Quantum Transport in Nanoporous Graphene

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Abstract: Abstract...

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 Project Repository: https://github.com/rwiuff/QuantumTransport

I. INTRODUCTION

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II. QUANTUM TRANSPORT

A. Ballistic quantum transport

As graphene is a two dimensional material that consists of carbon atoms arranged in a hexagonal pattern, features in such a material can approach nanometer and sub nanometer scales. Because of the small scale the electrical properties and the electrical nature of the material is greatly changed. Normal drift-diffusion current models describe electric charges per area and current per area, but because the conductor is graphene, it can be considered one dimensional. This makes drift-diffusion models insufficient to describe the electrical transport and properties of graphene because the drift-diffusion model is based on scattering of multiple electrons and the mean free path between scattering. Because of the strong binding between atoms in graphene hardly any phonons are present in the material, even at room temperature. In the ballistic model, this means that electrons are not affected by phonons, i.e. no electrons will be excited by phonons, and that they move through the material as waves. Furthermore the model looks at only one electron at a time in the presence of an electron gas. This model has been used with big success for regular graphene and it seems the model also gives a good approximation for NPG.

B. π-orbitals and π-electrons

The main scope of this paper is dealing with electron transport in novel nanoporous graphene devices. When modeling such transport one needs to address the orbital structure of carbon lattices and later this will motivate the use of tight-binding and Green's functions. In its basic form graphene can be divided into rings of carbon atoms as shown in Fig. 1. In the (x, y)-plane the carbon atoms are bound in sp^2 orbitals as shown in Fig. 2.
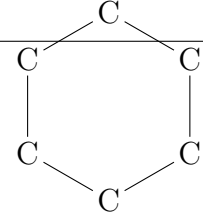
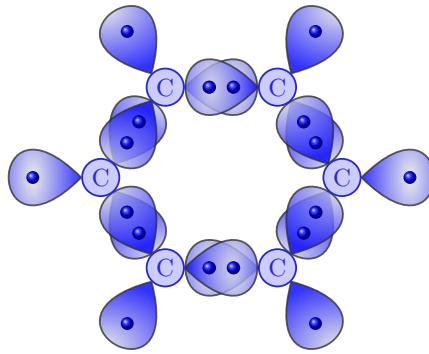**Figure 1:** *Graphene lattices consists of hexagonal arrangements of carbon atoms.*

Figure 2: *Carbon atoms in a hexagonal lattice are sp^2 hybridised in the (x, y)-plane.*

This hybridisation lock all but one valence electron for the carbon atoms. These electrons exists in a p-orbital in the z-direction. Fig. 3 shows the valence orbitals of carbon.
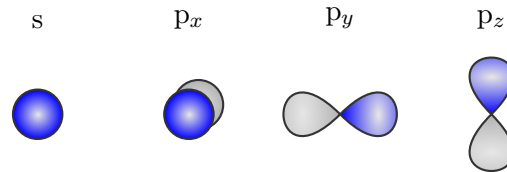

Figure 3: *The valence orbitals of carbon.*

The last electron in the p_z orbital does not mix with the tightly bound s, p_x and p_y electrons and moves more freely. Thus these electrons have higher energies compared to the sp^2 electrons and occupy states at the Fermi level. These electrons dominates transport

in the graphene lattice. The p_z orbital is also known as the π-orbital and as such the electron lying there is called a π-electron. Through a carbon lattice the π-electrons will travel through π-orbitals, switching sign as they go as shown in Fig. 4.
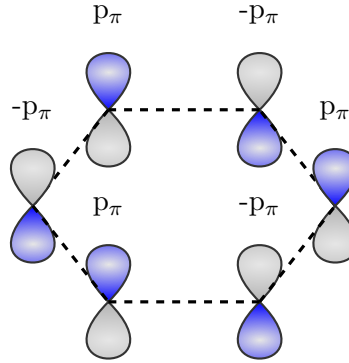

Figure 4: *When jumping from one carbon atom to another, the π-electron goes between p_π and $-p_\pi$. Such a jump is described by two matrix elements in the system's Hamiltonian.*

