Test Calculations on Silicon: Insights from Quantum Espresso

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- Self-Consistent Field Calculation
- Structure Optimization
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- Band structure Calculation
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BAND THEORY

Band theory is a fundamental concept in condensed matter physics that explains the behavior of electrons in solids and their energy distribution.

Key concepts in Band theory associated in our test calculations:

- Energy bands
- Conduction bands & Valence bands
- Electronic Structure & Band Structure
- Density of states
- Fermi Level
- Band Diagram
- Electronic energy levels & Energy band alignment

Why study Silicon?

Silicon is a fundamental material in the field of semiconductor technology.

By studying its properties through computational methods, we can gain insights into its behavior and potentially uncover new applications.

https://noahchemicals.s3.amazonaws.com/wp-content/uploads/2021/05/16202726/shutterstock_1021725241.jpg

Self-Consistent Field Calculation

Understanding Electronic Structure

meyn@LAPTOP-C0A2DPIS: ~/q-e-qe-7.1/test_calculation

```
&CONTROL
calculation = 'scf'
prefix = 'silicon'
outdir = './tmp/'
pseudo_dir = '/home/meyn/q-e-qe-7.1/pseudo/'
verbosity = 'high'
/

&SYSTEM
ibrav = 2,
celldm(1) = 10.26,
nat = 2,
ntyp = 1,
ecutwfc = 30
nbnd = 8
/

&ELECTRONS
mixing_beta = 0.6
/

ATOMIC_SPECIES
Si 28.086 Si.pz-vbc.UPF

ATOMIC_POSITIONS (alat)
Si 0.0 0.0 0.0
Si 0.25 0.25 0.25

K_POINTS (automatic)
6 6 6 0 0 0
~
```

Input file

How is the crystal structure defined?

Diamond lattice is a fcc (face centered cubic) lattice with two atoms per unit cell. So, we specified:

Ibrav =2 : Bravais lattice index, which is 2 for FCC structure

celldm(1) = 10.26 : How many and which parameters are needed to completely define Bravais lattice geometry

nat = 2 : number of atoms in an unit cell

ntyp = 1 : number of different types of atom in the cell

Output file

```
meyn@LAPTOP-C0A2DPIS:~/q-e-qe-7.1/test_calculation$ pw.x < silicon.in > silicon.out
meyn@LAPTOP-C0A2DPIS:~/q-e-qe-7.1/test_calculation$ cat silicon.out
```

```
meyn@LAPTOP-C0A2DPIS:~/q-e-qe-7.1/test_calculation$ vi silicon.out
meyn@LAPTOP-C0A2DPIS:~/q-e-qe-7.1/test_calculation$ grep -e 'total energy' -e estimate silicon.out
     total energy              =     -15.84834964 Ry
     Harris-Foulkes estimate   =     -15.86759222 Ry
     estimated scf accuracy    <       0.06203207 Ry
     total energy              =     -15.85013015 Ry
     Harris-Foulkes estimate   =     -15.85115036 Ry
     estimated scf accuracy    <       0.00475170 Ry
     total energy              =     -15.85037880 Ry
     Harris-Foulkes estimate   =     -15.85039758 Ry
     estimated scf accuracy    <       0.00011449 Ry
!    total energy              =     -15.85039450 Ry
     Harris-Foulkes estimate   =     -15.85039488 Ry
     estimated scf accuracy    <       0.00000091 Ry
     The total energy is the sum of the following terms:
meyn@LAPTOP-C0A2DPIS:~/q-e-qe-7.1/test_calculation$
```

Structure Optimization

Achieving the Optimal Configuration

meyn@LAPTOP-C0A2DPIS: ~/q-e-qe-7.1/test_calculation

```
&CONTROL
calculation = 'vc-relax'
prefix = 'silicon'
outdir = './tmp/'
pseudo_dir = '/home/meyn/q-e-qe-7.1/pseudo/'
etot_conv_thr = 1e-5
forc_conv_thr = 1e-4
/

&SYSTEM
ibrav=2,
celldm(1) =14,
nat=2,
ntyp=1,
ecutwfc=30
/

&ELECTRONS
conv_thr=1e-8
/

&IONS
/

&CELL
cell_dofree='ibrav'
/

ATOMIC_SPECIES
Si 28.0855 Si.pz-vbc.UPF

ATOMIC_POSITIONS (alat)
Si 0.0 0.0 0.0
Si 0.25 0.25 0.25

K_POINTS (automatic)
6 6 6 1 1 1
~
~
```

