

VASP exercises

Introduction



- VASP (Vienna Ab-initio Simulation Package)
 - <http://cms.mpi.univie.ac.at/vasp/> - manual



Go up to the homepage!

V A S P - GROUP



VASP (or also VAMP) . . . an (Austrian) high quality product.



. . . with some help of a (German) friend

VAMP/VASP is a package for performing ab-initio quantum-mechanical molecular dynamics (MD) using pseudopotentials and a plane wave basis set. The approach implemented in VAMP/VASP is based on a finite-temperature local-density approximation (with the free energy as variational quantity) and an exact evaluation of the instantaneous electronic ground state at each MD-step using efficient matrix diagonalization schemes and an efficient Pulay mixing. These techniques avoid all problems occurring in the original Car-Parrinello method which is based on the simultaneous integration of electronic and ionic equations of motion. The interaction between ions and electrons is described using ultrasoft Vanderbilt pseudopotentials (US-PP) or the projector augmented wave method (PAW). Both techniques allow a considerable reduction of the necessary number of plane-waves per atom for transition metals and first row elements. Forces and stress can be easily calculated with VAMP/VASP and used to relax atoms into their instantaneous groundstate.

For a more detailed Introduction read [VAMP/VASP the GUIDE](#) (HTML 2.2)

You can also download the postscript file:

- 1 page per page: [vasp.pdf.gz](#) or [vasp.pdf](#)
- 1 page per page: [vasp.ps.Z](#) or [vasp.ps.gz](#)
- 2 pages per page: [vasp_2.ps.Z](#) or [vasp_2.ps.gz](#)
- letter format: [vasp_letter.ps.Z](#) or [vasp_letter.ps.gz](#)

Related documents are available on [related documents](#)

Pdf files of the talks and hands-on sessions from the latest Vasp-workshop can be found [here](#). For beginners these documents are preferable to the VASP guide!



a visualisation utility for VASP can be found [here](#).



is a comprehensive graphical interface and computational environment for VASP. It comprises tools to prepare, perform and monitor VASP calculations and to evaluate and visualize the computed data. GoVASP is exclusively distributed and supported by [Windiks Consulting](#), not by the VASP group in Vienna. Hence, the VASP group in Vienna declines any responsibility for the installation of and any results obtained by using GoVASP.



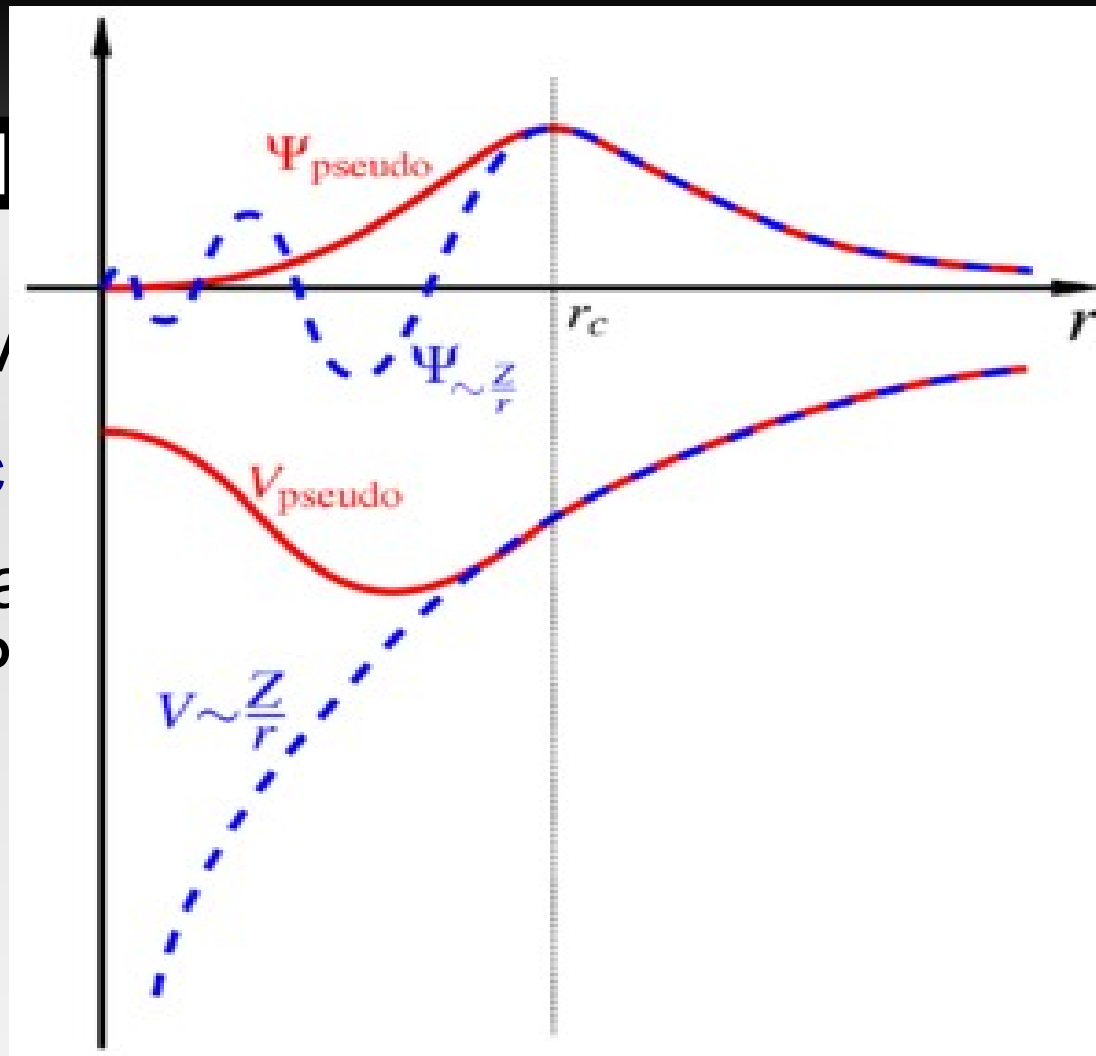
STRender - a java program for 3D visualization of atomic and magnetic structures, isoplanes, STM images is [here](#) in the section Downloads.

