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1 Graphene

1.1 Electronic structure

1.1.1 Crystal structure

A two dimensional crystal has all the atoms regularly placed on a plane. A particularly interesting example is graphene that is obtained exfoliating graphite. The graphene flakes are generally deposited on a substrate. Figure 1 shows a STM image of grapheme deposited on silicon carbide. As

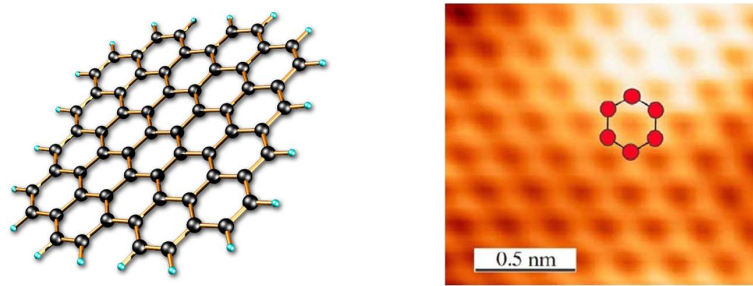


Figure 1: A model and a STM image of graphene deposited on SiC. (STM image from Lauffer et al, PRB 77, 155426 (2008))

the picture shows, the carbon atoms occupy the vertices of regular hexagons so that each atom has other three as first neighbour. The hexagons sides is just the C-C bond length whose value is 1.4 \AA .

We shall be using the Tight Binding Method for computing the graphene band structure. The first step is the identification of the Bravais lattice. Looking at Fig.1 it should be quite evident that the crystal shown there is not a Bravais lattice: it is in fact impossible to define two primitive vectors whose linear combination with integers reproduces the entire crystal. It is therefore necessary to introduce a basis. Figure 2 shows a possible choice of primitive vectors and basis. It is easy to see that

$$\begin{aligned} \mathbf{a}_1 &= a\hat{x} + b\hat{y} \\ \mathbf{a}_2 &= a\hat{x} - b\hat{y} \end{aligned} \quad (1)$$

where we have defined

$$\begin{cases} a &= \frac{3}{2}a_0 \\ b &= \frac{\sqrt{3}}{2}a_0 \end{cases} \quad (2)$$

Here a_0 is the bond length.

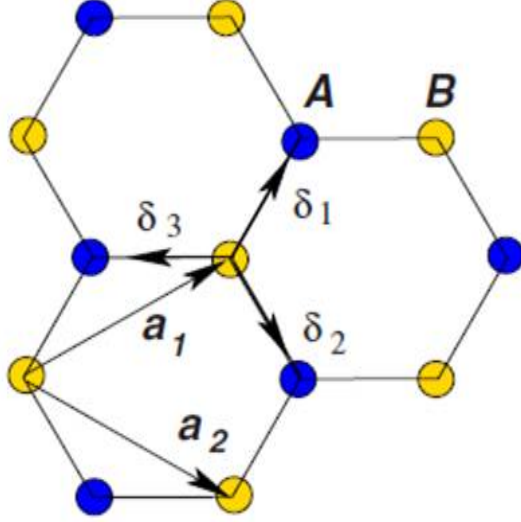


Figure 2: Graphene primitive vectors \mathbf{a}_1 and \mathbf{a}_2 . The basis within the primitive cell is made of two atoms indicated as A and B. The vectors δ_1 , δ_2 and δ_3 point to the first neighbors.

1.1.2 Tight binding matrix

For computing the electronic structure we need to choose the atomic orbitals. Carbon has 6 electrons with the structure $1s^2 2s^2 2p^2$ and with a valence of 4. When a carbon atom interacts with its first neighbors, the orbitals s , p_x and p_y hybridize forming three oriented σ bonds while the p_z orbitals combine forming a π structure. Both cases are shown in Fig 3.

If we construct the graphene wave function as a linear combination of the atomic orbitals s , p_x , p_y and p_z centered on the two atoms of the primitive cell, we expect 6 bands originating from the sp^2 hybridization plus other 2 coming from the π structure. An accurate analysis of the hamiltonian matrix elements shows that the 8×8 matrix splits in two independent blocks: one 6×6 block, which we indicate as σ , containing the matrix elements between s , p_x and p_y plus one 2×2 block, which we indicate as π , containing the matrix elements involving the p_z orbitals. It is important

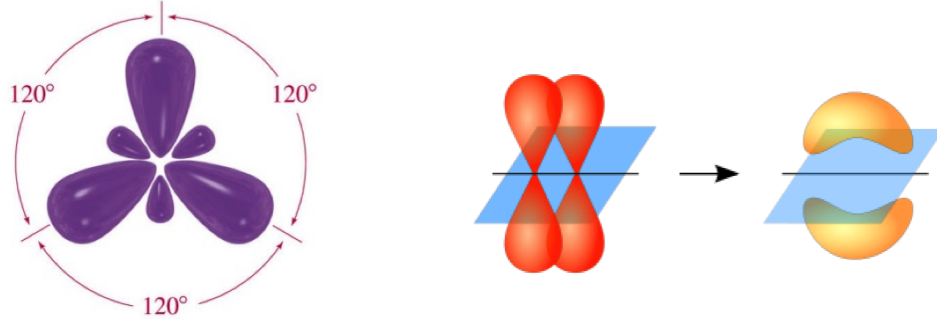


Figure 3: sp^2 (left) and π (right) hybridisation

to underline that this sharp separation into independent blocks is a direct consequence of the orthogonality of p_z orbitals to the graphene plane. If graphene were not perfectly flat, the hamiltonian matrix would not have this blocks structure.

