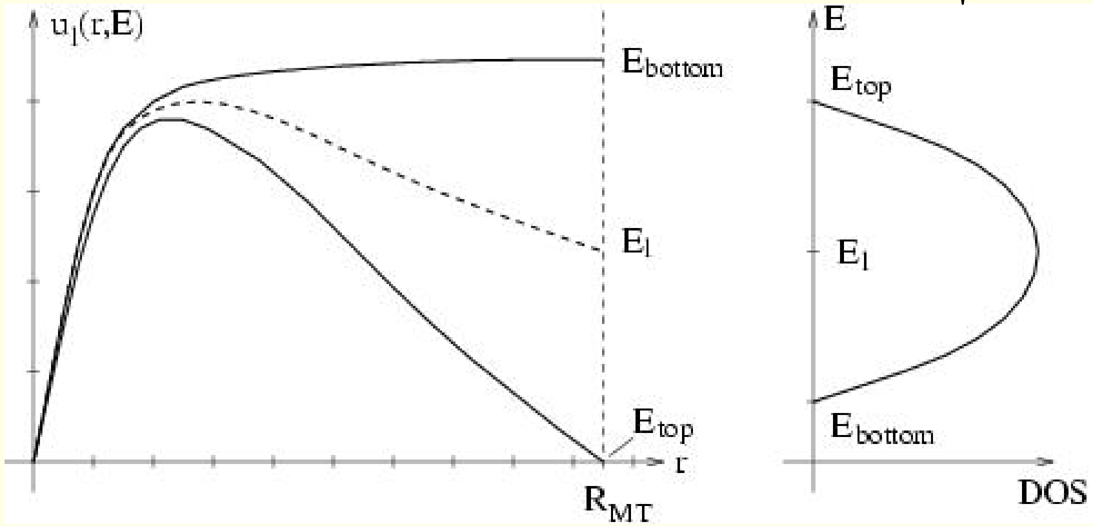
case.in1

```
WFFIL                          (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
```

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

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

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



case.in1 (cont.), case.in2

```
K-VECTORS FROM UNIT:4     -7.0     1.5     emin/emax window
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
```

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

run_lapw -ql 0.05 -in1new 1

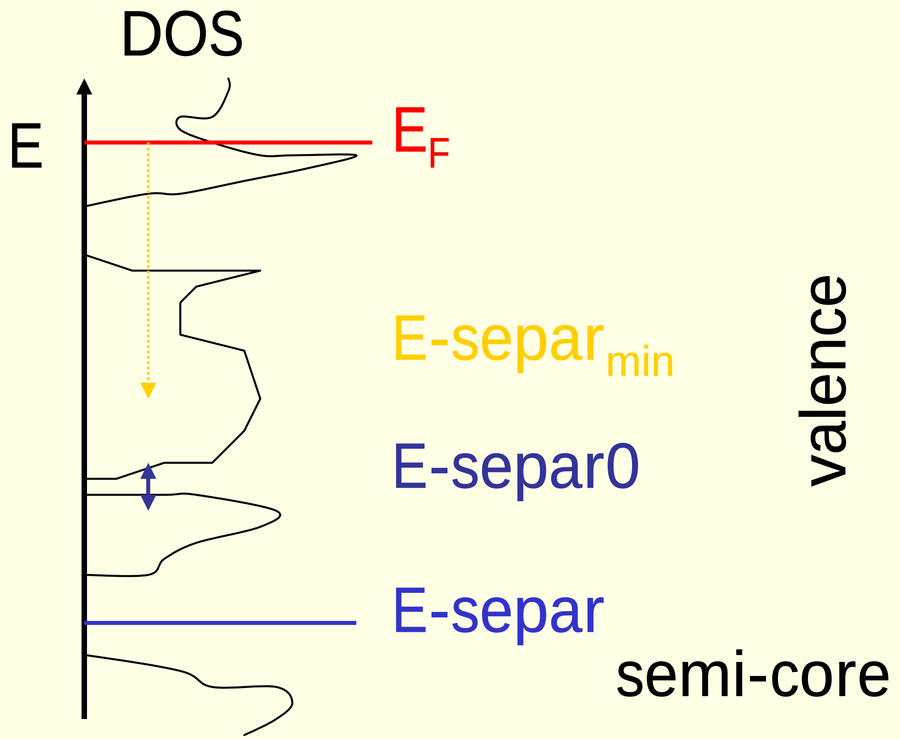
- Alternative case.in1 file produced by write_in1:

case.scf2:

```
Energy to separate semicore and valencestates:   0.34941
:FER  : F E R M I - ENERGY(TETRAH.M.)=   0.79528
       Q-s-low E-s-low   Q-p-low E-p-low   Q-d-low E-d-low
:EPL01:1.9813 -2.6852    5.5892 -1.1099    0.0873  0.0910
       Q-s-hi  E-s-hi    Q-p-hi  E-p-hi    Q-d-hi  E-d-hi
:EPH01:0.0668  0.5152    0.1752  0.6174    1.0614  0.6181
```

➔ case.in1:

```
WFFIL         (WFPRI, SUPWF)
  7.00         10     4
 .49528   6    0
 0     0.515     0.000 CONT 1
 0    -2.685     0.000 CONT 1
 1     0.617     0.000 CONT 1
 1    -1.110     0.000 CONT 1
 2     0.618     0.000 CONT 1
 2     0.091     0.000 CONT 1
 ...
```



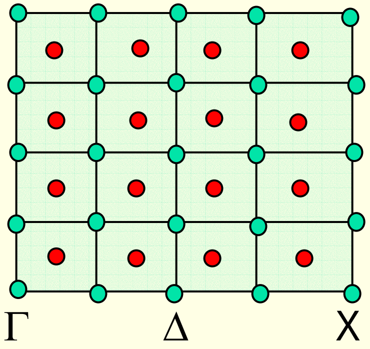
BZ integration, “FERMI”-methods

- 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 0.005)
      - temperature broadening (TEMP 0.005)
  - *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)
  - *always "add inversion" except in magnetic spin-orbit calculations*
    - time inversion holds and E(k) = E(-k)
  - *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*
  - *continue later with finer mesh*
    - mesh was good if nothing changes and scf terminates after few (3) iterations
  - *use an even finer meshes for DOS, spectra, optics,…*

Program execution:

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

  x lapw2 –up –c

- 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*

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.

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*

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 cells*
  - *Phonons via supercells*
    - interface to PHONON (K.Parlinski) – bands, DOS, thermodynamics, neutrons
- 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)*

Properties with WIEN2k - III

- New developments (in progress)
  - *non-collinear magnetism (available on request: www.wien2k.at)*
  - *transport properties (Fermi velocities, Seebeck, conductivity, thermoelectrics, ..) (G.Madsen's BotzTrap code)* www.chem.au.dk/~webuorg/new/groups/gm/gm.html)
  - *non-linear optics (available on request)*
  - *Bethe-Salpeter equation (Excitons)*
  - *Compton profiles*
  - *linear response (phonons, E-field) (C.Ambrosch-Draxl)*
  - *stress tensor (C.Ambrosch-Draxl)*
  - *approximate HartreeFock (+Hybrid functionals), exact exchange, GW*
  - *grid-computing*

Cohesive energy

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

- $E^{crystal}$: 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 FCC box (identical RMT, RKmax, 1 k-point, spinpolarized)

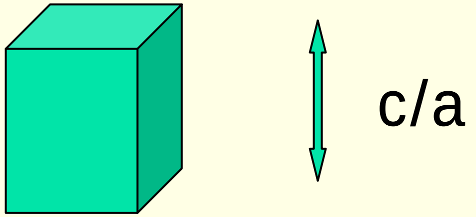
Structural optimizations:

- Lattice parameters, volume, c/a ratio only via total energies:
  - *x optimize: create 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)
      - different “save_lapw” (into a directory with specific names)
      - replace “run_lapw” by “runsp_lapw” or min_lapw –I –j “run_lapw –I –fc 1”
  - *execute optimize.job*
  - *plot (analyse) the results*

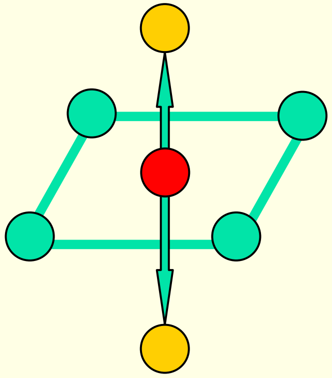
  - *combinations of volume and c/a are possible:*
    - “x optimize” always uses case_initial.struct (if present)
    - do a “volume” optimization to create case_vol_xx.struct files
    - copy the respective case_vol_xx.struct file to case_initial.struct
    - x optimize with “c/a” for this particular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



Total energies and atomic forces

(Yu et al.; Kohler et al.)

