

# VASP tutorial 2010-2014

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# Preliminary

→ your account is up and running?

→ key is requested?

→ add to your `.bashrc`

```
export MODULEPATH=$VSC_DATA_VO/vsc40201/modules:$MODULEPATH
```

→ move to raichu:

```
module swap cluster/raichu
```

→ Load HIVE toolbox:

```
module load HIVE
```

# What is VASP?

VASP is a package for performing ab-initio quantum-mechanical molecular dynamics (MD) using pseudo-potentials and a plane wave basis set. Both LDA and GGA potentials/functionals are available. This code can be used to obtain electronic and structural properties of small atomic systems (roughly up to 100-200 atoms).

## 1) Periodic boundary conditions



**Good for bulk materials**  
( = not so good for isolated systems i.e. molecules)



**Ideal for Plane wave basis-sets**

# What is VASP?

VASP is a package for performing ab-initio quantum-mechanical molecular dynamics (MD) using pseudo-potentials and a plane wave basis set. Both LDA and GGA potentials/functionals are available. This code can be used to obtain electronic and structural properties of small atomic systems (roughly up to 100-200 atoms).

## 2) Pseudo-potentials



**To make life easier with the plane waves**



**Different flavors: LDA, GGA, hybrid (> v5)**

# What is VASP?

VASP is a package for performing ab-initio quantum-mechanical molecular dynamics (MD) using pseudo-potentials and a plane wave basis set. Both LDA and GGA potentials/functionals are available. This code can be used to obtain electronic and structural properties of small atomic systems (roughly up to 100-200 atoms).

## 3) Small systems



**100 atoms are already large systems.  
Relaxation on 32 cores can take a week (real time!).**



**Periodic Boundary conditions allow you to simulate Bulk.**

# Lock and Load



Go to: `$VSC_DATA_VO/shared/VASP_TUTORIAL`

And copy the tar-zipped file with your name to a location on your account, and untar using: `tar -xzvf`

# Basics: Self Consistent Calculation I

VASP always needs minimum 4 files:

- 1) **INCAR** : *contains all the settings of the program parameters you wish to use. (energy cutoff, parallelism, smearing,...)*
- 2) **KPOINTS** : *all the information with regard to your k-point set.*
- 3) **POSCAR** : *all the information with regard to the actual geometry of your system.*
- 4) **POTCAR** : *the information regarding the potentials/functionals used  
→ this one you get from a database*

Let's finally get started:

→ Make a folder with the name of your system. Inside this folder make a new folder named: SelfConsistent.

# Basics: SC Calculation II → POSCAR-file

## Ge-Bulk

## CO-molecule

The diagram illustrates the structure of two POSCAR files: Ge-Bulk and CO-molecule. It highlights key differences and similarities between them.

**Ge-Bulk POSCAR:**

```
POSCAR
Ge_Bulk
5.6575
0.50 0.50 0.00
0.00 0.50 0.50
0.50 0.00 0.50
2
Cartesian
0.00 0.00 0.00
0.25 0.25 0.25
```

**CO-molecule POSCAR:**

```
POSCAR [----] 15 L:[ 1+ 3 4
CO_molecule
1.00
10.00 0.00 0.00
0.00 10.00 0.00
0.00 0.00 10.00
1 1 ! 1 Carbon and 1 O atom
Cartesian
0.00 0.00 0.00 ! C-atom
0.00 0.00 1.128 ! O-atom
```

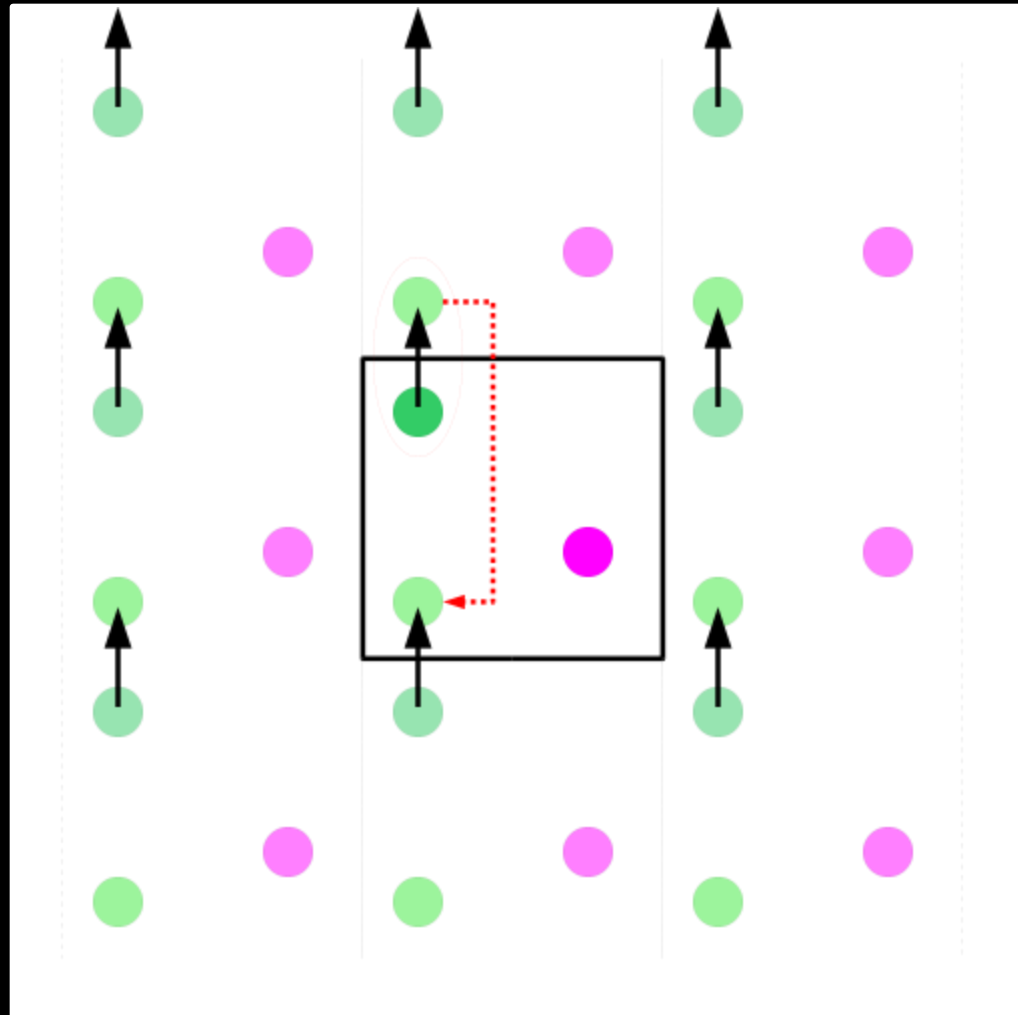
**Annotations:**

- Comment-tag:** Points to the title line (e.g., "Ge\_Bulk" or "CO\_molecule").
- Scale factor:** Points to the lattice constant (5.6575 for Ge-Bulk, 1.00 for CO-molecule).
- 3 lattice vectors:** Points to the 3x3 lattice vector matrix.
- Type and #atoms:** Points to the line indicating the number of atoms and their types (e.g., "2" for Ge-Bulk, "1 1" for CO-molecule).
- Type coordinates: Direct or Cartesian:** Points to the coordinate system specification ("Cartesian").
- Positions of the atoms:** Points to the atomic coordinates.
- Comments:** Points to the explanatory text at the end of the CO-molecule file.

