Electronic Property Calculations using VASP: Example of Bulk (Silicon) and 2D material systems

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A) Silicon Bulk

(1) Geometry Optimization (Lattice Relaxation)

(a) POSCAR:

```
Si8
   1.0000000000000000
     5.4684574509260617     0.0000000000000000     0.0000000000000003
     0.0000000000000009     5.4684574509260617     0.0000000000000003
    -0.0000000000000000     0.0000000000000000     5.4684574509260617
   Si
     8
Direct
  0.7500000000000000  0.7500000000000000  0.2500000000000000
  0.0000000000000000  0.5000000000000000  0.5000000000000000
  0.7500000000000000  0.2500000000000000  0.7500000000000000
  0.0000000000000000  0.0000000000000000  0.0000000000000000
  0.2500000000000000  0.7500000000000000  0.7500000000000000
  0.5000000000000000  0.5000000000000000  0.0000000000000000
  0.2500000000000000  0.2500000000000000  0.2500000000000000
  0.5000000000000000  0.0000000000000000  0.5000000000000000
```

(b) KPOINTS:

```
Automatic mesh
0
Gamma
10 10 10
0  0  0
```

(c) INCAR:

```
#Global Parameters
  ISTART      = 1
  LREAL       = Auto
  PREC        = Normal
  LWAVE       = .TRUE.
  LCHARG      = .TRUE.
```

```
   ADDGRID      = .TRUE.

#Lattice Relaxation
  NSW          = 300
  ISMEAR       = 0
  SIGMA        = 0.05
  IBRION       = 2
  ISIF         = 3
  EDIFFG       = -1.5E-02
  PREC         = Accurate

# Parallelization
 LPLANE        = T
 NCORE         = 8
 LSCALU        = F
 NSIM          = 4
```

(d) POTCAR

Check here for selecting the correct pseudopotential file:
https://www.vasp.at/wiki/index.php/Available_PAW_potentials

(2) Band structure

To do band structure calculation, one need to prepare a primitive cell and corresponding K points path (K-path) alone Irreducible Brillouin Zone. Irreducible Brillouin Zone is the first Brillouin zone reduced by all of the symmetries in the points group of the lattice (point group of the crystal). Recognize and select high symmetry points, and link them along edges of Irreducible Brillouin Zone. This example will investigate the Band structure of Si with spin polarization and without spin-orbital coupling.

1. At first, do geometry optimization, and then do a **single-point self-consistent calculation** to get the CHGCAR. The INCAR for that is given below.

```
        SYSTEM          = Si

        #1 Startparameter for this Run:
        NWRITE          = 2
        ISTART          = 0
        INIWAV          = 1
        IWAVPR          = 1
        ICHARG          = 2
        LCHARG          = .TRUE. # writes the CHGCAR file
```

2

```
LWAVE              = .FALSE.


#2 Electronic Relaxation 1
NELM               = 100
EDIFF              = 1E-06
BMIX               = 3.00
ENCUT              = 500


#3 Electronic Relaxation 1
IALGO              = 38
LDIAG              = T
LREAL              = .FALSE.
PREC               = Accurate


#4 Ionic Relaxation
NSW                = 0 # for single point calculation
NBLOCK             = 1
KBLOCK             = 10
IBRION             = 2
ISIF               = 3
ISYM               = 2
SYMPREC        =  1e-6
LCORR              = T
EDIFFG             = -1E-03
POTIM              = 0.50
SMASS              = 3.00


#5 DOS related values
ISMEAR             = 0
SIGMA              = 0.05
LORBIT             = 11


#6 Parallelizationoption
LPLANE             = T
NCORE              = 8
LSCALU             = F
NSIM               = 4
ISPIN              = 2
```

2. Use a high dense KPOINTS for the accurate results. I used a 15x15x15, as shown below.

```
KPT-Resolved Value to Generate K-Mesh: 0.030
0
Monkhorst-Pack
15   15   15
0.0  0.0  0.0
```

3. After the successful completion of the SCF run, do a non-SCF calculation. The KPATH selection (which is referred to as the KPOINTS for NSCF calculation) for band structure calculations is important and there are different ways to find out the K-path automatically by using (a) pymatgen (https://pymatgen.org/, (b) seek-path (https://www.materialscloud.org/work/tools/seekpath), etc.

