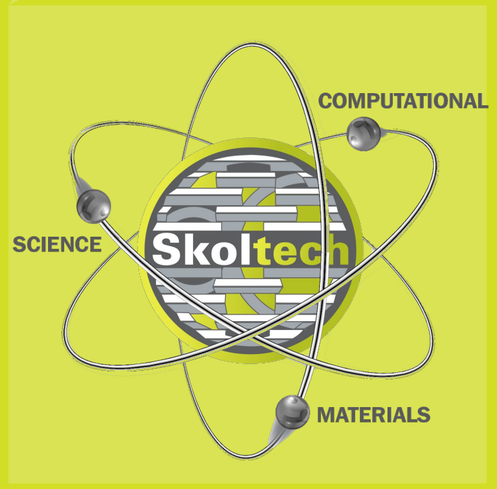
Tutorial 4: Crystals with DFT
Lab 4. VASP



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Tutorial 4 agenda

1. **Prerequisites for Lab 4**
    a. DFT for crystals
    b. Set-up your environment
2. **Lab 4. VASP**
    a. How to set-up your lab
    b. Units
    c. Basic commands and functions
    d. Lab tasks

Bloch's waves

Idea: In periodic system, one-electron wavefunction can be chosen to be a plane wave times the periodicity of the Bravais lattice.

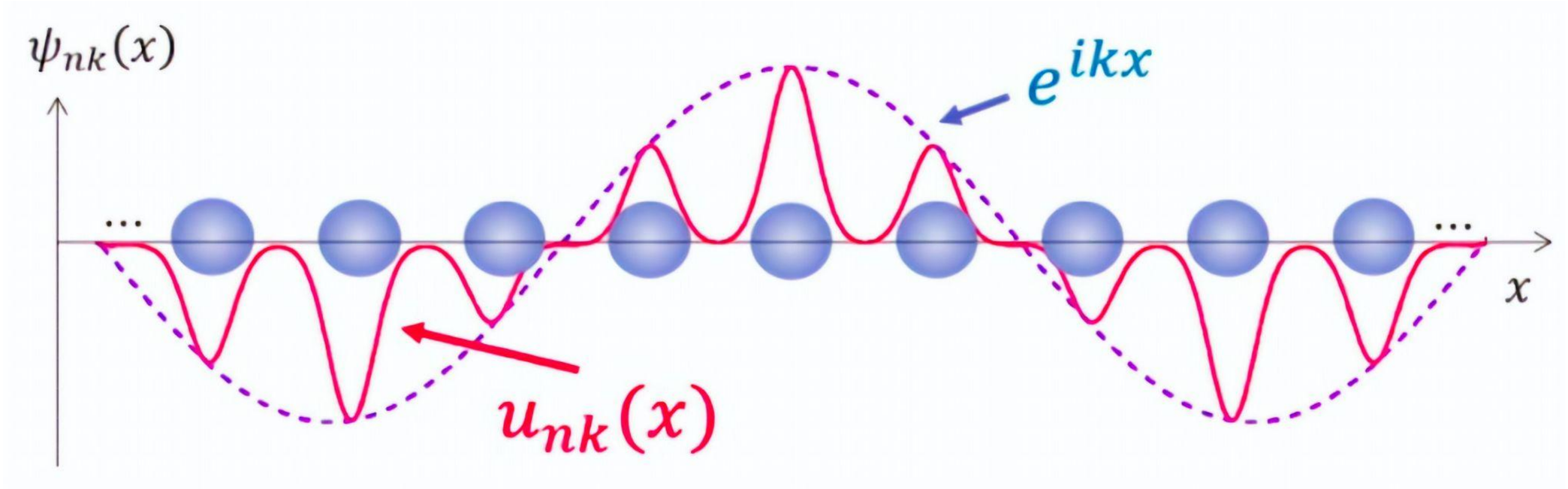
Periodic function with periodicity of the crystal

$$\phi_{\mathbf{k},n}(\mathbf{r}) = u_{\mathbf{k},n}(\mathbf{r}) e^{i\mathbf{k}\mathbf{r}}$$

- ***k*** - new quantum number, vector in reciprocal space!
- ***n*** is band number from the solution of reduced spectral problem with PBC.
- only one reciprocal cell → finite volume problem.
- e^{ikr} - invariant with respect ***k = k+G***, where ***G*** is translation vector.

Bloch's waves

$$\psi_{\mathbf{k},n}(\mathbf{x}) = u_{\mathbf{k},n}(\mathbf{x})e^{i\mathbf{kx}}$$



Bloch’s waves

- Fourier coefficients stored in regular grid.
- Not atom-centered → unbiased.
- Efficient FFT algorithms between *r*- and *G*-space representation.
- Complete and orthonormal basis set.
- Systematically improvable by increasing the cut-off radius.
- O(*N*^2) scaling on CPU.

- Large set of basis coefficients. Hamiltonian cannot be stored.
- Calculation of vacuum as expensive as atoms.
- Sharp nodes of wave functions of core electrons are very expensive. Need pseudo-potential.