**Important:** The order of the atom positions in the POSCAR file needs to be the same as in the POTCAR file!



# Intermezzo: PBC



# Basics: SC Calculation III → INCAR-file

```
mc - /gpfs/h06/tcmsdany/Ugent/VASPles/COmolecule/SelfConsistent
INCAR      [----] 15 L:[ 1+12  13/ 17] *(522 / 714b)=
general:
  SYSTEM = CO-molecule
  ISTART = 0  ! 0 start from scratch, 1 use old WAVECAR
  ICHARG = 2  ! 1 use old CHGCAR, 2 superposition atoms
              ! 10+ Fix CHG
  ISMEAR = 0  ! -5 Tetra+Blochl, 0 Gaussian, >=1 MP
  SIGMA = 0.1 ! width smearing
  EDIFF = 1.0E-7 ! electronic convergence criterium
  PREC = High  ! used precision
  LWAVE = .FALSE. ! do not write the WAVECAR file
  LCHARG = .TRUE. ! write the CHGCAR file
  LVTOT = .FALSE. ! do not write the potetial file
  ENCUT = 400 ! kinetic energy cutoff
              ! for <1meV convergence Ge in normal POTCAR
dynamic:
  IBRION = -1 ! -1 fix atoms, 2 ConjGrad for relax
  NSW = 0    ! number of ionic steps

1Help  2Save  3Mark  4Replac  5Copy  6Move  7Search  8Delete
```

→ More information and parameters can be found in the VASP manual.

# Basics: SC Calculation IV → KPOINTS-file

## Ge-Bulk

```
mc - /gpfs/h06/tcmsda
KPOINTS
K-points
0
Monkhorst Pack
21 21 21
0 0 0
```

## CO-molecule

```
mc - /gpfs/h06/tcms
KPOINTS
K-points
0
Monkhorst Pack
1 1 1
0 0 0
```

#K-points, 0 → automatic grid

Type of automatic grid:  
Monkhorst Packing  
Gamma Centered (→ hexagonal)

K-point grid + shift (second line)

Vacuum directions only need 1 k-point

⇒ molecule: 1,1,1 (=Gamma point only)

If your lattice-vectors have different length, then this needs to be reflected in the k-point set (could give errors otherwise)

→ e.g. lattice vectors with lengths:  $a_1=1$ ,  $a_2=2$ ,  $a_3=10$

→ k-points: 6 3 1

# Basics: SC Calculation V → POTCAR-file

VASP provides potential files for all chemical elements. Each of these files is called POTCAR, and VASP only recognizes a file named POTCAR as potential file.

```
mc - /gpfs/h06/tcmsdany/Ugent/VASPles/GeBulk/SelfConsistent
```

```
Danny2@OwnH ~/Ugent/VASPles/GeBulk/SelfConsistent $ head -30 POTCAR
```

```
P&W Ge 03Mar1998
4.000000000000000000
parameters from PSCTR are:
VRHEIM = Ge: s2p2
LEXCH = CA
EATOM = 106.1908 eV, 7.8048 Ry

TITEL = P&W Ge 03Mar1998
LULTRA = F use ultrasoft PP ?
IUNSCR = 1 unscreen: 0-lin 1-nonlin 2-no
RPACOR = 2.170 partial core radius
POMASS = 72.610; ZVAL = 4.000 mass and valenz
RCORE = 2.300 outmost cutoff radius
RWIGS = 2.300; RWIGS = 1.217 wigner-seitz radius (au Å)
ENMAX = 173.969; ENMIN = 130.477 eV
ICORE = 3 local potential
LCOR = T correct aug charges
LPAW = T paw PP
EAUG = 385.843
DEXC = -.107
RMAX = 3.496 core radius for proj-oper
RAUG = 1.300 factor for augmentation sphere
RDEP = 2.318 core radius for depl-charge
QCUT = -3.576; QGAM = 7.152 optimization

Description
  1   E      TYP  RCUT      TYP  RCUT
  0   .000    23  2.300
  0   .000    23  2.300
  1   .000    23  2.300
```

This is a PAW potential for Ge

# electrons: 4 valence electrons for this Ge potential, there also exists a Ge potential including the d-electrons in the valence shell → 14e-

Type of exchange-functional: CA=Ceperley-Alder → LDA

**What if you have multiple/different kinds of atoms in your system?**  
e.g. CO molecule  
> cat POTCAR\_C POTCAR\_O >> POTCAR

```
Danny2@OwnH ~/Ugent/VASPles/GeBulk/SelfConsistent $
```

# Run, Raichu. Run!

```
> cd static/  
> qsub jobscript.sh
```



```
#!/bin/sh  
#PBS -N Solid_Static  
#PBS -m e  
#PBS -l nodes=1:ppn=4  
#PBS -l walltime=0:30:00  
#
```

```
STARTDIR=$PBS_O_WORKDIR
```

```
newgrp g_vasp5
```

```
module purge
```

```
module load cluster/raichu
```

```
module load VSC-tools
```

```
module load VASP/5.3.3-ictce-4.1.13-mt-dftd3
```

```
cd $STARTDIR
```

```
echo "Job started at : "`date` >> out.dat
```

```
mympirun vasp >> out.dat
```

```
echo "Job ended at : "`date` >> out.dat
```

```
wait
```

# Basics: SC Calculation VI → Spoils of War

huygens.sara.nl - PuTTY

ERROR: 0031-652 Error reading STDIN

running on 4 nodes

distr: one band on 1 nodes, 4 groups

vasp.4.6.31 08Feb07 complex

POSCAR found: 2 types and 2 ions

LDA part: xc-table for Ceperly-Alder, standard interpolation

POSCAR, INCAR and KPOINTS ok, starting setup

FFT: planning ... 1

reading WAVECAR

entering main loop

	N	E	dE	d eps	ncg	rms	rms (c)
DAV:	1	0.802627564386E+02	0.80263E+02	-0.18301E+03	24	0.351E+02	
DAV:	2	-0.519100429888E+01	-0.85454E+02	-0.84840E+02	44	0.103E+02	
DAV:	3	-0.164287208724E+02	-0.11238E+02	-0.11231E+02	44	0.549E+01	
DAV:	4	-0.164968585937E+02	-0.68138E-01	-0.68135E-01	40	0.424E+00	
DAV:	5	-0.164968988604E+02	-0.40267E-04	-0.40266E-04	24	0.110E-01	0.640E+00
DAV:	6	-0.157610906861E+02	0.73581E+00	-0.34616E+00	24	0.102E+01	0.323E+00
DAV:	18	-0.155756565134E+02	-0.31059E-05	-0.14470E-07	24	0.100E-01	0.300E-01
DAV:	19	-0.155756569455E+02	-0.43206E-06	-0.10795E-08	24	0.100E-01	0.300E-01
DAV:	20	-0.155756572651E+02	-0.31962E-06	-0.43656E-09	24	0.339E-04	0.205E-05
DAV:	21	-0.155756574599E+02	-0.19483E-06	-0.12021E-09	28	0.213E-04	0.158E-05
DAV:	22	-0.155756574963E+02	-0.3642E-07	0.55017E-10	32	0.625E-05	

