Spacegroup $P4_2/mnm$

Structure given by:

- spacegroup
- lattice parameter
- positions of atoms (basis)

Rutile TiO_2:

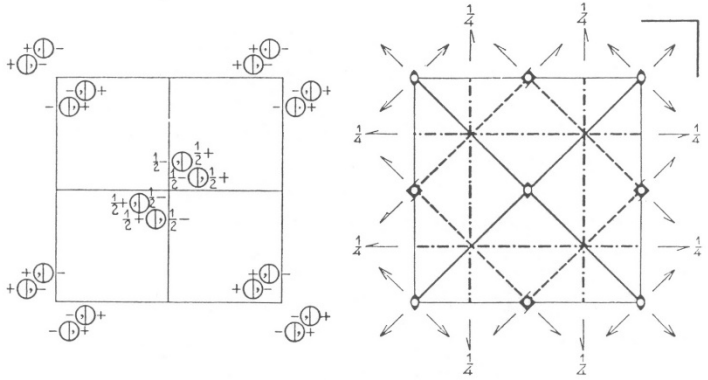
$P4_2/mnm$ (136)

a=8.68, c=5.59 bohr

Ti: (0,0,0)

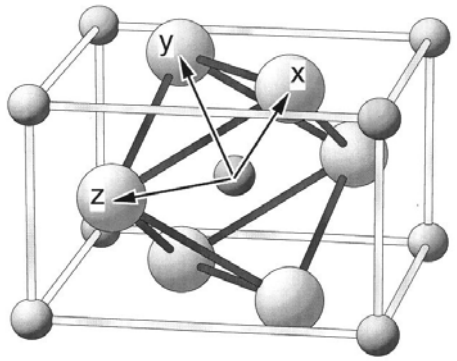
O: (0.304,0.304,0)

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



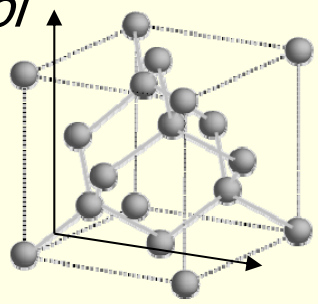
Origin at centre (*mmm*)

Number of positions, Wyckoff notation, and point symmetry			Co-ordinates of equivalent positions	Conditions limiting possible reflections
				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 *hk*0: No conditions 0*kl*: $k+l=2n$ *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