The most interesting part of the band structure is that originating from the p_z orbitals. For each atom in the primitive cell, the Bloch sum is

$$\psi_\alpha = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} |\mathbf{R}, \alpha\rangle \quad (3)$$

where α identifies one of the two atoms in the basis and N is the number of primitive cells. From Eq.(3) the hamiltonian matrix elements are

$$\langle \psi_\alpha | H | \psi_\beta \rangle = \frac{1}{N} \sum_{\mathbf{R}, \mathbf{R}'} e^{i\mathbf{k} \cdot (\mathbf{R} - \mathbf{R}')} \langle \mathbf{R}', \alpha | H | \mathbf{R}, \beta \rangle \quad (4)$$

The sum on \mathbf{R} , for each fixed value of \mathbf{R}' , gives always the same number.¹ We can therefore fix a reference cell, for instance $\mathbf{R}' = 0$, and multiply by N so that

$$\langle \psi_\alpha | H | \psi_\beta \rangle = \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} \langle \mathbf{0}, \alpha | H | \mathbf{R}, \beta \rangle \quad (5)$$

For computing the matrix elements (5) we shall take into account only the terms involving first neighbours sites. Following Fig.4 the computation is easy. The diagonal element is

$$\langle \psi_A | H | \psi_A \rangle = \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} \langle \mathbf{0}, A | H | \mathbf{R}, A \rangle \quad (6)$$

¹This is a consequence of the periodic boundary conditions. We would, of course, obtain the same result if we fix \mathbf{R} and sum over \mathbf{R}' .

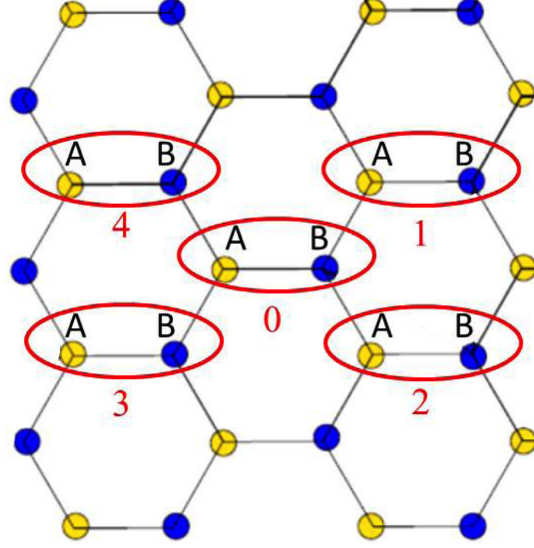


Figure 4: The 4 neighbouring cells of the one chosen as reference. (Figura da rifare)

From Fig.4 it is seen that atom A in the reference cell $\mathbf{0}$ has as first neighbours only atoms of type B so that the sum in Eq.(6), when limited to first neighbors, contains only the term $\mathbf{R} = \mathbf{0}$. The result is

$$\langle \psi_A | H | \psi_A \rangle = \langle \mathbf{0}, A | H | \mathbf{0}, A \rangle = E_0 \quad (7)$$

where we are indicating with E_0 the actual value of the matrix element. We now proceed with off diagonal element

$$\begin{aligned} \langle \psi_A | H | \psi_B \rangle &= \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} \langle \mathbf{0}, A | H | \mathbf{R}, B \rangle = \\ &\langle \mathbf{0}, A | H | \mathbf{0}, B \rangle + \\ &e^{-i\mathbf{k} \cdot \mathbf{a}_2} \langle \mathbf{0}, A | H | \mathbf{3}, B \rangle + \\ &e^{-i\mathbf{k} \cdot \mathbf{a}_1} \langle \mathbf{0}, A | H | \mathbf{4}, B \rangle \end{aligned} \quad (8)$$

We note that the cells $\mathbf{1}$ and $\mathbf{2}$ in Fig.4 do not contribute because atoms B in these cells are not first neighbours of atom A in cell $\mathbf{0}$. Since the matrix elements $\langle \mathbf{0}, A | H | \mathbf{0}, B \rangle$, $\langle \mathbf{0}, A | H | \mathbf{3}, B \rangle$ and $\langle \mathbf{0}, A | H | \mathbf{4}, B \rangle$ are all equal, indicating with γ the common value, we have

$$\langle \psi_A | H | \psi_B \rangle = \gamma (1 + e^{-i\mathbf{k} \cdot \mathbf{a}_2} + e^{-i\mathbf{k} \cdot \mathbf{a}_1}) \quad (9)$$

Defining

$$f(\mathbf{k}) = 1 + 2e^{ik_x a} \cos(k_y b) \quad (10)$$

the hamiltonian matrix is

$$H(\mathbf{k}) = \begin{pmatrix} E_0 & \gamma f(\mathbf{k}) \\ \gamma f^*(\mathbf{k}) & E_0 \end{pmatrix} \quad (11)$$

