The $k \cdot p$ method and its application to graphene, carbon nanotubes and graphene nanoribbons: the Dirac equation

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Summary. — The $k \cdot p$ method is a semi-empirical approach which allows to extrapolate the band structure of materials from the knowledge of a restricted set of parameters evaluated in correspondence of a single point of the reciprocal space. In the first part of this review article we give a general description of this method, both in the case of homogeneous crystals (where we consider a formulation based on the standard perturbation theory, and Kane’s approach) and in the case of non-periodic systems (where, following Luttinger and Kohn, we describe the single-band and multi-band envelope function method and its application to heterostructures). The following part of our review is completely devoted to the application of the $k \cdot p$ method to graphene and graphene-related materials. Following Ando’s approach, we show how the application of this method to graphene results in a description of its properties in terms of the Dirac equation. Then we find general expressions for the probability density and the probability current density in graphene and we compare this formulation with alternative existing representations. Finally, applying proper boundary conditions, we extend the treatment to carbon nanotubes and graphene nanoribbons, recovering their fundamental electronic properties.

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1. Introduction

To understand the physical properties of semiconductors it is necessary to know their electronic band structure, i.e. the behavior of energy as a function of the wave vector $k$ in the reciprocal lattice of the crystal. Several numerical methods can be successfully applied to find the band structure and the corresponding wave functions, such as the tight binding, the pseudopotential, the orthogonalized plane wave, the augmented plane wave, the Green’s function and the cellular methods [1-3]. These methodologies can yield the desired results throughout the $k$-space.

Many phenomena, for example in the study of electrical transport (due to both electrons and holes) and of optical properties (such as absorption or gain due to electronic transitions caused by an incident optical wave), involve only the top of the valence band and the bottom of the conduction band. Indeed, low-energy electrons and holes are situated in these regions and also electronic transitions occur near the band edges of direct band gap semiconductors. Therefore a technique to obtain the band structure in such regions is of great interest.

The $k \cdot p$ method [4-27] allows to extrapolate the band structure of materials from the knowledge of a restricted set of parameters (a limited number of energy gaps and of momentum matrix elements between band lattice functions), evaluated in correspondence of a single point $k_0$ of the reciprocal space, which are generally treated as fitting parameters, that can be obtained from experiments or ab initio calculations. Even though, considering quite a large number of bands and thus of parameters, the $k \cdot p$ method can be used to obtain the band structure all over the Brillouin zone of the material [28-32], its primary use is to explore with great detail the dispersion relations around the considered point $k_0$. In particular, it allows to obtain the band structure of materials in the regions of the reciprocal space near the band extrema, expanding the eigenvalues and eigenvectors of the single-electron Hamiltonian as a function of $k$ around the wave vector $k_0$ corresponding to the band maximum or minimum. It has been shown to be very useful to study structures containing a large number of atoms, for which atomistic approaches would be computationally too expensive.

This method, first introduced by J. Bardeen [33] and F. Seitz [34], was developed and adopted by W. Shockley [35] and G. Dresselhaus, A. F. Kip and C. Kittel [36] in well-known papers on the energy band structures of semiconductors. It received a general formulation with E. O. Kane [10-12,37-39] and with J. M. Luttinger and W. Kohn [40,41]. It was later applied to strained materials (by G. E. Pikus and G. L. Bir [14]) and to heterostructures (for example by G. Bastard [42-44], M. Altarelli [45-47] and M. G.
Burt [48-53]), proving to be a very useful and straightforward way to study the local properties of materials.

In the last few years, a significant theoretical and experimental effort has been devoted to the study of graphene and graphene-related materials, which appear as promising candidates for many technological applications and are characterized by very unusual and interesting physical properties. In particular, the application of the \( k \cdot p \) method to the study of the electronic properties of graphene, systematically pursued by T. Ando [54-56] and other authors, results in a description of the graphene properties in terms of the Dirac equation, the same relation that describes the relativistic behavior of elementary spin-(1/2) particles. This is at the basis of the experiments aiming to observe in graphene, at non-relativistic speeds, the analogous of purely relativistic quantum phenomena [57-61]. The application of proper boundary conditions to the relations found for a sheet of graphene allows to obtain the electronic properties of carbon nanotubes and graphene nanoribbons, materials which (contrary to unconfined graphene) can exhibit (depending on their geometrical details) a non-zero energy gap.