Parallel 4-cpu calculation

Our Bulk Ge system has only one type of atoms: Ge, 2 atoms in our unit cell

Total ground-state energy

1 F = -.15575657E+02 EO = -.15575657E+02 d E = -.284847E-11

#Irreducible Brillouin zone K-points (VASP scales ~linear with IBZKPT)

Danny2@OwnH ~/Ugent/VASPles/COmolecule/SelfConsistent \$ grep NBANDS OUTCAR

k-Points NKPTS = 1 number of bands NBANDS= 12

#bands (2e<sup>-</sup> per band)

Danny2@OwnH ~/Ugent/VASPles/COmolecule/SelfConsistent \$ grep LOOP OUTCAR |tail -5

```
LOOP: VPU time 0.68: CPU time 0.69
LOOP: VPU time 0.62: CPU time 0.62
LOOP: VPU time 0.67: CPU time 0.69
LOOP: VPU time 0.49: CPU time 0.49
LOOP+: VPU time 18.15: CPU time 18.42
```

Time per electronic step (LOOP) and ionic step (LOOP+)

Danny2@OwnH ~/Ugent/VASPles/COmolecule/SelfConsistent \$

# Relaxation I: Setup

The structures we used for the SC calculations were not optimized. To optimize them some parameters need to be changed.

→ make a new folder : relax, and copy your 4 input files (INCAR, KPOINTS, POSCAR and POTCAR) of the SC calculation.

## Modifications:      POSCAR

```
mc - /gpfs/h06/tcmsdany/Uge
POSCAR [-----]
Ge_Bulk
5.6575
0.50 0.50 0.00
0.00 0.50 0.50
0.50 0.00 0.50
2
Selective Dynamics
Cartesian
0.00 0.00 0.00 F F F
0.30 0.30 0.30 T T T
```

Add the line  
Selective dynamics

Indicate which atom  
coordinates to update.

Modify atom positions ☺

## KPOINTS

→ Reduce the k-point set to 11x11x11 for the Ge bulk system.

## INCAR

```
mc - /gpfs/h06/tcmsdany/Ugent/VASPles/GeBulk/relax
INCAR [-----] 11 L:[ 1+10 11/ 22] *(420 / 931k
general:
SYSTEM = relax Ge Bulk
ISTART = 0 ! 0 start from scratch
ICHARG = 2 ! 2 superposition atoms
ISMEAR = 1 ! >=1 Methfessel-Paxton
SIGMA = 0.1 ! width smearing
EDIFF = 1.0E-6 ! electronic convergence criterium
EDIFFG = -0.001 ! ionic relaxation stops if all
! forces are smaller than 1meV
! To use a stopping criterium similar to the electronic
! steps => use a positive value for EDIFFG
PREC = High ! high precision
LWAVE = .TRUE. ! write the WAVECAR file
LCHARG = .TRUE. ! write the CHGCAR file
LVTOT = .FALSE. ! do not write the potetial file
ENCUT = 345 ! kinetic energy cutoff
ISIF = 2 ! 2: relax ions only
! 3: also relax volume and shape of cell
! 4: relax ions + cellshape, volume=fixed
dynamic:
IBRION = 2 ! 2 Conjugate Gradient method for relax
NSW = 100 ! No more than 100 ionic steps
```

**Be careful using ISIF in combination with vacuum systems: molecules, surfaces,...**

# Run, Raichu. Run!

```
> cd relax/  
> qsub jobscript.sh
```





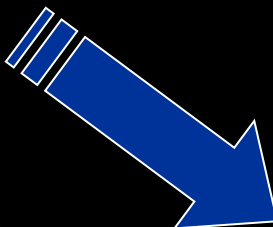
# Relaxation II: Results

## CO-molecule

## POSCAR

```
mc - /gpfs/h06/tcmsdany/Ugent/VASPles/COmolecule/relax
Danny2@OwnH ~/Ugent/VASPles/COmolecule/relax $ cat POSCAR
CO_molecule
10.00
1.00 0.00 0.00
0.00 1.00 0.00
0.00 0.00 1.00
1 1 ! 1 Carbon and 1 O atom
Selective Dynamics
Cartesian
0.00 0.00 0.00 F F F ! C-atom
0.00 0.00 1.20 T T T ! O-atom
Danny2@OwnH ~/Ugent/VASPles/COmolecule/relax $
```

C-O bond length of 1.134998A  
Not bad compared to the  
experimental value of 1.128A  
→ ~0.6% larger



## CONTCAR

```
mc - /gpfs/h06/tcmsdany/Ugent/VASPles/COmolecule/relax
Danny2@OwnH ~/Ugent/VASPles/COmolecule/relax $ cat CONTCAR
CO_molecule
10.000000000000000000
1.000000000000000000 0.000000000000000000 0.000000000000000000
0.000000000000000000 1.000000000000000000 0.000000000000000000
0.000000000000000000 0.000000000000000000 1.000000000000000000
1 1
Selective dynamics
Direct
0.000000000000000000 0.000000000000000000 0.000000000000000000 F F F
0.000000000000000000 0.000000000000000000 0.1134997654412192 T T T
0.000000000E+00 0.000000000E+00 0.000000000E+00
0.000000000E+00 0.000000000E+00 0.000000000E+00
Danny2@OwnH ~/Ugent/VASPles/COmolecule/relax $
```

The CONTCAR file is a POSCAR file you can use to continue either your relaxation (if 100 ionic steps was not enough) or start a SC calculation. The CONTCAR file is written at the end of each ionic step. (don't forget to rename it POSCAR is you want to use it)

# Relaxation III: Results

```

mc - /gpfs/h06/tcmsdany/Ugent/VASPles/COmolecule/relax
Danny2@OwnH ~/Ugent/VASPles/COmolecule/relax $ grep LOOP+ OUTCAR
LOOP+: VPU time      21.76: CPU time      21.91
LOOP+: VPU time      13.14: CPU time      13.18
LOOP+: VPU time      12.53: CPU time      12.58
LOOP+: VPU time      16.57: CPU time      16.65
LOOP+: VPU time      11.48: CPU time      11.53
LOOP+: VPU time      11.53: CPU time      11.56
LOOP+: VPU time      10.84: CPU time      10.88
LOOP+: VPU time      10.26: CPU time      10.29
LOOP+: VPU time       9.62: CPU time       9.69
LOOP+: VPU time       8.31: CPU time       8.39
LOOP+: VPU time       7.17: CPU time       7.24
LOOP+: VPU time       1.86: CPU time       1.92
Danny2@OwnH ~/Ugent/VASPles/COmolecule/relax $ grep F OSZICAR
 1 F= -.65091160E+01 EO= -.65129813E+01 d E =-.650912E+01
 2 F= -.10665642E+02 EO= -.10669508E+02 d E =-.415653E+01
 3 F=  0.28428453E+03 EO=  0.28428260E+03 d E =0.290794E+03
 4 F= -.10764686E+02 EO= -.10768551E+02 d E =-.425557E+01
 5 F= -.13878135E+02 EO= -.13880068E+02 d E =-.736902E+01
 6 F= -.13132131E+02 EO= -.13134064E+02 d E =-.662302E+01
 7 F= -.15350382E+02 EO= -.15352314E+02 d E =-.884127E+01
 8 F= -.15480047E+02 EO= -.15481980E+02 d E =-.897093E+01
 9 F= -.15567923E+02 EO= -.15569855E+02 d E =-.905881E+01
10 F= -.15572778E+02 EO= -.15574710E+02 d E =-.906366E+01
11 F= -.15572844E+02 EO= -.15574777E+02 d E =-.906373E+01
12 F= -.15572845E+02 EO= -.15574777E+02 d E =-.906373E+01
Danny2@OwnH ~/Ugent/VASPles/COmolecule/relax $