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

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

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

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

- 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

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

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

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

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

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:
  - *run_lapw –fc 1.0   (mRy/bohr)*
    - grep :for002 case.scf
      - 200.
      - -130.
      - 140.
      - 135   only F_{HF} + F_{core}
      - 120
      - 122   forces converging
      - 121
      - -12.3 F_{HF} + F_{core} + F_{val}, only this last number is correct
- Forces are usefull for
  - *structural optimization (of internal parameters)*
  - *phonons*

Structural optimization of internal parameters

- /home/pblaha/tio2> min_lapw -h
  - *OPTIONS:*
    - -j JOB -> job-file JOB (run_lapw -I -fc 1. -i 40)
    - -p -> does a k-point parallel calculation
    - -sp -> does a spin-polarized calculation (runsp_lapw)
    - -NI/-I -> without/with initialization of input-files (after inM changes)
    - -i NUMBER -> max. NUMBER (50) of structure changes
  - *CONTROL FILES:*
    - .minstop stop after next structure change
- /home/pblaha/tiO2> cat tio2.inM
    - PORT 2.0 #(NEW1, NOSE, MOLD, tolf (a4,f5.2))
    - 1.0 1.0 1.0 0.7 # Atom1
    - 1.0 1.0 1.0 0.7 # Atom2 (NEW1: 1,2,3:delta, 4:eta(1=MOLD))
- monitor minimization in file case.scf_mini
  - *contains last iteration of each geometry step*
  - *If minimizations gets stuck or oscillates:*
    - change deltas, rm case.tmpM

Optimization of atomic posistions (E-minimization via forces)

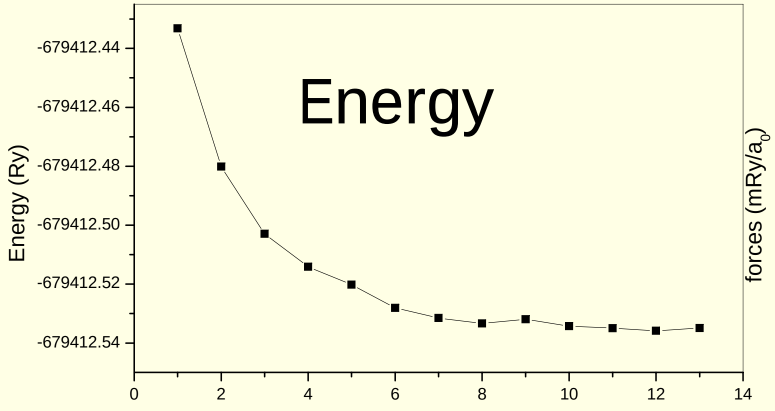
- damped Newton mechanics scheme

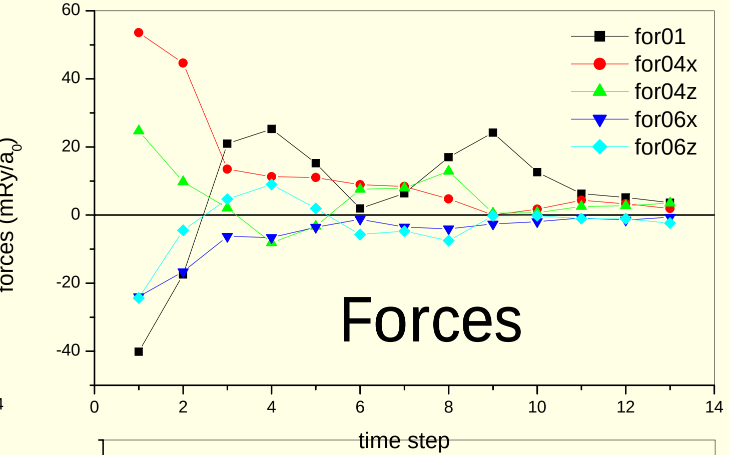
(at the moment not very user friendly, input adjustment by hand)

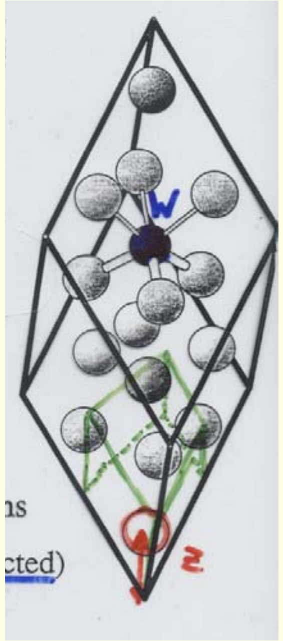
$$\vec{F}_i = -\frac{\partial E}{\partial \vec{R}_i}$$

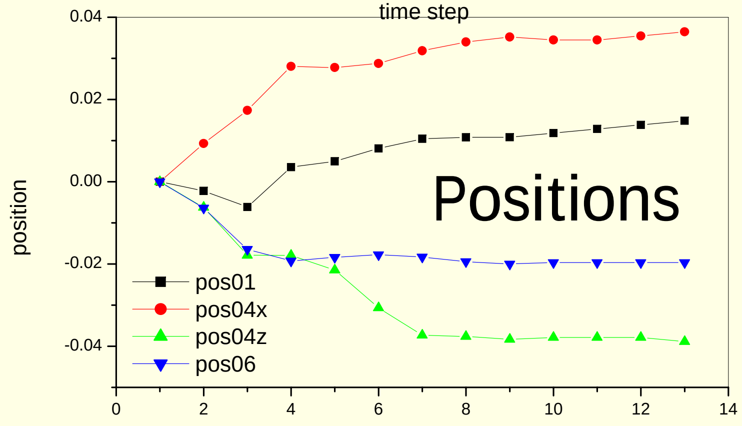
- new quite efficient quasi-Newton (Broyden) scheme

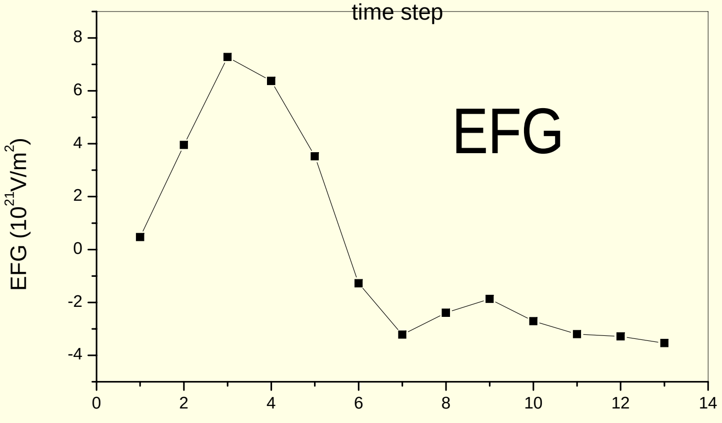
W impurity in Bi (2x2x2 supercell: $Bi_{15}W$)



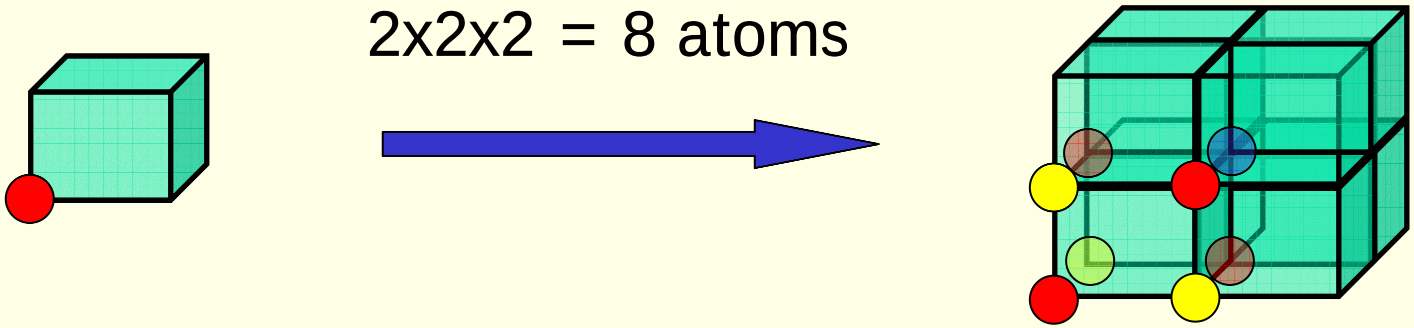








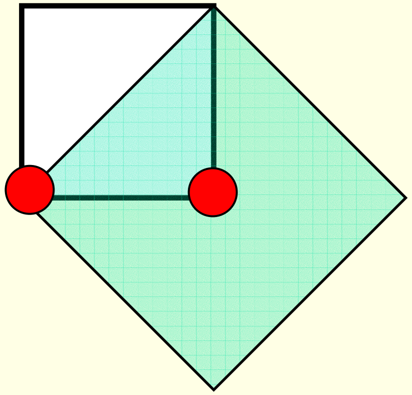
Supercells


2x2x2 = 8 atoms

(0,0,0)	P➔ 8 atoms	(0,0,0)	(.5,0,0)	(.5,.5,0)	(.5,.5,.5)
			(0,.5,0)	(.5,0,.5)	
			(0,0,.5)	(0,.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

Supercells

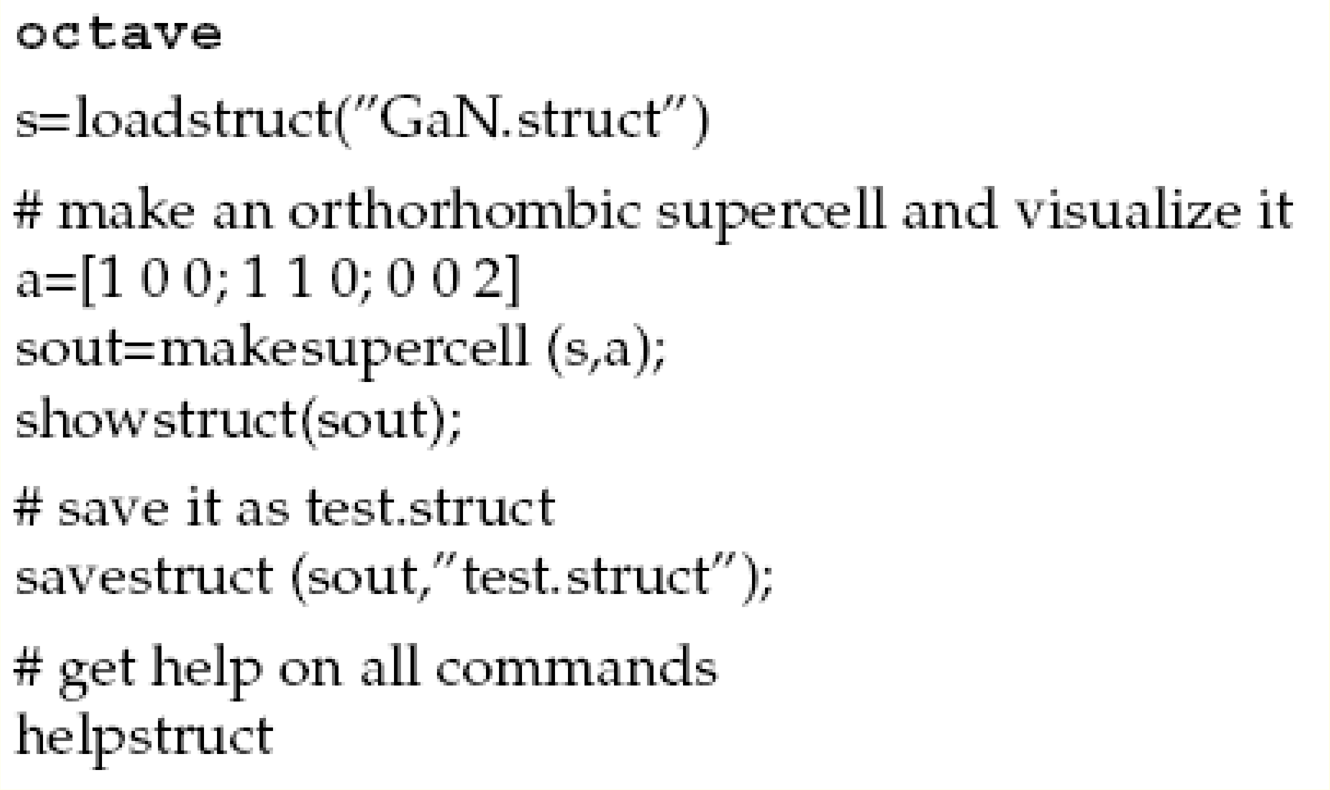


$\sqrt{2}x\sqrt{2}$ supercells (1 ➔ 2 atoms)

- 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!!!
  - *replace (impurities, vacancies) or displace (phonons) at least 1 atom*
- At present „supercell“ works only along unit-cell axes!!!