Input file

Two types of structural optimization calculations in Quantum espresso:

1. relax: where only the atomic positions are allowed to vary
2. **vc-relax:** which allows to vary both the atomic positions and lattice constants.

etot_conv_thr = 1e-5: sets the convergence threshold for the total energy during the optimization.

forc_conv_thr = 1e-4: sets the convergence threshold for the atomic forces during the optimization.

ecutwfc=30: sets the energy cutoff for the wavefunction expansion.

conv_thr=1e-8: sets the convergence threshold for the self-consistency loop of the electronic structure calculation.

Output file

```
meyn@LAPTOP-C0A2DPIS:~/q-e-qe-7.1/test_calculation$ pw.x -inp si_relax.in > si_relax.out
```

```
meyn@LAPTOP-C0A2DPIS:~/q-e-qe-7.1/test_calculation$ grep "Final enthalpy" si_relax.out
     Final enthalpy =     -15.8536258866 Ry
```

```
     Final enthalpy =     -15.8536258866 Ry
Begin final coordinates
     new unit-cell volume =    265.89459 a.u.^3 (    39.40151 Ang^3 )
     density =      2.36727 g/cm^3

CELL_PARAMETERS (alat= 14.00000000)
  -0.364556739   0.000000000   0.364556739
   0.000000000   0.364556739   0.364556739
  -0.364556739   0.364556739   0.000000000

ATOMIC_POSITIONS (alat)
Si       -0.000000000   0.000000000   0.000000000
Si        0.182278370   0.182278370   0.182278370
End final coordinates
```

Density of States Calculation

Probing Electronic Density

Fixed-ion self consistent filed (scf) calculation

Input file

```
meyn@LAPTOP-C0A2DPIS:~/q-e-qe-7.1/test_calculation$ cat si_scf_dos.in
&CONTROL
calculation = 'scf',
restart_mode = 'from_scratch',
prefix = 'silicon',
outdir = './tmp/'
pseudo_dir = '/home/meyn/q-e-qe-7.1/pseudo/'
verbosity = 'high'
/

&SYSTEM
ibrav = 2,
celldm(1) = 10.2076,
nat = 2,
ntyp = 1,
ecutwfc = 50,
nbnd = 8
/

&ELECTRONS
conv_thr = 1e-8,
mixing_beta = 0.6
/

ATOMIC_SPECIES
Si 28.086 Si.pz-vbc.UPF

ATOMIC_POSITIONS (alat)
Si 0.0 0.0 0.0
Si 0.25 0.25 0.25

K_POINTS (automatic)
8 8 8 0 0 0
```

Output file

```
meyn@LAPTOP-C0A2DPIS:~/q-e-qe-7.1/test_calculation$ pw.x < si_scf_dos.in > si_scf_dos.out
```

```
     bravais-lattice index     =            2
     lattice parameter (alat)  =      10.2076  a.u.
     unit-cell volume          =     265.8955 (a.u.)^3
     number of atoms/cell      =            2
     number of atomic types    =            1
     number of electrons       =         8.00
     number of Kohn-Sham states=            8
     kinetic-energy cutoff     =      50.0000  Ry
     charge density cutoff     =     200.0000  Ry
     convergence threshold     =      1.0E-08
     mixing beta               =       0.6000
     number of iterations used =            8  plain     mixing
     Exchange-correlation      = SLA PZ NOGX NOGC ( 1  1  0  0 0 0)

     celldm(1)=  10.207600  celldm(2)=   0.000000  celldm(3)=   0.000000
     celldm(4)=   0.000000  celldm(5)=   0.000000  celldm(6)=   0.000000

     crystal axes: (cart. coord. in units of alat)
               a(1) = (  -0.500000   0.000000   0.500000 )
               a(2) = (   0.000000   0.500000   0.500000 )
               a(3) = (  -0.500000   0.500000   0.000000 )

     reciprocal axes: (cart. coord. in units 2 pi/alat)
               b(1) = ( -1.000000 -1.000000  1.000000 )
               b(2) = (  1.000000  1.000000  1.000000 )
               b(3) = ( -1.000000  1.000000 -1.000000 )
```