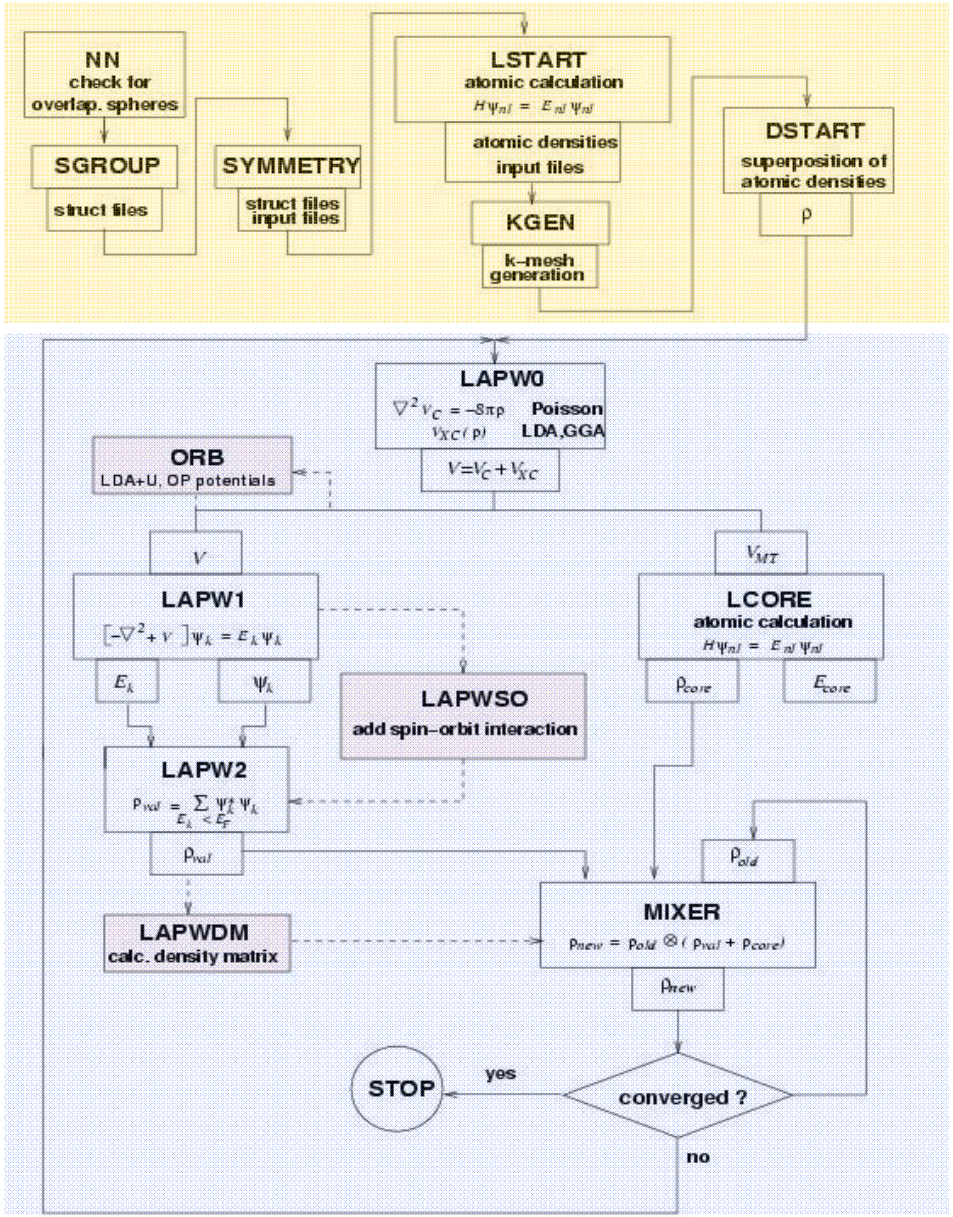
- Specify:
  - *Number of nonequivalent atoms*
  - *lattice type (P, F, B, H, CXY, CXZ, CYZ) or spacegroup symbol*
    - if existing, you must use a SG-setting with inversion symmetry:
      - Si: ±(1/8,1/8,1/8), not (0,0,0)+(1/4,1/4,1/4)!
  - *lattice parameters a,b,c (in Å or bohr)*
  - *name of atoms (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), but not larger than 2.5 bohr*
  - *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*



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:

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

- increasing Rkmax by 10 %
  ⟹ doubles cputime

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

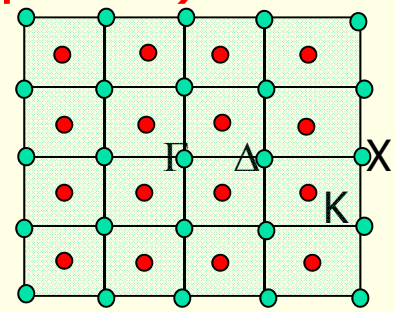
START with **SMALL** Rkmax (relaxation), **increase/test** later

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 0.005)
      - temperature broadening (TEMP/TEMPS 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)
  - *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);*
  - *reduce mixing in case.inm slightly; rm *.broyd* case.scf; x dstart*
  - *check E-parameters (see above), check :NEC01 (correct number of e^-)*