C.   Tight-binding

Now that the transport carrying electrons are defined, one must choose a formalism for the transport itself. Introducing: **"The Tight-Binding approximation"**. In this approximation the electrons are considered being tightly bound to the atoms. Contrary to a free electron gas approximation, the electrons does not spend time in between orbitals, but jump from orbital in atom a to orbital in atom b. In this world view the Hamiltonian contains a matrix of hopping elements for a collection of neighbouring atomic orbitals, i.e. molecular orbitals, as well as the energy contained within each orbital (which will be addressed later on). This can be done by describing the orbitals as a Linear Combination of Atomic Orbitals (LCAO). The solution to the Schrödinger equation is then:

$$\Psi_{\mathrm{MO}} = \sum_{\alpha,R} c_{\alpha,R} \phi_\alpha(R) \tag{C.1}$$

where $\phi_\alpha(R)$ is some atomic orbital at position R, with α denoting the valence of the orbital $(2s, 2p_x, 2p_y, 2p_z)$. In electron transport the states close to the Fermi level is of interest. These are namely the highest occupied molecular orbitals (HOMO), or the lowest unoccupied molecular orbitals (LUMO). As stated earlier only the π-electrons is then of interest. The electrons' motion can be described with the hopping matrix of elements:

$$V_{pp\pi} = \langle \phi_\pi(1)| \hat{H} |\phi_\pi(2)\rangle \tag{C.2}$$

Physically this means that there is a potential between the π orbitals of neighbouring atoms 1 and 2. The element

$$\epsilon_0 = \langle \phi_\pi(1)| \hat{H} |\phi_\pi(1)\rangle \tag{C.3}$$

is the average energy of the electron on atom 1 and, it is normal to define the hopping energy relative to this:

$$\epsilon_0 = 0 \tag{C.4}$$

If the atoms or their environment differs, so does the on-site potential.

D.   The benzene molecule

As an example the Hamiltonian of benzene is considered. In Fig. 5 one can see the indices of a benzene molecule. Remember that $\langle \phi_\pi(1)| \hat{H} |\phi_\pi(1)\rangle = 0$ and Eq. (C.2), the Hamiltonian reads:
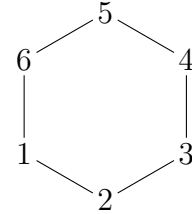
Figure 5: *Indices of a benzene molecule*

$$\mathbf{H} = V_{pp\pi} \begin{array}{c} \\ 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ 6 \end{array} \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 1 \\ 1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 1 \\ 1 & 0 & 0 & 0 & 1 & 0 \end{pmatrix} \tag{D.1}$$

As a helping aid, Eq. (D.1) shows the atomic indices of the atom on the top and to the left of the matrix. This will give an understanding of how to work with such matrices. The structure of the benzene molecule is rotationally symmetric and rotating the indices one sixth must yield the same Hamiltonian. Consider the energy eigenvector:

$$\phi = \begin{pmatrix} c_1 & c_2 & c_3 & c_4 & c_5 & c_6 \end{pmatrix} \tag{D.2}$$

There must exist an operator that rotates the indices as such:

$$C_6\phi = \begin{pmatrix} c_2 & c_3 & c_4 & c_5 & c_6 & c_1 \end{pmatrix} \tag{D.3}$$

The rotated Hamiltonian is the same, and thus C_6 and $\mathbf{H}$ commutes. The rotated vector must be an eigenvector with the same energy and it should be possible to find simultaneous eigenvectors to C_6 and $\mathbf{H}$.

$$C_6\phi = \begin{pmatrix} c_2 & c_3 & c_4 & c_5 & c_6 & c_1 \end{pmatrix} = \lambda \begin{pmatrix} c_1 & c_2 & c_3 & c_4 & c_5 & c_6 \end{pmatrix} \tag{D.4}$$

This operator C_6 is represented with the matrix:

$$\mathbf{C}_6 = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \tag{D.5}$$

It can quickly be shown that the normalised eigenvectors to C_6 are

$$\phi_n = \frac{1}{\sqrt{6}} \begin{pmatrix} \lambda_n^0 & \lambda_n^1 & \lambda_n^2 & \lambda_n^3 & \lambda_n^4 & \lambda_n^5 \end{pmatrix}, \quad \lambda_n = \exp\{-i2\pi n/6\}, \quad n = 0, 1, 2, 3, 4, 5 \tag{D.6}$$

These eigenvectors are also eigenvectors for $\mathbf{H}$ with the eigenvalues:

$$\varepsilon_n = \lambda_n + \lambda_{n-1} = 2\cos n\pi/3 \tag{D.7}$$

Thus thanks to the rotational symmetry it was possible to find the eigenvectors and eigenenergies for the Hamiltonian.