Non-self consistent field (nscf) calculation

Input file

```
meyn@LAPTOP-C0A2DPIS:~/q-e-qe-7.1/test_calculation$ vi si_nscf_dos.in
meyn@LAPTOP-C0A2DPIS:~/q-e-qe-7.1/test_calculation$ cat si_nscf_dos.in
&CONTROL
calculation = 'nscf',
restart_mode = 'from_scratch',
prefix = 'silicon',
outdir = './tmp/'
pseudo_dir = '/home/meyn/q-e-qe-7.1/pseudo/'
verbosity = 'high'
/

&SYSTEM
ibrav = 2,
celldm(1) = 10.2076,
cat = 2,
ntyp = 1,
ecutwfc = 50,
nbnd = 8,
occupations='tetrahedra'
/

&ELECTRONS
conv_thr = 1e-8
mixing_beta = 0.6
/

ATOMIC_SPECIES
Si 28.086 Si.pz-vbc.UPF

ATOMIC_POSITIONS (alat)
Si 0.0 0.0 0.0
Si 0.25 0.25 0.25

K_POINTS (automatic)
12 12 12 0 0 0
```

```
meyn@LAPTOP-C0A2DPIS:~/q-e-qe-7.1/test_calculation$ pw.x < si_scf_dos.in > si_scf_dos.out
```

Density of States Calculation

```
meyn@LAPTOP-C0A2DPIS:~/q-e-qe-7.1/test_calculation$ vi si_dos.in
meyn@LAPTOP-C0A2DPIS:~/q-e-qe-7.1/test_calculation$ cat si_dos.in
&DOS
prefix='silicon',
outdir='./tmp/',
fildos='si_dos.dat',
emin=-9.0,
emax=16.0
/
```

