Quantum Transport in Nanoporous Graphene

Rasmus Kronborg Finnemann Wiuff (s163977)[*]

and Christoffer Vendelbo Sørensen (163965)[†]

Technical University of Denmark[‡]

(Dated: May 1ˢᵗ 2019)

Abstract: Abstract...

I. INTRODUCTION

Lorem ipsum dolor sit amet, consectetuer adipiscing elit. Ut purus elit, vestibulum ut, placerat ac, adipiscing vitae, felis. Curabitur dictum gravida mauris. Nam arcu libero, nonummy eget, consectetuer id, vulputate a, magna. Donec vehicula augue eu neque. Pellentesque habitant morbi tristique senectus et netus et malesuada fames ac turpis

---

[*] E-mail at rwiuff@dtu.dk

[†] E-mail at chves@dtu.dk

[‡] Homepage of the Technical University of Denmark http://www.dtu.dk/english/;

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

egestas. Mauris ut leo. Cras viverra metus rhoncus sem. Nulla et lectus vestibulum urna fringilla ultrices. Phasellus eu tellus sit amet tortor gravida placerat. Integer sapien est, iaculis in, pretium quis, viverra ac, nunc. Praesent eget sem vel leo ultrices bibendum. Aenean faucibus. Morbi dolor nulla, malesuada eu, pulvinar at, mollis ac, nulla. Curabitur auctor semper nulla. Donec varius orci eget risus. Duis nibh mi, congue eu, accumsan eleifend, sagittis quis, diam. Duis eget orci sit amet orci dignissim rutrum.

[1]

II.   QUANTUM TRANSPORT

A.   Ballistic quantum transport

As graphene is 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 they are based on scattering of multiple electrons and the mean free path between scattering. In graphene only a few electrons at a time are considered when modeling electron transport and it is therefore necessary to use quantum mechanics to describe the transport of electrons in the material.

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 adress 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 devided 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.
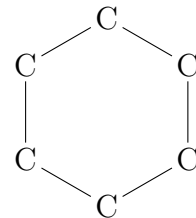

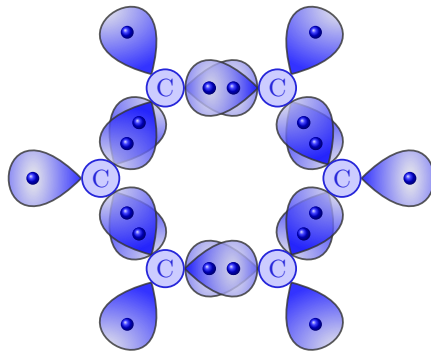**Figure 1:** *Graphene lattices consists of hexagonal arrangements of carbon atoms.*

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.
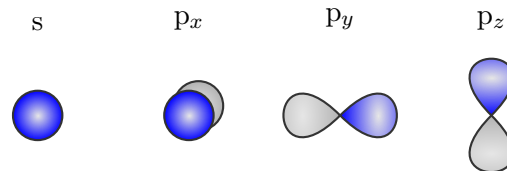

Figure 3: *The valence orbitals of carbon.*

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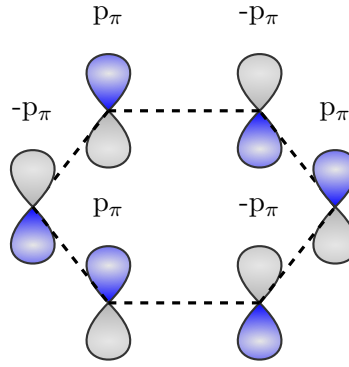
Figure 4: *When jumping from one carbon atom to another, the π-electron goes between p_π and -p_π. Such a jump is described by two matrix elements in the system's Hamiltonian.*

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 gass 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 adressed 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:

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

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 moelcular 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:
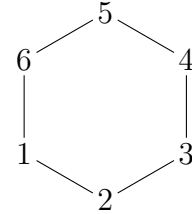

Figure 5: *Indices of a benzene molecule*

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

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 normalized 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.

ACKNOWLEDGMENTS

[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).

LIST OF FIGURES

LIST OF TABLES

LISTINGS

Appendices

Appendix A: Project overview

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

2019

| Feb | Mar | Apr | May |

| 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 |

Report writing

Course 33442

Ch. 1 & 2

Ch. 3

Ch. 4 & 5

Python code

Py TB scripts

Small NPG systems simulations

Proof of Concept with Python ◆

Large scale TB

SISL & TBtrans tutorial

Setup NPG variations

Generate data

Hand in report ◆