```

Only 12 ionic steps were needed to relax to the final structure.

```

huygens.sara.nl - PuTTY
$3" "$6}' ~/Ugent/VASPles/COm
2.00000 -8.312127
1.59900 -12.420791
0.39600 1866.430615
1.59105 -12.488259
0.99353 28.385187
1.40848 -12.936392
1.20101 -6.226605
1.09727 5.139860
1.14418 -1.070337
1.13609 -0.131998
1.13498 0.001876
1.13500 0.000941
Danny2@OwnH ~/Ugent/VASPles/COm

```

Position 2<sup>nd</sup> atom  
at the end of each  
ionic step

Force eV/A

# Your turn

>> Did the lattice parameter change?

To get the initial lattice parameters:

```
hive3.exe getlattice POSCAR
```

To get the final lattice parameters:

```
hive3.exe getlattice CONTCAR
```

>> How did the atomic positions change, what are the relative coordinates?

>> Is this a good relaxation if you want to obtain the optimum lattice parameter?

→ What should be changed?

# Run, Raichu. Run!

```
> cd relax/  
> qsub jobscript.sh
```



## More advanced: Density of States (DOS) I

Both DOS and band-structure calculations are 2-step calculations.

1. Do a SC calculation to get a ready converged charge density
2. Do a Non-self consistent Calculation with high K-point density, using the charge density obtained in the SC calculation.

Make a new directory: DOS and copy POSCAR, POTCAR, INCAR, KPOINTS and CHGCAR to this folder from your SC calculation.

The files CHGCAR, POTCAR and POSCAR remain unchanged for the DOS calculation. However, to get a good DOS we would like a denser k-point grid than the one we used up to now. (Charge density and effective potential converge rapidly wrt. k-points, so we can use a “small” k-point set to get the charge density)

**→ Increase your k-point set in the file KPOINTS to e.g. 41x41x41  
(btw this is also the maximum that VASP can handle)**

# Run, Raichu. Run!

```
> cd DOS/  
>qsub jobscript.sh
```



# More advanced: DOS II

The only file left to modify is the INCAR file.

```
mc - /gpfs/h06/tcmsdany/Ugent/VASPls/GeBulk/DOS
INCAR [----] 45 L:[ 1+17 18/ 21] *(749 / 922b)=
general:
  SYSTEM = Ge Bulk DOS
  ISTART = 0 ! 0 start from scratch, 1 use old WAVECAR
  ICHARG = 11 ! 1 use old CHGCAR 10+ Fix CHG
  ISMEAR = -5 ! -5 Tetra+Blochl
  EDIFF = 1.0E-8 ! electronic convergence criterium
  PREC = High ! used precision
  LWAVE = .FALSE. ! do not write the WAVECAR file
  LCHARG = .TRUE. ! write the CHGCAR file
  LVTOT = .FALSE. ! do not write the potetial file
  ENCUT = 345 ! kinetic energy cutoff
dynamic:
  IBRION = -1 ! -1 fix atoms, 2 ConjGrad for relax
  NSW = 0 ! number of ionic steps
Density of States:
  LORBIT = 1 ! DOSCAR+lm decomposed PROCAR, RWIGS needed
  RWIGS = 1.22 ! Wigner Seitz radius (Å) for each ion-type
  NPAR = 1 ! to get site projected dos
  EMIN = -20 ! lower boundary (eV) for energy plot
  EMAX = 15 ! upper " " " " "
  NEDOS = 3500 ! # of gridpoints in dos-plot -> here 10meV
1Help 2Save 3Mark 4Replac 5Copy 6Move 7Search 8Delete
```

Set ICHARG=1+10=11  
→1: read the CHGCAR from our SC calc.

→ 10: keep the Charge density fixed during the calculation. (only wave function update)

Increase convergence criterion slightly

To get a good PDOS, you do not want the spheres of the atoms to overlap → chance to see states from atom A in the PDOS of atom B

Optional.  
These allow you to specify the part of the DOS you are interested in, and the resolution you wish to have.

# More advanced: DOS III: Results Ge Bulk

```
mc - /gpfs/h06/tcmsdany/Ugent/VASPles/GeBulk/DOS
```

```
Danny2@OwnH ~/Ugent/VASPles/GeBulk/DOS $ cat out.dat
ERROR: 0031-652 Error reading STDIN
running on 4 nodes
distr: one band on 4 nodes, 1 groups
vasp.4.6.31 08Feb07 complex
POSCAR found : 1 types and 2 ions
LDA part: xc-table for Ceperly-Alder, standard interpolation
POSCAR, INCAR and KPOINTS ok, starting setup
WARNING: wrap around errors must be expected
FFT: planning ... 1
reading WAVECAR
charge-density read from file: Ge
entering main loop
      N      E      dE      d eps      ncg      rms
DAV:  1      0.784100864734E+01      0.78410E+01      -0.26759E+03      28384      0.590E+02
DAV:  2      -0.100723362603E+02      -0.17913E+02      -0.17620E+02      42960      0.763E+01
DAV:  3      -0.103508880907E+02      -0.27855E+00      -0.27855E+00      34016      0.127E+01
DAV:  4      -0.103512686934E+02      -0.38060E-03      -0.38060E-03      42088      0.508E-01
DAV:  5      -0.103512688485E+02      -0.15507E-06      -0.15507E-06      33648      0.741E-03
DAV:  6      -0.103512688488E+02      -0.36107E-09      -0.36103E-09      41728      0.234E-04
      1 F= -.10351269E+02 E0= -.10351269E+02 d E =0.000000E+00
```

ICHARG=11, CHGCAR was read from the SC calc.

```
Danny2@OwnH ~/Ugent/VASPles/GeBulk/DOS $ grep "volume of typ" OUTCAR
volume of typ      1: 33.6 %
Danny2@OwnH ~/Ugent/VASPles/GeBulk/DOS $ grep -A 5 "# of ion" OUTCAR
# of ion      s      p      d      tot
-----
  1      0.991      1.059      0.049      2.099
  2      0.991      1.059      0.049      2.099
-----
tot      1.98      2.12      0.10      4.20
Danny2@OwnH ~/Ugent/VASPles/GeBulk/DOS $
```

Is this a good value?

