IDNM 680: ELECTRONIC PHONON BAND STRUCTURE OF GRAPHENE

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In this assignment, we are going to perform DFT calculations on graphene using the software QuantumEspresso. We begin by downloading the relevant files

```
wget https://github.com/pranabdas/espresso/blob/main/src/*
```

While QuantumEspresso is already installed on the Beowulf server, we can make use of all the relevant graphene files found at

`/home/idnm2023/IDNM680/Della-Giustina/espresso-main/src/graphene`.

For each of the `.in` files, we need to make and then change the `\tmp` and `\pseudos` directories listed at the top of each input file. Create both directories and download the pseudo-potentials file by executing

```
mkdir tmp
mkdir pseudos
cd pseudos
wget http://pseudopotentials.quantum-espresso.org/upf_files/C.pbe-rrkjus.UPF
```

First, we must calculate the self-consistent field calculations to obtain Kohn-Sham orbitals and their energies. The solution to the Kohn-Sham Equation (1), a one electron Schrödinger like equation, give us the electron density $\rho(r)$ of the system, which are used to calculate the total energy of the system.

$$\left[-\frac{\hbar^2}{2m}\Delta + G(\mathbf{r},[\rho])\right]\varphi_\lambda(\mathbf{r}) = \epsilon_\lambda\varphi_\lambda(\mathbf{r}) \tag{1}$$

The idea of the Kohn-Sham method is that the ground state properties of a many-electron system are determined solely by its electron density, which is given by Equation (2).

$$\rho(\mathbf{r}) = 2\sum_{\lambda=1}^{N_e/2}|\varphi_\lambda(\mathbf{r})|^2 \tag{2}$$

Note that these solutions are approximations of the many-body problem of interacting electrons mapped into that of a system consisting of non-interacting electrons. To perform the calculations, execute the following

```
mpirun -np 4 /opt/qe-7.2/bin/pw.x -i graphene_scf.in > graphene_scf.out &
```

Now, we perform the non-self-consistent field calculations. This uses the output of the self-consistent field equations, the Kohn-Sham orbitals and their energies, to find a fixed potential $V(r)$, as opposed to the local potential $G(\mathbf{r},[\rho])$ in Equation (1), to solve Equation (3) with a finer k-point mesh for a more accurate approximation.

$$\left[-\frac{\hbar^2}{20m}\nabla^2 + V(\mathbf{r})\right]\varphi_i(\mathbf{r}) = \varepsilon_i\varphi_i(\mathbf{r}) \tag{3}$$

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The output of such a calculation will inform us the electronic states close to the Fermi level, or the amount of thermodynamic work required to add one electron to the body. The calculation is made with the following command

```
mpirun -np 4 /opt/qe-7.2/bin/pw.x -i < graphene_nscf.in > graphene_nscf.out &
```

Next, we calculate the density of states, which quantifies the number of states per interval of energy for *each* energy level available to be occupied. Density of states can be calculated from the eigenvalues ϵ_λ of the Kohn-Sham Equations (3):

$$D(\epsilon) = 2\sum_{\lambda} \delta\left(\epsilon - \epsilon_\lambda\right) \tag{4}$$

```
mpirun -np 4 /opt/qe-7.2/bin/dos.x -i < graphene_dos.in > graphene_dos.out &
```

To post-process the band calculations output, we run the following

```
mpirun -np 4 /opt/qe-7.2/bin/bands.x -i < graphene_bands_pp.in >
   graphene_bands_pp.out &
```

To plot the results, we make use of the `Python` script found on the tutorial at `https://pranabdas.github.io/espresso/hands-on/graphene/`, using the `graphene_bands.dat.gnu` file.

```
import numpy as np
import matplotlib.pyplot as plt

data = np.loadtxt('graphene_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(0.921, linestyle=(0, (8, 10)), linewidth=0.75, color='k', alpha
   =0.5)
# High symmetry k-points (check bands_pp.out)
plt.axvline(0.6667, linewidth=0.75, color='k', alpha=0.5)
plt.axvline(1, linewidth=0.75, color='k', alpha=0.5)
# text labels
plt.xticks(ticks= [0, 0.6667, 1, 1.5774], labels=['$\Gamma$', 'K', 'M', '$\
   Gamma$'])
plt.ylabel("Energy (eV)")
plt.show()
```

Which outputs a visualization of the band structure in the Brillouin zone, the Fourier transformed lattice of Wigner-Seitz primitive cells, and is displayed in Figure 1. Each 'band' represents the change in energy as an electron moves along this path. The dashed line represents the Fermi energy, which is the highest energy level that can be occupied by an electron at absolute zero.

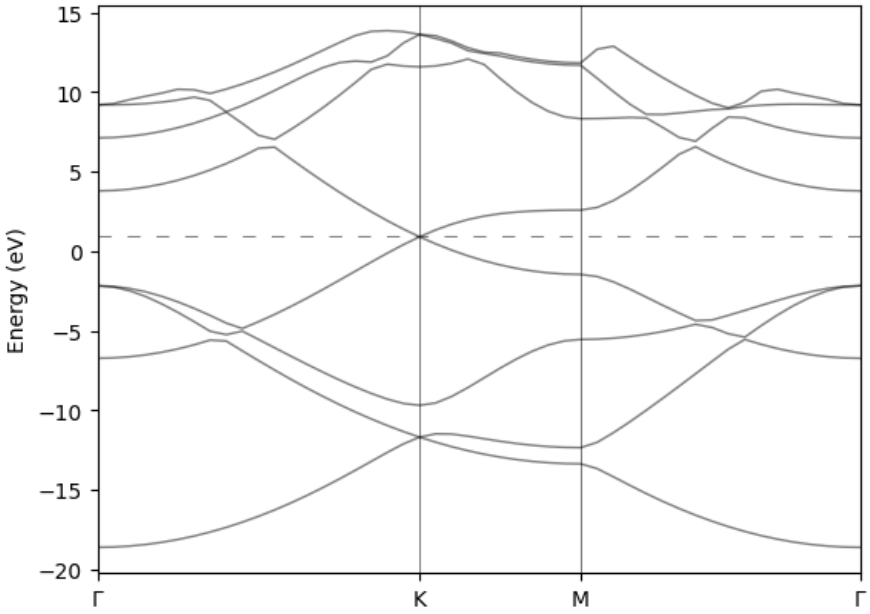

FIGURE 1. Energy band structure of graphene obtained from the QuantumEspresso calcultations.

References

[1] Leonid Kantorovich. *Quantum theory of the Solid State: An introduction*. **volume** 136. Fundamental Theories of Physics. Springer Science, 2004. DOI: 10.1007/978-1-4020-2154-1.