Structeditor (by R.Laskowski)

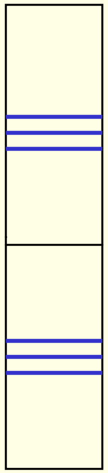
- requires octave (mathlab) and opendx (visualization)
- allows complex operations on struct-files



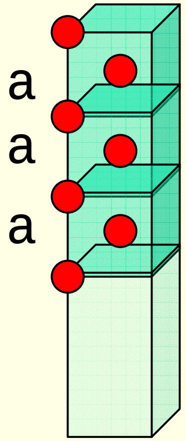
```
octave
s=loadstruct("GaN.struct")
# make an orthorhombic supercell and visualize it
a=[1 0 0; 1 1 0; 0 0 2]
sout=makesupercell (s,a);
showstruct(sout);
# save it as test.struct
savestruct (sout,"test.struct");
# get help on all commands
helpstruct
```

Surfaces

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

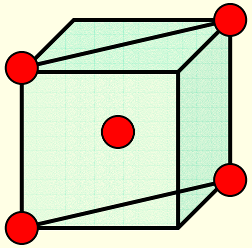
shift to
➔
inversion

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

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

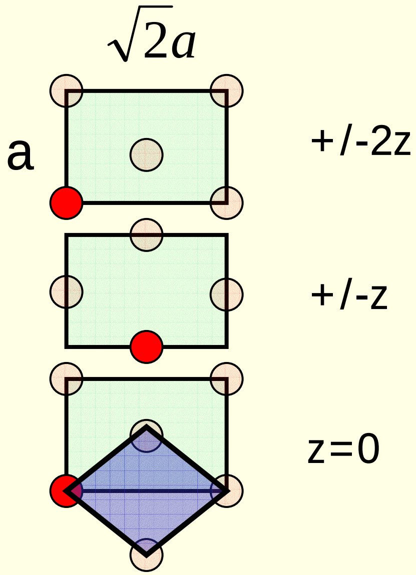
z= a/2c

bcc (110):

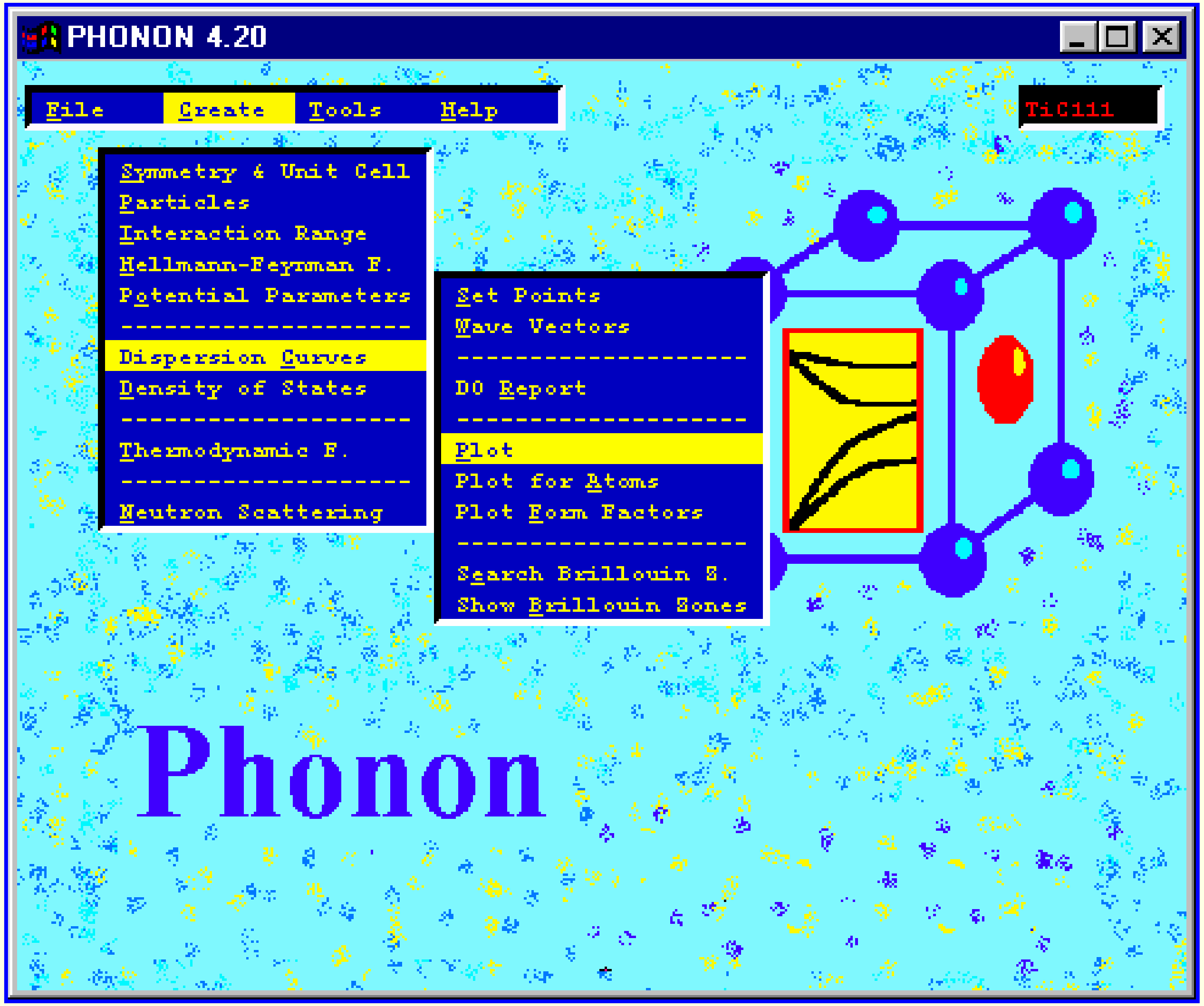


orthorhombic CXY-lattice: a, $\sqrt{2}a$, c

(0 0 0) z=a/$\sqrt{2}a$ c
(0 .5 +/-z)
(0 0 +/-2z)

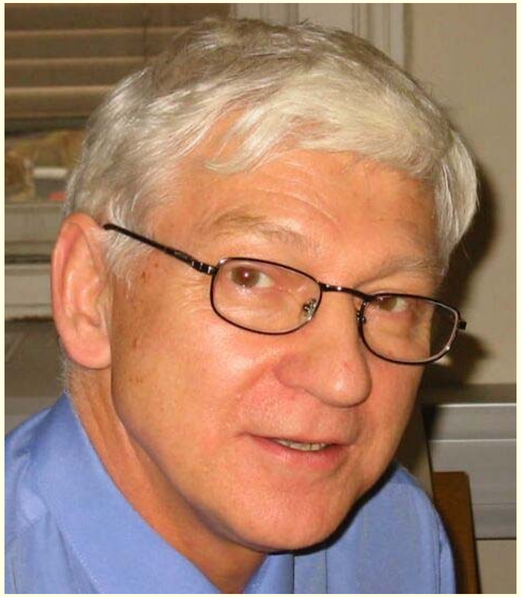


Calculations of Phonons: The Direct Method



WIEN2k + Phonon

Copyright by K.Parlinski



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

(alternatively use D.Alfe`s PHON code
+W2P-interface from G.Madsen)

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 $\frac{\partial E}{\partial \mathbf{R}_i(\mathbf{n},\mu)} \mid_o = 0$.

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.

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.

