Appendix A

Appendix

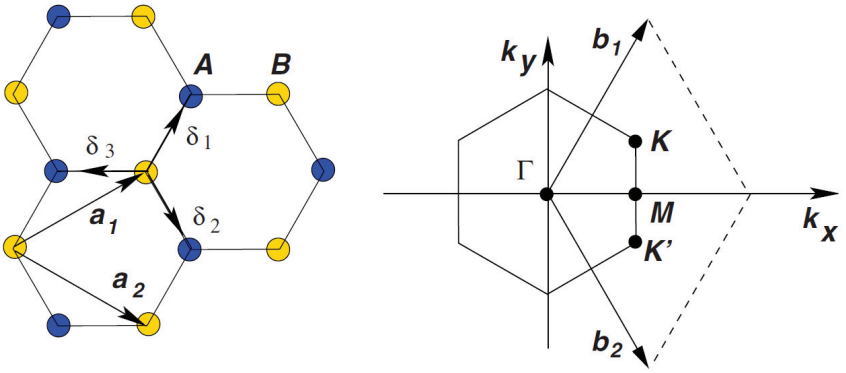

Figure A.1: Left: Real space structure of graphene displaying a honeycomb lattice made of two triangular sub-lattices indicated by A and B. The unit cell vectors a_1 and a_2 are drawn. Right: First Brillouin zone of graphene in reciprocal space. The reciprocal unit cell vectors b_1 and b_2 are indicated. k_x and k_y refer to the components of the electron momentum in the x and y directions, respectively. The main symmetry points in the Brillouin zone are also marked. Images taken from ref. [1]

Fundamental properties of graphene

Graphene is a two dimensional (2D) allotrope of carbon, it is made of (sp^2) carbon atoms arranged in a honeycomb lattice.[1] It has to be distinguished from multilayer graphene and graphite where few or many layers of graphene are present. In the thesis the word *graphene* always refers to single layer graphene. The 2D planar structure of graphene is due to the hybridization of one s orbital and two p orbitals. The σ bonding gives to graphene its mechanical robustness while the p orbitals form a half-filled π band that crosses the Fermi energy and defines graphene's electronic properties. The σ band is instead a deep valence band that does not contribute to the charge transport. Figure A.1 shows the graphene structure in real space as well as the first Brillouin zone of graphene in reciprocal space. The carbon-carbon bond measures $a = 1.42$ Å and the honeycomb structure can be described by two interpenetrating triangular lattices with a unit cell consisting of two non-equivalent carbon atoms indicated by A and B in Figure A.1. The lattice vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ measure 2.46 Å and include an angle of 60°. The vectors in

reciprocal space are indicated by $\mathbf{b}_1$ and $\mathbf{b}_2$ and measure 2.95 Å^{-1}. The vectors can be also expressed with their respective coordinates in real and reciprocal space as following:

$$\boldsymbol{a_1} = \frac{a}{2}(3, \sqrt{3}) \qquad \boldsymbol{a_2} = \frac{a}{2}(3, -\sqrt{3}) \tag{A.1}$$

$$\boldsymbol{b_1} = \frac{2\pi}{3a}(1, \sqrt{3}) \qquad \boldsymbol{b_2} = \frac{2\pi}{3a}(1, -\sqrt{3}) \tag{A.2}$$

The electronic properties of graphene can be described by a tight-binding Hamiltonian considering that electrons can hop to both nearest- and next-nearest-neighbor atoms.