The first part of this review is a short introduction to the \( k \cdot p \) method in some of its most common formulations.

In particular, sect. 2 describes the application of the \( k \cdot p \) method to homogeneous crystals, where, due to the periodicity of the material, the electron wave functions are Bloch functions and thus the unperturbed Bloch lattice functions are adopted as a basis for the method. We first describe (following W. T. Wenkebach [5]) how the \( k \cdot p \) approach can be derived by just applying the standard perturbation theory to the Schrödinger-Bloch equation and how this formulation can be adopted to study the dispersion relations of semiconductors with the diamond or zincblende structure. Then we briefly summarize the alternative formulation by Kane, consisting in the exact diagonalization of the Schrödinger-Bloch Hamiltonian for a subset of bands, and in the inclusion of the effect of the other energy bands with the Löwdin perturbation theory.

In sect. 3, instead, we describe how the \( k \cdot p \) method can be applied to the case of non-periodic systems, where the phase factor (involving the wave vector measured from the considered extremum point) of the Bloch lattice functions has to be replaced by properly defined envelope functions. Following J. M. Luttinger and W. Kohn, we derive the single-band and multi-band envelope function equations, and then we briefly outline the main approaches followed in the application of the envelope function theory to the study of heterostructures.

The second part of the review is devoted to the application of the \( k \cdot p \) method, and in particular of the envelope function approach, to graphene, carbon nanotubes and graphene nanoribbons.

In sect. 4, following T. Ando, we perform a first-order expansion of a simple tight-binding description of graphene, obtaining the Dirac equation for the envelope functions (corresponding to the two degeneration points of graphene) in the presence of a generic external potential, and we analytically solve this equation for the case of null potential. Starting from this formulation, we also derive general expressions for the probability density and for the probability current density in graphene, and we compare them with those used, adopting a valley-isotropic representation, by C. W. J. Beenakker et al. [62, 61].

In sect. 5 we extend the previous treatment to the study of carbon nanotubes, enforcing a periodic boundary condition along the chiral vector, that univocally characterizes these tubules. In particular, we show how this periodic condition on the overall wave function translates in terms of the envelope functions, and we analytically solve the
Dirac problem in the absence of an external potential, obtaining the conditions for which nanotubes have a semiconducting or a metallic behavior.

Finally, in sect. 6 we discuss the case of graphene nanoribbons. Adapting the approach adopted by L. Brey and H. A. Fertig [63,64] to the mathematical formulation of graphene proposed by T. Ando, we study both zigzag and armchair nanoribbons, obtaining an analytical solution in the absence of an external potential, and recovering the fundamental properties of these structures.

2. – The $k \cdot p$ method in homogeneous crystals: derivation based on the standard perturbation theory and Kane’s model

We begin our overview of the $k \cdot p$ method describing its formulation in the case of homogeneous crystals.

In a pure crystal an electron is subject to a periodic potential energy

$$U_L(r) = U_L(r + R),$$

with $R$ any linear combination of the lattice vectors, and thus also the Hamiltonian is invariant under translation by the lattice vectors. Therefore, if $\psi^a_k(r)$ is the wave function of an electron moving in the crystal, also $\psi^a_k(r + R)$ will be a solution of the Schrödinger equation and therefore will coincide with $\psi^a_k(r)$, apart from a constant with unit modulus (otherwise the wave function could grow to infinity, if we repeated the translation $R$ indefinitely). Thus the general form of the electron wave functions will be

$$\psi^a_k(r) = e^{ik \cdot r} u^a_k(r),$$

where $\psi^a_k(r)$ is usually called “Bloch function”, while $u^a_k(r)$ is called “Bloch lattice function” and is periodic with the lattice periodicity

$$u^a_k(r + R) = u^a_k(r)$$

(Bloch’s theorem) [65].