III.   BAND STRUCTURE OF NPG

A.   Creating on-site Hamiltonian and hopping matrices for the system

In order to calculate and visualise the band structure of the NPG within a unit cell, the on-site Hamiltonian along with its hopping matrices must be defined. The on-site Hamiltonian lies within the unit cell of the system. As the unit cell is repeated periodically the on-site Hamiltonian fills out one full period of the system. The unit cell is defined with respect given unit vectors which determine the periodicity of the system. By these definitions the elements of the hopping matrices represents hops between the repeated unit cells with respect to the periodicity. See **??** for a visual representation of the structure with its peridicity.

On the premise of the Tight Binding Model, the next step to find all the nearest neighbouring atoms within the given set of atom coordinates to define the on-site Hamiltonian $\mathbf{h_0}$ and then define the hopping matrices $\mathbf{V}$ and its conjugate $\mathbf{V}^{\dagger}$. This is because the Tight Binding model only allow for hopping of electrons between nearest neighbours which in this case is the periodic boundary conditions set for the system.

Maybe implement code pieces or explain code terms that executes these operations. i.e. "By using two for loops and the numpy function np.subtract(), we get the all the combinations of... etc. This should be considered throughout the section. This can be done simply by taking what is similar to an outer product of the coordinate matrix with itself only here every combination of coordinates are subtracted not multiplied, hereafter taking the norm of all those combinations. This will produce a matrix which contain all distances between all atoms in the NPG. Once obtained a threshold will be applied to sort out the nearest neighbours within the matrix. In this specific case the coordinates given was with respect to unit vectors with a lattice constant of 1.00 Å, which means that the threshold in this case should be 1.60 Å which is the inter-atomic distance for nearest neighbours in a graphene mesh. All distances above 1.60 Å will be changed to a 0-element in the on-site Hamiltonian as no hopping of electrons is possible between atoms that are more than one inter-atomic distance apart. All distances below the threshold will be changed to 1 to represent a hop between to atoms. The on-site Hamiltonian is then multiplied by at scalar which is the on-site potential V_{ppi} which in this case is -1. Now the on-site Hamiltonian is complete and the construction of the hopping matrices can begin.

As the on-site Hamiltonian represents a (three)two-dimensional structure one has to make sure that hopping between the nearest neighbour atoms relative to that of a repeated unit cell (on-site Hamiltonians) can described in all directions in the plane. Effectively this means that six hopping matrices should be created. One in the x-direction, one in the y-direction, one in the xy-direction and their hermitian conjugates. Graphically this corresponds to a structure of this kind:
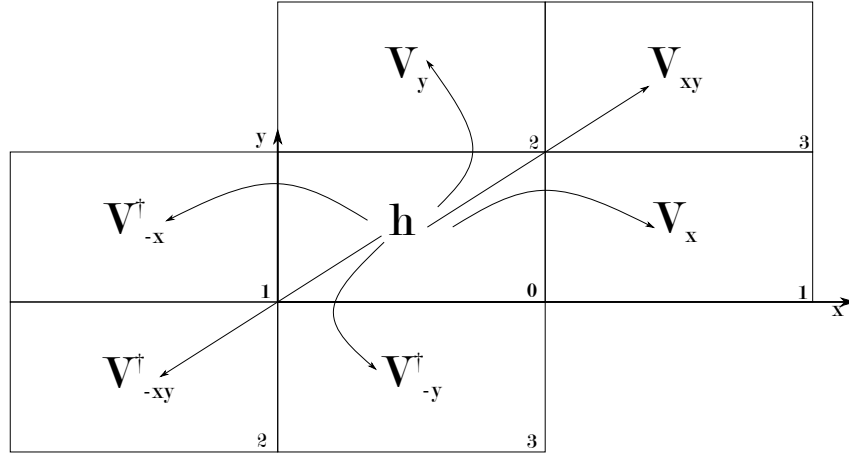
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2019

Figure 6: *Representative figure of how the on-site Hamiltonian along with its hopping matrices are structured*