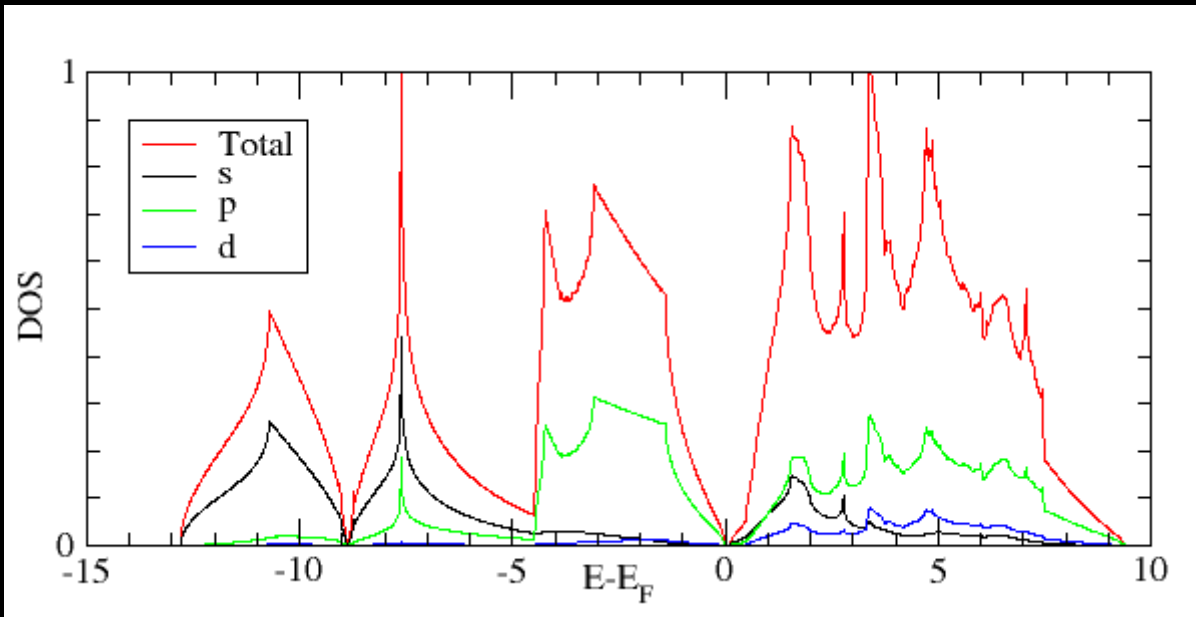
Yes: Packing factor for diamond is  $(\pi \cdot \sqrt{3})/16 \approx 34.0087\%$

Spreading in s, p, and d states per ion

**NOTE: 4 electrons accounted for...is this correct?**



# More advanced: DOS IV: Results

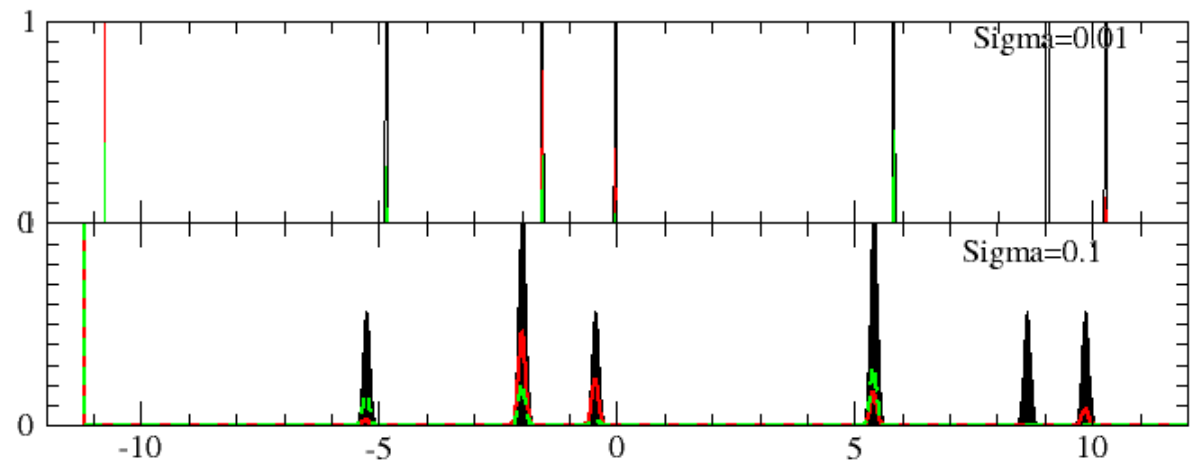


Ge Bulk DOS

## CO DOS

Be very careful with the smearing width!

→ Check the PROCAR



hive3.exe dosgrabber?

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# Band gap

system	Band Gap @302K (eV)
C (diamond)	5.5
Si(diamond)	1.11
Ge(diamond)	0.67
Sn(diamond)	0

# More advanced: DOS V: Results CO molecule

```

PROCAR lm decomposed
# of k-points: 1 # of bands: 9 # of ions: 2

k-point 1 : 0.00000000 0.00000000 0.00000000 weight = 1.00000000

band 1 # energy -27.19882901 # occ. 2.000000000
ion s py pz px dxy dyz dz2 dxz dx2 tot
1 0.090 0.000 0.064 0.000 0.000 0.000 0.007 0.000 0.000 0.161
2 0.507 0.000 0.049 0.000 0.000 0.000 0.002 0.000 0.000 0.558
tot 0.597 0.000 0.114 0.000 0.000 0.000 0.009 0.000 0.000 0.720

band 2 # energy -14.07206692 # occ. 2.000000000
ion s py pz px dxy dyz dz2 dxz dx2 tot
1 0.196 0.000 0.009 0.000 0.000 0.000 0.000 0.000 0.000 0.206
2 0.139 0.000 0.278 0.000 0.000 0.000 0.003 0.000 0.000 0.420
tot 0.335 0.000 0.287 0.000 0.000 0.000 0.003 0.000 0.000 0.626

band 3 # energy -10.79645775 # occ. 2.000000000
ion s py pz px dxy dyz dz2 dxz dx2 tot
1 0.000 0.045 0.000 0.069 0.000 0.002 0.000 0.003 0.000 0.118
2 0.000 0.174 0.000 0.264 0.000 0.001 0.000 0.001 0.000 0.440
tot 0.000 0.219 0.000 0.333 0.000 0.002 0.000 0.004 0.000 0.558

band 4 # energy -10.79645775 # occ. 2.000000000

```

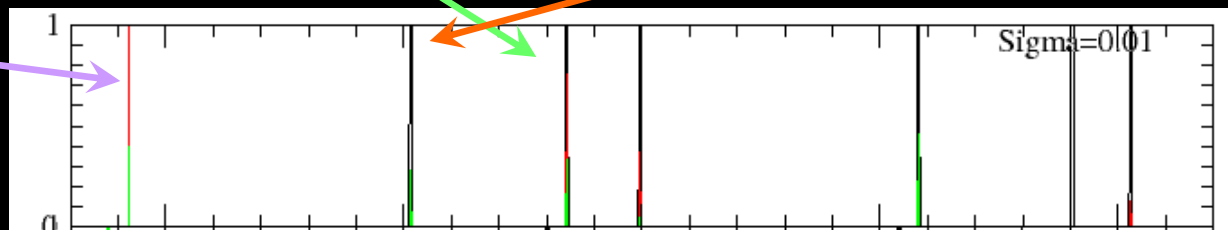
Be very careful with the smearing width!