case.in1

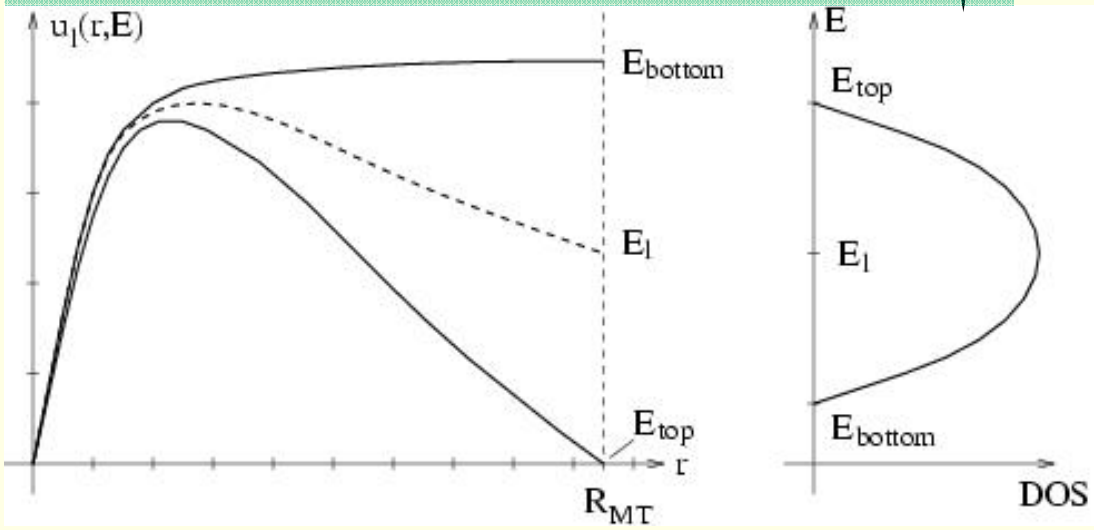
set E_l to E_F-0.2 Ry

```
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
```

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

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

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



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
```

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

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

x lapw2 -qtl	Calculate partial charges ☑ interactively
edit TiC.int	Edit input-file for TETRA
x tetra	Calculate partial DOS ☑ interactively
edit TiC.outputt	Check output of TETRA
dosplot	Plot DOS

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

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

contine with DOS | Save | Download this file:

Header from TiC.qtl:

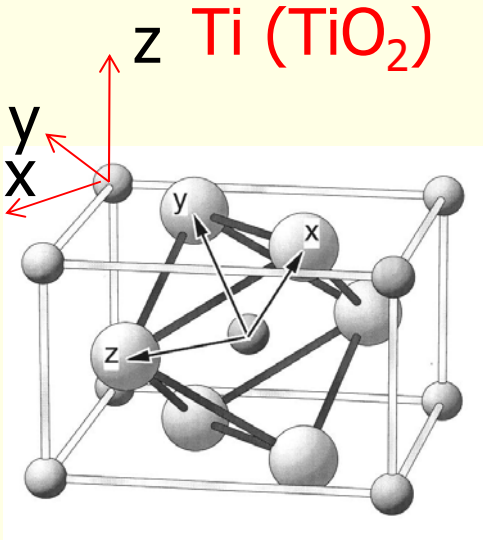
```
ATOM   1  tot,0,1,2,3,xdos(i,j),j=1,i),i=1,lxdos2)
ATOM   2  tot,0,1,2,D-eg,D-t2g,3
```