Introduction

- VASP (Vienna Ab-initio Simulation Package)
 - <http://cms.mpi.univie.ac.at/vasp/> - manual
 - DFT based periodic ab-initio package (mostly => HF/MP2 only experimental)
 - Local density approximation (LDA) or generalized gradient approximation GGA used (non-local exchange also available, e.g. B3LYP, but only experimental)
 -

Introdu

- VASP (V)
- <http://c>
- DFT ba
HF/MP



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mostly =>

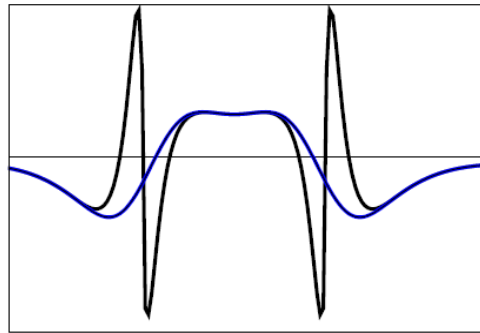
or generalized
(non-local
YP, but only

- Basis sets
 - pseudopotential used – ultrasoft (US-PP)
 - “pseudized” smooth wavefunction(potential) in the core region – no nodes
 - valence (interatomic) region (from r_c) - correct shape

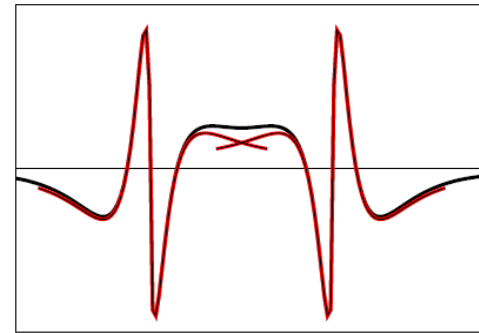
Introduct

- VASP (Vienna <http://www.vasp.at>)
- DFT based
- HF/MP2

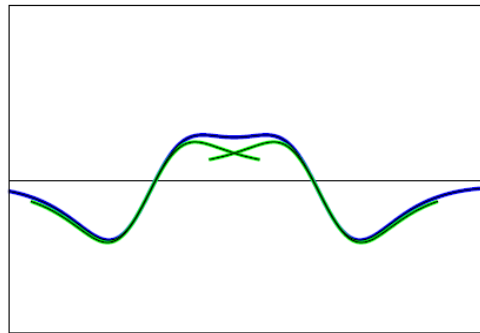
$$|\Psi\rangle = |\tilde{\Psi}\rangle + |\Psi^1\rangle - |\tilde{\Psi}^1\rangle = |\tilde{\Psi}\rangle + \sum_i (|\phi_i\rangle - |\tilde{\phi}_i\rangle) \langle \tilde{p}_i | \tilde{\Psi} \rangle$$



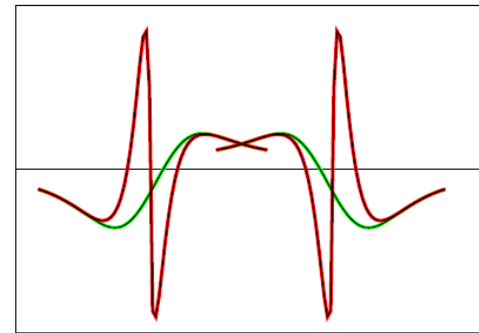
$|\Psi\rangle, |\tilde{\Psi}\rangle$



$|\Psi\rangle, |\Psi^1\rangle$



$|\tilde{\Psi}\rangle, |\tilde{\Psi}^1\rangle$



$|\Psi^1\rangle, |\tilde{\Psi}^1\rangle$

- Basis sets
 - pseudopotential used – ultrasoft (US-PP)
 - projector-augmented wave method (PAW)
 - atomic WFs in core region augmented with “pseudized” WF in valence regions