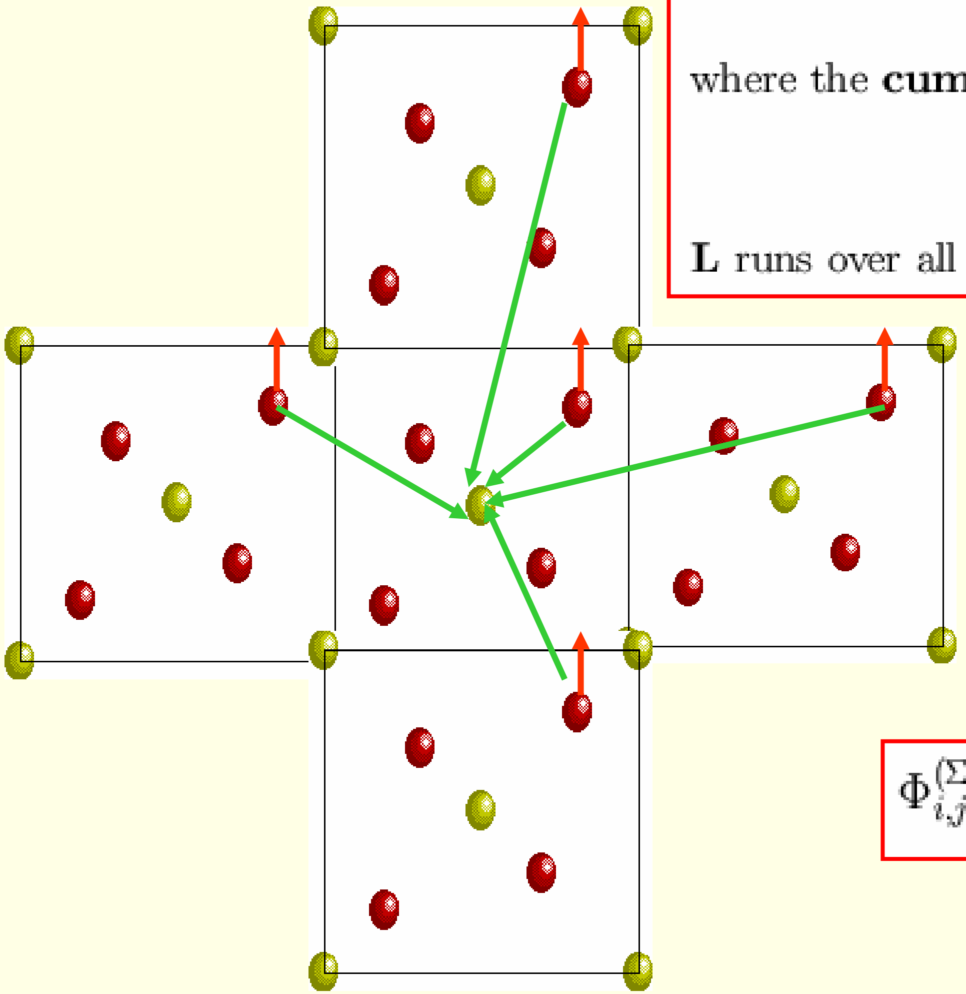
or

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

where the **cummulant force constant** is

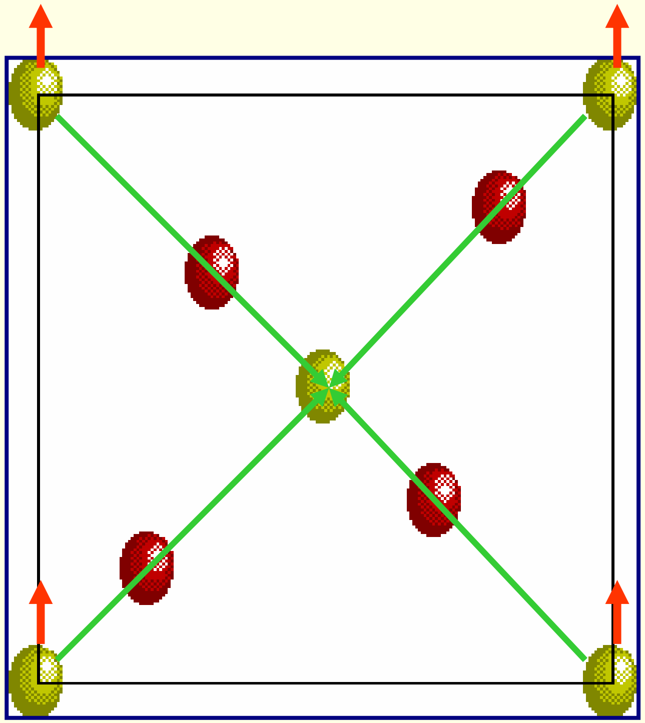
$$\Phi^{(\Sigma)}_{i,j}(\mathbf{n},\mu,\mathbf{m},\nu) = \sum_{\mathbf{L}} \Phi_{i,j}(\mathbf{n},\mu,\mathbf{m}+\mathbf{L},\nu)$$

$\mathbf{L}$ 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 Force Constants



For atoms at supercell surface, edges, corners we define **supercell force constants** (SC)

$$\boxed{\Phi_{i,j}^{(SC)}(\mathbf{n},\mu,\mathbf{m},\nu) = \frac{1}{n_{\mathbf{m}}}\Phi_{i,j}^{(\Sigma)}(\mathbf{n},\mu,\mathbf{m}+\mathbf{L},\nu)}$$

n_m – number of equivalent atoms, on surfaces, edges, or corners of supercell.
n_m = 1 for all inner atoms of supercell

Master equation of direct method

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

Sum (**m**, ν) over atoms within the supercell

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):

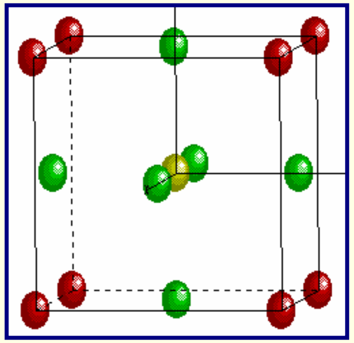
$$exp\{-2\pi i\mathbf{k}_s\cdot\mathbf{L}\}=1$$

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.