```
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

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



  - *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)*

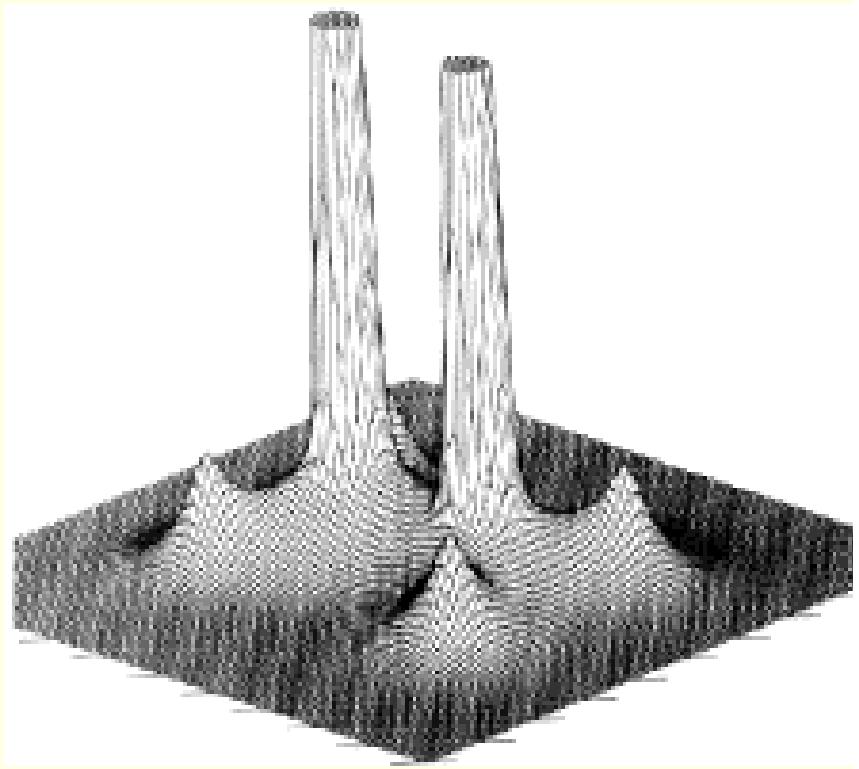
Properties with WIEN2k - I

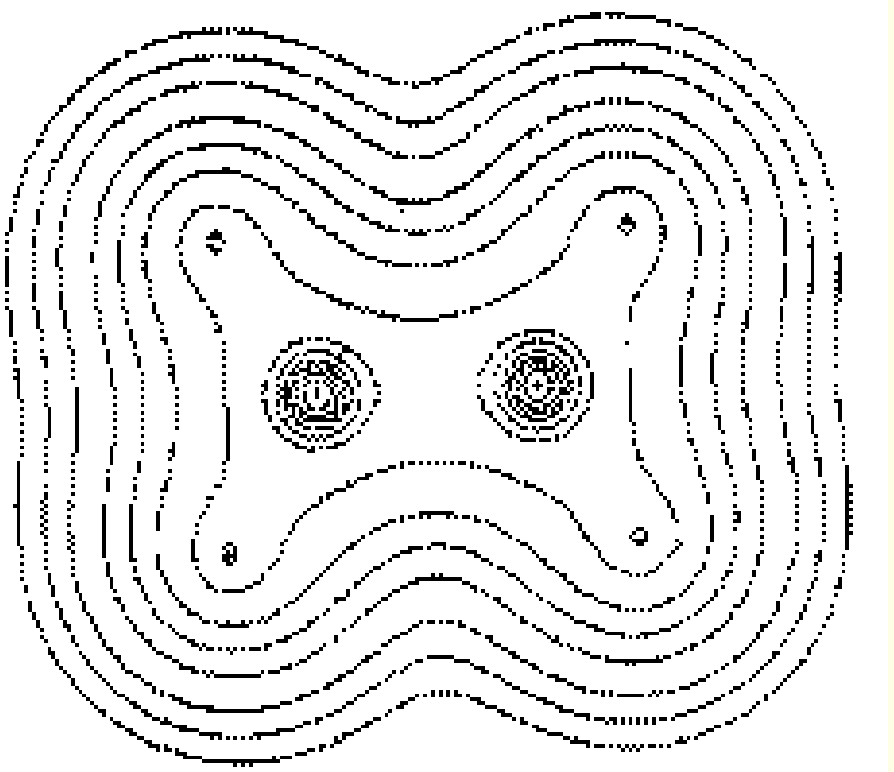
- Energy bands
  - *classification of irreducible representations*
  - *´character-plot´ (emphasize a certain band-character)*
- Density of states
  - *including partial DOS with l and m- character (eg. p_x , p_y , p_z)*
- Electron density, potential
  - *total-, valence-, difference-, spin-densities, 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*
  - *NMR chemical shifts*