In practice this is done by shifting the original coordinates by the given unit vectors of the system in each direction, adding the unit vector to the coordinate matrix making three new matrices. Now that three shifted matrices has been obtained, the same routine to find the distances as with the on-site Hamiltonian can be utilised, the only difference being that the outer subtraction will be between the on-site Hamiltonian and the shifted matrices respectively to make sure it is the distance between the on site Hamiltonian and the shifted matrices that is calculated. Again by replacing the distances in the shifted matrices with 1 and 0 according to the inter-atomic threshold, the hopping matrices are obtained. The three hopping matrices denoted $\mathbf{V}_{1x}$, $\mathbf{V}_{2y}$ and $\mathbf{V}_{3xy}$ represent hopping in the "forward" direction (left-to-right). To create the hopping matrices hopping in the "backwards" (right-to-left) direction one simply has to transpose the hopping matrices. These matrices are denoted with a dagger: $\mathbf{V}_{1x}^{\dagger}$, $\mathbf{V}_{2y}^{\dagger}$ and $\mathbf{V}_{3xy}^{\dagger}$. Fig. 7 is a figure of the resulting matrix-maps from the calculation, stitched together like in Fig. 6.
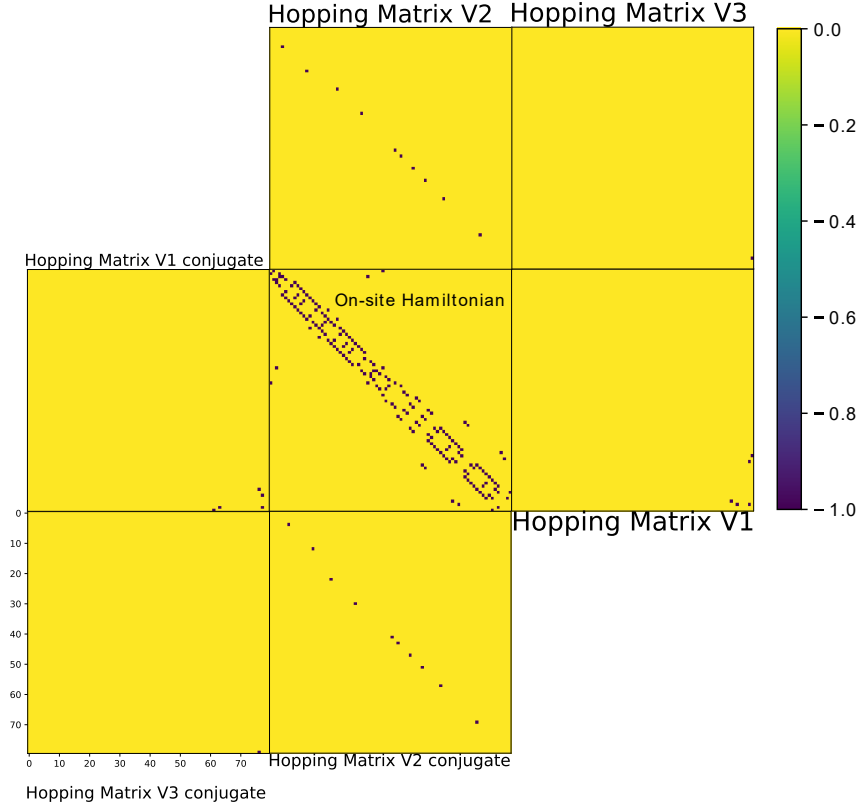
Figure 7: *Matrix maps from calculation on the NPG. The on-site Hamiltonian along with all its hopping matrices are stitched together like the representative figure Fig. 6. All the dark spots represents a hopping of an electron to its nearest neighbour.*

B.   Defining the full Hamiltonian and solving the Schrodinger equation

Now that the on-site Hamiltonian along with its hopping matrices has been defined, the next step is to create the full Hamiltonian in order to solve the Schrodinger equation for system, which is a eigen-value/vector problem. In essence the full Hamiltonian denoted **H** is a sum of the on-site Hamiltonian and its corresponding hopping matrices multiplied by a complex exponential function that has the appropriate phase relative to the hopping matrix:

$$\begin{aligned}
\mathbf{H}(k_x, k_y) =& \mathbf{h}_0 + (\mathbf{V}_{1x}e^{-ik_x} + \mathbf{V}_{1x}^\dagger e^{ik_x} + \mathbf{V}_{2x}e^{-ik_y} + \mathbf{V}_{2x}^\dagger e^{-ik_y} \\
& + \mathbf{V}_{3xy}e^{-ik_x}e^{-ik_y} + \mathbf{V}_{3xy}^\dagger e^{ik_x}e^{ik_y})
\end{aligned} \tag{B.1}$$