→ Check the PROCAR file for more information on the nature of the spikes

Band 1: O-s

Band 2: C+O s →  $\sigma$

Band 3,4,5: C+O p →  $\pi$ ?



# Blast from the past: Relaxation.



- >> What happened to the lattice parameter?  
`hive3.exe getlattice CONTCAR`
- >> Is it the same as the experimental one?
- >> Is it the same as for your neighbour?

## More advanced: BANDS I

Similar as to the DOS calculation, a band-structure calculation consists of two parts:

1. Do a SC calculation to get a ready converged charge density
2. Do a Non-self consistent Calculation with high K-point density along lines of high symmetry, using the charge density obtained in the SC calculation.

Make a new directory: bands and copy POSCAR, POTCAR, INCAR, KPOINTS and CHGCAR to this folder from your SC calculation.

The files CHGCAR, POTCAR and POSCAR remain unchanged for the band-structure calculation. Since we only use K-points along lines of high symmetry, a SC calculation is out of the question. → all k-points need to be treated independently.

# Run, Raichu. Run!

```
> cd bands/  
> qsub jobscript.sh
```



# More advanced: BANDS II

```
mc - /gpfs/h06/tcmsdany/Uge
KPOINTS [-M--]
K-points L-G-X
25
line mode
reciprocal
0.5 0.5 0.5
0 0 0
0 0 0
0.5 0.5 0
```

For band-structures we use k-points along certain lines

In this calculation we will use 25 k-points per line segment

2 line segments:  $L \rightarrow \Gamma$  and  $\Gamma \rightarrow X$

Total: 50 Irreducible K-points in our calculation

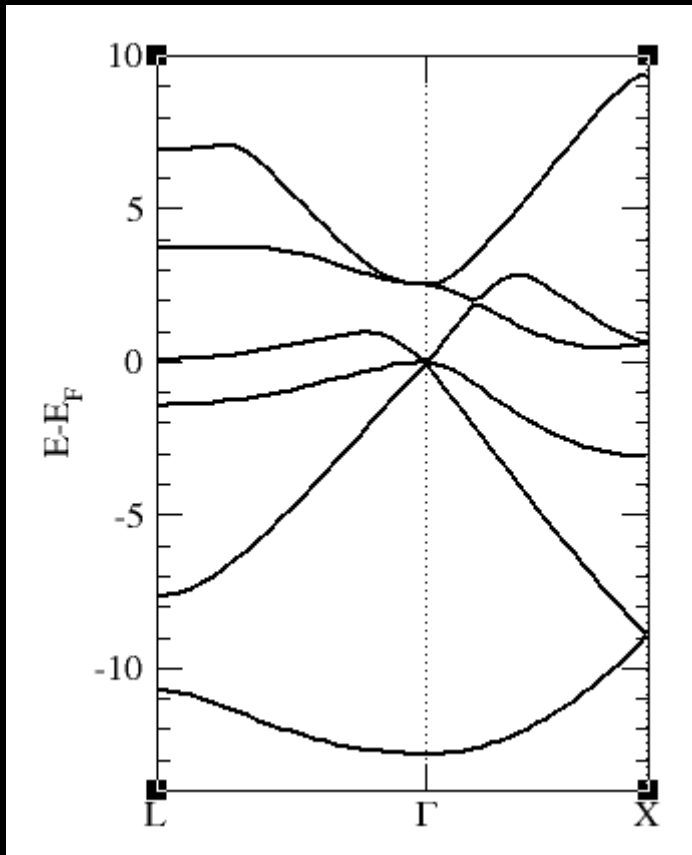
```
INCAR [-M--] 0 L:[ 1+16 17/ 17] *(431 /
general:
SYSTEM = Ge Bands
ISTART = 0
ICHARG = 11 ! 1 use old CHGCAR,10+ Fix CHG
ISMEAR = 1 ! -5 Tetra+Blochl, 0 Gaussian, >=1 MP
SIGMA = 0.1
EDIFF = 1.0E-7
PREC = High
LWAVE = .FALSE. ! do not write the WAVECAR file
LCHARG = .TRUE. ! write the CHGCAR file
LVTOT = .FALSE.
ENCUT = 345
LORBIT = 11 ! we want the PROCAR file
dynamic:
IBRION = -1
NSW = 0
```

Do a non-SC calculation

Since the k-points form lines, it is impossible to make tetrahedra, so a different integration scheme is necessary.

The PROCAR file is always useful to have if you are interested in the character of your bands (cf. CO DOS)

# More advanced: BANDS II: Result



The energy values for all bands at each k-point can be found in the EIGENVAL-file → this can be used to generate a band-structure (as seen on the left)

hive3.exe bandgrabber?

```
mc - ~/temp_huygens/temp/bands
File: EIGENVAL      Line 1 Col 0      10938 bytes
  2   2   1   1
0.2263517E+02  0.4000457E-09  0.4000457E-09  0.4000457E-09
0.100000000000000005E-03
CAR
Ge Bands
  8   50   8
0.5000000E+00  0.5000000E+00  0.5000000E+00  0.2000000E-01
1      -6.9535
2      -3.8686
3       2.3622
4       2.3622
5       3.8525
6       7.4759
7       7.4759
8      10.7085
0.4791667E+00  0.4791667E+00  0.4791667E+00  0.2000000E-01
1      -6.9731
2      -3.8381
3       2.3659
4       2.3659
5       3.8562
6       7.4775
```

K-point

bands



## More advanced: Partial Charge Density → STM

Between molecules and bulk we find surfaces. These systems can also be studied with VASP. Periodic boundary conditions make sure your system extends infinitely in both x and y direction. In the z-direction we will have copies of the same slab (just like we had for the molecule), and a vacuum region thick enough to negate interaction needs to be added. As a consequence you should not try to perform cell-optimizations, in which you allow the volume to change (your vacuum will implode).

### How do you set up a slab calculation?

1 Make a POSCAR and POTCAR file just as before

→ try to center your slab around a zero-plane

→ watch out for the symmetry (sometimes 1 extra layer might halve the number of IBZKPTS)

→ fix layers that should represent bulk

2 Make a KPOINTS file with 1 k-point in the direction perpendicular to the surface (e.g. 8x8x1, for a slab in the xy-plane)

3 Setup an INCAR file just as before

Next to DOS and band-structure calculations you can also do a Partial Charge Density calculation. The results of such a calculation could then be used to simulate STM images.

# More advanced: Partial Charge Density → STM II

A Partial Charge Density calculation is the shortest calculation you can run, it doesn't even perform a single electronic step.