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



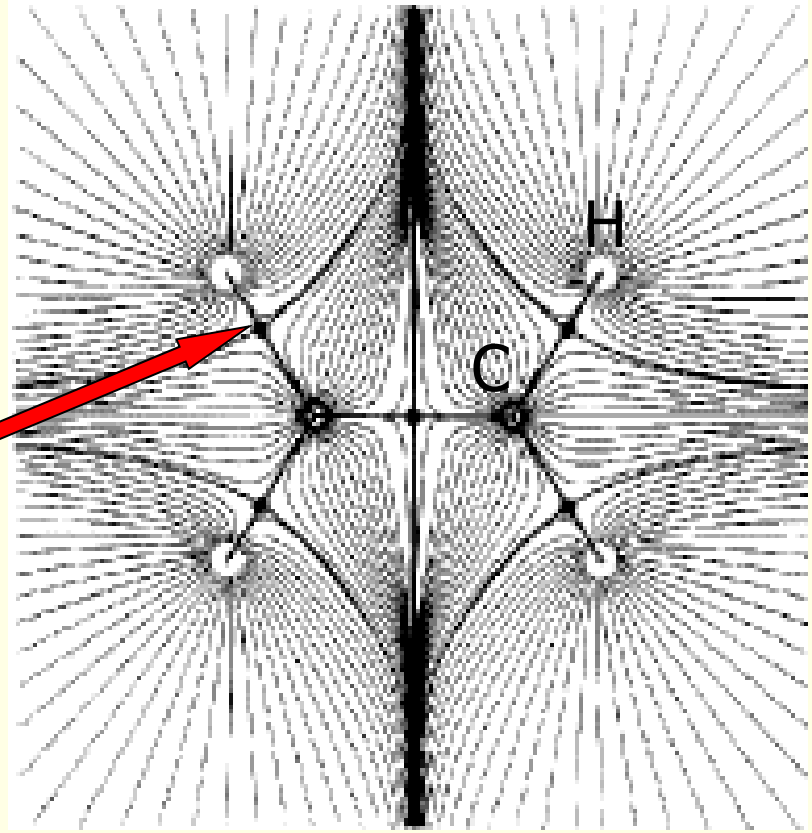


AIM-II

- Bonds are characterized by „critical points", where $\nabla\rho = 0$

  - density maximum: (3,-3); 3 negative curvatures λ, (at nucleus or non-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