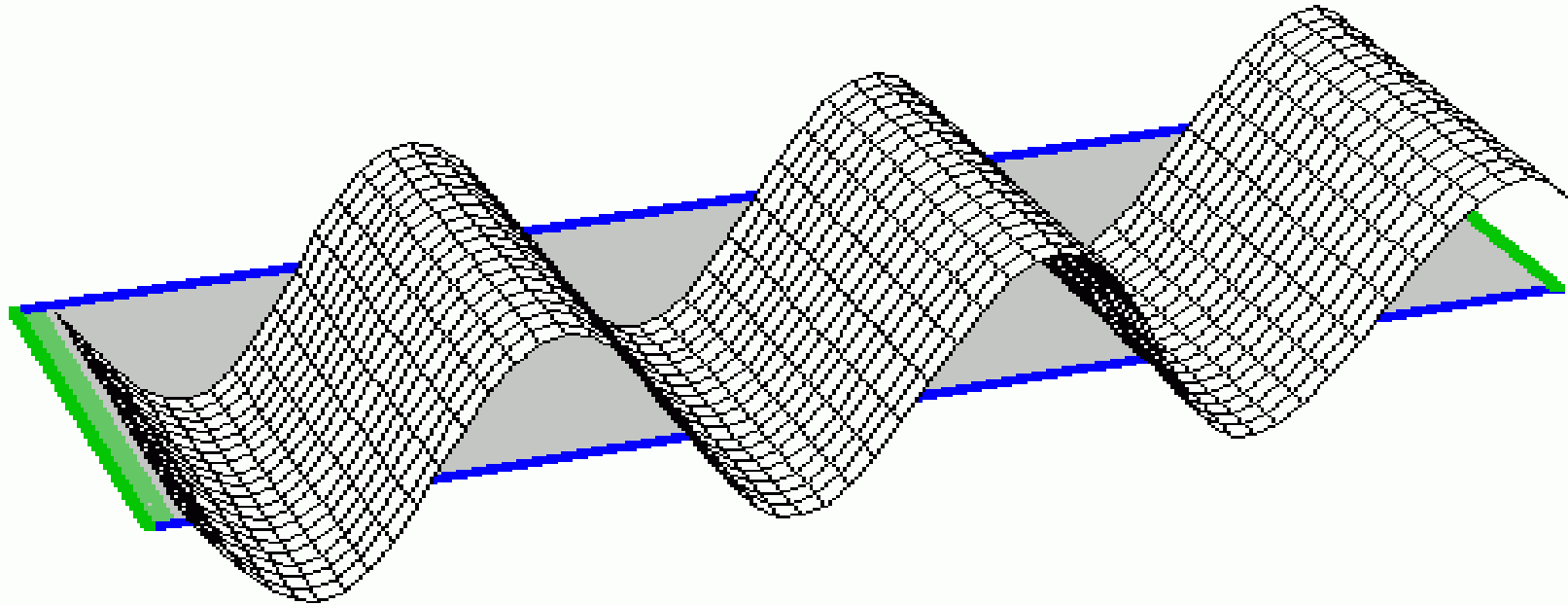
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(non-local
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Introduction



- BASIS SETS

- pseudopotential used – ultrasoft (US-PP)
- projector-augmented wave method (PAW)
- Plane waves used $u(\mathbf{x}, t) = Ae^{i(\mathbf{k} \cdot \mathbf{x} - \omega t)}$ $|\mathbf{k}| = 2\pi/\lambda$
 $Re[u(\mathbf{x}, t)] = |A| \cos(\mathbf{k} \cdot \mathbf{x} - \omega t + \arg A)$

Introduction – Basis set

- Basis set quality

$$|\mathbf{G} + \mathbf{k}| < G_{\text{cut}} \quad \text{with} \quad E_{\text{cut}} = \frac{\hbar^2}{2m} G_{\text{cut}}^2$$

- determined by the plane wave energy cutoff
- all plane waves considered with the kinetic energy smaller than E_{cut}

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

- \mathbf{G}_{cut} – the allowed k-vectors; $\mathbf{G} = x_1^* \mathbf{b}_1 + x_2^* \mathbf{b}_2 + x_3^* \mathbf{b}_3$; x_1, x_2, x_3 – integers and $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ – reciprocal vectors
- notice that the basis set changes with the cell size
 - larger cell size – larger basis set
 - basis set incompleteness problem when volume changes (see exercise fcc Si) – Pulay stress

Introduction

- Capabilities
 - cluster(ex. 1), surface(ex. 3) and bulk (ex. 2) calculation
 - Band-structure (ex. 2 & 3)
 - density of states (ex. 2 & 3)
 - properties (characterization)
 - structural – ionic (atomic) and lattice relaxation (lattice parameters) – all ex.
 - optical (e.g. lattice vibrations – phonons, adsorbed molecule characterization – vibrational frequency – ex. 1 & 3)
 - magnetic

Outline

- Warm-up example (see `~grajciar/School/QCH_VASP_exercises/`)
 - carbon monoxide
 - Input/Output (I/O) files

Input files - POSCAR

- POSCAR – structural data
 - atomic positions
 - atomic names (types) - (optional)
 - lattice vectors

CO molecule	!title
1.0	!scaling parameter
8.0 0.0 0.0	!lattice vector a
0.0 8.0 0.0	!lattice vector b
0.0 0.0 8.0	!lattice vector c
O C	!atomic type(s) - optional
1 1	!number of atoms for each at.type
Cartesian	!positions given in cartesian coordinates
0 0 0	!position vectors
0 0 1.12	!position vectors

Input files - POSCAR

- POSCAR – structural data
 - atomic positions
 - atomic names (types) - (optional)
 - lattice vectors

CO on Ni surface

3.53

0.70710678	0.00000000	0.00000000	!a
-0.35355339	0.6123724	0.00000000	!b
0.000000000	0.00000000	5.196152	!c

Ni C O

5 1 1

Direct

!positions in fractional coordinates

0.000000000	0.000000000	0.000000000
0.33333333	0.66666667	0.11111111
0.66666667	0.33333333	0.22222222
0.000000000	0.000000000	0.33333333
0.33333333	0.66666667	0.44444444
0.33333333	0.66666667	0.54029062
0.33333333	0.66666667	0.60298866

!example => $0.33*a+0.66*b+0.11*c$

Input files - POTCAR

- POTCAR – pseudo-potential file
- Copy POTCAR from pseudopotential database:

```
cat  
~grajciar/School/QCH_VASP_exercises/potpaw_PBE/O/POTCAR  
~grajciar/.../potpaw_PBE/C/POTCAR > POTCAR
```
- pseudo-potential description + data for potential generation
- number of valence electrons (pseudo-potential size)
- atomic mass
- required energy cutoff (~basis set quality)

```
PAW_PBE O 08Apr2002  
6.000000000000000000  
parameters from PSCTR are:  
VRHFIN =O: s2p4                                !number of valence electrons  
LEXCH = PE  
EATOM = 432.3788 eV, 31.7789 Ry  
  
TITEL = PAW_PBE O 08Apr2002  
LULTRA = F use ultrasoft PP ?  
IUNSCR = 0 unscreen: 0-lin 1-nonlin 2-no  
RPACOR = .000 partial core radius  
POMASS = 16.000; ZVAL = 6.000 mass and valenz !at. mass  
RCORE = 1.520 outmost cutoff radius  
RWIGS = 1.550; RWIGS = .820 wigner-seitz radius (au A)  
ENMAX = 400.000; ENMIN = 300.000 eV !required cutoff  
ICORE = 2 local potential  
LCOR = T correct aug charges  
LPAW = T paw PP  
EAUG = 605.392  
DEXC = .000  
RMAX = 2.264 core radius for proj-oper  
RAUG = 1.300 factor for augmentation sphere  
RDEP = 1.550 radius for radial grids  
QCUT = -5.520; QGAM = 11.041 optimization parameters  
  
.  
.  
.  
.  
.  
.  
..
```