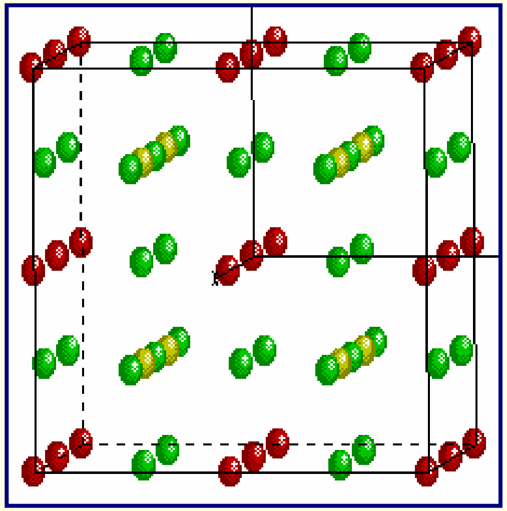
Exact wave vectors

1x1x1



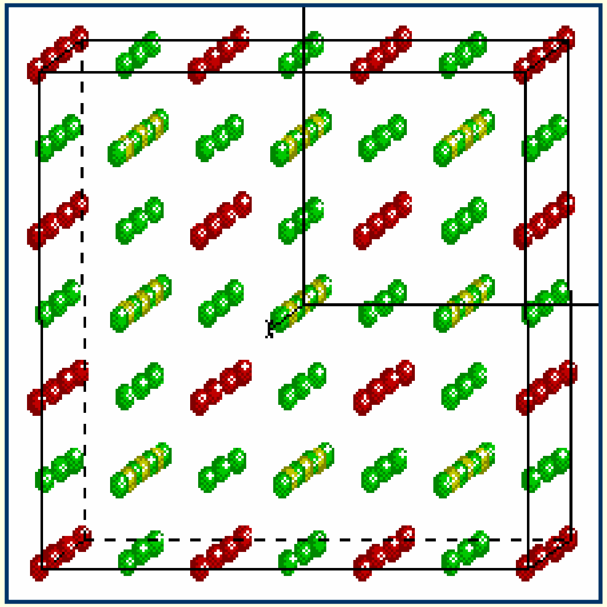
Exact: Γ

2x2x2



Exact: Γ, X, M, R

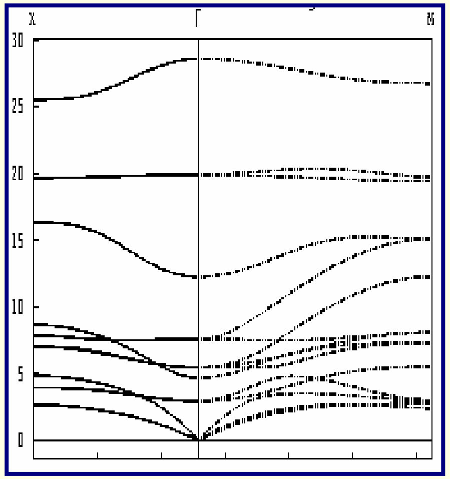
3x3x3

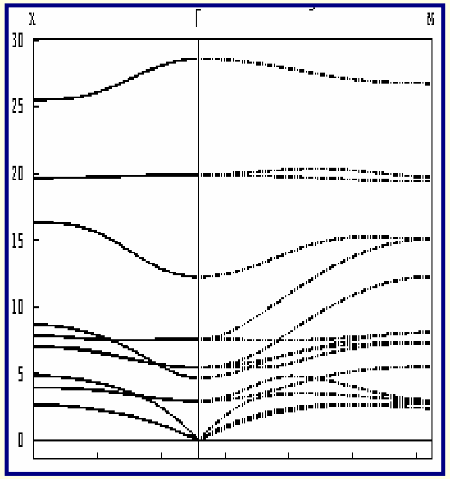


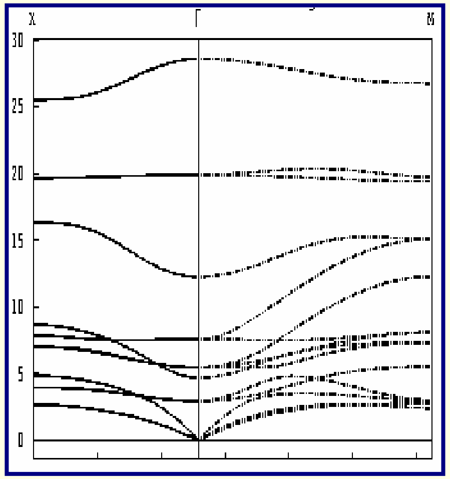
Exact: Γ

X Γ M

↓ Γ ↓



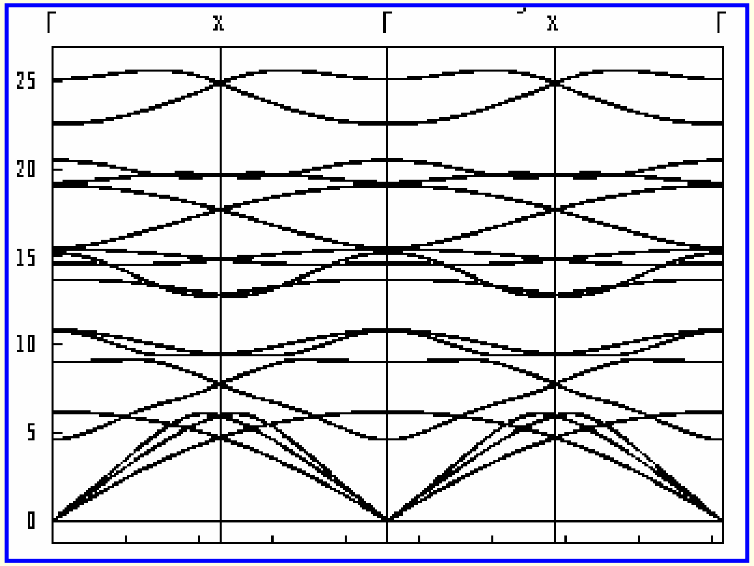




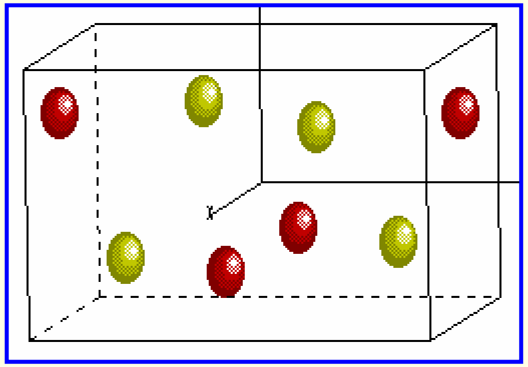
Phonon dispersions + density of states

Frequency

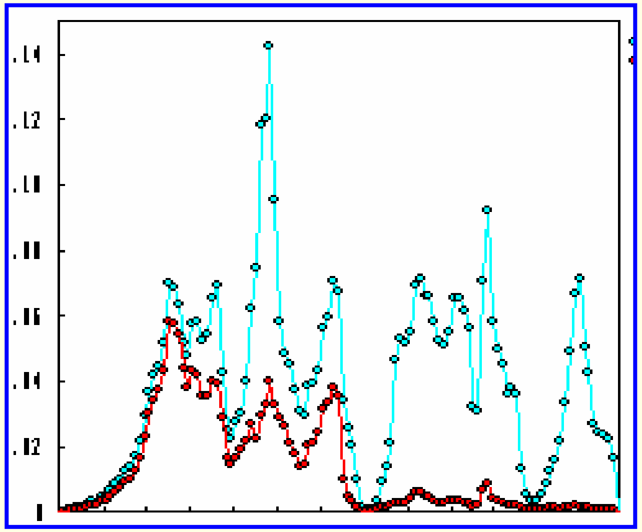
ω



GeO_2 P4_2/mnm

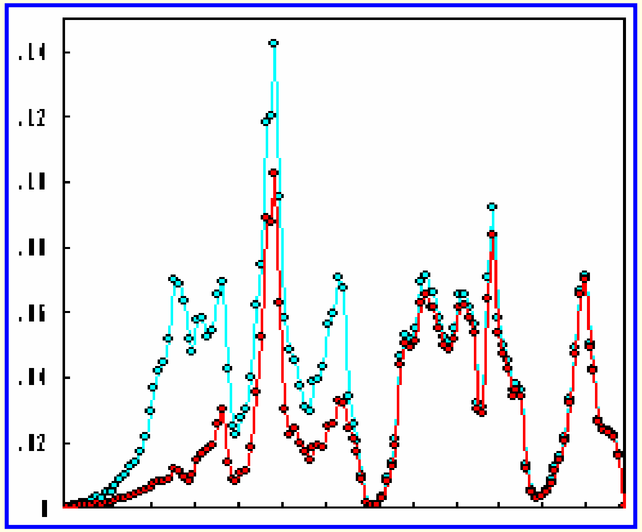


Total + Germanium



ω

Total + Oxygen



ω

Thermodynamic functions of phonon vibrations

Internal energy:

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

Free energy:

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

Entropy:

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

Heat capacity C$_v$:

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

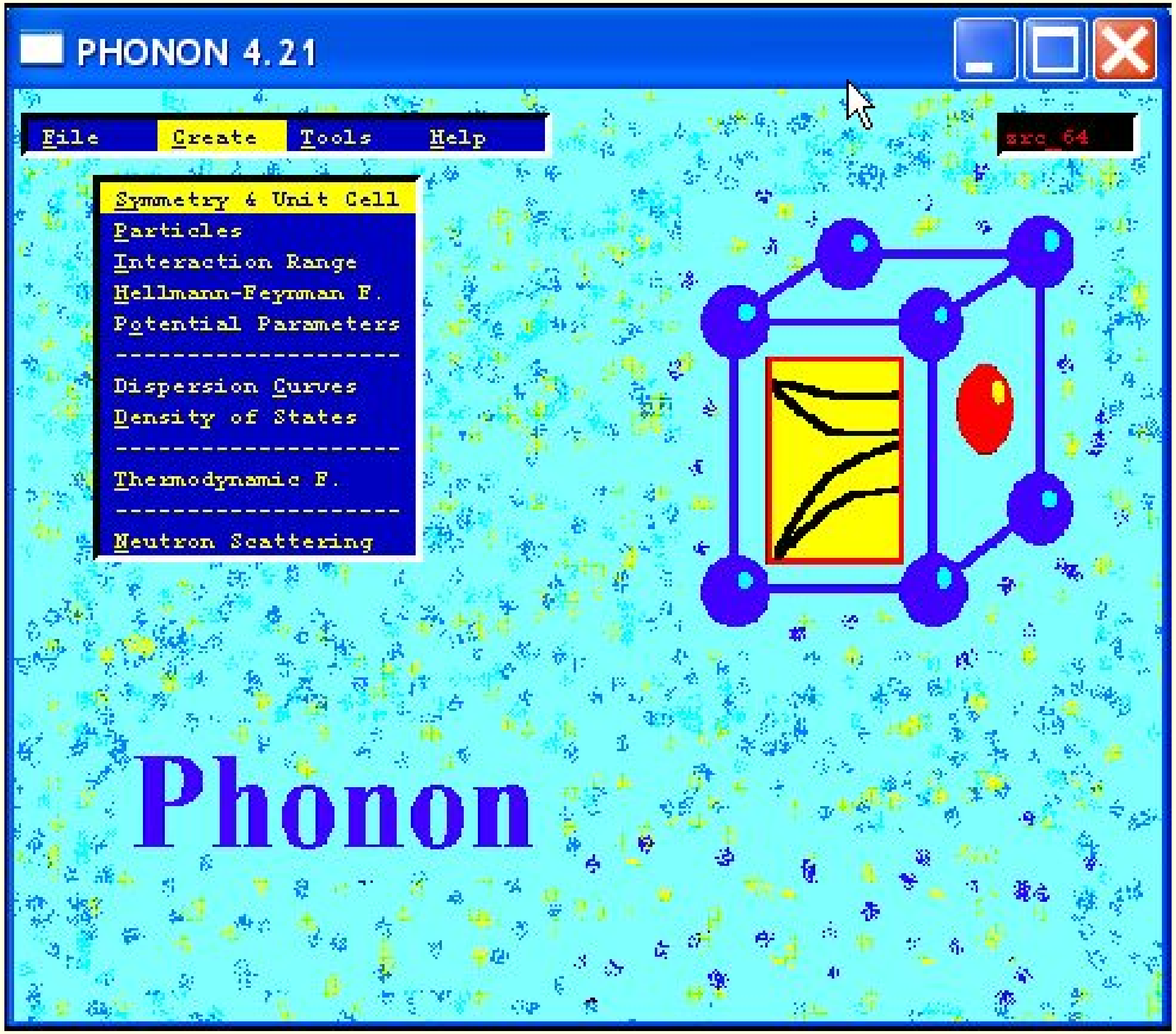
Thermal displacements:

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

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

PHONON-I

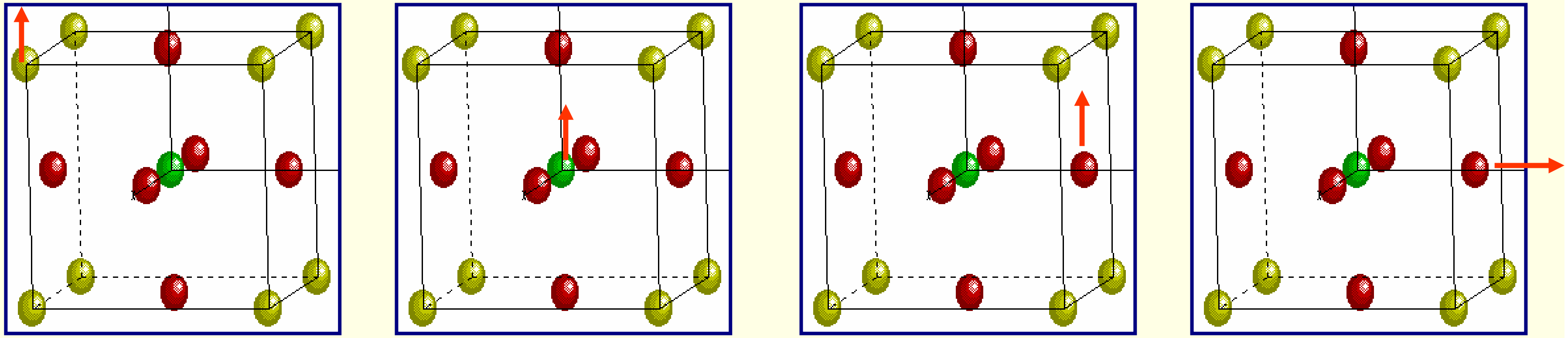
- PHONON
  - *by K.Parlinski (Crakow)*
  - *runs under MS-windows*
  - *uses a „direct“ method to calculate Force-constants with the help of an ab initio program*
  - *with these Force-constants phonons at arbitrary k-points can be obtained*
- Define your spacegroup
- Define all atoms



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

Phonons:

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



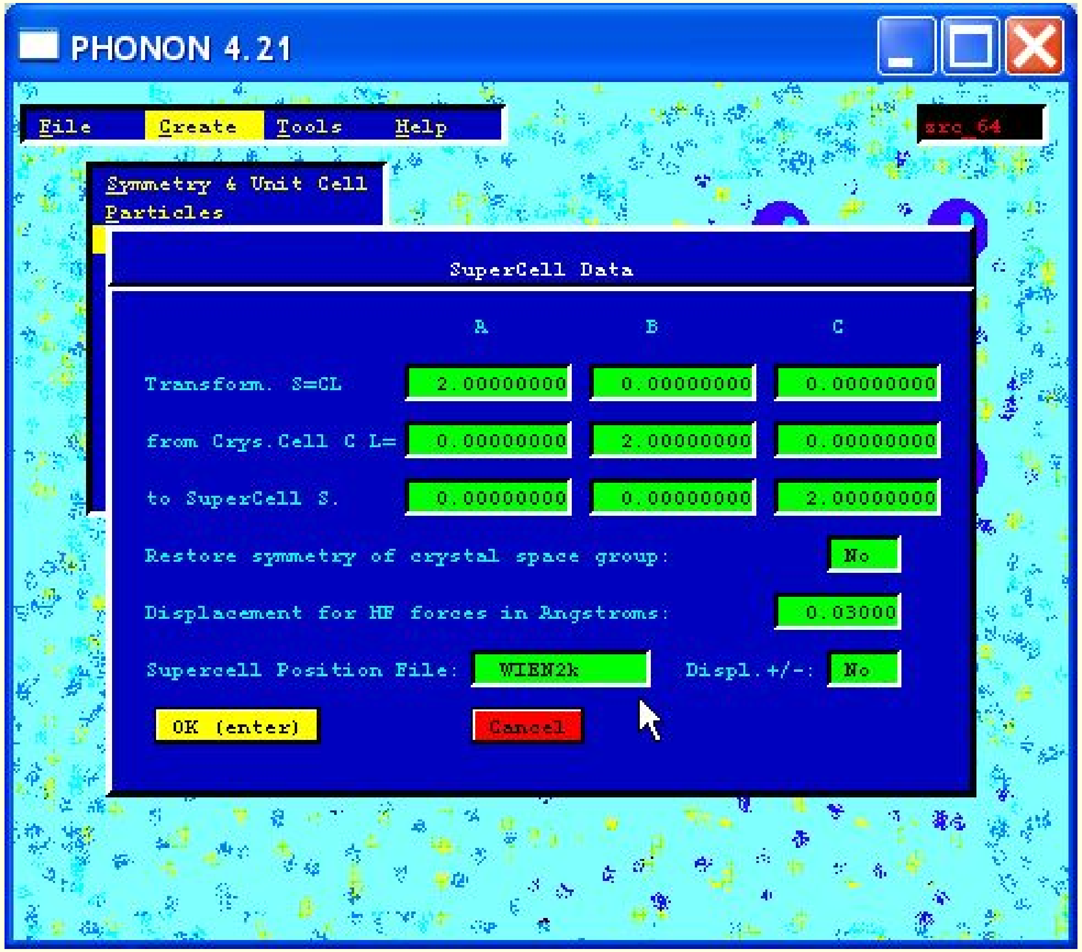
(Displacement pattern for cubic perovskite)

- *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

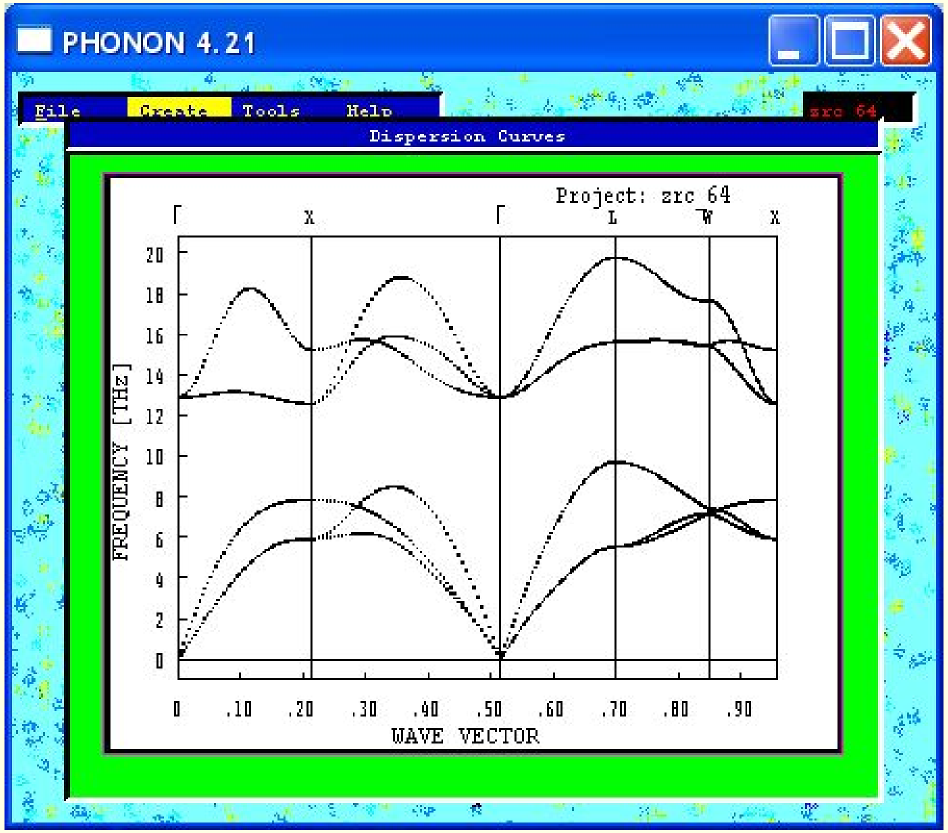
Supercell Position File: WIEN2k Displ.+/-: No

OK (enter) Cancel

- 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

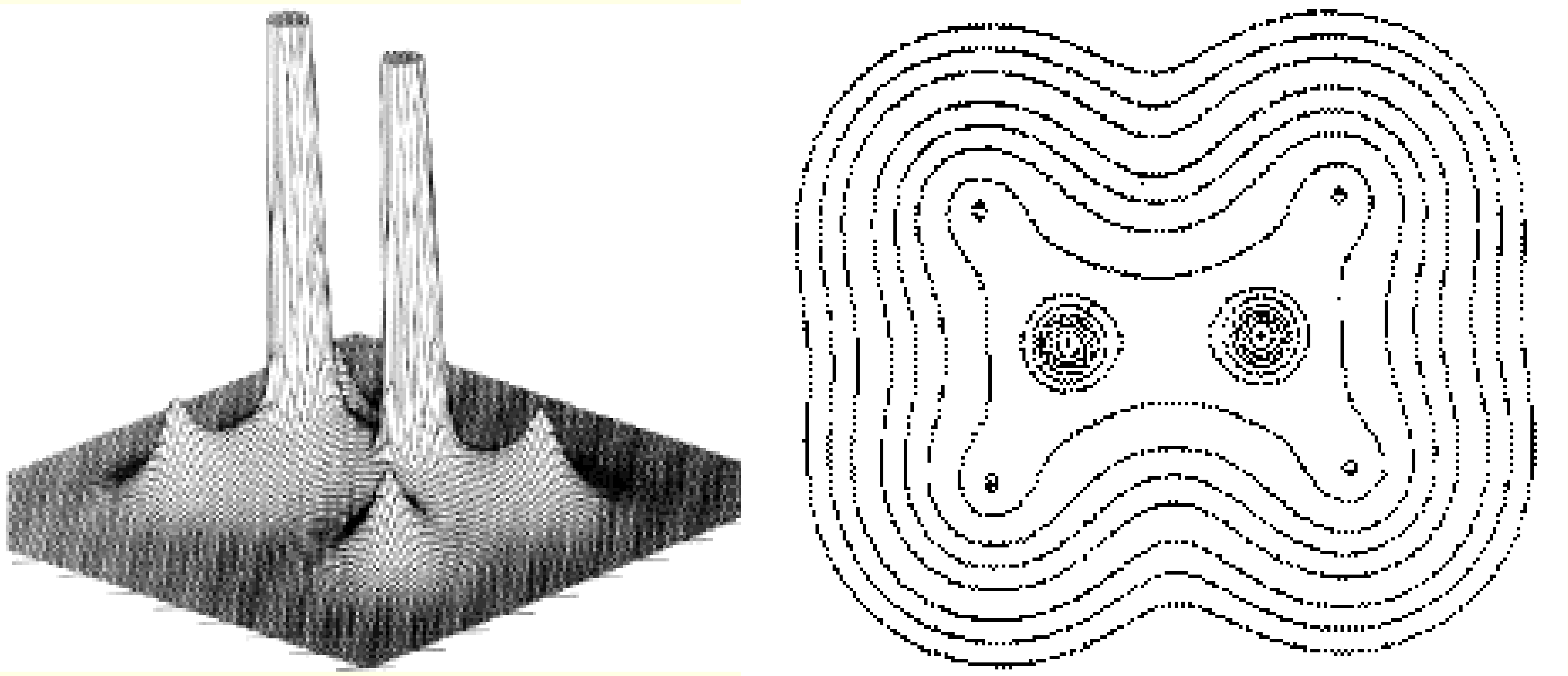
- analyze_phonon_lapw
  - *reads the forces of the scf runs*
  - *generates „Hellman-Feynman“ file case.dat and a „symmetrized HF-file case.dsy (when you have displacements in both directions)*
    - check quality of forces:
    - sum F_x should be small (0)
    - abs(F_x) should be similar for +/- displacements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



Atoms in Molecules

- Theory to characterize atoms and chemical bonds from the topology of the electron density, by R.F.Bader (http://www.chemistry.mcmaster.ca/faculty/bader/aim/aim_0.html)

