VASP exercises

Introduction

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

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 utilty for VASP can be found here.

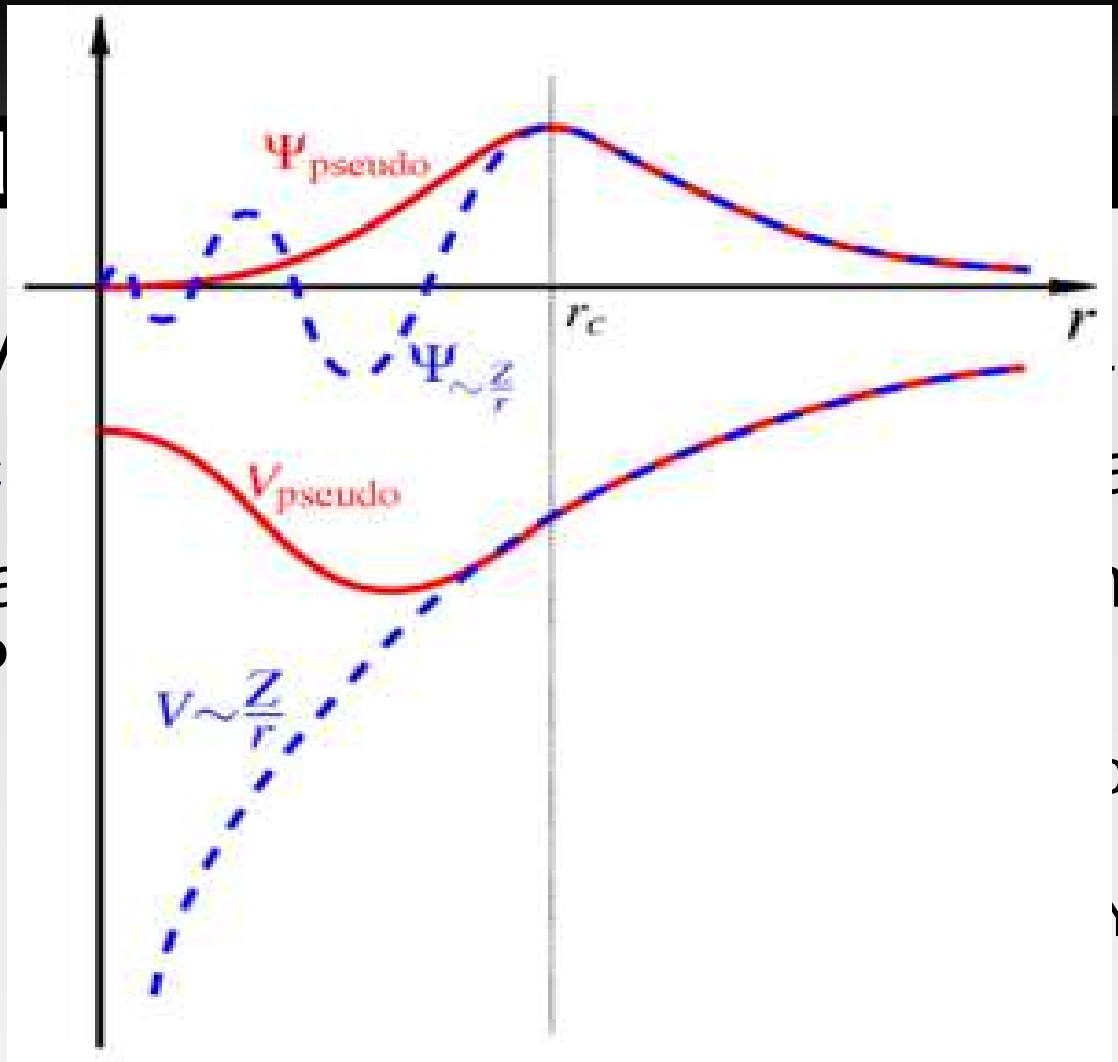
is a comprehensive graphical interface and computational environment for VASP. It comprises tools to prepare, perform and monitor VASP calculations and to evaluate and visualize the computed data. GoVASP is exclusively distributed and supported by Windiks Consulting , not by the VASP group in Vienna. 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)
  -