1.1.3 Eigenvalues and eigenvectors

The linear equations to be solved are

$$\begin{pmatrix} E_0 & \gamma f(\mathbf{k}) \\ \gamma f^*(\mathbf{k}) & E_0 \end{pmatrix} \begin{pmatrix} C_A \\ C_B \end{pmatrix} = \varepsilon \begin{pmatrix} C_A \\ C_B \end{pmatrix} \quad (12)$$

where C_A and C_B are the coefficient weighting the two Bloch sums (3) of atoms A and B in the unit cell. The solution of Eq.(12) gives the following eigenvalues

$$\varepsilon(\mathbf{k}) = E_0 \pm \gamma |f(\mathbf{k})| \quad (13)$$

The two eigenvectors corresponding to the two eigenvalues for each \mathbf{k} can easily be obtained from (12) together with the normalization condition

$$|C_A|^2 + |C_B|^2 = 1 \quad (14)$$

The result corresponding to the band with the plus sign in (13), the conduction band, is

$$\begin{aligned} C_{A,c} &= \frac{f(\mathbf{k})}{|f(\mathbf{k})|} \frac{1}{\sqrt{2}} \\ C_{B,c} &= \frac{1}{\sqrt{2}} \end{aligned} \quad (15)$$

where the added the index c stands for *conduction*. The band with the minus sign in (13), the valence band, gives the eigenvector

$$\begin{aligned} C_{A,v} &= -\frac{f(\mathbf{k})}{|f(\mathbf{k})|} \frac{1}{\sqrt{2}} \\ C_{B,v} &= \frac{1}{\sqrt{2}} \end{aligned} \quad (16)$$

where the added index v stands for *valence*.

1.1.4 Reciprocal lattice

For studying the feature of the band structure (13) we need first to work out the graphene reciprocal lattice. From the Bravais lattice primitive vectors (1) it is easy to see that the reciprocal lattice primitive vectors are

$$\begin{aligned} \mathbf{A}_1 &= \frac{\pi}{a} \hat{\mathbf{x}} + \frac{\pi}{b} \hat{\mathbf{y}} \\ \mathbf{A}_2 &= \frac{\pi}{a} \hat{\mathbf{x}} - \frac{\pi}{b} \hat{\mathbf{y}} \end{aligned} \quad (17)$$

The reciprocal lattice together with the first Brillouin zone is shown in Fig.5. An important observation to be made is the following. As shown in Fig.5, the first Brillouin zone is a hexagon whose vertices coordinates are indicated in the same figure. The vertices with the same color are equivalent. Here equivalent means that any couple with the same color differ for a reciprocal vector. Let us consider, as an example, the points $(0, 2\pi/3b)$ and $(\pi/a, -\pi/3b)$. If we take the difference of the two vector pointing on these two vertices, we obtain $(-\pi/a, \pi/b)$ which is exactly $-\mathbf{A}_2$. The same is true for all the other pairs. The vertices of the first Brillouin zone are known as Dirac points, are often indicated as K points and they play, as we shall see, a very important role in many of the graphene properties.

1.1.5 Band structure

The overall band structure obtained by (13) is shown in Fig.6. In this figure the zero of the energy has been chosen in such a way that $E_0 = 0$ in (13). The lower band, that with negative energy, is completely full with electrons while the upper one is empty. The argument to see why the bands are filled up in this way is as follow. Since there are two atom per cell with four valence electrons each, if N is the number of primitive cell we need to place

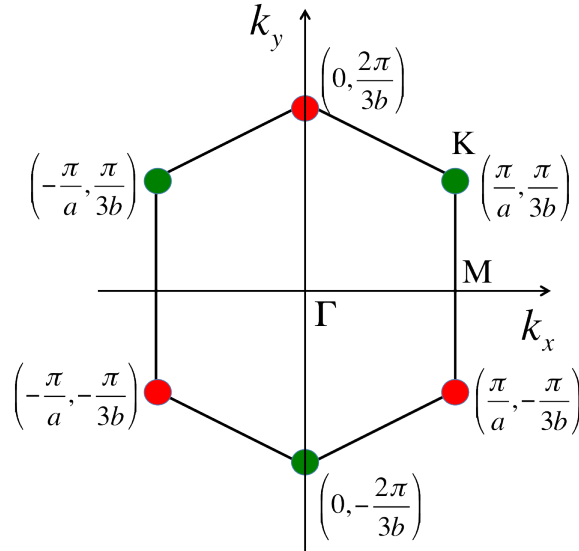


Figure 5: Graphene first Brillouin zone.

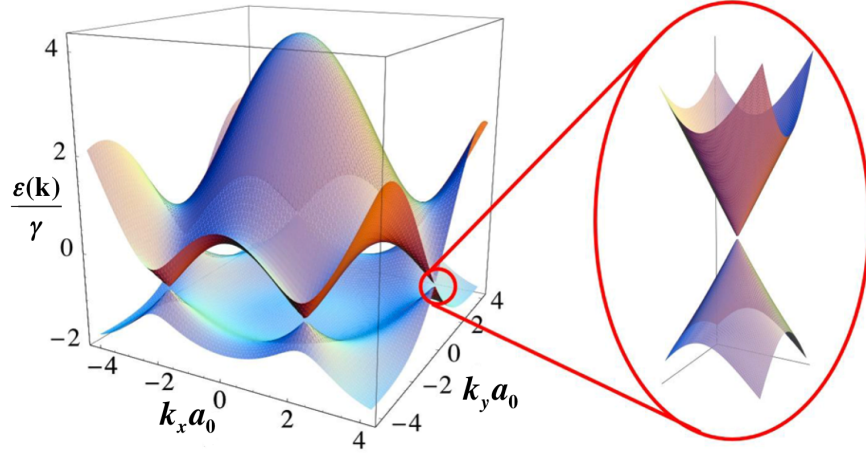


Figure 6: Graphene band structure represented as surfaces. The upper and lower bands touch each other at the Dirac points, the vertices of the first Brillouin zone.

8N electrons. As already argued, a tight binding calculation with 4 valence atomic orbitals for each atom in the primitive cell gives 8 bands. Three of them are related to the σ bonding (see Fig.3) and, taking into account the spin, are full with 6N electrons. Of the other two bands, the ones we are considering here, one is full with 2N electrons and the other is therefore empty. As a consequence, the low temperature Fermi level is at zero energy, that is, it is exactly placed at the touching point between the valence and conduction bands.