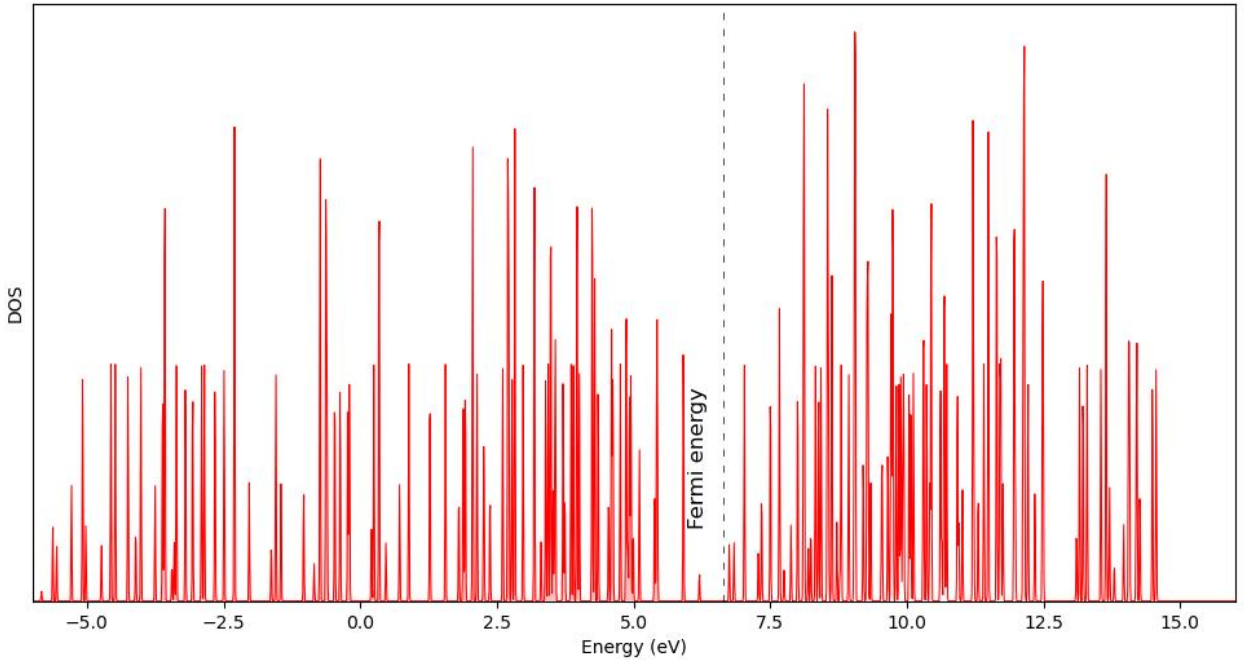
Output file

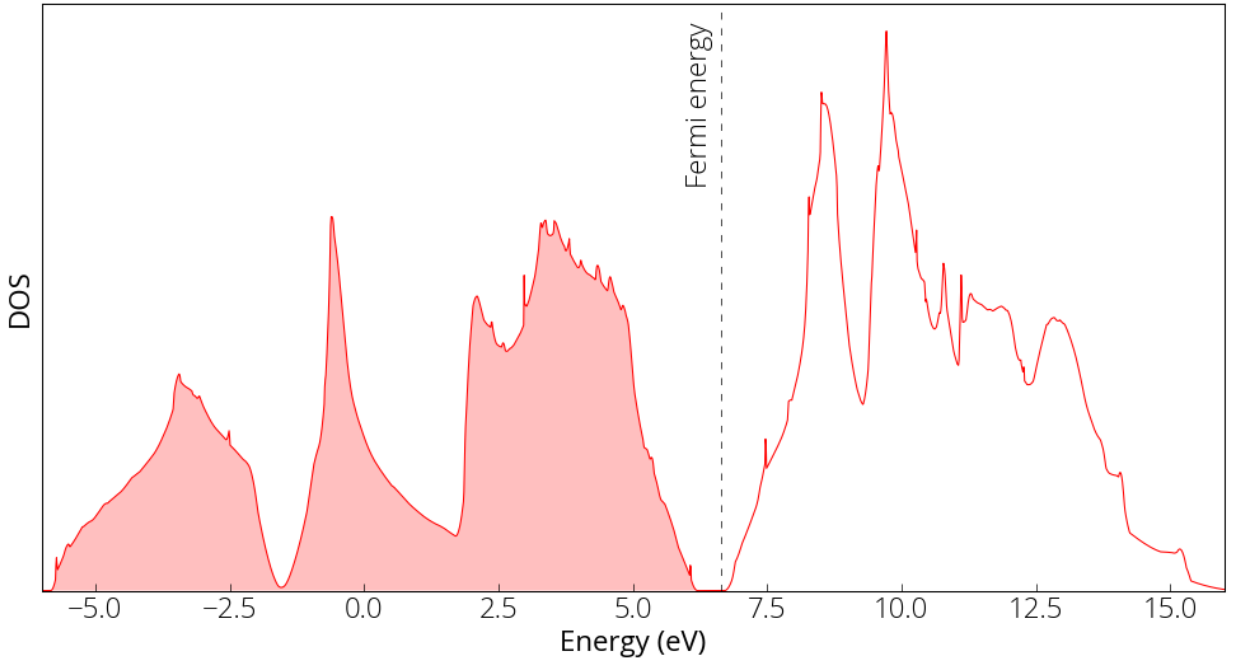
```
meyn@LAPTOP-C0A2DPIS:~/q-e-qe-7.1/test_calculation$ dos.x < si_dos.in > si_dos.out
meyn@LAPTOP-C0A2DPIS:~/q-e-qe-7.1/test_calculation$ cat si_dos.dat
#  E (eV)   dos(E)     Int dos(E) EFermi =    0.000 eV
  -9.000  0.1249E-83  0.1249E-85
  -8.990  0.1249E-83  0.2498E-85
  -8.980  0.1249E-83  0.3748E-85
  -8.970  0.1249E-83  0.4997E-85
  -8.960  0.1249E-83  0.6246E-85
  -8.950  0.1249E-83  0.7495E-85
  -8.940  0.1249E-83  0.8745E-85
  -8.930  0.1249E-83  0.9994E-85
  -8.920  0.1249E-83  0.1124E-84
  -8.910  0.1249E-83  0.1249E-84
  -8.900  0.1249E-83  0.1374E-84
  -8.890  0.1249E-83  0.1499E-84
  -8.880  0.1249E-83  0.1624E-84
  -8.870  0.1249E-83  0.1749E-84
  -8.860  0.1249E-83  0.1874E-84
  -8.850  0.1249E-83  0.1999E-84
  -8.840  0.1249E-83  0.2124E-84
  -8.830  0.1249E-83  0.2249E-84