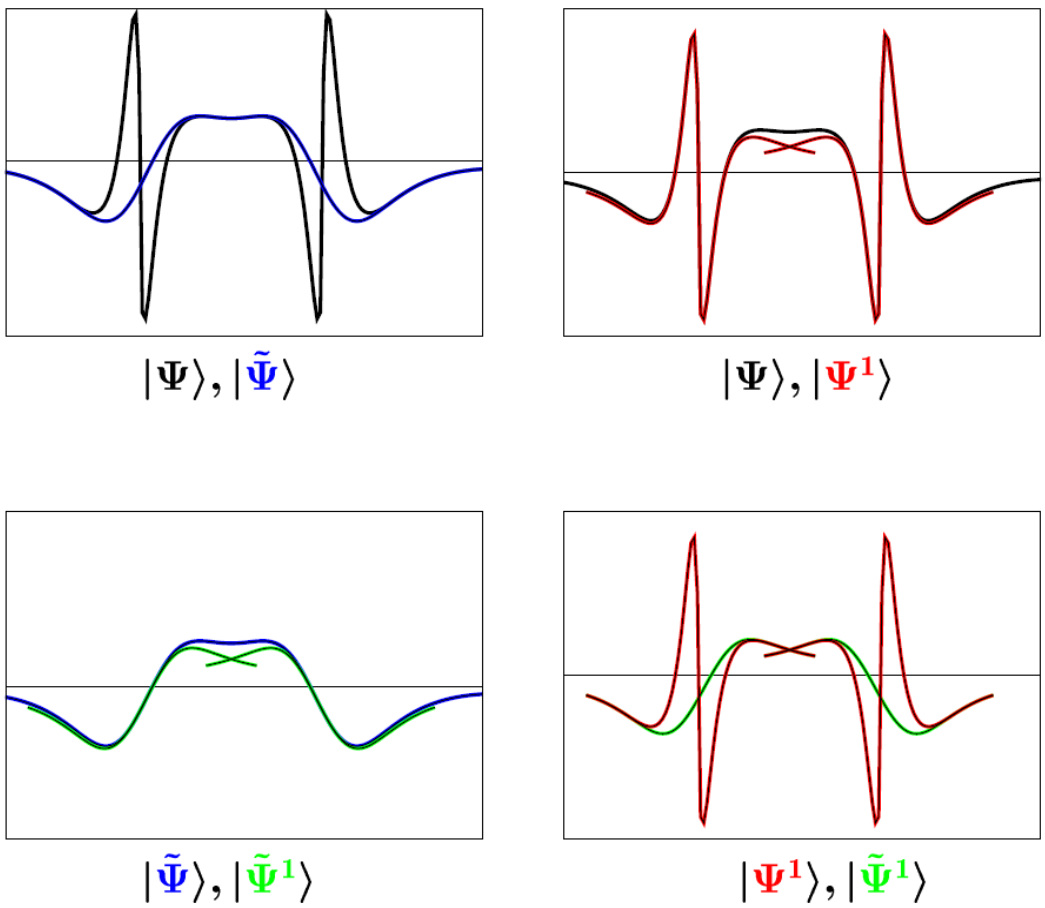
Introdu



- VASP (V ... ckage)
  - http://c ... al
  - DFT ba ... nostly => HF/MP ...
    ... 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