1.1.6 Metal or semimetal ?

It is well known that the classification of a material from the point of view of the conductivity can be done analyzing the band structure. In Fig.7 we show, very schematically, the most important cases. The band structure of panel (a) is typical of either a semiconductor or an insulator, the difference being just the amplitude of the principal gap. There is a full band and an empty one separated by an energy gap so that the Fermi level lies inside the gap. Panel (c) shows the band structure that is characteristic of a metal: the Fermi level cuts a band which is therefore partially full. Panel (b) shows the case of a semimetal. Its peculiar feature is that there are two bands that overlap in energy at two different \mathbf{k} values. This is, for instance, the case of Bismuth. Graphene can be classified as a semimetal because there are two bands that touch at the K points with the Fermi level just crossing

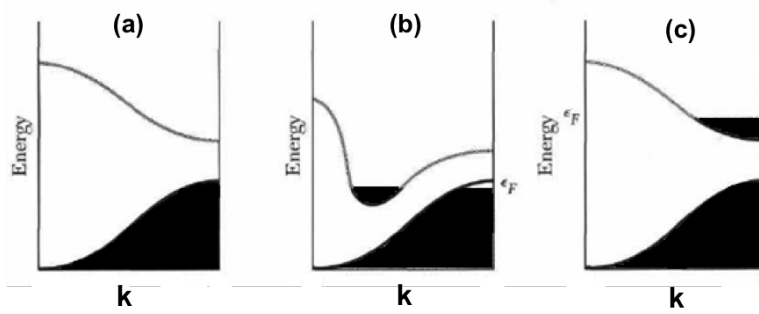


Figure 7: Schematics of the band structures of (a) a semiconductor, (b) a semimetal and (c) a metal. The shadowed portions correspond to filled band states.

them. However, this classification should not be considered in a strict sense because experiments show that in graphene the position of the Fermi level may depend on the substrate.

1.1.7 Dirac cone

Let us now analyze the graphene band structure near the vertices (K points) of the hexagonal first Brillouin zone of Fig.6. The interest in this analysis resides in the fact that it is on these points that the valence and conduction bands touch and, in addition, it is there that the Fermi level is placed. As first step let us calculate the K points coordinates shown in Fig.6. Clearly these are the zeros of $f(\mathbf{k})$. From (10) the zeros are the solution of

$$e^{ik_x a} \cos(k_y b) = -\frac{1}{2} \quad (18)$$

Since the right hand side of this equation is a real number, such must be the left hand side. This implies that $k_x a$ is either zero or a multiple of π . We need just $k_x a = 0$ and $k_x a = \pi$. In the first case Eq.(18) is satisfied when $k_y = \pm 2\pi/3b$ while in the second we have $k_y = \pm\pi/3b$. These points are exactly those shown in Fig.5.

For looking at the bands near the K points, we need to calculate the Taylor expansion of $f(\mathbf{k})$ around those points. Let us take, for instance, the point $(0, 2\pi/3b)$. Here it comes a subtlety which need to be discussed. In general, for calculating the Taylor expansion around a given point, we need the values of the function and of its derivatives in a circle centered on that point. In our case this means that we need to go out of the first Brillouin

zone, at least partially. However, we have seen that the six K points of Fig.5 are equivalent in groups of three so that the parts that lie within the first zone around two points of a group can be folded outside as shown by Fig.8. With this procedure, we can complete a circle around a K point and proceed with the Taylor expansion. Around the point A of Fig.8 we have

$$f(k_x, k_y) = f\left(0, \frac{2\pi}{3b}\right) + \left.\frac{\partial f}{\partial k_x}\right|_{0, \frac{2\pi}{3b}} (k_x - 0) + \left.\frac{\partial f}{\partial k_y}\right|_{0, \frac{2\pi}{3b}} \left(k_y - \frac{2\pi}{3b}\right) \quad (19)$$

For the derivatives we have

$$\left.\frac{\partial f}{\partial k_x}\right|_{0, \frac{2\pi}{3b}} = -ia$$

$$\left.\frac{\partial f}{\partial k_y}\right|_{0, \frac{2\pi}{3b}} = -b\sqrt{3}$$

and from this we have

$$f(k_x, k_y) = -iak_x - b\sqrt{3} \left(k_y - \frac{2\pi}{3b}\right) \quad (20)$$

Recalling the definition (2) and considering that we can always shift the origin of the reciprocal space on the K point, the above equation becomes

$$f(k_x, k_y) = -\frac{3a_0}{2} (ik_x + k_y) \quad (21)$$

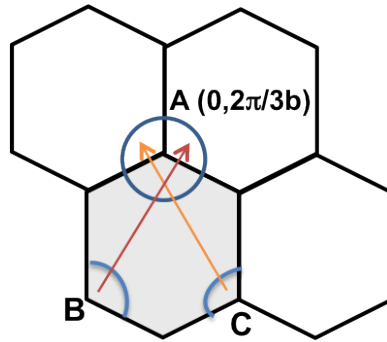


Figure 8: Folding of two equivalent points in the first Brillouin Zone for completing a circle around the third point.

From (13) and (21) we have

$$\varepsilon(k_x, k_y) = \pm \gamma \frac{3a_0}{2} |ik_x + k_y| = \pm \frac{3a_0}{2} \gamma \sqrt{k_x^2 + k_y^2}$$

The final result is therefore

$$\varepsilon(\mathbf{k}) = \pm \frac{3}{2} a_0 \gamma |\mathbf{k}| \quad (22)$$

Around the K point we have a dispersion relation in which the energy is proportional to the amplitude of \mathbf{k} . A similar energy-wave vector dependence occurs for the acoustic phonons of large wavelength and for photons. Electrons near the K points have a vanishing effective mass.