4. The KPOINTS file for band and density of states calculation is given below. Always cross check this with the seek-path (https://www.materialscloud.org/work/tools/seekpath

```
K-Path for Si
   20
Line-Mode
Reciprocal
   0.0000000000   0.0000000000   0.0000000000      G
   0.5000000000   0.0000000000   0.5000000000      X

   0.5000000000   0.0000000000   0.5000000000      X
   0.6250000000   0.2500000000   0.6250000000      U

   0.3750000000   0.3750000000   0.7500000000      K
   0.0000000000   0.0000000000   0.0000000000      G

   0.0000000000   0.0000000000   0.0000000000      G
   0.5000000000   0.5000000000   0.5000000000      L

   0.5000000000   0.5000000000   0.5000000000      L
   0.5000000000   0.2500000000   0.7500000000      W

   0.5000000000   0.2500000000   0.7500000000      W
   0.5000000000   0.0000000000   0.5000000000      X
```

5. To perform an NSCF calculation and generate a band structure in VASP, use the below provided INCAR file for the NSCF calculation. This INCAR file should read the CHGCAR output from the previous single-point SCF calculation (step 1).

```
SYSTEM            = Si


#1 Startparameter for this Run:
NWRITE            = 2
ISTART            = 1
INIWAV            = 1
IWAVPR            = 1
ICHARG            = 11 #reads the CHGCAR file
LWAVE             = .FALSE.


#2 Electronic Relaxation 1
NELM              = 100
EDIFF             = 1E-06
BMIX              = 3.00
ENCUT             = 500


#3 Electronic Relaxation 1
IALGO             = 38
LDIAG             = T
LREAL             = .FALSE.
PREC              = Accurate
# NBANDS          = 30


#4 Ionic Relaxation
NSW               = 0
NBLOCK            = 1
KBLOCK            = 10
IBRION            = 2
ISIF              = 3
ISYM              = 0
# SYMPREC         =  1e-6
LCORR             = T
EDIFFG            = -1E-03
POTIM             = 0.50
SMASS             = 3.00
LCHARG            = .TRUE.


#5 DOS related values
ISMEAR            = 0
SIGMA             = 0.05
LORBIT            = 11
EMIN              = -20
```

```
EMAX                = 20
NEDOS               = 3001

#6 Parallelizationoption
LPLANE              = T
NCORE               = 8
LSCALU              = F
NSIM                = 4
ISPIN               = 2
```

6. After calculation, do band structure post-processing. I would recommend to use a Python based utility, https://smtg-ucl.github.io/sumo/sumo-bandplot.html