Input files - KPOINTS

- determines the k-point sampling
- number of k-points
- explicit or automatic generators
- atoms and molecules – single k-point
- Band structure calculation – specific format (cvceni 2 a 3)

Example 1 – explicit listing:

Gamma-point only	!title section
1	!number of k-points
rec	!k-point position in reciprocal lattice coordinates
0 0 0 1	!b1 b2 b3 (coordinates) and weight

Example 2 – automatic generation:

Automatic mesh	
0	!automatic generation ('zero')
Monkhorst Pack	!method of automatic generation
1 1 1	!num. of subdivisions along reciprocal vectors
0 0 0	!shift of the k-point mesh

Input files - KPOINTS

- determines the k-point sampling
- number of k-points
- explicit or automatic generators
- atoms and molecules – single k-point
- Band structure calculation – specific format (cvceni 2 a 3)

$$\sum_n \frac{1}{\Omega_{BZ}} \int_{\Omega_{BZ}} \epsilon_{n\mathbf{k}} \Theta(\epsilon_{n\mathbf{k}} - \mu) d\mathbf{k},$$

k-points convergence?

- metallic/insulator? - metallic systems need more k-points (partially filled bands)
- convergence speed highly system-dependent
- usage of different smearing methods to facilitate the convergence:
replacement of the delta function $\Theta(\epsilon_{n\mathbf{k}} - \mu)$ by various smooth functions
controlled by the ISMEAR and SIGMA keywords set in **INCAR**

Input files - INCAR

- INCAR provides keywords for calculation (if not provided, defaults used)
- ISMEAR keyword
 - smearing method
- SIGMA keyword
 - parameter of smearing and indirectly of k-point mesh size convergence
 - smearing “size” or also “electronic” temperature
- All set - run VASP by typing

VASP=5.2.12 iq-4 4 1G

```
SYSTEM = CO molecule  !title (optional)
ISMEAR = 0             !smearing method
```

ISMEAR:

= 0 – Gaussian smearing (function)
insulator/semiconductors and large cells

= 1 – Methfessel-Paxton method
metals

= -5 – linear tetrahedron method
DOS and very accurate energies

$$f\left(\frac{\epsilon - \mu}{\sigma}\right) = \frac{1}{\exp\left(\frac{\epsilon - \mu}{\sigma}\right) + 1}$$

SIGMA:

~ 0.05 – insulators

~ 0.2 (default) or larger for metals

Output files - OSZICAR

- condensed information about the run
 - iteration count – N
 - total(free) energy – E
 - energy change – dE
 - final line → F – total E(ref. atom energy subtracted), E0 – E for sigma->0 (no entropy), dE change with respect to the last step (for static run entropy times SIGMA)

	N	E	dE	d eps	ncg	rms	rms(c)	
DAV:	1	0.736805827675E+02	0.73681E+02	-0.20503E+03	18	0.516E+02		
DAV:	2	-0.817837805683E+01	-0.81859E+02	-0.81650E+02	35	0.152E+02		
...								
DAV:	12	-0.147629595575E+02	-0.63689E-03	-0.87791E-05	20	0.589E-02	0.108E-02	
DAV:	13	-0.147638417598E+02	-0.88220E-03	-0.13454E-04	20	0.559E-02	0.419E-03	
DAV:	14	-0.147639840488E+02	-0.14229E-03	-0.10703E-05	20	0.181E-02	0.222E-03	
DAV:	15	-0.147640632736E+02	-0.79225E-04	-0.67256E-06	18	0.129E-02		
1 F= -.14764063E+02 E0= -.14764063E+02 d E =-.147641E+02								

Output files - OUTCAR

- main output file

- Input files reading
- Nearest neighbor distances
- keywords (INCAR/defaults)
summary of lattice parameters, k-points, position
- basis set info (plane wave number)
- electronic step info
- Eigenvalues
- total energy and forces (stress) info
- Memory and timing

```

vasp.5.2.2 15Apr09 complex
executed on      LinuxIFC date 2010.05.20  09:30:23
running on  1 nodes
distr:  one band on  1 nodes,  1 groups

```

INCAR:

POTCAR: PAW PBE O 08Apr2002

POTCAR: PAW_PBE C 08Apr2002

POTCAR: PAW_PBE O 08Apr2002

VRHFIN = 0: s2p4

LEXCH = PE

EATOM = 432.3788 eV, 31.7789 Ry

TITEL = PAW_PBE_O_08Apr2002

LULTRA = \bar{F} use ultrasoft PP ?