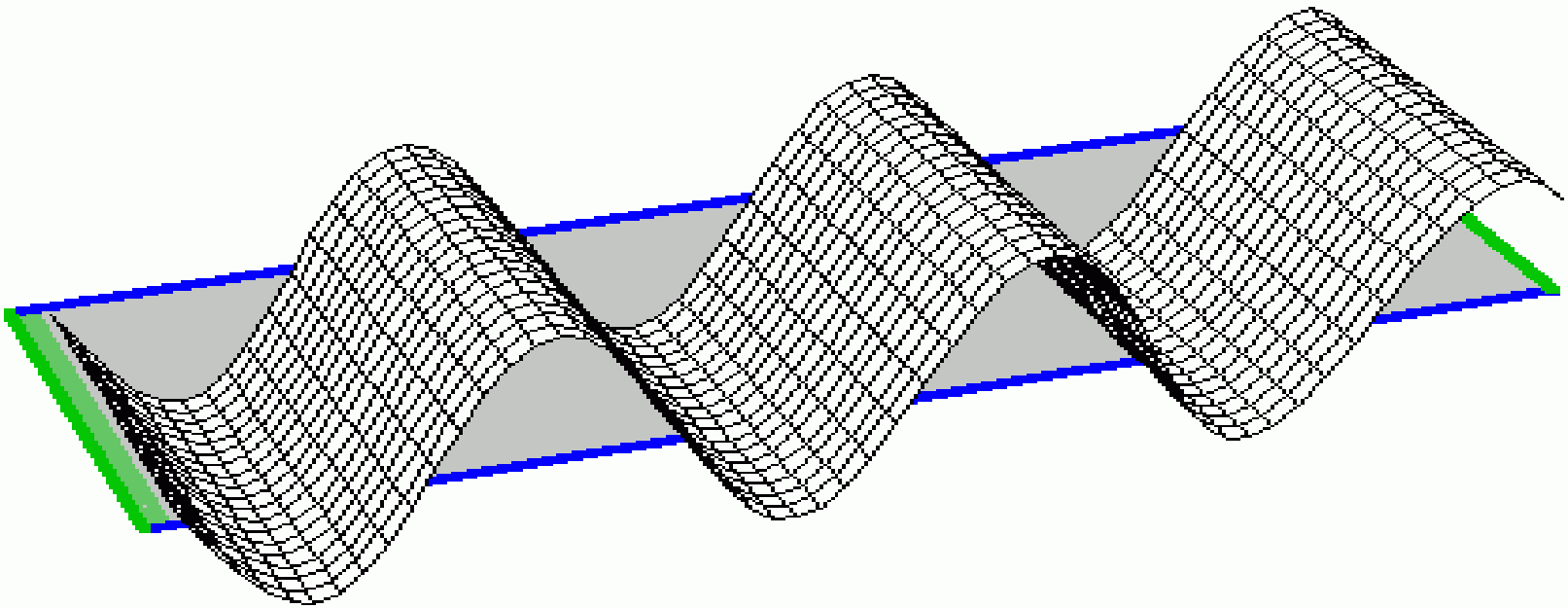
Introdu

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



- VASP (ckage)
  - http:// l
  - DFT b ostly => HF/MI
    r generalized (non-local ′P, but only
  - Basis sets
    - pseudopotential used – ultrasoft (US-PP)
    - projector-augmented wave method (PAW)
      - atomic WFs in core region augmented with “pseudized” WF in valence regions

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

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

- Basis set quality
  - determined by the plane wave energy cutoff
  - all plane waves considered with the kinetic energy smaller than E_{cut}
  - G_{cut} – the allowed k-vectors; $G = x_1 * b_1 + x_2 * b_2 + x_3 * b_3$; x_1, x_2, x_3 – integers and b_1, b_2, 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

$$\mathbf{b_1} = 2\pi \frac{\mathbf{a_2} \times \mathbf{a_3}}{\mathbf{a_1} \cdot (\mathbf{a_2} \times \mathbf{a_3})}$$

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    0.0000000    0.000000        !a
  -0.35355339    0.6123724    0.000000        !b
   0.00000000    0.0000000    5.196152        !c
  Ni C O
  5 1 1
Direct                                         !positions in fractional coordinates
   0.00000000    0.00000000    0.00000000
   0.33333333    0.66666667    0.111111111     !example => 0.33*a+0.66*b+0.11*c
   0.66666667    0.33333333    0.22222222
   0.00000000    0.00000000    0.33333333
   0.33333333    0.66666667    0.44444444
   0.33333333    0.66666667    0.54029062
   0.33333333    0.66666667    0.60298866
```

Input files - POTCAR

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

```
cat
~grajciar/School/QCH_VASP_exerci
ses/potpaw_PBE/O/POTCAR
~grajciar/.../potpaw_PBE/C/POTCA
R > 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
6.00000000000000000
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 (cviceni 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 generatioin
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 (cviceni 2 a 3)

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

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 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

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

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 =O: s2p4
   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
   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
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```
 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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  - electronic step info
  - Eigenvalues
  - total energy and forces (stress) info
  - Memory and timing

```
.
.
.
  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

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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

- 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

```
 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
  1.00000000000000
    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/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

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

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

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

- copy KPOINTS, POSCAR from ex_1
  - `cp ../ex_1/KPOINTS ../ex_1_3/POSCAR .`
- POTCAR is provided(don't change or use for other exercises)

