§15. Calculation by VASP.

§15.1 Introduction

VASP is an ab-initio package for quantum mechanical calculation the physical properties of bulk materials and molecules. The mathematical basis of package is DFT method and Hartree-Fock approximation implemented on paradigme of pseudopotentials. Ab-initio means that to calculate any physical properties of a material, you only need to know the initial positions and the type of atoms. VASP is a commercial package with total set of pseudopotential for any atom from periodical table of elements. The program is delivered as source code on Fortran 90 programming language. To compile the program you need any fortran compiler supporting standard of Fortran 90. For example gfortran-free fortran compiler or oneAPI - is a Intel set of compilers and tools. Both programs are free.

Due to high requirement of this type of programs to computational resources (large number of processors and much operating memory for parallel computations) it is make sense to run VASP on computational clusters with around 4GB of memory for one processor or thread (depending on the problem of course). Since 100% of compute clusters run the Linux operating system(OS), knowledge of this OS and understanding of work in command line is very desirable. Usually cluster is using to perform the calculations and desktop computer can be used to analyze the results of calculations, plotting the data and so on.

I want to emphasize that VASP can also be installed on a Linux desktop computer. But do not forget that calculations for systems with a large number of atoms on such computers with few processors and memory can take months, if at all possible (depending on the problem).

In our case the package already precompiled and can be used.

§15.1 Important files.

1. *File* **POSCAR** *contains the position and description of atoms.*

The format of date is following (as example we consider the crystal $BaTiO_3$):

POSCAR

BaTiO3	Line 1
1.0	Line 2
4.0 0.0 0.0	Line 3
0.0 4.0 0.0	Line 4
0.0 0.0 4.0	Line 5
Ba Ti O	Line 6
1 1 3	Line 7
Direct	Line 8
0. 0. 0.	Line 9
0.5 0.5 0.5	Line 10
0.5 0.5 0.0	Line 11
0.5 0.0 0.5	Line 12
0.0 0.5 0.5	Line 13

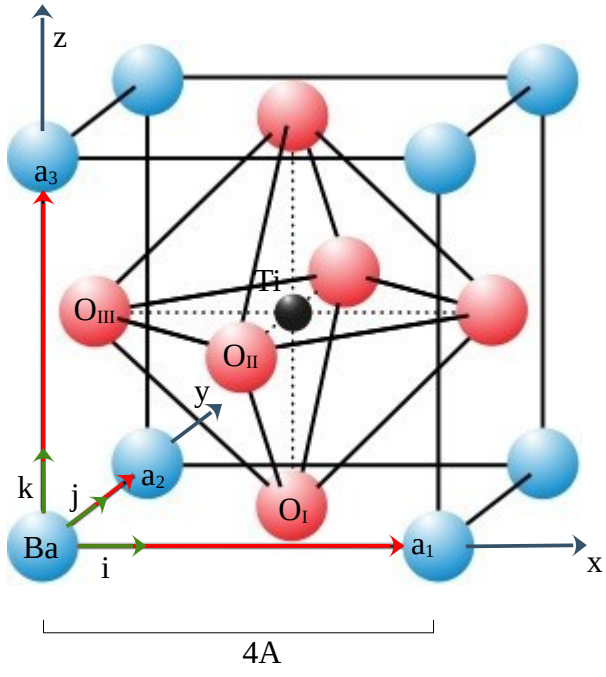

Figure 1

The unit cell of $BaTiO_3$ crystal is represented in Figure 1. The basis vectors $\mathbf{a_1}$, $\mathbf{a_2}$, $\mathbf{a_3}$ have the same lengths 4A.

The description of lines:
Line 1 - any comments
Line 2 – any real number. Basis vectors should be multiplied on it.
Line 3 – coordinates x,y, and z of the first basis vector $\mathbf{a_1}$. Units of measurement – angstrom (10^{-10}m).
Line 4 – coordinates x,y, and z of the second basis vector $\mathbf{a_2}$. Units of measurement – angstrom(10^{-10}m).
Line 5 – coordinates x,y, and z of the third basis vector $\mathbf{a_3}$. Units of measurement – angstrom(10^{-10}m).
Line 6 – chemical description of atoms. Only chemical symbols of elements.
Line 7 – the number of corresponding chemical elements in a unit cell. Must bi in the same sequence as in the previous row.
Line 8 – Can be DIRECT(or just D) or CARTESIAN (or just C).
CARTESIAN - means that atoms coordinates x,y and z presented in angstrom. For example for O_I atom $2.0\vec{i}+2.0\vec{j}+0.0\vec{k}$.
DIRECT – means that coordinates of atoms must be presented in units of basis vectors $x\vec{a}_1+y\vec{a}_2+z\vec{a}_3$.
For example for O_I atom $0.5\vec{a}_1+0.5\vec{a}_2+0.0\vec{a}_3$.
Line 9 – direct coordinates for Ba atom located in zero point
Line 10 – direct coordinates for Ti atom located in zero point
Line 11 – direct coordinates for O_I atom located in zero point
Line 12 – direct coordinates for O_{II} atom located in zero point
Line 13 – direct coordinates for O_{III} atom located in zero point

The POCAR file for coordinates of atoms presented in CARTESIAN format is looks like following:

```
BaTiO3
1.0
4.0  0.0  0.0
0.0  4.0  0.0
0.0  0.0  4.0
Ba Ti O
1 1 3
C
0.   0.   0.
2.0 2.0 2.0
2.0 2.0 0.0
2.0 0.0 2.0
0.0 2.0 2.0
```

The POSCAR file can be directly generated from **.cif** (https://en.wikipedia.org/wiki/Crystallographic_Information_File) file.
The **.cif** files for diffeerent structures you can find in any data base for example (http://www.crystallography.net/cod/).
The corresponding **.cif** file can be converted to POSCAR file by free visualization software VESTA (https://jp-minerals.org/vesta/en/).