IUNSCR = 0 unscreen: 0-lin 1-nonlin 2-no

RPACOR = .000 partial core radius

POMASS = 16.000; ZVAL = 6.000 mass and valenz

RCORE = 1.520 outmost cutoff radius

RWIGS = 1.550; RWIGS = .820 wigner-seitz radius (au A)

ENMAX = 400.000; ENMIN = 300.000 eV

ICORE = 2 local potential

LCOR = T correct aug charges

POSCAR: O atom
positions in cartesian coordinates
No initial velocities read in

Output files - OUTCAR

- main output file
 - Input files reading
 - Nearest neighbor distances
 - keywords (INCAR/defaults)
summary of lattice parameters, k-points, position
 - basis set info (plane wave number)
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 - Memory and timing

```
ion position          nearest neighbor table
  1 0.000 0.000 0.000- 2 1.12
  2 0.000 0.000 0.140- 1 1.12
.
.
.
I would recommend the setting:
  dimension x,y,z NGX = 39 NGY = 39 NGZ = 39
SYSTEM = CO molecule
POSCAR = CO molecule

Startparameter for this run:
  NWRITE = 2 write-flag & timer
  PREC = normal medium, high low
  ISTART = 0 job : 0-new 1-cont 2-samecut
  ICHARG = 2 charge: 1-file 2-atom 10-const
  ISPIN = 1 spin polarized calculation?
  LNONCOLLINEAR = F non collinear calculations
  LSORBIT = F spin-orbit coupling
  INIWAV = 1 electr: 0-lowe 1-rand 2-diag
  LASPH = F aspherical Exc in radial PAW
  METAGGA = F non-selfconsistent MetaGGA calc.

Electronic Relaxation 1
  ENCUT = 400.0 eV 29.40 Ry 5.42 a.u. 13.05 13.05
13.05*2*pi/ulx,y,z
  ENINI = 400.0 initial cutoff
  ENAUG = 605.4 eV augmentation charge cutoff
  NELM = 60; NELMIN= 2; NELMDL= -5 # of ELM steps
  EDIFF = 0.1E-03 stopping-criterion for ELM
.
.
.
```

Output files - OUTCAR

- main output file
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summary of lattice parameters, k-points, position
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```
.
.
.
energy-cutoff :    400.00
volume of cell :    512.00
  direct lattice vectors          reciprocal lattice vectors
    8.000000000  0.000000000  0.000000000  0.125000000
0.000000000  0.000000000
    0.000000000  8.000000000  0.000000000  0.000000000
0.125000000  0.000000000
    0.000000000  0.000000000  8.000000000  0.000000000
0.000000000  0.125000000

length of vectors
    8.000000000  8.000000000  8.000000000  0.125000000
0.125000000  0.125000000

k-points in units of 2pi/SCALE and weight: Gamma-point only
0.00000000  0.00000000  0.00000000  1.000

k-points in reciprocal lattice and weights: Gamma-point only
0.00000000  0.00000000  0.00000000  1.000

position of ions in fractional coordinates (direct lattice)
0.00000000  0.00000000  0.00000000
0.00000000  0.00000000  0.14000000

position of ions in cartesian coordinates (Angst):
0.00000000  0.00000000  0.00000000
0.00000000  0.00000000  1.12000000
.
```

Output files - OUTCAR

- main output file
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summary of lattice parameters, k-points, position
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k-point 1 : 0.00000.00000.0000 plane waves: 9315

maximum and minimum number of plane-waves per node : 9315
9315

----- Iteration 1(1) -----

POTLOK: cpu time 0.79: real time 0.80

SETDIJ: cpu time 0.00: real time 0.00

EDDAV: cpu time 0.34: real time 0.34

DOS: cpu time 0.00: real time 0.00

LOOP: cpu time 1.14: real time 1.15

eigenvalue-minimisations : 18

total energy-change (2. order) : 0.7368058E+02 (-0.2050338E+03)

number of electron 10.0000000 magnetization

augmentation part 10.0000000 magnetization

Free energy of the ion-electron system (eV)

alpha Z PSCENC = 0.85010715

Ewald energy TEWEN = 55.03899630

-1/2 Hartree DENC = -516.02856099

-exchange EXHF = 0.00000000

-V(xc)+E(xc) XCENC = 39.95561961

PAW double counting = 283.82984571 -286.83001101

entropy T*S EENTRO = -0.00000342

eigenvalues EBANDS = -82.52583049

atomic energy EATOM = 579.39041991

free energy TOTEN = 73.68058277 eV

energy without entropy = 73.68058619 energy(sigma->0) =
73.68058448

Output files - OUTCAR

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E-fermi : -7.7274 XC(G=0): -1.1671 alpha+bet : -0.3423
add alpha+bet to get absolut eigen values

k-point 1 : 0.0000 0.0000 0.0000
band No. band energies occupation
1 -29.3296 2.00000
2 -13.7471 2.00000
3 -11.6698 2.00000
4 -11.6698 2.00000
5 -8.7140 2.00000
6 -1.6278 0.00000
7 -1.6278 0.00000
8 -0.2404 0.00000
9 1.7218 0.00000

General timing and accounting informations for this job:

=====

Total CPU time used (sec): 8.245
User time (sec): 7.348
System time (sec): 0.896
Elapsed time (sec): 9.412

Maximum memory used (kb): 0.
Average memory used (kb): 0.

Minor page faults: 93915
Major page faults: 67
Voluntary context switches: 96

Output files - OUTCAR

- Total energy and forces

FREE ENERGIE OF THE ION-ELECTRON SYSTEM (eV)

free energy TOTEN = -14.764063 eV

energy without entropy= -14.764063 energy(sigma->0) = -14.764063

CHARGE: cpu time 0.08: real time 0.08
FORLOC: cpu time 0.04: real time 0.04
FORNL : cpu time 0.03: real time 0.03
STRESS: cpu time 0.20: real time 0.19
FORHAR: cpu time 0.23: real time 0.23
MIXING: cpu time 0.03: real time 0.04

FORCE on cell =-STRESS in cart. coord. units (eV):

Direction XX YY ZZ XY YZ ZX

Alpha Z 0.85011 0.85011 0.85011
Ewald -85.97175 -85.97175 226.98245 0.00000 0.00000 0.00000
Hartree 142.41395 142.41395 253.05695 0.00000 0.00000 0.00000
E(xc) -43.93132 -43.93132 -42.74412 0.00000 0.00000 0.00000
Local -193.38373 -193.38373 -587.29040 0.00000 0.00000 0.00000
n-local -18.75410 -18.75410 -30.41055 0.00000 0.00000 0.00000
augment 6.26448 6.26447 5.60305 0.00000 0.00000 0.00000
Kinetic 191.74366 191.74366 176.45336 0.00000 0.00000 0.00000
Fock 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000

Total -0.76871 -0.76871 2.50084 0.00000 0.00000 0.00000
in kB -2.40549 -2.40549 7.82575 0.00000 0.00000 0.00000
external pressure = 1.00 kB Pullay stress = 0.00 kB

Output files - OUTCAR

- Total energy and forces