$$H = -t \sum_{<i,j>,\sigma} (a^{\dagger}_{\sigma,i} b_{\sigma,j} + H.c.) - t^{'} \sum_{<<i,j>>,\sigma} (a^{\dagger}_{\sigma,i} a_{\sigma,j} + b^{\dagger}_{\sigma,i} b_{\sigma,j} + H.c.) \tag{A.3}$$

where $\hbar = 1$, $a^{\dagger}_{\sigma,i}$ ($a_{\sigma,i}$) creates (annihilates) an electron at position r_i with spin σ inside the sub lattice A, the same applies for $b^{\dagger}_{\sigma,i}$ for the sub lattice B, $t \simeq 2.8$ eV ($t^{'} \simeq [0.2 - 0.02]t$) is the nearest (next-nearest) neighbor hopping energy and H.c. is the Hamiltonian conjugated term.[1,2] The theoretical π band structure of freestanding (non-doped) graphene is reported in Figure A.2 and can be expressed as

$$E_{\pm}(\boldsymbol{k}) = \pm t\sqrt{3 + f(\boldsymbol{k})} - t^{'} f(\boldsymbol{k}) \tag{A.4}$$

with

$$f(\boldsymbol{k}) = 2\cos(\sqrt{3}k_y a) + 4\cos(\frac{\sqrt{3}}{2}k_y a)\cos(\frac{3}{2}k_x a) \tag{A.5}$$

The $\pm$ sign refers to conduction ($\pi*$) and valence (π) band that become symmetric for $t^{'} = 0$. In the case of freestanding neutral graphene, the π band crosses the Fermi energy at exactly 6 points (K-K$^{'}$) in the Brillouin zone. Expanding the full band structure close to these K ($K^{'}$) points, one can obtain the dispersion close to the these points.[3]

$$E_{\pm}(\boldsymbol{q}) \simeq \pm v_F |\boldsymbol{q}| + O[(q/K)^2] \tag{A.6}$$

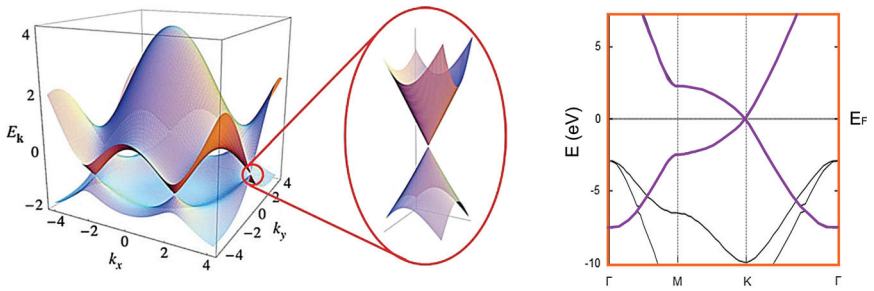

Figure A.2: Left: 3D representation of the π-$\pi*$ bands of graphene. Image from ref.[1] Right: 2D cut of the graphene band structure along the main symmetry directions in reciprocal space. π-$\pi*$ bands are indicated by the purple curve.

where $|\boldsymbol{q}| << |\boldsymbol{K}|$ is the momentum measured relatively to the K point with $\boldsymbol{k} = \boldsymbol{K} + \boldsymbol{q}$. The Fermi velocity $v_F = 3ta/2$ is about $1 \cdot 10^6$ m/s. Eq. A.6 shows that close to the K (K$'$) points the dispersion is linear. The particular linear dispersion of electrons close to these points (only valid at low energies) mimics the physics of quantum electrodynamics of massless fermions. For this reason, these points are called Dirac points. In fact, electrons in graphene completely lose their effective mass showing a quasi-particle behavior that is described by a Dirac-like equation rather than the Schrödinger equation. However, electrons in graphene close to the Fermi energy move with a velocity v_F that is about 300 times slower than c.

The peculiarity of the electronic properties of graphene is connected with the unusual way in which massless Dirac fermions behave compared to ordinary electrons. For example, if a magnetic field is applied, new physical phenomena can be observed such as the anomalous integer quantum Hall effect.[4–6] Moreover, electrons in graphene can travel for very long distances (micrometers) without being scattered by the carbon lattice. In other words they are ballistic. The ballistic electron propagation in graphene is important for applications such as spintronic devices where the electrons must keep their spin coherence over a long distance. Many other astonishing effects can happen in graphene and we refer to ref[1] for more details.

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