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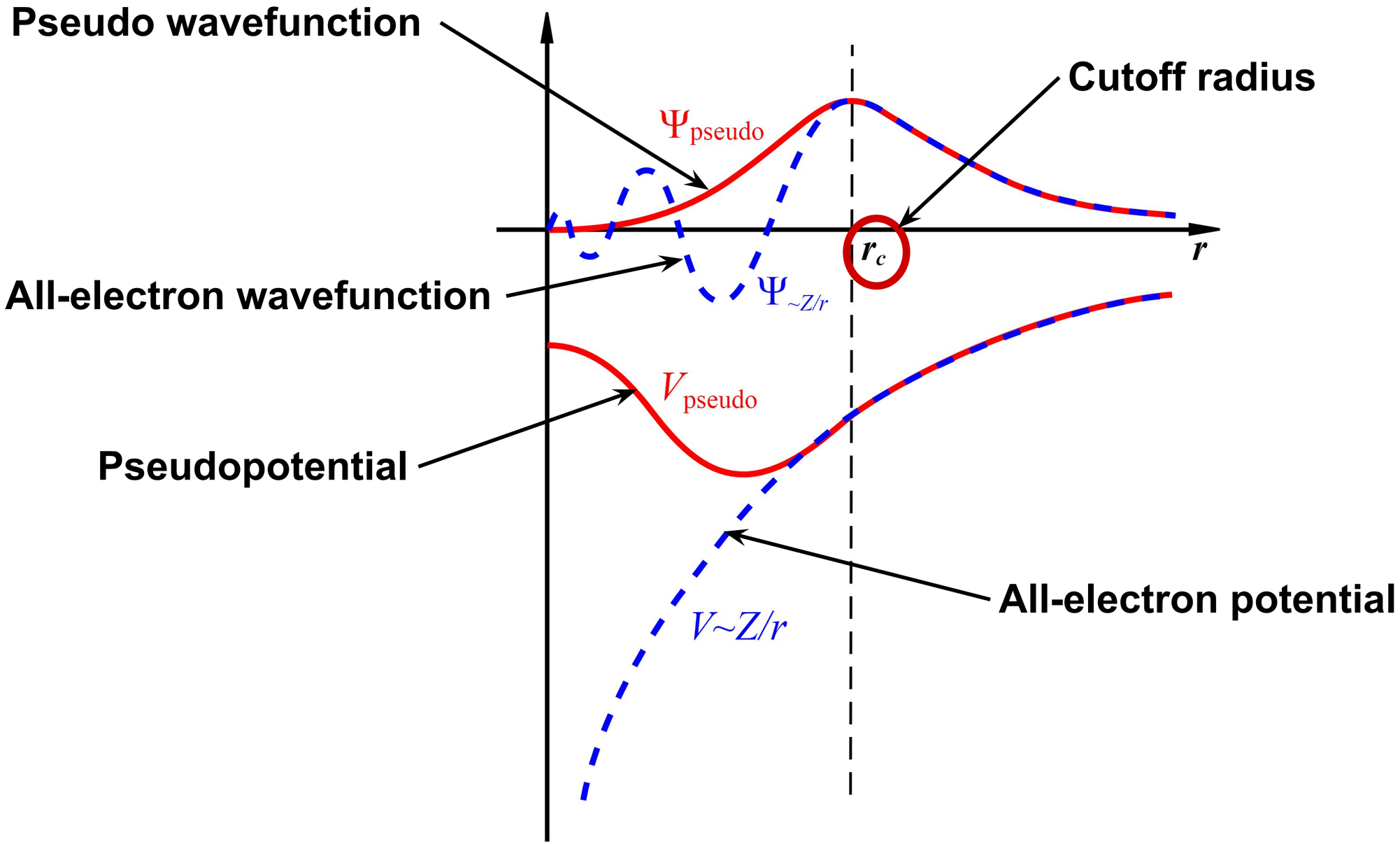
Pseudopotentials



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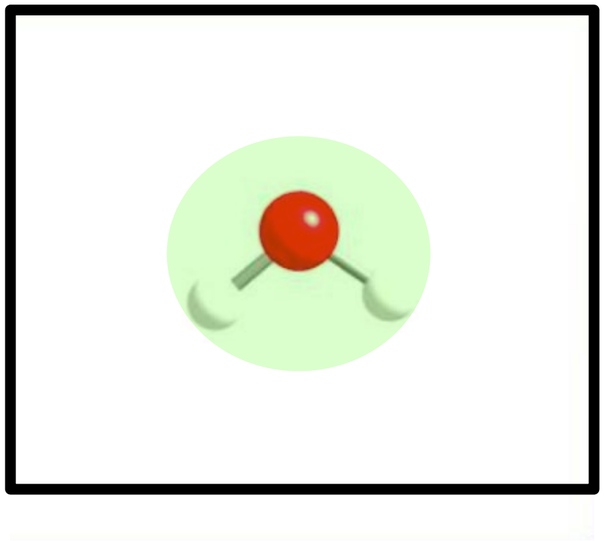
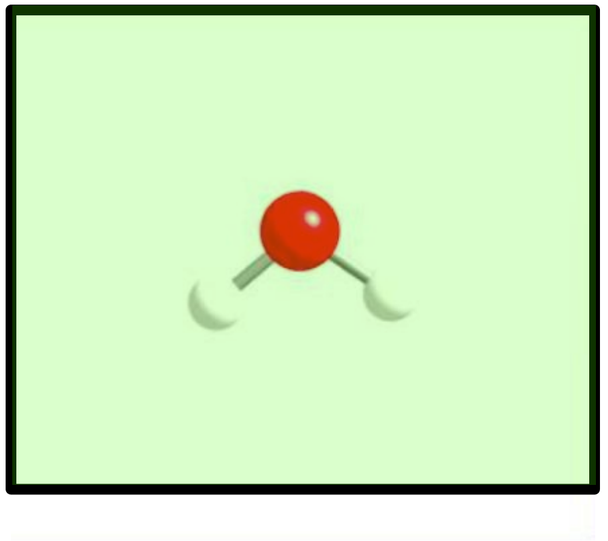
When a plane-wave basis is not good

Localized basis set



Can be localized on atoms and vacuum is not calculated.