```
FORCES acting on ions
electron-ion (+dipol)      ewald-force      non-local-force      convergence-correction
-----
 0.280E-14 0.183E-14 0.208E+03  0.294E-16 0.352E-16 -.272E+03  0.000E+00 0.000E+00 0.612E+02  0.169E-13 0.391E-14 0.334E-
02
 0.611E-14 0.103E-13 -.241E+03  0.269E-16 0.693E-16 0.272E+03  0.000E+00 0.000E+00 -.281E+02  0.194E-13 0.114E-13 0.402E-
03
-----
 0.891E-14 0.122E-13 -.331E+02  0.563E-16 0.105E-15 0.000E+00  0.000E+00 0.000E+00 0.331E+02  0.364E-13 0.153E-13 0.374E-
02

POSITION                      TOTAL-FORCE (eV/Angst)
-----
 0.00000  0.00000  0.00000  0.000000  0.000000  -2.915079
 0.00000  0.00000  1.12000  0.000000  0.000000  2.915079
-----
total drift:                0.000000  0.000000  -0.000468
```


OUTPUT files - CONTCAR

- CONTCAR
 - final atomic positions (from the last ionic step)
 - in POSCAR format
 - in order to restart i.e. optimization just copy CONTCAR to POSCAR...

```
CO molecule
1.0000000000000000
 8.0000000000000000  0.0000000000000000  0.0000000000000000
 0.0000000000000000  8.0000000000000000  0.0000000000000000
 0.0000000000000000  0.0000000000000000  8.0000000000000000
O   C
1   1
Direct
0.00000000 0.00000000 0.00000000
0.00000000 0.00000000 0.14000000

0.00000000E+00 0.00000000E+00 0.00000000E+00
0.00000000E+00 0.00000000E+00 0.00000000E+00
```

CO - restart

- Copy all files to directory ex_2; `cp * ../ex_1_2`
- move to ex_2 and run VASP
- compare OSZICARs from ex_1 and ex_2; `diff ex_1_1/OSZICAR ex_1_2/OSZICAR`
- fast convergence in ex_2 !!!

```
2,17c2,4
< DAV: 1 0.736805827675E+02 0.73681E+02 -0.20503E+03 18 0.516E+02
< DAV: 2 -0.817837805683E+01 -0.81859E+02 -0.81650E+02 35 0.152E+02
...
< DAV: 10 -0.147599549579E+02 -0.10131E-02 -0.10470E-03 20 0.231E-01 0.349E-02
< DAV: 11 -0.147623226663E+02 -0.23677E-02 -0.59106E-04 18 0.136E-01 0.213E-02
< DAV: 12 -0.147629595575E+02 -0.63689E-03 -0.87791E-05 20 0.589E-02 0.108E-02
< DAV: 13 -0.147638417598E+02 -0.88220E-03 -0.13454E-04 20 0.559E-02 0.419E-03
< DAV: 14 -0.147639840488E+02 -0.14229E-03 -0.10703E-05 20 0.181E-02 0.222E-03
< DAV: 15 -0.147640632736E+02 -0.79225E-04 -0.67256E-06 18 0.129E-02
< 1 F= -.14764063E+02 E0= -.14764063E+02 d E =-.305075E-11
---
> DAV: 1 -0.147640782426E+02 -0.14764E+02 -0.27441E-06 18 0.854E-03 0.163E-03
> DAV: 2 -0.147640781892E+02 0.53443E-07 -0.72215E-07 20 0.549E-03
> 1 F= -.14764078E+02 E0= -.14764078E+02 d E =-.584429E-11
```

CO - restart

- In ex_2 VASP is restarted with WAVECAR present
- WAVECAR stores the wavefunction from the run
- great starting function – possible slight modification of run parameters/position etc.
- drawback – large size
 - controlled by keyword LWAVE in INCAR
 - LWAVE = .FALSE. (no WAVECAR written)
 - default LWAVE = .TRUE.

Outline

- Warm-up example
 - carbon monoxide
- cut-off study

CO - cut-off study

$$|\mathbf{G} + \mathbf{k}| < G_{\text{cut}} \quad \text{with} \quad E_{\text{cut}} = \frac{\hbar^2}{2m} G_{\text{cut}}^2$$

ENCUT: cut-off energy for plane wave basis set in eV
=[real]
=(default) – largest ENMAX as read from POTCAR

- `cd ../ex_1_3/`
- basis set quality controlled by value of the cut-off – determines the number of the plane waves by limiting their maximal kinetic energy
- the cut-off value is controlled by the ENCUT keyword in INCAR
- copy KPOINTS, POSCAR from ex_1_1
 - `cp ../ex_1_1/KPOINTS
../ex_1_3/POSCAR .`
- POTCAR is provided(don't change or use for other exercises)

SYSTEM = CO molecule !title (optional)
ISMEAR = 0 !smearing method
ENCUT = 400 !cut-off

CO - cut-off study

- we shall use small bash script to obtain the E vs cut-off scan – scan.sh
- run by
`./scan_cuttutoff.sh`
- it generates
`cutoff_scan.dat`