We can, in any case, calculate the group velocity. From (22) we get

$$\begin{cases} v_x = \frac{1}{\hbar} \frac{\partial \varepsilon}{\partial k_x} = \frac{3a_0\gamma}{2\hbar} \frac{k_x}{\sqrt{k_x^2 + k_y^2}} \\ v_y = \frac{1}{\hbar} \frac{\partial \varepsilon}{\partial k_y} = \frac{3a_0\gamma}{2\hbar} \frac{k_y}{\sqrt{k_x^2 + k_y^2}} \end{cases} \quad (23)$$

The velocity modulus is

$$v_F = \frac{3a_0\gamma}{2\hbar} \quad (24)$$

With the numerical values $\gamma = 3.033$ eV, $a_0 = 0.14$ nm the velocity is $v_F = 9.7 \times 10^7$ cm/sec. We can then rewrite (22) as

$$\varepsilon(\mathbf{k}) = \pm \hbar v_F |\mathbf{k}| \quad (25)$$

The surface of constant energies are therefore two cones touching at the K point as depicted in Fig.9

1.1.8 Density of states

The density of states is defined as the number of electronic states per unit energy. It can be calculated from

$$D(E) = \sum_{\mathbf{k}} \delta(E - \varepsilon(\mathbf{k})) \quad (26)$$

where the sum over \mathbf{k} must be done in the first Brillouin zone. Let us consider a piece of graphene of length L and width W as shown in Fig.10. Since the graphene layer is made of a large number of unit cells, we can

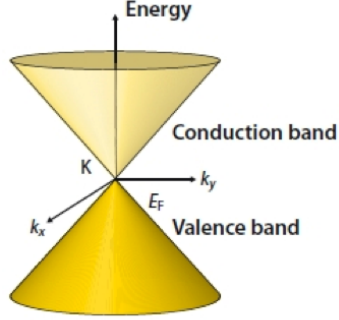


Figure 9: The Dirac cones.

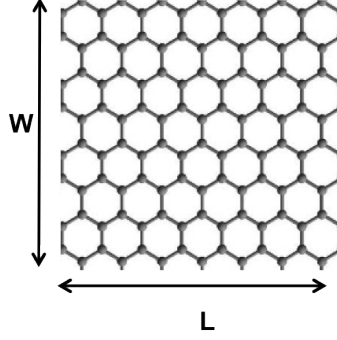


Figure 10: A portion of graphene of length L and width W . Periodic boundary condition are imposed on both the length and the width.

transform the sum into an integral

$$D(E) = \frac{WL}{(2\pi)^2} \int \delta(E - \varepsilon(\mathbf{k})) dk_x dk_y \quad (27)$$

Since the energy depends only on the amplitude of \mathbf{k} and not on its direction, it is convenient to rewrite the integral using polar coordinate

$$D(E) = \frac{WL}{(2\pi)^2} \int_0^{2\pi} d\theta \int_0^{k_0} k dk \delta(E - \varepsilon(k)) \quad (28)$$

In writing this integral we are replacing the hexagonal first Brillouin zone with a circle of radius k_0 chosen in such a way that the circle area is equal

to that of hexagonal first Brillouin zone. From (28) we have

$$D(E) = \frac{WL}{2\pi} \int_0^{k_0} k dk \delta(E - \varepsilon(k))$$

We can now do a change of variables from k to the energy ε using (25)

$$D(E) = \frac{WL}{2\pi} \frac{1}{(\hbar v_F)^2} \int_0^{\varepsilon_0} \varepsilon \delta(E - \varepsilon) d\varepsilon$$

where $\varepsilon_0 = \hbar v_F k_0$. Because of the properties of the δ function, the above integral has a non vanishing contribution only when $0 \leq E \leq \varepsilon_0$. Moreover, we have to multiply by a factor of two due to the electronic spin plus another factor of two due to the second non equivalent K point in the first Brillouin zone. The bottom line is

$$D(E) = \frac{2WL}{\pi(\hbar v_f)^2} |E| \quad (29)$$

The modulus in this equation accounts for the valence and conduction bands. The density of states is proportional to the energy and as shown in Fig. 11.

1.1.9 Electron density

If a graphene layer is suspended, that is, is not in direct contact with a substrate, the Fermi level E_F crosses the K point. However, if there is a contact with the substrate and/or a gate potential, E_F can either go in the valence band or into the conduction band. These shift of E_F is related to the transfer of charges between the graphene layer and the substrate.

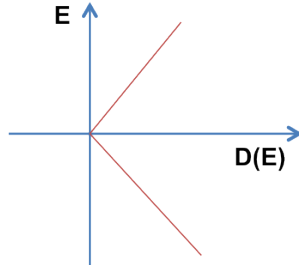


Figure 11: The graphene density of states.