Plane-wave basis set

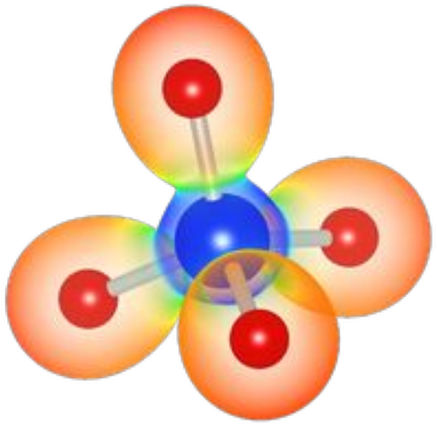


No need to localize on atoms, but the **vacuum is calculated**.

Ideas behind the Lab 4

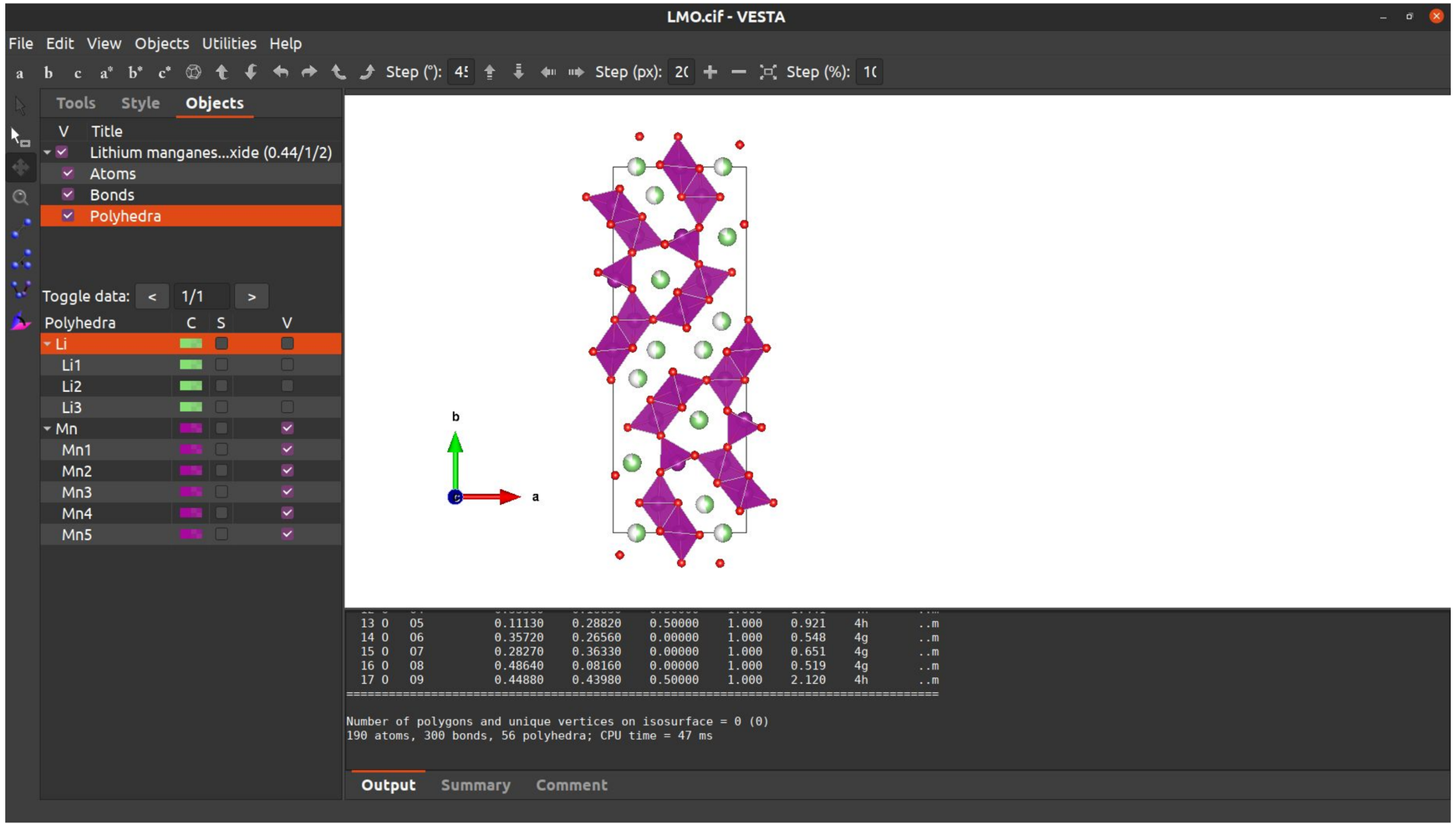
- **Learn** how to perform DFT calculations for crystals
- **Get familiar** with plane-wave basis set
- **Get familiar** with electronic band structure
- **Get familiar** with phonon calculations

Construction of crystals for VASP



VESTA visualization program

Visualization program for structural models, volumetric data such as electron/nuclear densities, and crystal morphologies. Some of the novel features of VESTA are listed below.