**You need:**

**WAVECAR**-file (LWAVE=.TRUE. → INCAR SC calc.)

Keep everything the same as for your SC calculation only modify the INCAR file like this:  
(use a new folder, if something goes wrong or your want to do multiple runs you can simply copy the WAVECAR file again)

```
mc - -/calc_vasp/nanowire2/b4as_ptl3_p2c025_nwge_4x4cell/STMrun
INCARmod [-M--] 0 L:[ 1+22 23/ 24] *(913 / 914b)= .
general:
  SYSTEM = surface system
  ICHARG = 0 ! use old WAVECAR to generate the CHGCAR.
  ISMEAR = 1 ! MP since we have to few k-points
  SIGMA = 0.1
  EDIFF = 1.0E-6 ! fast relax
  PREC = High ! to make ROPT = 2.0E-4 with LREAL = Auto
  LREAL = Auto ! huge cell
  ENCUT = 345 !.
dynamic: !static calculation
  IBRION = -1 ! fix atoms
  NSW = 0 ! only electronic steps
Banddecomposed Chargedensity:
  LPARD = .TRUE. ! calculate Band decomposed chargecars
  NBMOD = -3 ! Calculate partial charges for.
  ! e- with eigenvalues in interval EINT->Ei
  EINT = -1.50
Moral support to keep VASP on the right track
  ISTART = 1 ! explicitly tell to use old one
  NBANDS = 584 ! different amount of cpus.
  ! = different amount of bands.
  ! = VASP refuses to use WAVECAR
```

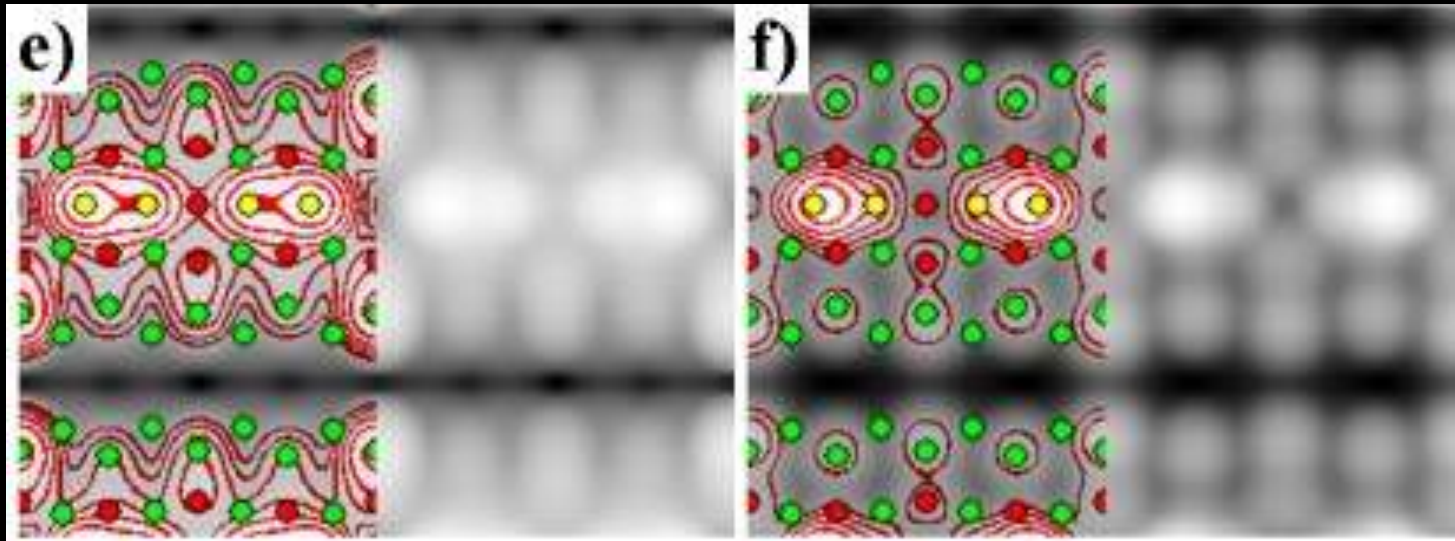
This tells VASP to just read the WAVECAR files and then start writing the PARCHG files

How the Partial charge needs to be generated

VASP tend to generate a new random WAVECAR at every possible chance. So be very careful and mind the #bands, #CPU,...

## More advanced: Partial Charge Density → STM III

VASP will now generate files called PARCHG, which have the same formatting as a normal CHGCAR file...in combination with some programming you can now generate STM images of your surface under study.



# It's all true ... for certain values of true

Of course you wish your calculations to reflect reality to perfection, however, infinite precision and numerical never fit in the same sentence in the absence of a negation.

- 1) ENCUT: energy cutoff for the kinetic energy (any contribution above is assumed negligible (and hoped zero))
- 2) (finite) k-point grids → continuous functions are approximated by points on a discrete grid. This grid is then made as coarse as possible to reduce the number of points to evaluate (while trying to maintain as much accuracy as possible)
- 3) Functionals: each flavor will give you quantitatively different results (qualitative results can also differ (e.g.: CO-adsorption site on Pt(111))), and their value can only be assessed by comparison to reality. (e.g.: Metallic Ge bulk)
- 4) Convergence criteria