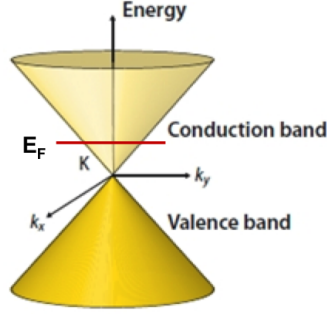


Figure 12:

Let us consider the case in which electrons move from the substrate to graphene. In this case E_F crosses the conduction band as shown in Fig. 12. At very low temperature (formally at $T = 0$) the number of electrons in the conduction band is given by

$$N = \int_0^{E_F} D(E) dE \quad (30)$$

With the density of states (29) it is easy to see that the electron density n is

$$n = \frac{N}{WL} = \frac{E_F^2}{\pi(\hbar v_F)^2} \quad (31)$$

The fact that the electron density is proportional to the square of E_F is a peculiarity of the linearity of the density of states with the energy. It is not due to the graphene two-dimensional nature. For appreciating this point, let us calculate the electron density of a two-dimensional crystal with a standard quadratic $\varepsilon(k)$ band

$$\varepsilon(k) = E_0 + \frac{\hbar^2 k^2}{2m^*} \quad (32)$$

where m^* is the effective mass. It is easy to see that the density of states of (32) is

$$D(E) = \begin{cases} 0 & \text{if } E < E_0 \\ \frac{LW}{2\pi} \frac{m^*}{\hbar^2} & \text{if } E \geq E_0 \end{cases} \quad (33)$$

We see that in this case $D(E)$ is constant rather than proportional to E . With this density of states, the electron concentration is given by

$$n = \frac{m^*}{2\pi\hbar^2} (E_F - E_0) \quad (34)$$

This shows that now n is proportional to E_F .

1.2 Graphene light absorption

An interesting feature of graphene has to do with its opacity to visible light. As the experimental data of Fig.13 shows, the absorption of light is very low: only about 2.3% of the incident light is absorbed. But there is more than this; the absorption coefficient does not depend on the material parameters being proportional to the fine structure constant. Moreover, if light is transmitted through multilayer graphene, the overall absorption is just that of a single layer multiplied by the number of layer. This intriguing features deserves some discussion and this is the aim of this section.

1.2.1 The absorption coefficient

The ratio between the incident power I (energy per unit time) of the electromagnetic field and the absorbed power I_a at a fixed frequency is, by definition, the absorption coefficient η

$$\eta = \frac{I_a}{I} \quad (35)$$

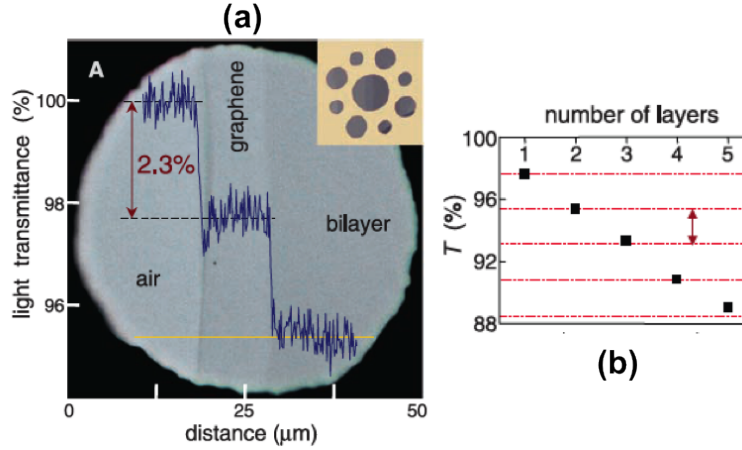


Figure 13: Panel (a): Visible light transmission through single and bilayer graphene. Panel (b): The light transmission through multilayer graphene is just an integer multiple of that of a single layer (Taken from: Science 320, 1308 (2008))

Let us discuss in some more detail (35). For the incident electromagnetic power I we can reason as follows. The total number of photons arriving on a surface of area S in the time interval t in the direction normal to the surface is

$$N_f = ctSn_f \quad (36)$$

where c is the speed of light and n_f is the average (with respect to time) number of photons per unit volume. Dividing N_f by t and multiplying by the energy $\hbar\omega$ of a single photon we obtain the incident power

$$I = cSn_f\hbar\omega \quad (37)$$

whose dimensions are J/sec . Let us now consider an electric plane wave of the form

$$\mathbf{E} = \hat{\mathbf{e}}E_0\cos(\mathbf{k} \cdot \mathbf{r} - \omega t) \quad (38)$$

where $\hat{\mathbf{e}}$ is the polarization direction. The energy density² is $\epsilon_0|E|^2$. From (38) it results that the time average over one period is $\epsilon_0|E_0|^2/2$ so that the time averaged number of photon per unit volume is $n_f = \epsilon_0|E_0|^2/2\hbar\omega$. We can therefore rewrite (37) as

$$I = c\frac{\epsilon_0|E_0|^2}{2}S \quad (39)$$

For the calculation of I_a we have to consider that an elementary absorption process consists in a electron transition from an initial state $|m\rangle$ to a final state $|n\rangle$. Quantum mechanics dictates that this process occurs with a probability per unit time P . The absorbed power is therefore

$$I_a = \hbar\omega P \quad (40)$$

The fact that I_a is a power comes from the dimensions of P which are sec^{-1} .

For computing the probability P , we need the interaction energy between the field and the electrons. It can be shown that this interaction is³

$$H_{em} = \frac{e}{m}\mathbf{A} \cdot \mathbf{p} \quad (41)$$

where e is the electron charge, \mathbf{p} is the electron momentum operator and \mathbf{A} is the vector potential whose connection to \mathbf{E} is

$$\mathbf{E} = -\frac{\partial \mathbf{A}}{\partial t} \quad (42)$$

²The electromagnetic total energy density in vacuum is $\epsilon_0|E|^2/2 + |B|^2/2\mu_0$. But for a plane wave $B = E\sqrt{\epsilon_0\mu_0}$ so that the total energy density is $\epsilon_0|E|^2$.