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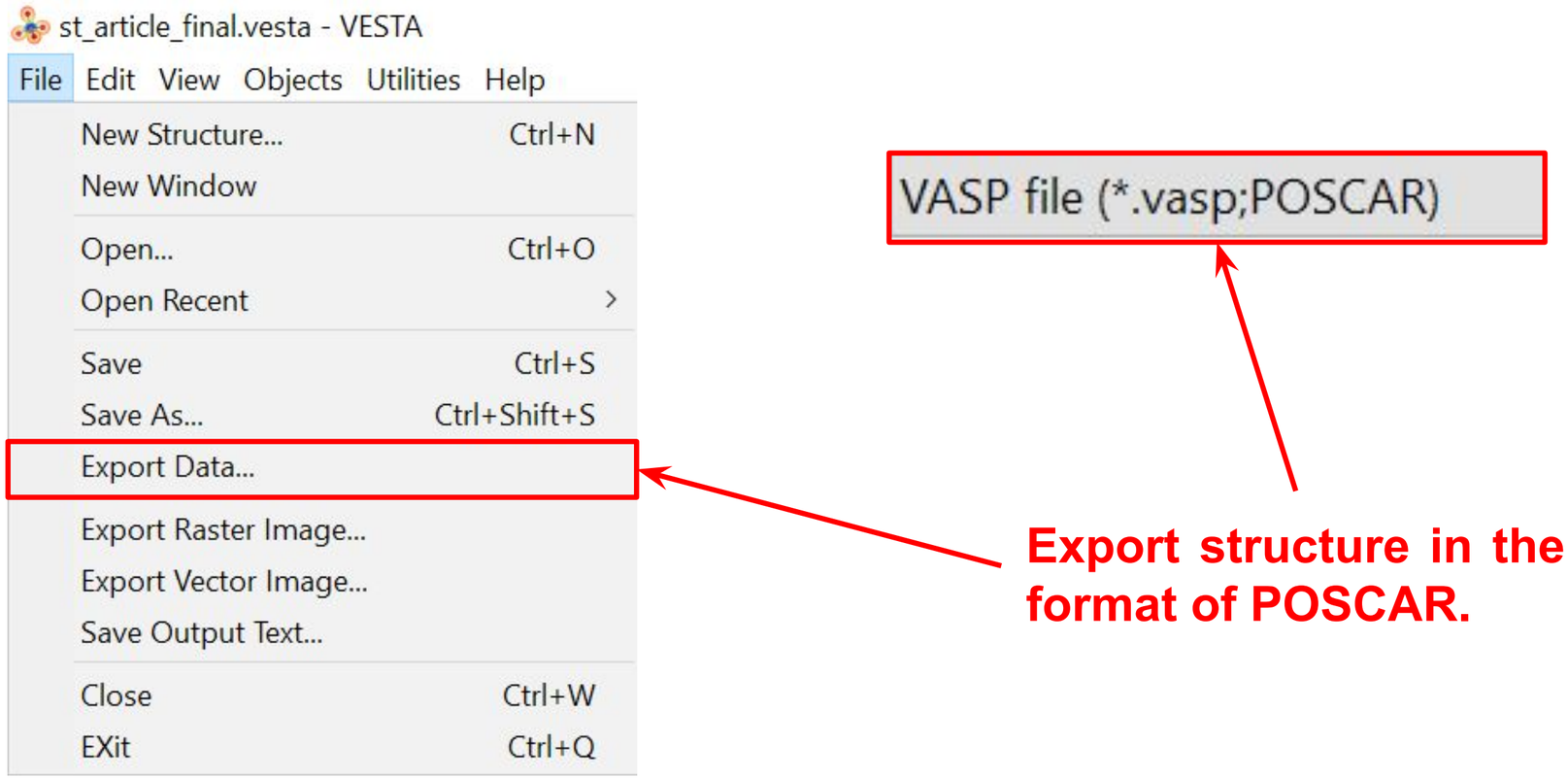

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Lab 4. Set up VASP and files

Settings the Lab on the Virtual Machine

Credentials for the Virtual Machine:
‘your_login’@10.30.16.180
‘your_password’

Download archive with **Lab files for silicon**.

Download archive with **Lab files for TiC**.