  -8.820  0.1249E-83  0.2374E-84
  -8.810  0.1249E-83  0.2498E-84
  -8.800  0.1249E-83  0.2623E-84
  -8.790  0.1249E-83  0.2748E-84
  -8.780  0.1249E-83  0.2873E-84
  -8.770  0.1249E-83  0.2998E-84
  -8.760  0.1249E-83  0.3123E-84
  -8.750  0.1249E-83  0.3248E-84
```

```python
import matplotlib.pyplot as plt
from matplotlib import rcParamsDefault
import numpy as np
%matplotlib inline
```

```python
# load data
energy, dos, idos = np.loadtxt('C:/Users/User/QE_calculation/si_dos.dat', unpack=True)
```

```python
plt.figure(figsize = (12, 6))
plt.plot(energy, dos, linewidth=0.75, color='red')
plt.yticks([])
plt.xlabel('Energy (eV)')
plt.ylabel('DOS')
plt.axvline(x=6.642, linewidth=0.5, color='k', linestyle=(0, (8, 10)))
plt.xlim(-6, 16)
plt.ylim(0, )
plt.fill_between(energy, 0, dos, where=(energy < 6.642), facecolor='red', alpha=0.25)
plt.text(6, 1.7, 'Fermi energy', fontsize= 12, rotation=90)
plt.show()
```