CO - cut-off study

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

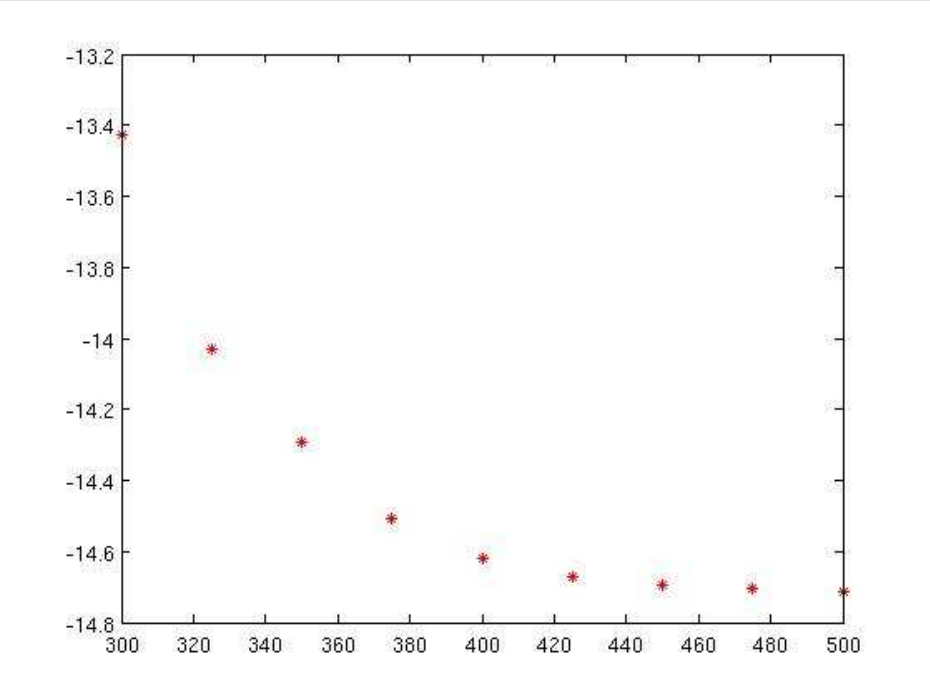
- load and visualize

```
#!/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 ../../co_molecule/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
   1.00000000000000
     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

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

- `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

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

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

$$\pm_{\mathrm{POTIM}} \times \hat{x}, \pm_{\mathrm{POTIM}} \times \hat{y}, \pm_{\mathrm{POTIM}} \times \hat{z}$$

$$\pm_{\mathrm{POTIM}} \times \hat{x} \text{ and } \pm_{2\,\mathrm{POTIM}} \times \hat{x}$$

$$\pm_{\mathrm{POTIM}} \times \hat{y} \text{ and } \pm_{2\,\mathrm{POTIM}} \times \hat{y}$$

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

CO molecule - PROCAR

- PROCAR
  - highest occupied bands

```
band   3 # energy  -11.43812617 # occ.  2.00000000

ion      s      py      pz      px     dxy     dyz     dz2     dxz     dx2     tot
  1  0.000  0.366  0.000  0.179  0.000  0.000  0.000  0.000  0.000  0.546
  2  0.000  0.105  0.000  0.051  0.000  0.000  0.000  0.000  0.000  0.156
tot  0.000  0.471  0.000  0.231  0.000  0.000  0.000  0.000  0.000  0.702

band   4 # energy  -11.43812617 # occ.  2.00000000

ion      s      py      pz      px     dxy     dyz     dz2     dxz     dx2     tot
  1  0.000  0.179  0.000  0.366  0.000  0.000  0.000  0.000  0.000  0.546
  2  0.000  0.051  0.000  0.105  0.000  0.000  0.000  0.000  0.000  0.156
tot  0.000  0.231  0.000  0.471  0.000  0.000  0.000  0.000  0.000  0.702

band   5 # energy   -8.77151667 # occ.  2.00000000

ion      s      py      pz      px     dxy     dyz     dz2     dxz     dx2     tot
  1  0.001  0.000  0.137  0.000  0.000  0.000  0.000  0.000  0.000  0.138
  2  0.171  0.000  0.260  0.000  0.000  0.000  0.000  0.000  0.000  0.432
tot  0.172  0.000  0.397  0.000  0.000  0.000  0.000  0.000  0.000  0.570
```