Upload the archive to the Virtual Machine:

```
scp lab4_silicon.zip a.burov@10.30.16.180:
```

Login to the Virtual Machine and unzip the archive:

```
unzip lab4_silicon.zip
```

Lab 4. VASP basics

VASP units

Mass	–	m_a
Energy	–	eV
Distance	–	Å
Force	–	eV/Å
Stresses	–	kBar, divide by 10 to get GPa
Charge	–	elementary charge
Dipole	–	electrons•Å
Temp	–	K
Time	–	fs (default, used in AIMD)

How to use VASP

To find input files for your calculations, you need go to *lab4_silicon/sampleinputs*

To run:

vasp_std > vasp.log

Note: *the following input files should be in the current directory:*

POSCAR – *contains crystal structure*

INCAR – *control parameters*

KPOINTS – *k-mesh in reciprocal space*

POTCAR – *PAW potential file*

POSCAR (input structure)

```
Si                                  # just any name
1.000                               # multiplier for vec
 0.00  2.71  2.71                   # Lattice vec 1, A
 2.71  0.00  2.71                   # Lattice vec 2, A
 2.71  2.71  0.00                   # Lattice vec 3, A
Si C
2  2                                # N atom for each type
Direct                              # type of coordinates
 0.00  0.00  0.00                   # atom 1 Si
 0.25  0.25  0.25                   # atom 2 Si
 0.00  0.00  0.00                   # atom 1 C
 0.25  0.25  0.25                   # atom 2 C
```

POTCAR (pseudopotential)

```
PAW_PBE Li 17Jan2003   # version
1.00000000000000000    # N of valence electrons
parameters from PSCTR are:
VRHFIN = Li: s1p0      # electronic configuration
LEXCH  = PE            # exch. cor PBE
EATOM  =  5.3001 eV # energy of atom in vacuum, it is
                    subtracted  from output total energy
```

POTCAR for several elements

For instance, for SiC system you should run

cat Si/POTCAR C/POTCAR > POTCAR

Note, the order should be the same as types of atoms follow in POSCAR

KPOINTS (sampling of reciprocal space)

```
Automatic Mesh
0
Monkhorst Pack
9 9 9
0 0 0
```

INCAR basic (control parameters)

```
ENCUT = 300      # eV, energy cut-off
ISIF = 3         # full optimization
ISMEAR = 2       # Smearing method, Methfessel-Paxton

KSPACING = 0.1 # spacing of k points, can be used
                 instead of KPOINTS file
```

INCAR reasonable (control parameters)

```
SYSTEM =  2 Li; # name
EDIFF = 0.0001  # eV, stopping criteria of SCF
EDIFFG = -0.01  # eV/A, stopping criteria of relaxation
NSW = 20        # number of relaxation steps
ENCUT = 150     # eV, energy cut-off
IBRION = 1      # optimization algo
ISIF = 3        # full optimization
ISMEAR = 2      # Smearing method, Methfessel-Paxton
SIGMA = 0.2     # eV, smearing broadening
NBANDS = 4      # number of bands
```

Output files

CONTCAR - file with output structure, the same format as **POSCAR**

OUTCAR - main file with energies, etc.

CHGCAR - charge density file

WAVECAR - wave function file

EIGENVAL - Kohn-Sham energies at k - required for band structure plotting

And others. For more details, see **VASP manual**.

Output file (grep commands)

```
grep reached OUTCAR - check that calculation is finished

grep TOTEN OUTCAR — print total energy at each SCF step

grep 'energy  without entropy'  OUTCAR
                - print total energy after each relax step
                  use energy(sigma->0) extrapolated energy
```

Output file (grep commands)

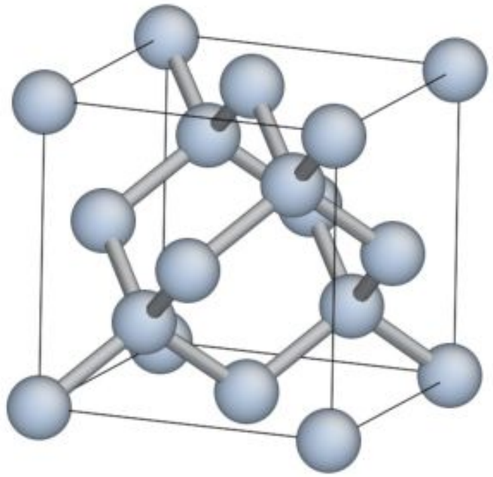
`grep 'in kB' OUTCAR`

- print stress tensor after each relax step,
  multiply by 100 to get MPa
  residual stress of 100 MPa is OK for most solids

`grep -A 3 TOTAL OUTCAR` – print positions and forces

`grep E-fermi OUTCAR` – print Fermi energy in eV

Lab 4. Silicon



0. Slurm task manager

`sbatch <task_name.sh>` – submit task task_name.sh

`squeue` – status of submitted tasks

```
JOBID PARTITION     NAME     USER ST       TIME  NODES NODELIST(REASON)
26164     class    em.sh  a.burov  R       0:02      1 cest-cms-amm
```

`scancel <JOBID>` – cancel the task with id: *JOBID*

For more details, see **Slurm manual**.