```
300 -.13428674E+02
325 -.14031929E+02
350 -.14293162E+02
375 -.14509072E+02
400 -.14619681E+02
425 -.14669528E+02
450 -.14694415E+02
475 -.14705667E+02
500 -.14711342E+02
```

- load and visualize

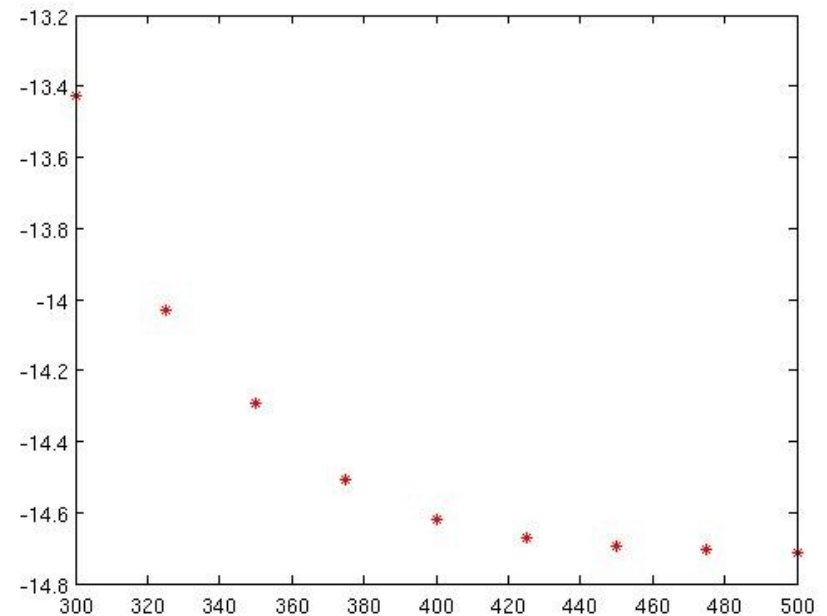
```
#!/bin/bash
rm CHGCAR CHG WAVECAR CONTCAR
for i in 300 325 350 375 400 425 450 475 500
#for i in 4.2 4.3
do
if [ -a OUTCAR ]
then
    rm OUTCAR
fi
touch OUTCAR
cat > INCAR <<EOF
SYSTEM = CO molecule
ISMEAR = 0
ENCUT = $i
EOF
echo "parameter = $i"
VASP mq 8 1.3G
while [ "General" != "$(grep 'General timing' OUTCAR|awk '{print $1}')" ];do
sleep 10
done

E=`tail -1 OSZICAR|awk '{print $3}'`
timing=`grep 'User time' OUTCAR|awk '{print $4}'`
echo $i $E >> cutoff_scan.dat
cp OUTCAR "OUTCAR_"$i
echo $i $timing >> timing.dat
done
```

CO - cut-off study

- load and visualize
 - the energy converges nicely
 - the energy for the default cut-off value is almost converged
 - one has to consider the higher time requirements when going to higher cut-off values

Note: the VASP by default uses the correction to total energy that might cause that with enlargement of the basis the energy rises. See VASP manual for details.



Outline

- Warm-up example
 - carbon monoxide
- cut-off study
- relaxation

CO molecule - Relaxation

- cd ../ex_1_4

- POSCAR

```
CO molecule           !title
1.0                   !scaling parameter
8.0  0.0  0.0         !lattice vector a
0.0  8.0  0.0         !lattice vector b
0.0  0.0  8.0         !lattice vector c
O  C                  !atomic type(s) - optional
1  1                  !number of atoms for each at.type
Cartesian             !positions given in cartesian coordinates
0  0  0               !position vectors
0  0  1.12
```

- modify INCAR

```
SYSTEM = CO molecule  !title (optional)
ISMEAR = 0            !smearing method
NSW = 5               !maximum number of ionic(relaxation) steps
IBRION = 2            !do the relaxation and use conjugate gradient algorithm
```

CO molecule - Relaxation

- IBRION keyword

- determines how/whether the atoms are moved



IBRION:

=-1 – (default) do not update the atomic positions

=0 – run the molecular dynamics



=1-3 – various relaxation(optimization) algorithms

=5-8 - vibrational dynamics (see exercise co_molecule)

- IBRION = 1 – used when close to local minimum
- IBRION = 2 – most robust – recommended
- IBRION = 3 – used when far from minimum

- NSW keyword

- the maximum number of (ionic) relaxation steps

- run VASP

CO molecule - Relaxation

- OSZICAR

```
DAV: 15 -0.147640632736E+02 -0.79225E-04 -0.67256E-06 18 0.129E-02
1 F= -.14764063E+02 E0= -.14764063E+02 d E =-.147641E+02
--
DAV: 11 -0.126608002024E+02 -0.34260E-04 -0.38464E-06 18 0.138E-02
2 F= -.12660800E+02 E0= -.12660800E+02 d E =0.210326E+01
--
DAV: 11 -0.147479026196E+02 -0.31149E-04 -0.21949E-06 20 0.104E-02
3 F= -.14747903E+02 E0= -.14747903E+02 d E =0.161607E-01
--
DAV: 4 -0.147968306775E+02 -0.48712E-05 -0.16243E-04 18 0.128E-01
4 F= -.14796831E+02 E0= -.14796831E+02 d E =-.327674E-01
```

- note the change in the total energy
- note the change in the convergence rate

- CONTCAR

- contains the optimized CO molecule geometry