Some additional information with examples you can find on VASP cite (https://www.vasp.at/) and on VASP wiki (https://www.vasp.at/wiki/index.php/The_VASP_Manual).

2. *File* **KPOINTS** *contains the description the mesh of wave vector in IBZ.*

The calculating energy of electrons in periodical lattice depend on value of wave vector $E(\vec{k})$. The nonequivalent values for k-vectors located inside of Irreducible Brillouin Zone (IBZ) see lectures and server where you can find any needed information about symmetry properties of crystals (https://www.cryst.ehu.es/).

For $BaTiO_3$ IBZ is a cube with length of side $\frac{2\pi}{a}$. The components of wave vector k make sense to change in the range [-π/a,+π/a] (see Frigure 2) .

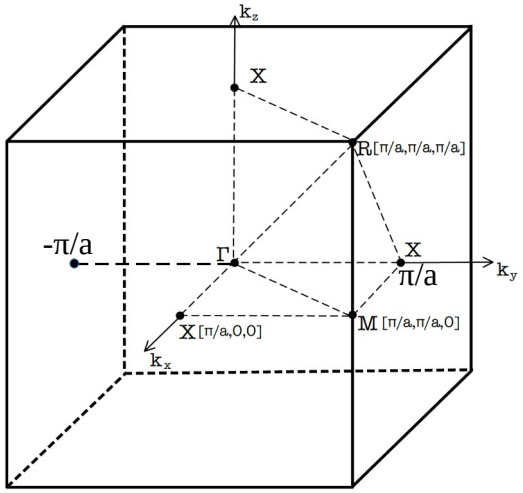

Figure 2

KPOINTS

Automatic mesh	Line 1
0	Line 2
Gamma	Line 3
4 4 4	Line 4
0. 0. 0.	Line 5

Line 1 – comment line
Line 2 - number of k-points =0, means that mesh of k-points will be generated automatic
Line 3 - zero point located at Γ point (central point in IBZ)
Line 4 - number of subdivisions along BZ lattice vectors.
In our case the components of wave vectors will be calculated with the next expression $k_x = \frac{\pi}{4 \cdot a} n_x$, here $n_x \in [0,1,2,3,4]$

Line 5 – the vector for addition shift zero point.
Actually we should change only parameters in Line 4. Too large value of the parameters (high density of k-points) leads to an increase in the demand for computer resources and an increase in the computation time. On the other hand, a high value increases the accuracy of the results. Therefore, you need to find a balance between the required accuracy and time of calculation to find an appropriate values of parameters.

3. *File* **POTCAR** *contains the pseudopotentials for atoms.*

File contains the pseudopotentials (chemical identity) for all atoms. This file must be created manually from the pseudo potential database provided with the VASP source code. The blocks for different atoms must be saved in the same sequence as in Line 6 of POSCAR file. The internal structure of this file is looks like following:

POTCAR

Block data for Ba atom should be read only 1 time as described in Line 7

Block data for Ti atom should be read only 1 time as described in Line 7

Block data for O atom should be read 3 time as described in Line 7

4. *File* **INCAR** *contains the description of task (what we have to do).*

The INCAR file have a simple format. Each line is looks like this:

TAG=value

The allowed TAGs for INCAR file you can find here *https://www.vasp.at/wiki/index.php/Category:INCAR*.
The valid choice of need tags depend on type of task. What are the tasks?
1. Optimization of structures (preliminary optimization of structure.)
2. Calculation of electron structure of material(band structure, DOS, PDOS).
3. Calculating of elastic properties (Full set of elastic parameters)
4. Calculation of phonons in Γ point. (Frequency of phonons, type of atoms displacements)
5. Calculating optical properties. (Dielectric function (real and imaginary parts))
6. Applying of external electric field.
7. Calculation of excites states (excitons)
8. Molecular dynamics calculations
and so on.

You can find a wide range of possible INCAR files for different types of calculations here:
https://www.vasp.at/wiki/index.php/Category:Examples

5. Additional software (free)

5.1 For visualization

- VESTA https://jp-minerals.org/vesta/en/
- VMD https://www.ks.uiuc.edu/Research/vmd/
- XcrysDen http://www.xcrysden.org/

5.2 VASP tools

- VTST Tools https://theory.cm.utexas.edu/vtsttools/scripts.html
- PYTMATGEN https://pymatgen.org/
- ASE https://wiki.fysik.dtu.dk/ase/_modules/ase/calculators/vasp/vasp.html
- PHONOPY https://phonopy.github.io/phonopy/
  useful program to calculate full phonon property of materials on basis of VASP calculations
- Useful link to VASP tools: https://www.vasp.at/resources/

5.3 Free software similar to VASP

- SIESTA https://departments.icmab.es/leem/siesta/
- EXPRESSO https://www.quantum-espresso.org/
- Abinit https://www.abinit.org/

- ELK https://elk.sourceforge.io/
- ORCA https://orcaforum.kofo.mpg.de/app.php/portal