³Here we use a gauge in which $\nabla \cdot \mathbf{A} = 0$

For a plane wave we have

$$\mathbf{A} = \hat{\mathbf{e}} A_0 \sin(\mathbf{k} \cdot \mathbf{r} - \omega t) \quad (43)$$

From (38) and (42) it is evident that

$$A_0 = \frac{E_0}{\omega} \quad (44)$$

It can be shown⁴ that the transition probability P per unit time from the initial state $|m\rangle$ to the final state $|n\rangle$ take the form

$$P = \frac{2\pi}{\hbar} \left(\frac{eA_0}{2m} \right)^2 |\langle n | \hat{\mathbf{e}} \cdot \mathbf{p} | m \rangle|^2 \delta(E_n - E_m - \hbar\omega) \quad (45)$$

Note that the presence of the delta function guarantees the energy conservation.

1.2.2 Transition probability in graphene.

In graphene, as well as in any crystal, we have a band structure so that there are many transitions possible from a band to another. The overall transition probability per unit time is a sum over all the states belonging to the two bands involved

$$P = \frac{2\pi}{\hbar} \left(\frac{eA_0}{2m} \right)^2 \sum_{\mathbf{k}} |\langle \psi_{\mathbf{k},c} | \hat{\mathbf{e}} \cdot \mathbf{p} | \psi_{\mathbf{k},v} \rangle|^2 \delta(E_c(\mathbf{k}) - E_v(\mathbf{k}) - \hbar\omega) \quad (46)$$

Note that this formula is very general and holds for any crystal in which we consider optical transitions between a valence band $E_v(\mathbf{k})$ and a conduction band $E_c(\mathbf{k})$. If the transitions occur at finite temperature and/or in the presence of doping, it may be important to include the occupation probabilities as given by the Fermi-Dirac distribution function. We will not treat this complication here. We just assume that the transitions always involve an occupied initial (valence) state and a final unoccupied (conduction state).

We have seen in §1.1.3 that the valence and conduction states in graphene are

$$\psi_{\mathbf{k},c} = C_{A,c} \psi_A + C_{B,c} \psi_B \quad (47)$$

$$\psi_{\mathbf{k},v} = C_{A,v} \psi_A + C_{B,v} \psi_B \quad (48)$$

⁴See chapter 11 of Kuno for a derivation

where the coefficients $C_{A,c}$ and $C_{B,c}$ are given by (15) while $C_{A,v}$ and $C_{B,v}$ are given by (16). For computing the transition probability we therefore need the momentum matrix elements between the Bloch sums (3)

$$\langle \psi_\alpha | \hat{\mathbf{e}} \cdot \mathbf{p} | \psi_\beta \rangle \quad (49)$$

Within the Tight Binding scheme, it can be proved that such matrix elements are given by the derivative with respect to \mathbf{k} of the corresponding hamiltonian matrix elements. For instance

$$\langle \psi_\alpha | p_x | \psi_\beta \rangle = \frac{m}{\hbar} \frac{\partial}{\partial k_x} H_{\alpha,\beta}(\mathbf{k}) \quad (50)$$

where, of course, ψ_α and ψ_β are, in our case, given by (3). In general we can write

$$\langle \psi_\alpha | \mathbf{p} | \psi_\beta \rangle = \frac{m}{\hbar} \nabla_{\mathbf{k}} H_{\alpha,\beta}(\mathbf{k}) \quad (51)$$

Form (11), (21) and (25) we can rewrite the hamiltonian matrix near the K point as

$$H(\mathbf{k}) = -\hbar v_F \begin{pmatrix} 0 & ik_x + k_y \\ -ik_x + k_y & 0 \end{pmatrix} \quad (52)$$

where, as usual, we are setting $E_0 = 0$. From now on we assume the vector potential as oriented along di $\hat{\mathbf{x}}$ direction so that, from (50) the momentum matrix elements are

$$p_x = -mv_F \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix} \quad (53)$$

We are now ready to write the p_x matrix elements between the graphene band states (47) and (48). As a first step we have

$$\langle \psi_{\mathbf{k},c} | p_x | \psi_{\mathbf{k},v} \rangle = C_{A,c}^* C_{B,v} \langle \psi_A | p_x | \psi_B \rangle + C_{A,v}^* C_{B,c} \langle \psi_B | p_x | \psi_A \rangle \quad (54)$$

where we have made use of the fact that the diagonal elements of p_x are zero as shown by (53). Since the coefficients $C_{A,c}$, $C_{B,c}$, $C_{A,v}$ and $C_{B,v}$ are given by (15) and (16), we need an expression for $f(\mathbf{k})/|f(\mathbf{k})|$. From (21) we have immediately an expression of this ratio near the K point

$$\frac{f(\mathbf{k})}{|f(\mathbf{k})|} = -\frac{ik_x + k_y}{\sqrt{k_x^2 + k_y^2}} \quad (55)$$

so that

$$\begin{aligned} C_{A,c} &= -\frac{ik_x + k_y}{k} \frac{1}{\sqrt{2}} \\ C_{B,c} &= \frac{1}{\sqrt{2}} \\ C_{A,v} &= \frac{ik_x + k_y}{k} \frac{1}{\sqrt{2}} \\ C_{B,v} &= \frac{1}{\sqrt{2}} \end{aligned} \quad (56)$$

Substituting (53) and (56) into (54) we have the following final result

$$\langle \psi_{\mathbf{k},c} | p_x | \psi_{\mathbf{k},v} \rangle = imv_F \frac{k_y}{k} \quad (57)$$

We can substitute this matrix element into the transition probability (46)

$$P = \frac{2\pi}{\hbar} \left(\frac{eA_0 v_F}{2} \right)^2 \sum_{\mathbf{k}} \left(\frac{k_y}{k} \right)^2 \delta(E_c(\mathbf{k}) - E_v(\mathbf{k}) - \hbar\omega) \quad (58)$$