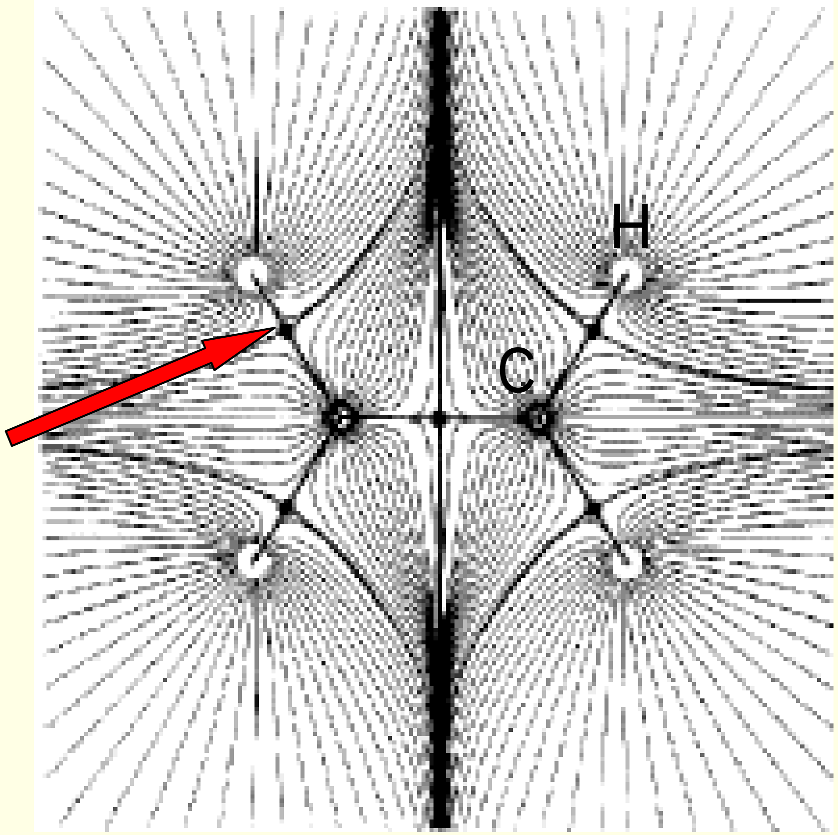
Electron density of C_2H_4



AIM-II

- Bonds are characterized by „critical points“, where $\nabla\rho = 0$
  - •density maximum: (3,-3); 3 negative curvatures λ, (nuclear max, N-NM)
  - •bond CP: (3,-1): 2 negative, 1 positive λ (saddle point)
    - •positive (and large) Laplacian: ionic bond
    - •negative Laplacian: covalent bond
  - •bridge CP: (3,1)
  - •cage CP: (3,3) (minimum)

(3,-1) BCP

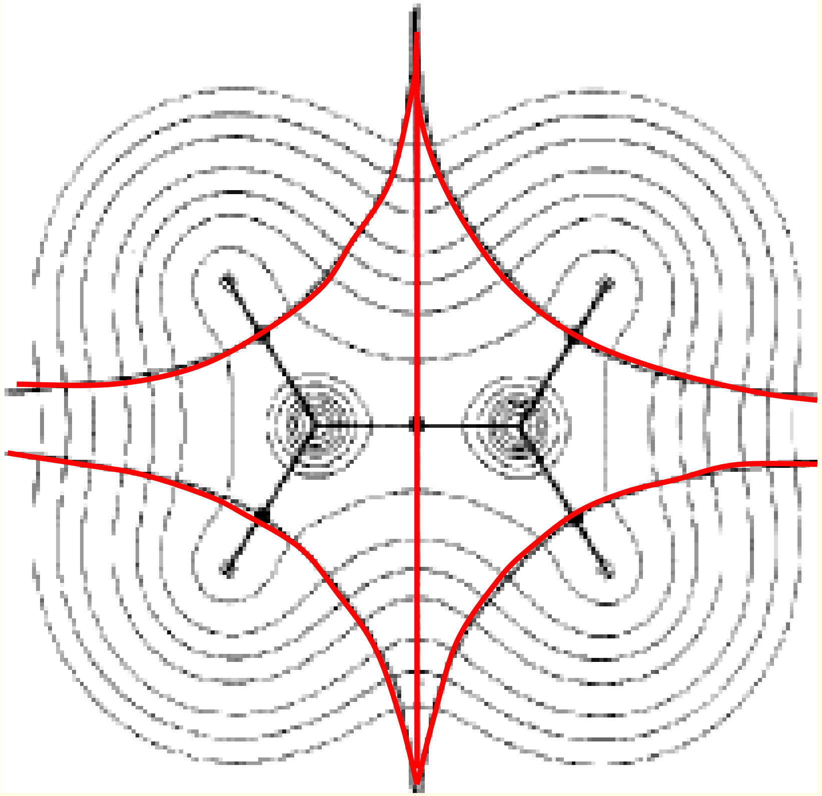


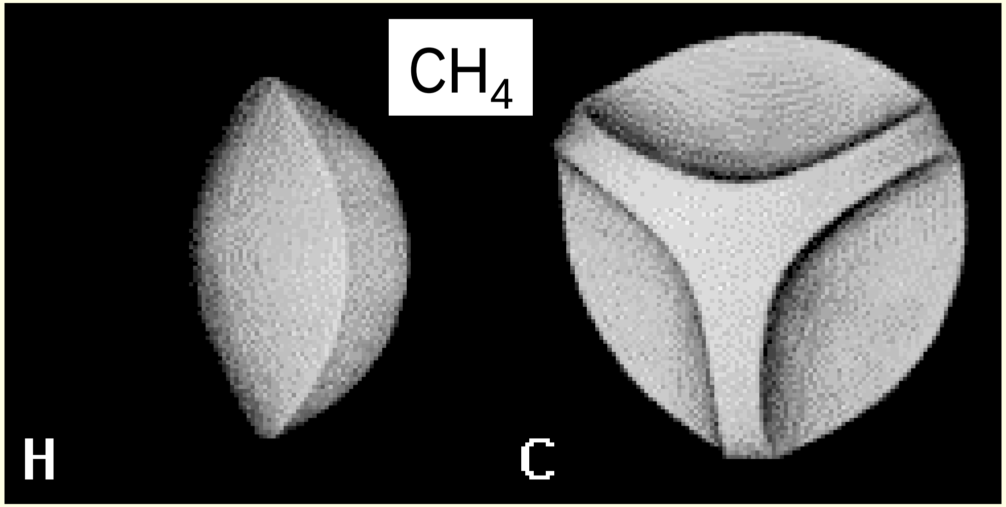
trajectories of constant $\nabla\rho$
originating at CPs in C_2H_4

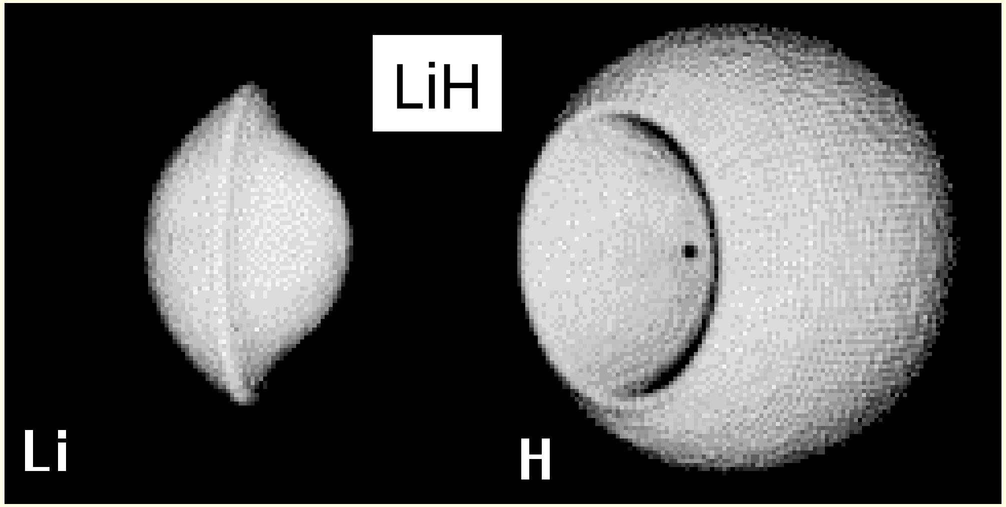
AIM-III

- "Atoms" are regions within a zero-flux surface $\vec{\nabla}\rho \cdot \vec{n} = 0$

ρ of C_2H_4 with zero-flux lines defining atomic basins







AIM-IV

- Bader analysis of some inorganic compounds:

	$\rho(e/A^3)$	$\Delta\rho(e/A^5)$	Q (e)
Cl_2	1.12	-6.1	-
I_2	0.48	-0.9	-
TiC	0.51	1.8	1.7
TiN	0.47	3.9	1.7
TiO	0.43	5.8	1.5
KCl	0.08	1.2	0.6

Cl_2 more covalent
then I_2

more ionic, but less charge?

less ionic then TiC ?

x aim [-c]

- You must have a “good” scf-density (case.clmsum)
  - *no core leakage, LMs up to L=8-10 in case.in2*

```
SURF
1                       atom in center of surface (including MULT)
20 0.0 1.570796327      theta, 20 points, from zero to pi/2
20 0.0 0.785398163      phi, from 0 to pi/4   (depends on symmetry!!)
0.07 1.0 4              step along gradient line, rmin (has reached an atom)
1.65 0.1                initial R for search, step (a.u)
3 3 3                   nshell
IRHO                    "INTEGRATE" rho
WEIT                    WEIT (surface weights are available in case.surf)
30                      30 radial points outside min(RMIN,RMT)
END
---------------------
CRIT
1                       atom around you search for critical points
ALL                     two, three, four, all    (dimers,trimers,....all=2+3)
3 3 3                   nshell
END
```

extractaim_lapw: ➔ critical_points_ang (converted units)

:PC x, y, z, λ_1, λ_2, λ_3, ch, laplacian, rho

WIEN2k- hardware/software

- WIEN2k runs on any Unix/Linux platform from PCs, workstations, clusters to supercomputers
  - *Pentium-IV with fast memory bus (1-2 Gb memory, 100Mbit net, IDE disks)*
  - *10 atom cells on 128Mb PC / 100 atom cells require 1-2 Gb RAM*
  - *installation support for most platforms*

- Fortran90 (dynamical allocation, modules)
  - *real/complex version (inversion)*
  - *many individual modules, linked together with C-shell or perl-scripts*

- *web-based GUI – w2web (perl)*

- f90 compiler, BLAS-library (ifort9+mkl), perl5, ghostscript (+jpg), gnuplot(+png), Tcl/Tk (Xcrysden), pdf-reader, www-browser, octave, opendx