1. Geometry optimization

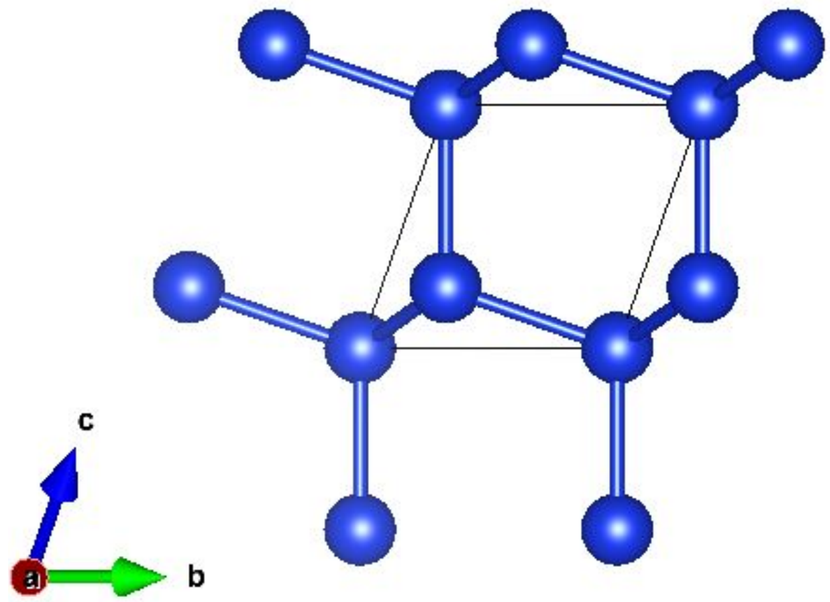
```
ENCUT = 600       # eV, energy cut-off
EDIFFG = -0.01    # force stopping criteria, 0.01 eV/A
ISIF = 3          # full optimization
IBRION = 2        # Quasi-Newton
NSW = 100         # Maximum Number of steps for optimization
ISMEAR = 0        # Smearing method, Gaussian
SIGMA = 0.1       # Smearing
LWAVE = .FALSE.   # do not save WAVECAR - usually huge ~1-10 GB

# EDIFFG reads as eV/A^3 for stresses. See "Total" in OUTCAR
and divide by N_at
```

1. Geometry optimization

The information on optimization routine is stored in **OUTCAR** file.

Can be examined with *grep* commands.

The optimized structure is located in **CONTCAR** file.



2. Equation of state

1. Perform optimization of atomic positions and cell shape (ISIF=4 or ISIF=1, ISIF=2 (option with 2 calculates the full stress tensor) for different volumes (lattice constants) of an input cell.

2. Construct an equation of state (EOS).

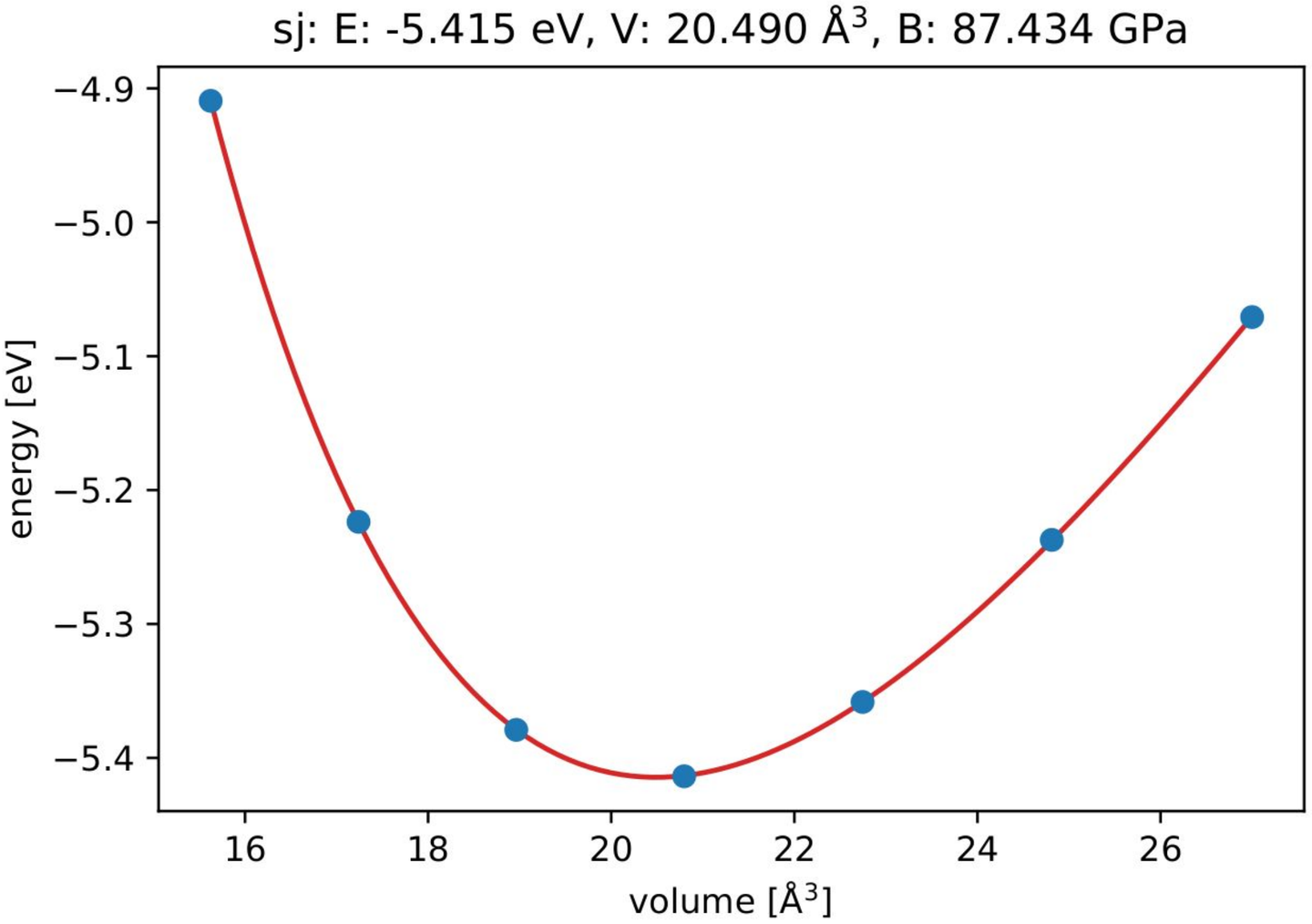
Birch–Murnaghan isothermal equation:

$$P(V) = \frac{3B_0}{2}\left[\left(\frac{V_0}{V}\right)^{7/3} - \left(\frac{V_0}{V}\right)^{5/3}\right]\left\{1 + \frac{3}{4}\left(B_0' - 4\right)\left[\left(\frac{V_0}{V}\right)^{2/3} - 1\right]\right\}$$

$$B_0 = -V\left(\frac{\partial P}{\partial V}\right)_{P=0} \qquad B_0' = \left(\frac{\partial B}{\partial P}\right)_{P=0}$$

3. Find a minimum volume and perform the optimization for it.

2. Equation of state



EOS, constructed with **SIMAN** package

3. Vibrational frequencies at Γ point

```
PREC = Accurate
ENCUT = 250
ISMEAR = 0
SIGMA = 0.1
IBRION = 6      # only symmetry inequivalent
POTIM = 0.015   # step size for finite difference method
LWAVE = .FALSE.
```

3. Vibrational frequencies at Γ point

`grep 'THz' OUTCAR_freq` – find vibrational modes in OUTCAR

```
1 f  =    15.069650 THz     94.685406 2PiTHz   502.669417 cm-1     62.323087 meV
2 f  =    15.069650 THz     94.685406 2PiTHz   502.669417 cm-1     62.323087 meV
3 f  =    15.069650 THz     94.685406 2PiTHz   502.669417 cm-1     62.323087 meV
4 f  =     0.000000 THz      0.000002 2PiTHz     0.000009 cm-1      0.000001 meV
5 f  =     0.000000 THz      0.000000 2PiTHz     0.000000 cm-1      0.000000 meV
6 f/i=     0.000000 THz      0.000001 2PiTHz     0.000006 cm-1      0.000001 meV
```

4. Elastic constants

```
PREC = Normal
ENCUT = 250
ISMEAR = 0
SIGMA = 0.1
IBRION = 6
ISIF = 3          #only symmetry inequivalent
POTIM = 0.015     #step size for finite difference method
LWAVE = .FALSE.
```

4. Elastic tensor

```
grep -10 "ELASTIC MODULI" OUTCAR_elastic | tail -11
```

TOTAL ELASTIC MODULI (kBar)

Direction	XX	YY	ZZ	XY	YZ	ZX
XX	1535.0824	561.8363	561.8363	0.0000	-0.0000	-0.0000
YY	561.8363	1535.0824	561.8363	0.0000	-0.0000	-0.0000
ZZ	561.8363	561.8363	1535.0824	0.0000	-0.0000	-0.0000
XY	0.0000	0.0000	0.0000	751.5350	-0.0000	-0.0000
YZ	-0.0000	-0.0000	-0.0000	-0.0000	751.5350	0.0000
ZX	-0.0000	-0.0000	-0.0000	-0.0000	0.0000	751.5350

To calculate elastic constants, you may use **MechElastic** software.

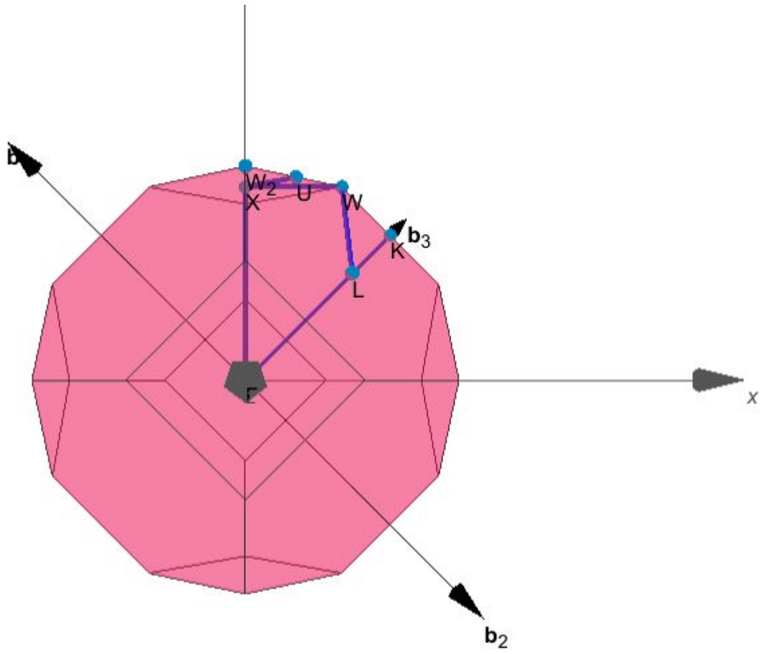
5. Band structure (INCAR)

```
ICHARG = 11    # obtain the eigenvalues (for band-structure
               plots) or the density of states (DOS)
ENCUT = 250
ISMEAR = 0
SIGMA = 0.01
LWAVE = .FALSE.
```