DOS PLOT

Band structure Calculation

Mapping Energy Bands

Single-point self consistent field calculation

```
meyn@LAPTOP-C0A2DPIS:~/q-e-qe-7.1/test_calculation$ vi si_bands_scf.in
```

Input file

```
&CONTROL
  calculation = 'scf',
  restart_mode = 'from_scratch',
  prefix = 'silicon',
  outdir = './tmp/'
  pseudo_dir = '/home/meyn/q-e-qe-7.1/pseudo/'
  verbosity = 'high'
/

&SYSTEM
  ibrav =  2,
  celldm(1) = 10.2076,
  nat =  2,
  ntyp = 1,
  ecutwfc = 50,
  ecutrho = 400,
  nbnd = 8,
!  occupations = 'smearing',
!  smearing = 'gaussian',
!  degauss = 0.005
/

&ELECTRONS
  conv_thr = 1e-8,
  mixing_beta = 0.6
/

ATOMIC_SPECIES
  Si 28.086 Si.pz-vbc.UPF

ATOMIC_POSITIONS (alat)
  Si 0.0 0.0 0.0
  Si 0.25 0.25 0.25

K_POINTS (automatic)
  8 8 8 0 0 0
~
~
~
```

Band calculation (non-self consistent field)

```
meyn@LAPTOP-C0A2DPIS:~/q-e-qe-7.1/test_calculation$ vi si_bands.in
```

```
&control
  calculation = 'bands',
  restart_mode = 'from_scratch',
  prefix = 'silicon',
  outdir = './tmp/'
  pseudo_dir = '/home/meyn/q-e-qe-7.1/pseudo/'
  verbosity = 'high'
/

&system
  ibrav =  2,
  celldm(1) = 10.2076,
  nat =  2,
  ntyp = 1,
  ecutwfc = 50,
  ecutrho = 400,
  nbnd = 8
 /

&electrons
  conv_thr = 1e-8,
  mixing_beta = 0.6
 /

ATOMIC_SPECIES
  Si 28.086  Si.pz-vbc.UPF

ATOMIC_POSITIONS (alat)
  Si 0.00 0.00 0.00
  Si 0.25 0.25 0.25

K_POINTS {crystal_b}
5
  0.0000 0.5000 0.0000 20  !L
  0.0000 0.0000 0.0000 30  !G
  -0.500 0.0000 -0.500 10  !X
  -0.375 0.2500 -0.375 30  !U
  0.0000 0.0000 0.0000 20  !G
```

```
meyn@LAPTOP-C0A2DPIS:~/q-e-qe-7.1/test_calculation$ pw.x < si_bands.in > si_bands.out
```

Postprocessing using bands.x utility

Input file

```
meyn@LAPTOP-C0A2DPIS:~/q-e-qe-7.1/test_calculation$ bands.x <si_bands_pp.in > si_bands_pp.out
```

```
meyn@LAPTOP-C0A2DPIS:~/q-e-qe-7.1/test_calculation$ vi si_bands_pp.in
meyn@LAPTOP-C0A2DPIS:~/q-e-qe-7.1/test_calculation$ cat si_bands_pp.in
&BANDS
  prefix = 'silicon'
  outdir = './tmp/'
  filband = 'si_bands.dat'
/
```

```
meyn@LAPTOP-C0A2DPIS:~/q-e-qe-7.1/test_calculation$ bands.x <si_bands_pp.in > si_bands_pp.out
```

Band structure Plot

```
import matplotlib.pyplot as plt
from matplotlib import rcParamsDefault
import numpy as np
%matplotlib inline