1.2.3 Absorbed energy

Because of the periodic boundary conditions and of the "macroscopic" size of the graphene layer, we can transform the sum on \mathbf{k} in (58) into an integral with the rule $\sum_{\mathbf{k}} \rightarrow \frac{S}{(2\pi)^2} \int$. Using, for convenience, polar coordinates we get

$$P = \frac{2\pi}{\hbar} \left(\frac{eA_0 v_F}{4\pi} \right)^2 S \int_0^{k_0} k dk \int_0^{2\pi} d\theta \left(\frac{k_y}{k} \right)^2 \delta(E_c(\mathbf{k}) - E_v(\mathbf{k}) - \hbar\omega) \quad (59)$$

Integrating over θ we have

$$P = \frac{e^2 A_0^2 v_F^2 S}{8\hbar} \int_0^{k_0} k \delta(2\hbar v_F k - \hbar\omega) dk \quad (60)$$

In this equation we have inserted in the δ function argument the bands (25). The final integration over k gives

$$P = \frac{e^2 A_0^2 \omega}{32\pi \hbar^2} S \quad (61)$$

so that the absorbed power is

$$I_a = \hbar\omega P = \frac{e^2 A_0^2 \omega^2}{32\hbar} \quad (62)$$

With (35), (39) and (62) we finally have the absorption coefficient

$$\eta = \frac{e^2}{4\pi\epsilon_0 c \hbar} \frac{\pi}{4} \quad (63)$$

Since the fine structure constant is defined as $\alpha = e^2/4\pi\epsilon_0 c \hbar$ and accounting for a factor of 2 due to spin and another factor of 2 for the two equivalent K points, we can rewrite (63) as

$$\eta = \pi\alpha \quad (64)$$

This is our fundamental result.

1.2.4 Transmitted power

The energy balance between the incident, reflected and absorbed power is

$$I = I_a + I_t + I_r \quad (65)$$

where I_t and I_r are, respectively, the transmitted and reflected powers. Since graphene practically does not reflect light, $I_r \simeq 0$. Taking into account the definition (35) of the absorption coefficient, (65) becomes

$$I = \eta I + I_t \quad (66)$$

Defining the transmission coefficient as

$$T = \frac{I_t}{I} \quad (67)$$

from (67) we have

$$T = 1 - \eta = 1 - \pi\alpha \quad (68)$$

Since the value of the fine structure constant is $1/137$, from (69) the transmission is $T = 0.977$ that does agree very well with the data of Fig.13.

1.2.5 Why is it ?

At this point one should ask why is it that the transmission depends only on the fundamental constant α . It is not easy to answer this question. We can, however, do an analysis computing the absorption coefficient of a two dimensional crystal with a parabolic rather than linear $E(\mathbf{k})$. After all, this is the main feature of graphene. In Fig.14 we show a pair of parabolic bands separated by a gap E_g . Let us calculate η . The hamiltonian matrix leading to the bands depicted in Fig.14 can be written in a form similar to (11)

$$H(\mathbf{k}) = \begin{pmatrix} 0 & f(\mathbf{k}) \\ f(\mathbf{k}) & 0 \end{pmatrix} \quad (69)$$

where now

$$f(\mathbf{k}) = \frac{E_g}{2} + \frac{\hbar^2}{2m}(k_x^2 + k_y^2) \quad (70)$$

The bands are given by $E = \pm f(\mathbf{k})$. The wave function coefficients are still given by (15) and (16) but now $f(\mathbf{k})/|f(\mathbf{k})| = 1$. From (50) the momentum matrix element is just $\hbar k_x$ so that the transition probability (58) now is

$$P = \frac{2\pi}{\hbar} \left(\frac{eA_0}{2m} \right)^2 \sum_{\mathbf{k}} (\hbar k_x)^2 \delta(E_c(\mathbf{k}) - E_v(\mathbf{k}) - \hbar\omega) \quad (71)$$

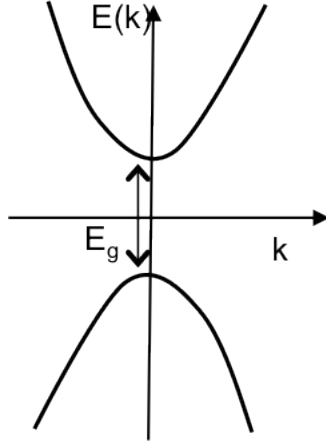


Figure 14: Parabolic bands separated by a gap E_g

With passages similar to that leading to (60) we have

$$P = \frac{\hbar e^2 A_0^2 S}{8m^2} \int_0^{k_0} k^3 \delta \left(E_g + \frac{\hbar^2 k^2}{m} - \hbar\omega \right) dk \quad (72)$$

The integration over k gives

$$P = \frac{e^2 A_0^2 \omega S}{16\hbar^2} \left(1 - \frac{E_g}{\hbar\omega} \right) \quad (73)$$

where, because of the presence of the gap E_g , it must be $\hbar\omega \geq E_g$. The absorbed energy is

$$I_a = \hbar\omega P = \frac{e^2 A_0^2 \omega^2 S}{16\hbar} \left(1 - \frac{E_g}{\hbar\omega} \right) \quad (74)$$

Taking into account the spin, the absorption coefficient for a single valley is

$$\eta = \alpha\pi \left(1 - \frac{E_g}{\hbar\omega} \right) \quad (75)$$

Note that if $E_g = 0$ then $\eta = \alpha\pi$. This is quite interesting because it shows that the fact that in graphene η is proportional to the fine structure constant α is *not* a consequence of the linear $E(\mathbf{k})$ relation but rather a direct consequence of dimensionality.