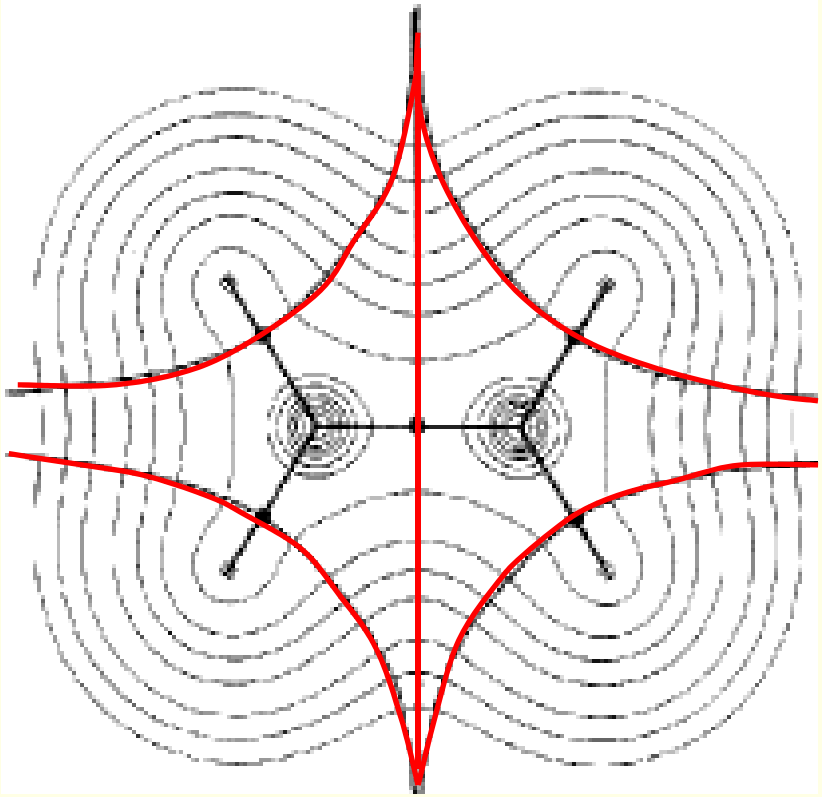


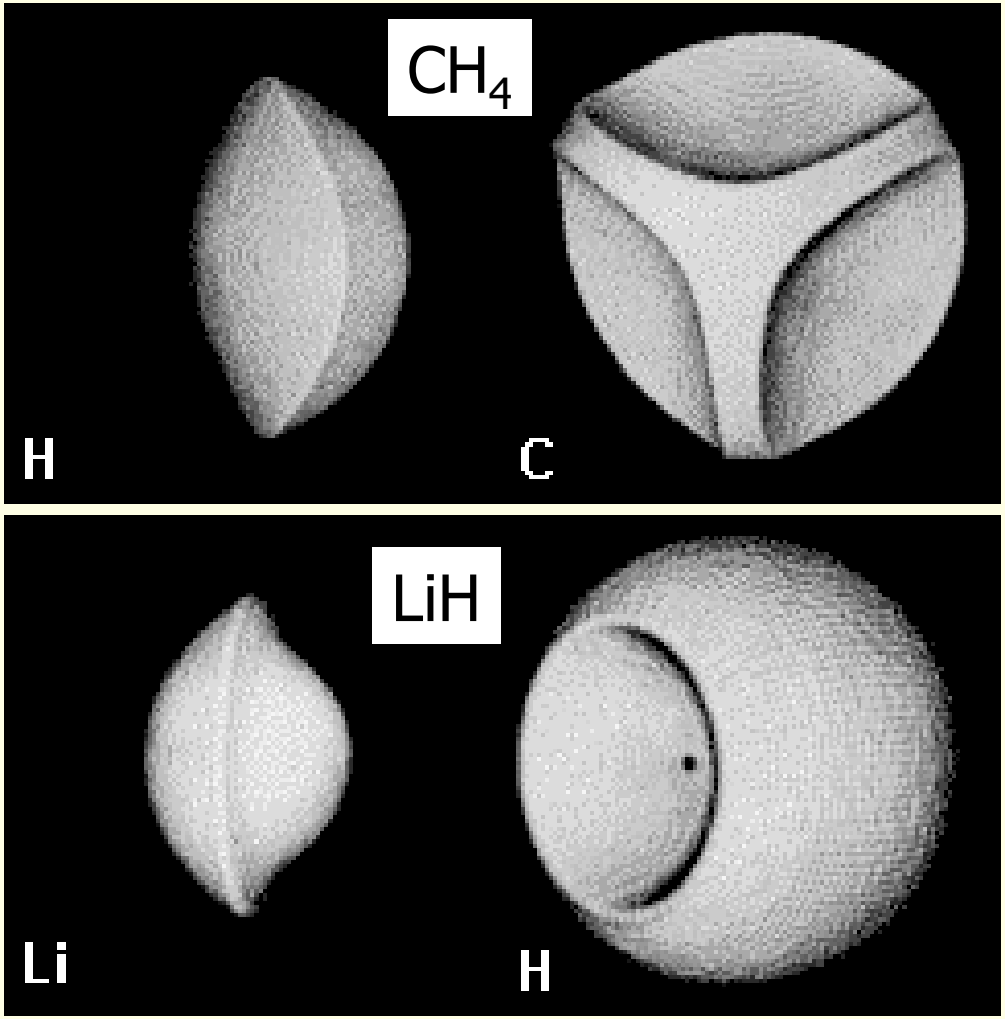
trajectories of constant $\nabla\rho$ originating at CPs in C_2H_4

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

- example of BN/Ni with "difference" to free atoms,
- workfunction shift
- 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

- 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
```

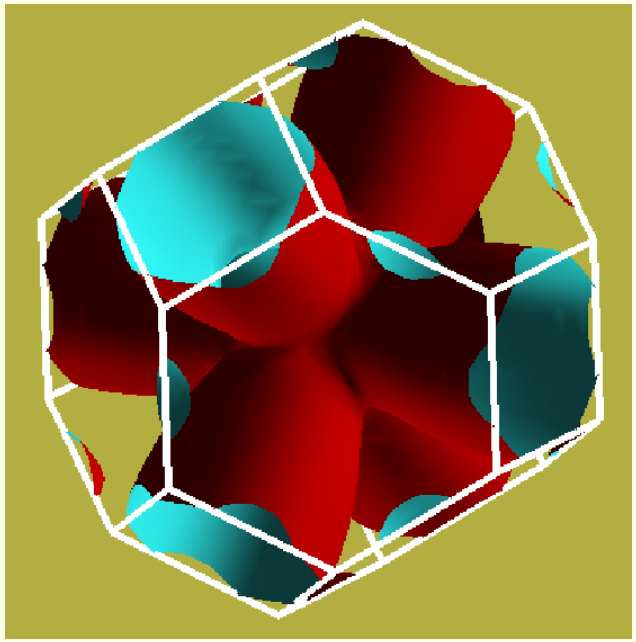
extractaim_lapw: ➔ critical_points_ang (converted units)
:PC x, y, z, λ_1, λ_2, λ_3, ch, laplacian, rho

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*