```

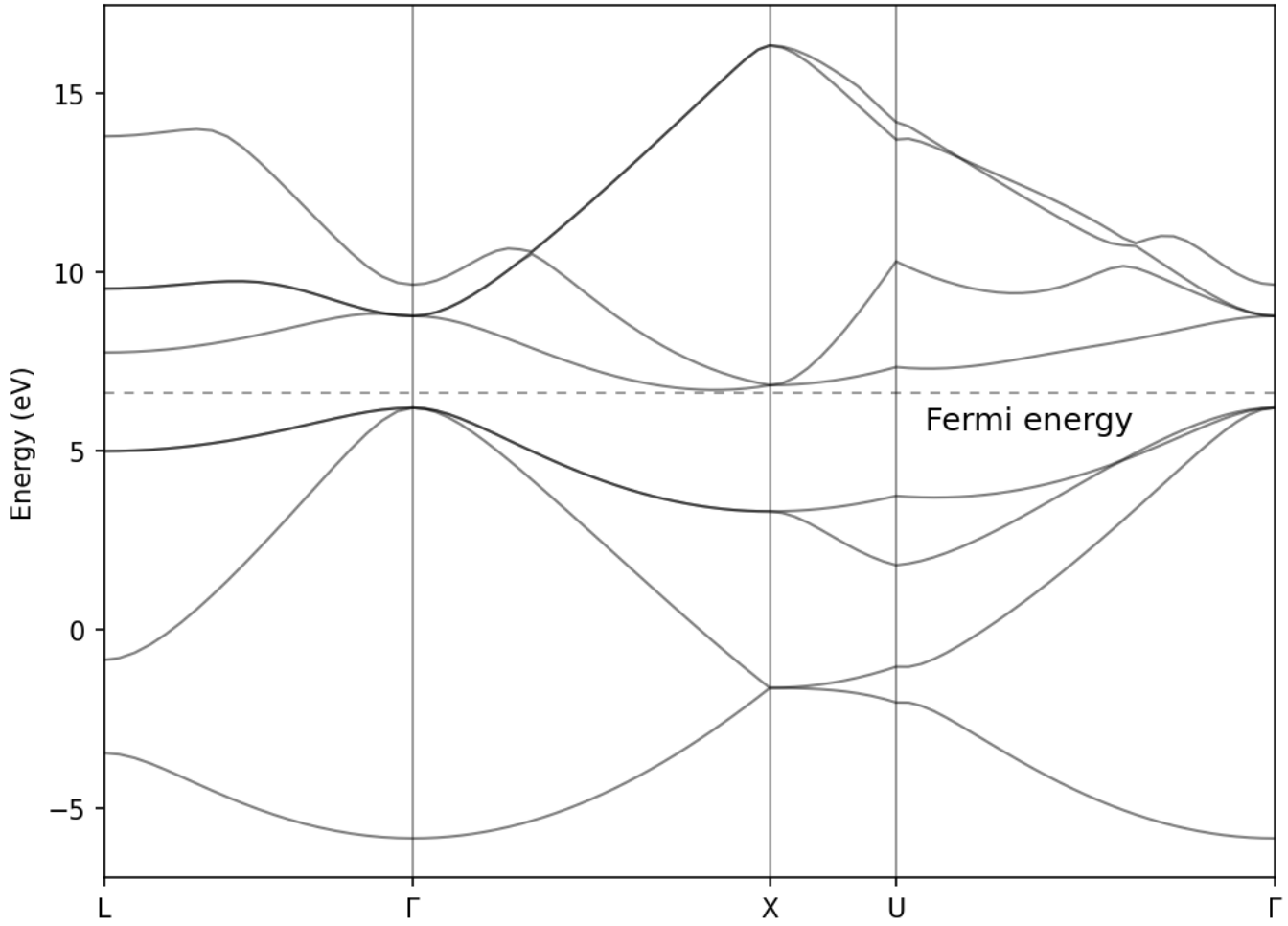
```
plt.rcParams["figure.dpi"]=150
plt.rcParams["figure.facecolor"]="white"
plt.rcParams["figure.figsize"]=(8, 6)
```

```
# load data
data = np.loadtxt('C:/Users/User/QE_calculation/si_bands.dat.gnu')

k = np.unique(data[:, 0])
bands = np.reshape(data[:, 1], (-1, len(k)))

for band in range(len(bands)):
    plt.plot(k, bands[band, :], linewidth=1, alpha=0.5, color='k')
plt.xlim(min(k), max(k))

# Fermi energy
plt.axhline(6.6416, linestyle=(0, (5, 5)), linewidth=0.75, color='k', alpha=0.5)
# High symmetry k-points (check bands_pp.out)
plt.axvline(0.8660, linewidth=0.75, color='k', alpha=0.5)
plt.axvline(1.8660, linewidth=0.75, color='k', alpha=0.5)
plt.axvline(2.2196, linewidth=0.75, color='k', alpha=0.5)
# text labels
plt.xticks(ticks= [0, 0.8660, 1.8660, 2.2196, 3.2802], \
           labels=['L', '$\Gamma$', 'X', 'U', '$\Gamma$'])
plt.ylabel("Energy (eV)")
plt.text(2.3, 5.6, 'Fermi energy', fontsize= 12)
plt.show()
```



Conclusion

- The Self-consistent field calculation offered a deep understanding of silicon’s electronic properties.
- The structure optimization calculation successfully obtained an optimized crystal structure for silicon, minimized the total energy, and established a stable configuration suitable for further analysis.
- The density of states calculation elucidated the distribution of energy states accessible to electrons and provided crucial information about the electronic density at various energy levels in silicon.
- The band structure calculation precisely mapped the energy bands in silicon and revealed key characteristics such as the bandgap, band dispersion, and symmetries of the energy levels.

References

- https://pranabdas.github.io/espresso/category/hands-on/
- https://www.britannica.com/science/band-theory
- https://www.power-and-beyond.com/semiconductor-materials-what-is-silicon-a-ba604a23f39215d0c410a14e5f071121/
- Sidebottom, D. (2012). Electrons: Band Theory. In Fundamentals of Condensed Matter and Crystalline Physics (pp.218-243). Cambridge University Press