Installation of WIEN2k

- Register via http://www.wien2k.at
- Create your $WIENROOT directory (e.g. ./WIEN2k)
- Download wien2k_06.tar and examples (executables)
- Uncompress and expand all files using:
  - *tar –xvf wien2k_06.tar*
  - *gunzip *.gz*
  - *chmod +x ./expand_lapw*
  - *./expand_lapw*
- This leads to the following directories:

./SRC	*(scripts, ug.ps)*
./SRC_aim	*(programs)*
...	
SRC_templates	*(example inputs)*
...	
SRC_usersguide_html	*(HTML-version of UG)*
example_struct_files	*(examples)*
TiC	

siteconfig_lapw

```
   ****************************************************
   *                      W I E N                     *
   *                 site configuration               *
   ****************************************************
      S    specify a system
      C    specify compiler
      O    specify compiler options, BLAS and LAPACK
      P    configure Parallel execution
      D    Dimension Parameters
      R    Compile/Recompile
      U    Update a package
      L    Perl path (if not in /usr/bin/perl)
      Q    Quit
```

D: define NMATMAX (adjust to your hardware/paging!):
NMATMAX=5000 ➔256Mb (real) or 500Mb (complex)
NMATMAX=10000 ➔ 1Gb (real) ➔ 80-150 atoms/unitcell

Always use „optimized“ BLAS library (ifort+mkl; ATLAS-BLAS, gotolib)

Compilation

- most common: Intels Fortran compiler (free for academic)
  - *ifc (7.1)*
    - -static linking
    - patch for 2 externals, see faq-web page or mailing-list digest
  - *ifort 9.0*
    - 8.0 buggy ?,
    - needs unlimited “stacksize” (limit stacksize=unlimited, otherwise: “segmentation fault”)
    - dynamic linking necessary (requires system and compiler libraries at runtime, may need $LD_LIBRARY_PATH)

  - *mkl 6.1 or higher; ATLAS-BLAS;* ***gotolib***
    - -L/opt/intel/mkl/lib –lmkl_em64t → libmkl_em64t.so
  - *compiler/linker options depend on compiler version + Linux-version !!*

userconfig_lapw

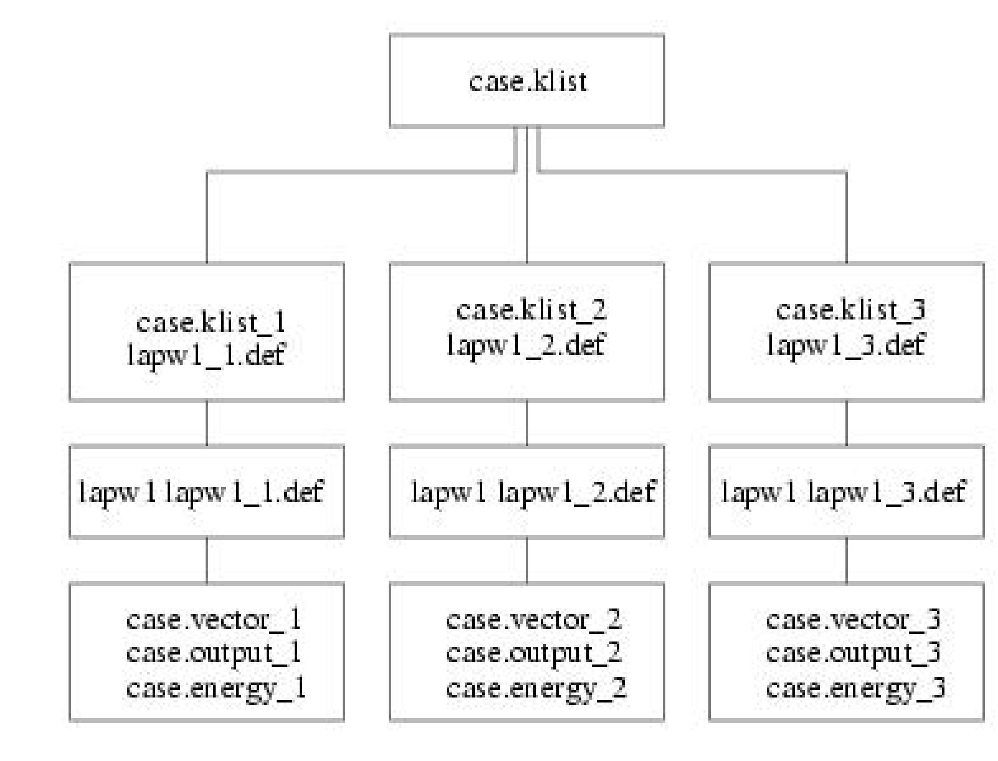
- Every user should run userconfig_lapw
  - *support for tcsh and bash*
  - *sets PATH to $WIENROOT, sets variables and aliases*
    - $WIENROOT, $SCRATCH, $EDITOR, $PDFREADER, $STRUCTEDIT_PATH
    - pslapw: ps –ef | grep lapw
    - lsi: ls –als *.in*
    - lso: *.output*
    - lss: *.scf*
    - lsc: *.clm*
    - limit stacksize unlimited
    - $OMP_NUM_THREADS (for mkl+dual core); $LD_LIBRARY_PATH
- w2web: acts as webserver on a userdefined (high) port.
  - *define „master“ and „slave“ nodes. (master knows all „projects“)*
  - *define user/password and port. (http://host.domain.xx:5000)*
  - *~/.w2web/hostname/conf/w2web.conf: (configuration file)*
    - deny=*.*.*.*
    - allow=128.130.134.* 128.130.142.10
    - define execution types: NAME=commands (eg.: batch=batch < %f)

Parallelization

- k-point parallel on clusters (slow network): lapw1+lapw2
  - *common NFS filesystem (files must be accessable with the same path on all machines)*
  - *rsh/ssh without password (.rhosts; private/public keys)*
    - .machines file:
      - 1:host1 (speed:hostname)
      - 2:host2
      - granularity:1 (1:10k+10k; 3: 3+3+3+3+3+3+rest ➔load balancing)
      - extrafine:1 (rest in junks of 1 k)
    - testpara (tests distribution); run_lapw -p
- fine-grain parallelization for big cases (>50 atoms) and fast network (Myrinet, Infiniband, shared memory machines)
  - *mpi + scalapack*
    - .machines file:
      - 1:host1:4 host2:4 8 mpi-parallel jobs on host1 and host2
      - lapw0:host1:4 host2:4 8 parallel jobs; atom-loops only!!!

Flow of parallel execution

lapw1para



case.klist

case.klist_1
lapw1_1.def

case.klist_2
lapw1_2.def

case.klist_3
lapw1_3.def

lapw1 lapw1_1.def

lapw1 lapw1_2.def

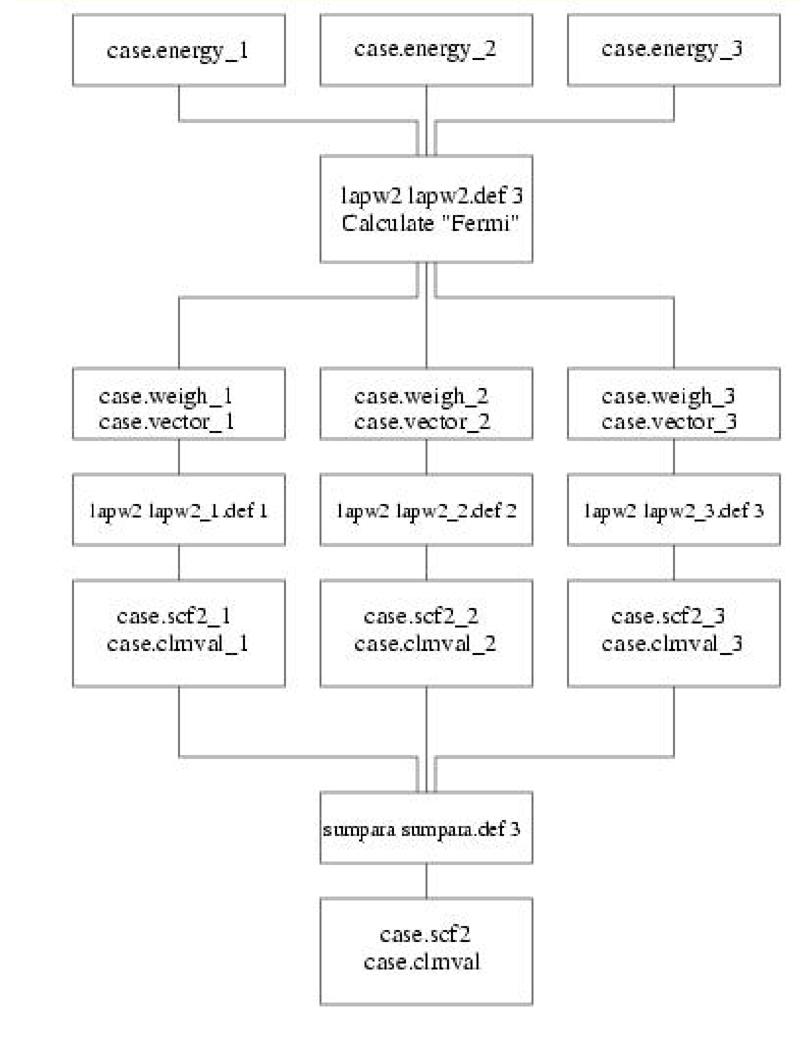
lapw1 lapw1_3.def

case.vector_1
case.output_1
case.energy_1

case.vector_2
case.output_2
case.energy_2

case.vector_3
case.output_3
case.energy_3

lapw2para



case.energy_1

case.energy_2

case.energy_3

lapw2 lapw2.def 3
Calculate "Fermi"

case.weigh_1
case.vector_1

case.weigh_2
case.vector_2

case.weigh_3
case.vector_3

lapw2 lapw2_1.def 1

lapw2 lapw2_2.def 2

lapw2 lapw2_3.def 3

case.scf2_1
case.clmval_1

case.scf2_2
case.clmval_2

case.scf2_3
case.clmval_3

sumpara sumpara.def 3

case.scf2
case.clmval