    Installation details can be found here: https://smtg-ucl.github.io/sumo/

    Band structure can also obtain by pymatgen package

    Check whether you're able to reproduce the band structure and density of states given below.
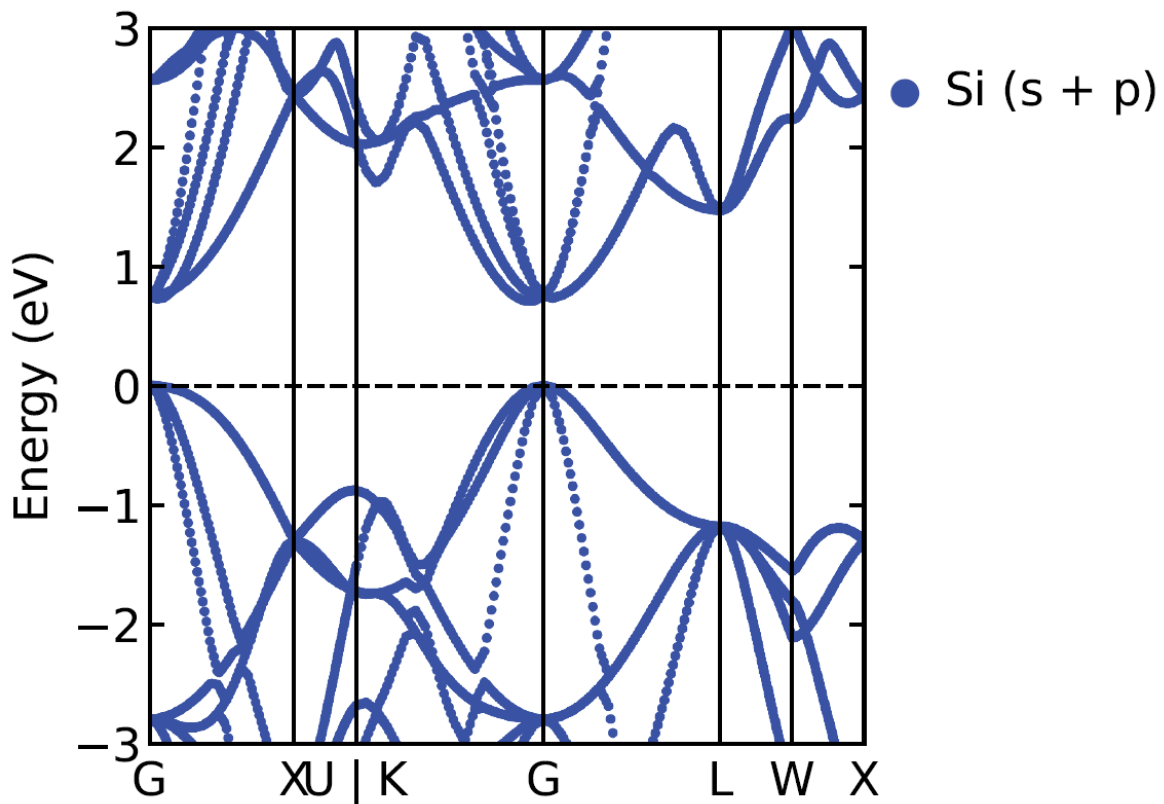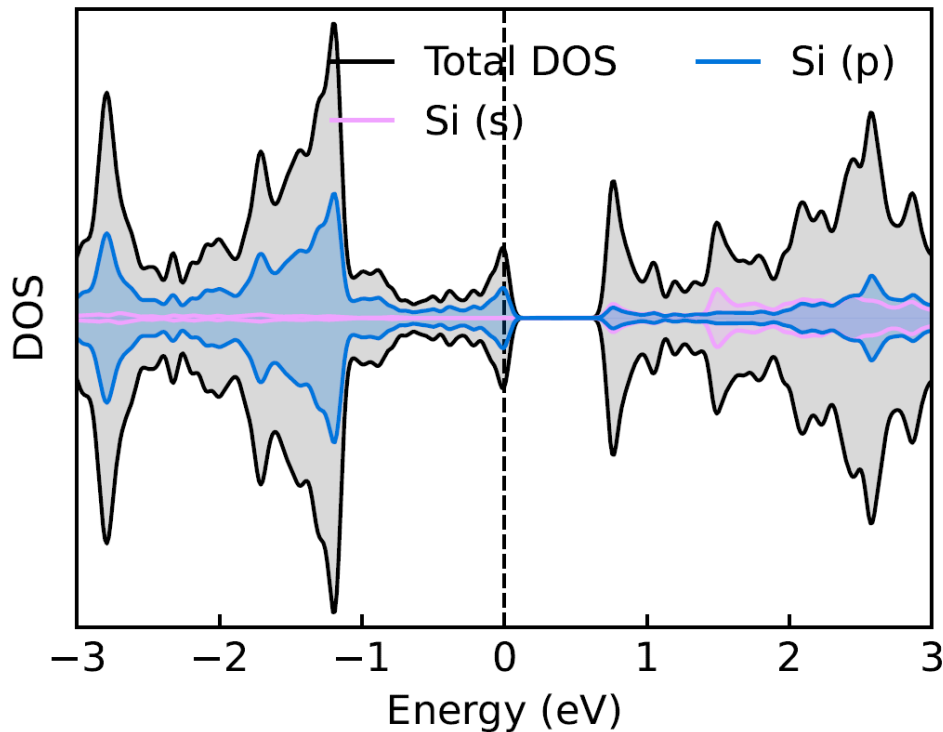
Note:

Q: Based on the calculation above, the bandgap of silicon was determined to be 0.707 eV. However, the experimentally estimated bandgap of silicon is 1.12 eV. How can we explain the significant difference between the experimentally determined bandgap and the bandgap obtained through the implementation of PBE-GGA in DFT (0.7073 eV)?