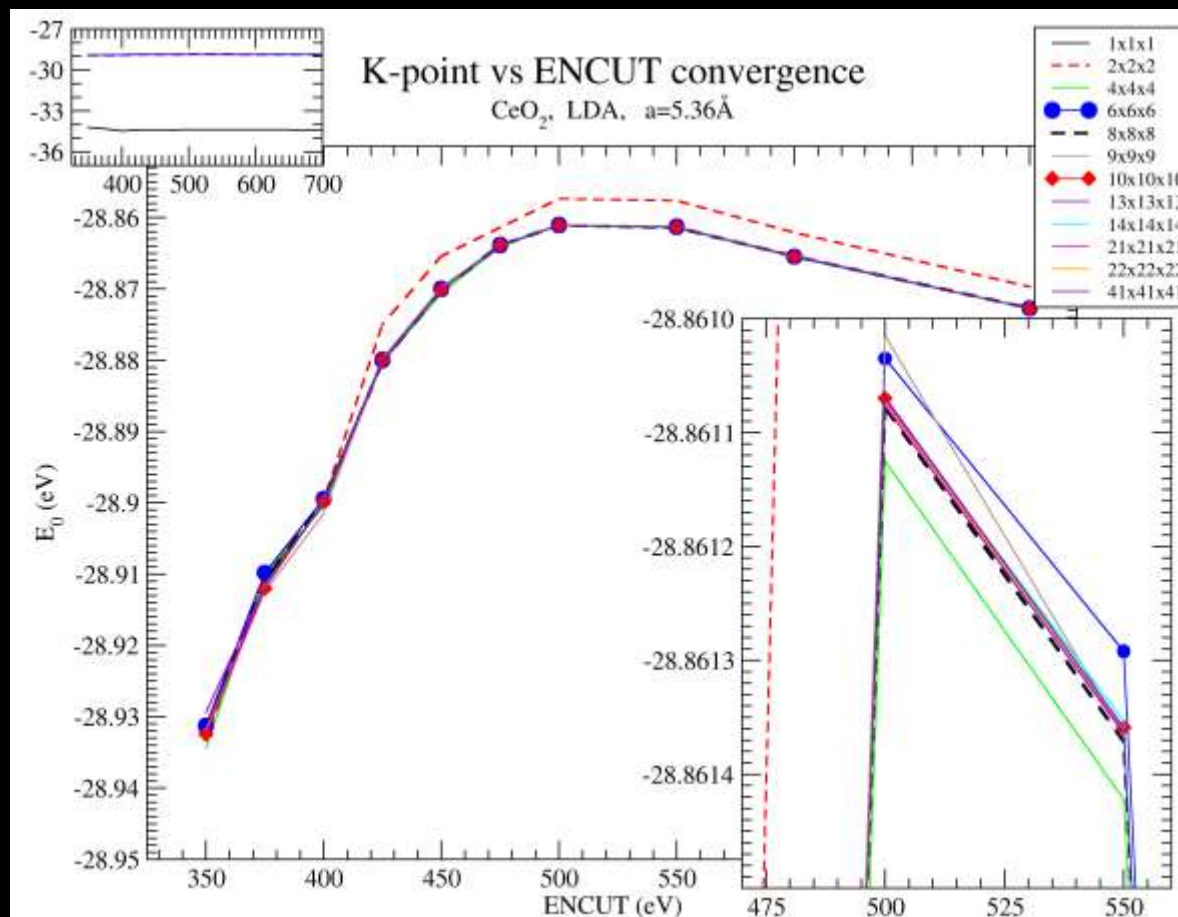


**Convergence tests are needed (for each new system)**

# It's all true ... k-points and ENCUT

First time VASP usage, first time study, or new study:

The ground-state energy of a system is connected to both K-points and kinetic energy cutoff  $\rightarrow$  spend some CPU-time on a 2D grid (k-points-ENCUT), to get a feel for the behavior of VASP



# It's all true ... k-points and ENCUT

## First time VASP usage, first time study, or new study:

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```
Danny2@OwnH ~/Ugent/CeO2_bulk/LDA/EcutKpoint $ grep "kinetic energy error" ENCUT*/KPT41/OUTCAR
ENCUT350/KPT41/OUTCAR: kinetic energy error for atom=      0.0667 (will be added to EATOM!!)
ENCUT350/KPT41/OUTCAR: kinetic energy error for atom=      0.3698 (will be added to EATOM!!)
ENCUT375/KPT41/OUTCAR: kinetic energy error for atom=      0.0553 (will be added to EATOM!!)
ENCUT375/KPT41/OUTCAR: kinetic energy error for atom=      0.2030 (will be added to EATOM!!)
ENCUT400/KPT41/OUTCAR: kinetic energy error for atom=      0.0456 (will be added to EATOM!!)
ENCUT400/KPT41/OUTCAR: kinetic energy error for atom=      0.1130 (will be added to EATOM!!)
ENCUT425/KPT41/OUTCAR: kinetic energy error for atom=      0.0367 (will be added to EATOM!!)
ENCUT425/KPT41/OUTCAR: kinetic energy error for atom=      0.0621 (will be added to EATOM!!)
ENCUT450/KPT41/OUTCAR: kinetic energy error for atom=      0.0301 (will be added to EATOM!!)
ENCUT450/KPT41/OUTCAR: kinetic energy error for atom=      0.0380 (will be added to EATOM!!)
ENCUT475/KPT41/OUTCAR: kinetic energy error for atom=      0.0250 (will be added to EATOM!!)
ENCUT475/KPT41/OUTCAR: kinetic energy error for atom=      0.0267 (will be added to EATOM!!)
ENCUT500/KPT41/OUTCAR: kinetic energy error for atom=      0.0213 (will be added to EATOM!!)
ENCUT500/KPT41/OUTCAR: kinetic energy error for atom=      0.0220 (will be added to EATOM!!)
ENCUT550/KPT41/OUTCAR: kinetic energy error for atom=      0.0169 (will be added to EATOM!!)
ENCUT550/KPT41/OUTCAR: kinetic energy error for atom=      0.0191 (will be added to EATOM!!)
ENCUT600/KPT41/OUTCAR: kinetic energy error for atom=      0.0146 (will be added to EATOM!!)
ENCUT600/KPT41/OUTCAR: kinetic energy error for atom=      0.0165 (will be added to EATOM!!)
ENCUT700/KPT41/OUTCAR: kinetic energy error for atom=      0.0104 (will be added to EATOM!!)
ENCUT700/KPT41/OUTCAR: kinetic energy error for atom=      0.0089 (will be added to EATOM!!)
ENCUT(=eV) 475 500 525 550
```

# It's all true ... optimizing your lattice

Although you might get a nice, high precision value for the lattice parameters of your system from experiment, this will probably not be the energy minimum for your calculation. Even more, the lattice parameters vary from functional to functional (and also depend on the accuracy of your k-pointset!).

## There are several ways to obtain the optimum lattice parameters

- 1) Lazy: just use the experimental value and ignore the above, or get it from a colleague working on the same system and same setup.
- 2) Quick (and sometimes dirty): a volume scan  
→ do a set of SC calculations with varying scale factor (line 2 in POSCAR) and find the minimum ground-state energy. Ideally at this point also the external pressure given by VASP should become zero.  
→ Works good for Ge

If you have more than one internal parameter (e.g. lattice vectors with different length) or the external pressure and the minimum energy don't coincide (i.e. they differ a lot) then you will need something more complex.

- 3) Fit to an equation of state: Do a set of fixed volume relaxations and fit these to the Equation of state of your choice. (cf [.exercise](#))  
→ advantage: no problem handling multiple internal parameters  
→ disadvantage: expensive compared to (2) + need to implement a fitting algorithm. (or use: [hive3.exe EOSfit](#) on E(V) data)

# VASP-speed

In the examples of this tutorial, the systems were small and it was possible to run a calculation on a single CPU within a few minutes. However, for a reasonable system of 100 atoms (you get there quickly) a relaxation can easily take half a week on 32 CPU's ...or even more.

→ VASP also exists in a parallel version

→ Next to a good parallel compilation, you might be able to speed up calculations by

- clever sequences of calculations (e.g. do a relaxation in multiple steps with increasing accuracy)
- use the CHGCAR and WAVECAR from a previous calculation to reduce the length of the first new ionic step. (can be a factor of 3)
- optimize some parallelization parameters in the INCAR file for your specific system(-size): NPAR, KPAR, LPLANE, NSIM (can give a global speedup of 20%)

→ Although such checks can be expensive at first, you can gain a lot in future calculations.



## Additional Information

- **VASP manual:** (make sure you have the latest newest version, older versions are still available online, but might contain 'wrong' information w.r.t. the function of INCAR-parameters of your VASP version (cf. NPAR))
- **Official VASP Tutorials**
- **VASP forum:** (if you have special questions, and time to wait for an answer...and for the site to load)
- **VESTA:** ((free) program (OPENGL + C++) to visualize crystal structures, CHGCARS, etc... short learning curve, export in images in most used formats (Win, Linux, Mac))
- **P4Vasp:** (a second visualization program (python+??), specifically aimed at VASP...however I would urge you to try VESTA ;))
- **Hive STM-plotter:** (if you are interested in generating STM images from your VASP data, this program (Delphi=pascal+GUI) will do the trick. Export images as bmp)
- **Hive3-tools:** Set of command-line tools available at the Ughent HP for post-processing your VASP data

**Up-to-date links:**

**<http://dannyvanpoucke.be/vasp-en/>**

...For real?