Here k represents a continuous variable between 0 and π along the x- and y-axis in inverse space. Using the full Hamiltonian, the Schrodinger equation can be solved

$$\mathbf{H}(k_x, k_y)\boldsymbol{\phi}_k = \boldsymbol{\epsilon}_n(k_x, k_y)\boldsymbol{\phi}_k \tag{B.2}$$

In practice this is all done by defining a function that takes the on-site Hamiltonian, the hopping matrices, and k as inputs and outputs the eigenvalues, using numpy's *numpy.linalg.eigh*. The number of eigenvalues in the output corresponds to the dimension of the full Hamiltonian. As the eigenvalues corresponds to the eigenenergies of the system, the band structures can be plotted.

C.   Plotting the band structures

The continuous variable k extends in two directions $(-k_x)$ and (k_y) which corresponds to the length along X and Γ in the Brillouin zone. It is therefore necessary to make two plots, one for each direction. The y-values in each plot corresponds to the eigenvalues obtained by the function described in Section III B. Each x-value along X and Γ therefore has associated with it the amount of y-values which the dimension of full Hamiltonian dictates. F.ex. if the full Hamiltonian has dimension 80×80 there is 80 eigenvalues associated with it and the amount of y-values for each x-value along X and Γ is 80. In this specific case, the full Hamiltonian for obtaining the eigenvalues that corresponds to X and Γ are:

$$X: \ \mathbf{H}_X = \mathbf{h}_0 + (\mathbf{V}_{1x}e^{ik_x} + \mathbf{V}_{1x}^{\dagger}e^{-ik_x} + \mathbf{V}_{2x} + \mathbf{V}_{2x}^{\dagger} + \mathbf{V}_{3xy}e^{ik_x} + \mathbf{V}_{3xy}^{\dagger}e^{-ik_x}) \qquad \text{(C.1)}$$

$$\Gamma: \ \mathbf{H}_\Gamma = \mathbf{h}_0 + (\mathbf{V}_{1x} + \mathbf{V}_{1x}^{\dagger} + \mathbf{V}_{2x}e^{-ik_y} + \mathbf{V}_{2x}^{\dagger}e^{ik_y} + \mathbf{V}_{3xy}e^{-ik_y} + \mathbf{V}_{3xy}^{\dagger}e^{ik_y}) \qquad \text{(C.2)}$$