A: DFT relies on approximations, and it is not always accurate in predicting the properties of materials, particularly when it comes to band structures and bandgaps.

One common issue with DFT is that it tends to underestimate the bandgap of semiconductors, including Si. This is because DFT calculations typically rely on the local density approximation (LDA) or the generalized gradient approximation (GGA), which are not accurate enough to capture the physics of the bandgap. The PBE-GGA approximation is a specific form of GGA that is known to underestimate bandgaps.

There are more advanced DFT methods, such as hybrid functionals (HSE) or GW approximation, that can improve the accuracy of bandgap predictions, but they are more computationally demanding and may not be feasible for large systems. In addition, experimental factors such as defects, impurities, and temperature can also affect the bandgap measurement, leading to discrepancies between theoretical predictions and experimental measurements.

B) 2D Materials

To compute the bandgap and density of states of 2D materials, please refer to the instructions provided for the bulk Silicon case. **It is important to make the necessary modifications in the INCAR file for the calculations associated with 2D materials**.

For the band and density of states calculations for materials such as graphene, h-BN, Si_2BN, Ti_2C MXenes, etc., you can use the KPOINTS file provided below. Always cross-check this with the seek-path tool (https://www.materialscloud.org/work/tools/seekpath) to ensure accuracy.

```
K-Path for 2D
20
Line-Mode
Reciprocal
0.0000000000   0.0000000000   0.0000000000      GAMMA
0.5000000000   0.0000000000   0.0000000000      M

0.5000000000   0.0000000000   0.0000000000      M
0.3333333333   0.3333333333   0.0000000000      K

0.3333333333   0.3333333333   0.0000000000      K
0.0000000000   0.0000000000   0.0000000000      GAMMA
```

Details about the Brillouin zones for 2D materials can be found here:
J. Phys. Chem. Lett. 2022, 13, 50, 11581–11594 (https://doi.org/10.1021/acs.jpclett.2c02972)
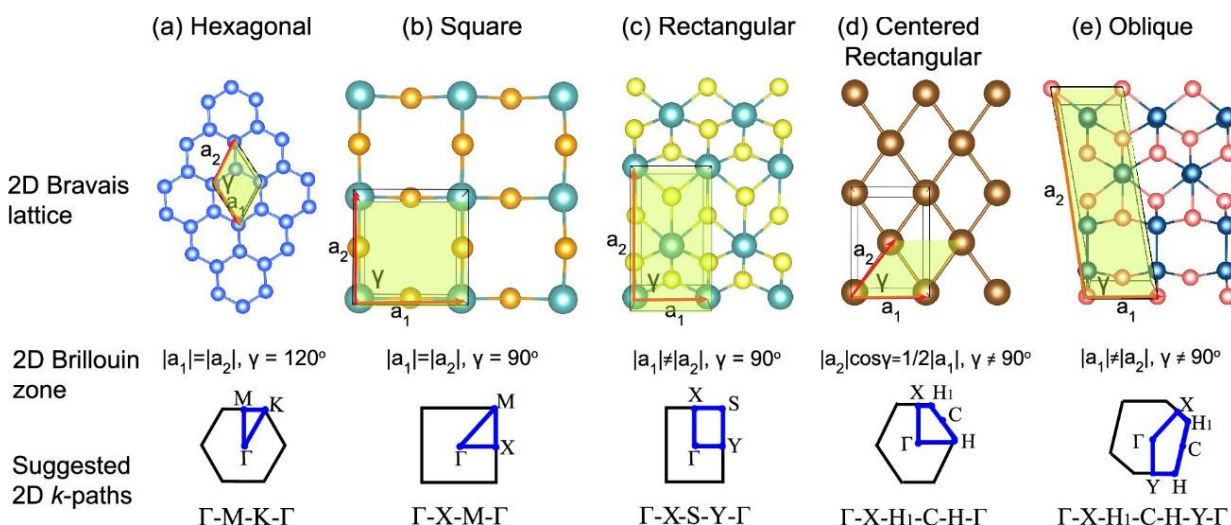
In addition to the above information,

there are other ways to find out the K-path automatically by using
1. pymatgen (https://pymatgen.org/)
2. seek-path（https://www.materialscloud.org/work/tools/seekpath）

TASK: Try to generate the band structure of graphene and Silicene. Check whether you're able to reproduce the band structure given below.