5. Band structure (KPOINTS)

```
kpoints for bandstructure L-G-X-U K-G
 40          ! 40 intersections
line         ! line mode
reciprocal   ! type of coordinates
  0.50000  0.50000  0.50000    !L
  0.00000  0.00000  0.00000    !G

  0.00000  0.00000  0.00000    !G
  0.00000  0.50000  0.50000    !X

  0.00000  0.50000  0.50000    !X
  0.25000  0.62500  0.62500    !U

  0.37500  0.7500   0.37500    !K
  0.00000  0.00000  0.00000    !G
```

To generate KPOINTS file for band structure calculations, you may use **SeekPath** soft.



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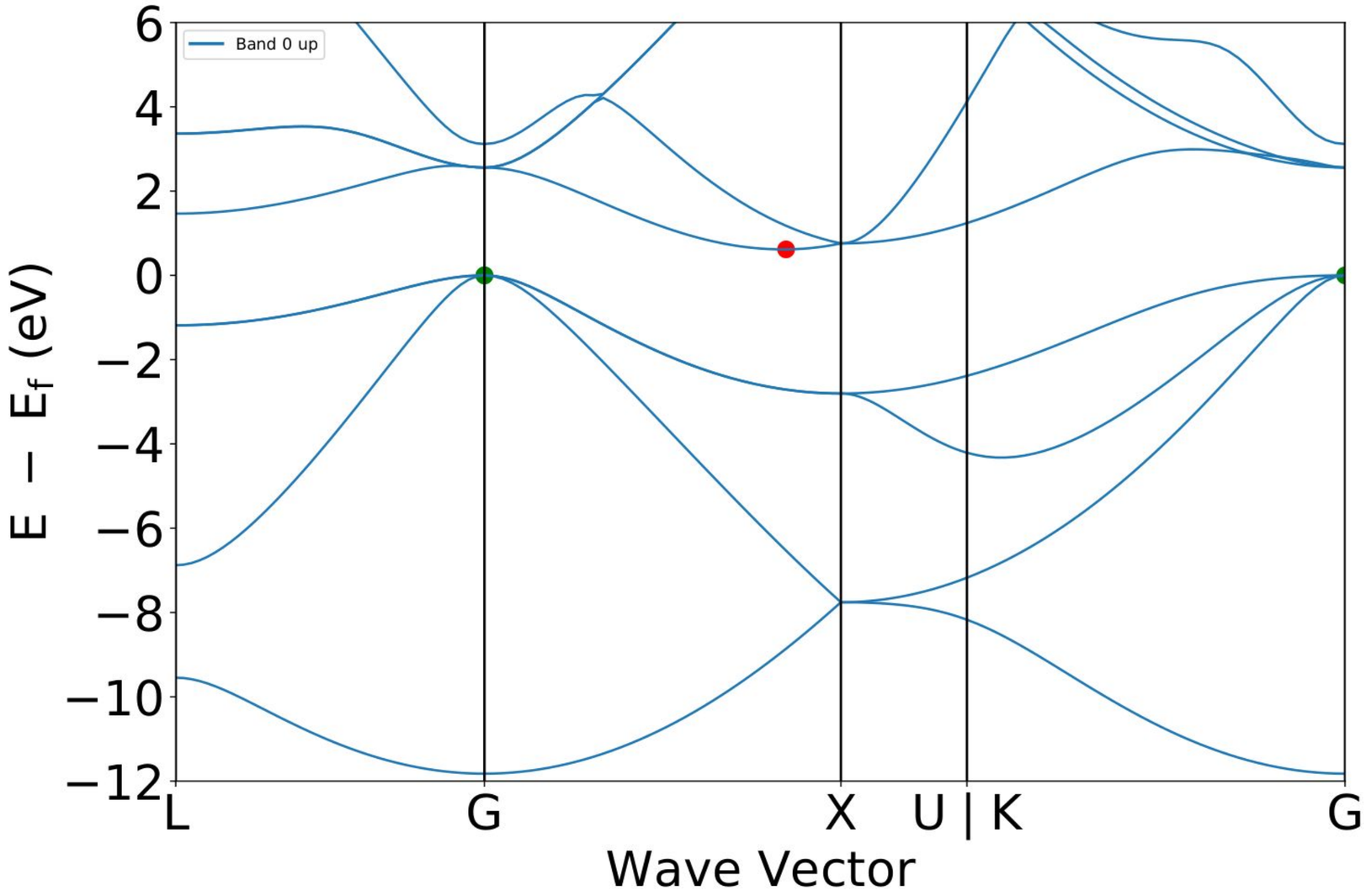
5. Band structure



To visualize it, you may use:

ASE

Pymatgen

Sumo

PyProcar

SIMAN

Any other software

Extra materials

- Vasp manual – all theory and input parameters for VASP
- Visualization of DOS plots: ASE, Pymatgen, Sumo, PyProcar, SIMAN

- Visualization software VESTA

- VASP tutorials – Official tutorials, some other

Thx

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