Using the eigenvalues as y-values in the two plots, putting the two plots together will yield a full plot of the band structure shown in Fig. 8.
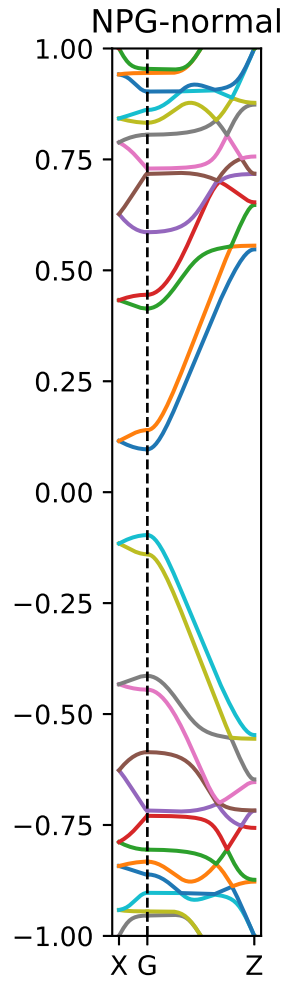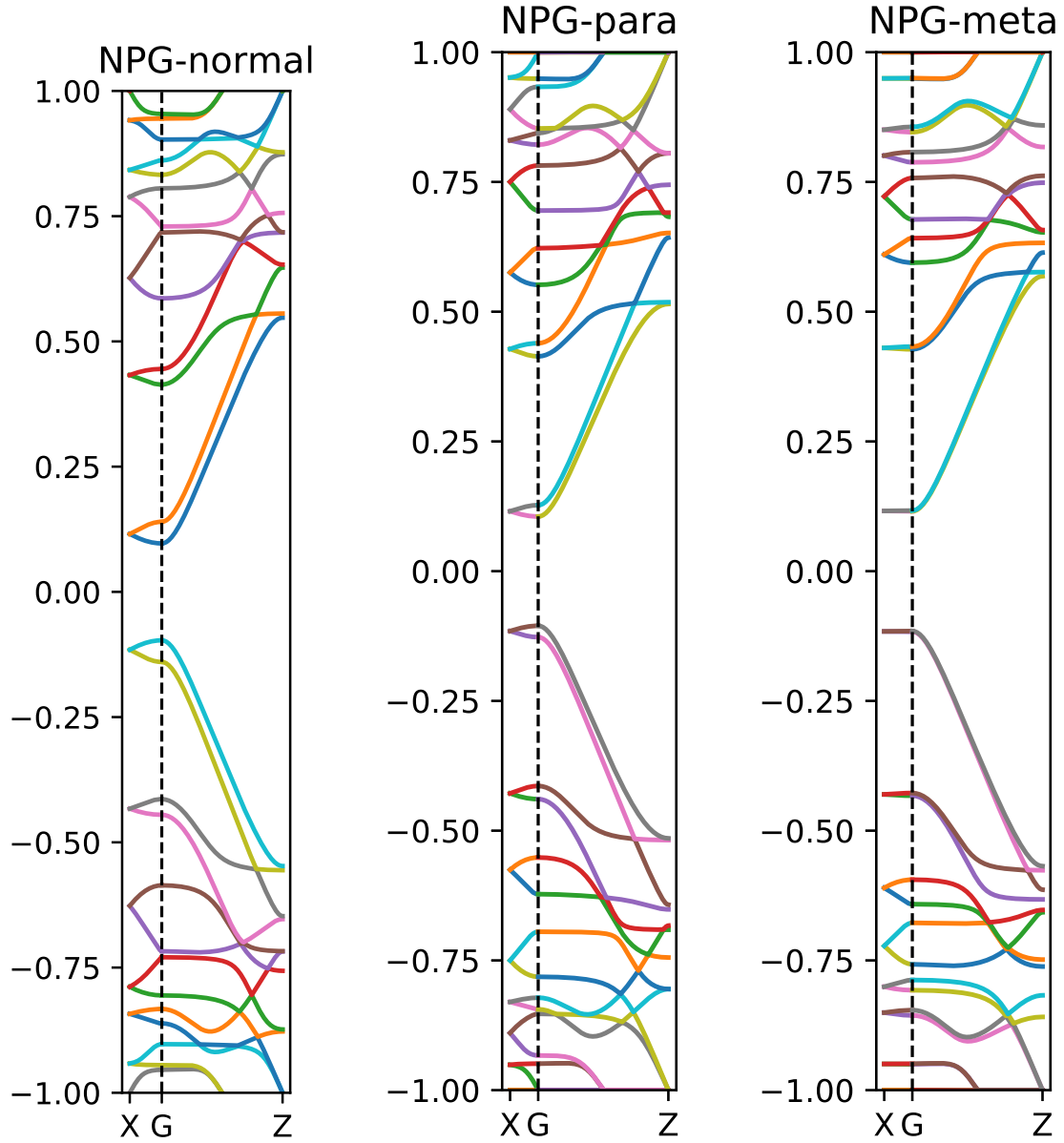
Figure 8: *Plot showing the band structure in the energy range -1 to 1 for NPG with normal bridges in the Γ- and X-direction*

(a) *Plot showing the band structure in the energy range -1 to 1 for NPG with normal bridges in the Γ- and X-direction*

(b) *Plot showing the band structure in the energy range -1 to 1 for NPG with para bridges in the Γ- and X-direction*

(c) *Plot showing the band structure in the energy range -1 to 1 for NPG with meta bridges in the Γ- and X-direction*

Figure 9: *Figure showing para, meta and normal NPG band structures*

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[1] G. Calogero, N. R. Papior, B. Kretz, A. Garcia-Lekue, T. Frederiksen, and M. Brandbyge, Electron Transport in Nanoporous Graphene: Probing the Talbot Effect, Nano Letters **19**, 576 (2019).

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LIST OF FIGURES

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Appendices

Appendix A: Project overview

A Gantt chart is provided on the next page. **Not Updated.**

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Course 33442

Ch. 1 & 2

Ch. 3

Ch. 4 & 5

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Py TB scripts

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Large scale TB

SISL & TBtrans tutorial

Setup NPG variations

Generate data

Hand in report ◆