```
CO molecule
1.0000000000000000
8.0000000000000000 0.0000000000000000 0.0000000000000000
0.0000000000000000 8.0000000000000000 0.0000000000000000
0.0000000000000000 0.0000000000000000 8.0000000000000000
O C
1 1
Direct
0.0000000000000000 0.0000000000000000 -0.0016335410386948
0.0000000000000000 0.0000000000000000 0.1416335410386953
```

Outline

- Warm-up example
 - carbon monoxide
- cut-off study
- relaxation
- vibration analysis

CO molecule - vibrations

$$H(f) = \begin{bmatrix} \frac{\partial^2 f}{\partial x_1^2} & \frac{\partial^2 f}{\partial x_1 \partial x_2} & \dots & \frac{\partial^2 f}{\partial x_1 \partial x_n} \\ \frac{\partial^2 f}{\partial x_2 \partial x_1} & \frac{\partial^2 f}{\partial x_2^2} & \dots & \frac{\partial^2 f}{\partial x_2 \partial x_n} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial^2 f}{\partial x_n \partial x_1} & \frac{\partial^2 f}{\partial x_n \partial x_2} & \dots & \frac{\partial^2 f}{\partial x_n^2} \end{bmatrix}$$

- cd ../ex_2/
- calculation of the vibrational frequencies from the numerical Hessian, i. e. the matrix of the second partial derivatives

- the vibrational motion can be treated as the harmonic (quadratic potential) spring oscillation

2. Newton law

$$m \frac{d^2 Q}{dt^2} + kQ = 0$$

Hook's law - approximation

- the solution of the ODR is

$$Q(t) = A \cos(2\pi\nu t); \quad \nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

frequency

- the potential energy is quadratic and is related to force by $\vec{F} = -\vec{\nabla}U$.

$$U(t) = \frac{1}{2}kx(t)^2 = \frac{1}{2}kA^2 \cos^2(\omega t + \varphi).$$

- thus the force constant is equal to second derivative of the potential with respect to coordinate

$$f = \frac{\partial^2 V}{\partial Q^2}$$

- the force constant is directly related to the vibrational motion frequency

CO molecule - vibrations

- `cd ../ex_2/`
- use the optimized geometry (CONTCAR) from previous run and copy it to POSCAR
- INCAR

```
SYSTEM = CO molecule
ISMEAR = 0
IBRION = 5                !vibration dynamics
NFREE = 2                !number of displacements from initial position
POTIM = 0.02              !size of displacement from initial position in angstrom
NSW = 1                  !in this case only – need to be > 0
```

POTIM:

If IBRION=1-3; i.e. the relaxation run => POTIM – step size (scaling constant for forces) for the relaxation steps

If IBRION=5-6; i.e. the vibrational dynamics run => POTIM – step size for the displacement for evaluation of the numerical Hessian

$$\pm \text{POTIM} \times \hat{x}, \pm \text{POTIM} \times \hat{y}, \pm \text{POTIM} \times \hat{z}$$

$$\pm \text{POTIM} \times \hat{x} \text{ and } \pm 2 \text{POTIM} \times \hat{x}$$

$$\pm \text{POTIM} \times \hat{y} \text{ and } \pm 2 \text{POTIM} \times \hat{y}$$

CO molecule - vibrations

- POSCAR

- selective dynamics line added
- specify the 'active' coordinates
 - in which the displacement is done

Selective dynamics	!vibrational dynamics tag
Cartesian	!positions given in cartesian coordinates
0 0 0 F F T	!first(oxygen) atom
0 0 1.12 F F T	!second(carbon) atom

- run VASP

CO molecules -vibrations

■ OUTCAR

- Hessian
- vibrational frequencies
- vibration vectors

OPTIONAL

- note the second frequency – imaginary => translation in z direction; should be zero but is not due to probably numerical inaccuracy
- change the convergence parameters (EDIFF keyword)
- change the precision (PREC keyword)
- step size (POTIM)
- number of steps (NFREE)

Finite differences progress:

Degree of freedom: 2/ 2

Displacement: 2/ 2

Total: 4/ 4

SECOND DERIVATIVES (NOT SYMMETRIZED)

```

      1Z      2Z
1Z -114.738087 114.738087
2Z  114.458017 -114.458017
```

Eigenvectors and eigenvalues of the dynamical matrix

1 f = 63.887568 THz 401.417428 2PiTHz 2131.059813 cm-1 264.217837 meV

X	Y	Z	dx	dy	dz
0.000000	0.000000	0.000000	0	0	-0.655282
0.000000	0.000000	1.143000	0	0	0.755384

2 f/i= 0.038643 THz 0.242802 2PiTHz 1.288994 cm-1 0.159815 meV

X	Y	Z	dx	dy	dz
0.000000	0.000000	0.000000	0	0	-0.755384
0.000000	0.000000	1.143000	0	0	-0.655282

PREC:

=Low |Medium|High|Normal(default)|Accurate

changes various default keyword settings with the overall effect on the accuracy in the systemic manner

EDIFF:

=real number

determines the convergence criteria for the self-consistent energy calculation

Default = 1E-4

CO molecule - 'charge distribution'

- 'charge distribution/population analysis'
 - spd site projected wavefunction character of eigenstates(bands) - provides information on wavefunction 'composition' from particular atoms
 - stored in PROCAR file
 - controlled in INCAR by LORBIT keyword

LORBIT:

=10 – l(quantum number) decomposed wavefunction written to PROCAR

=11 – lm decomposed wavefunction written to PROCAR - in this case possible to tell apart p_x (p_y) and p_z states

SYSTEM = CO molecule

ISMEAR = 0

LORBIT = 11

!PROCAR file written?

- copy the input files to ../ex_3/ and run VASP