Starting from the Schrödinger equation (in the absence of a magnetic field) for $\psi^a_k(r)$

$$H^{(0)} \psi^a_k(r) = E^n_k \psi^a_k(r),$$

with (in the absence of a magnetic field)

$$H^{(0)} = -\frac{\hbar^2}{2m_e} \nabla^2 + U_L(r)$$

(where $m_e$ is the electron mass and $\hbar$ is the reduced Planck constant) and substituting
\( \psi_k^n(r) \) with the generic expression of the Bloch function, we obtain

\[
\left( -\frac{\hbar^2}{2m_e} \nabla^2 + U_L(r) \right) e^{ik \cdot r} u_k^n(r) = \]

\[
-\frac{\hbar^2}{2m_e} \nabla \cdot \left( e^{ik \cdot r} (\nabla u_k^n(r)) + (\nabla e^{ik \cdot r}) u_k^n(r) + U_L(r) e^{ik \cdot r} u_k^n(r) \right) = \]

\[
\frac{\hbar^2}{2m_e} \left( e^{ik \cdot r} \nabla \cdot (\nabla u_k^n(r) + i k u_k^n(r)) + U_L(r) e^{ik \cdot r} u_k^n(r) \right) = \]

and thus

\[
(7) \quad H u_k^n(r) = (H^{(0)} + H^{(1)}) u_k^n(r) = E_k^n u_k^n(r), \]

with

\[
(8) \quad H^{(1)} = -\frac{i \hbar^2}{m_e} k \cdot \nabla + \frac{\hbar^2 k^2}{2m_e} \]

(where \( k = |k| \)). What we have just obtained is clearly an equation for the Bloch lattice functions (the Schrödinger-Bloch equation), which needs to be solved only for a single primitive cell with the boundary condition that the function \( u_k^n(r) \) must be periodic with the lattice periodicity. For each value of \( k \) this equation has a periodic solution only for selected values \( E_k^n \) of the energy \( E \). Noting that \( H^{(1)}(r) \) reduces to zero when \( k \) approaches 0 and thus that this part of the Hamiltonian can be treated as a perturbation around \( k = 0 \), we can locally solve this equation using the time-independent perturbation theory, assuming to know the eigenfunctions and eigenvalues of \( H^{(0)}(r) \), i.e. the Bloch lattice functions and the energy band values for \( k = 0 \).

For most of the semiconductors the maximum of the valence band is in the Γ-point (the center of the first Brillouin zone represented with the Wigner-Seitz method) and therefore corresponds to \( k = 0 \); the minimum of the conduction band instead is for \( k = 0 \) only for direct-gap semiconductors. When the extremum point of the energy band
we have that the value of $H$ (and thus the interesting region) is for a generic $k_0$, we can easily extend this argument observing that, if we define the value of $H$ in $k_0$ as

\begin{equation}
H_{k_0} = H^{(0)} - i \frac{h^2}{m_e} k_0 \cdot \nabla + \frac{h^2 k_0^2}{2 m_e},
\end{equation}

we have that the value of $H$ in $k$ is

\begin{equation}
H = H^{(0)} + H^{(1)} = H_{k_0} + \left[ - i \frac{h^2}{m_e} (k - k_0) \cdot \nabla + \frac{h^2}{2 m_e} (k^2 - k_0^2) \right] =
\end{equation}

and for $k$ near $k_0$ the term between square brackets can be treated as a perturbation of $H_{k_0}$ [10]. For the sake of simplicity, in the following we will consider $k_0 = 0$.

An important point to notice is that, for any selected $k$, the functions $u_n^k(r)$ form an orthogonal and complete set (in the restricted sense that any function with the lattice periodicity can be expanded in terms of the Bloch lattice functions corresponding to the selected $k$).

To describe the main results of time-independent perturbation theory [66,67], we have to distinguish the case in which the unperturbed energy levels are non-degenerate from the case in which such a degeneration exists (in the following we will use the notation of W. T. Wenckebach [66]). Let us begin from the first case. The problem we have to solve is

\begin{equation}
[H^{(0)} + H^{(1)}]|n\rangle = E_n |n\rangle,
\end{equation}

where $H^{(0)}$ is the unperturbed Hamiltonian and $H^{(1)}$ the perturbation. If we expand the eigenvalues $E_n$ and the eigenfunctions $|n\rangle$:

\begin{equation}
E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)} + \cdots,
\end{equation}

\begin{equation}
|n\rangle = |n\rangle^{(0)} + |n\rangle^{(1)} + |n\rangle^{(2)} + \cdots,
\end{equation}

we insert these expressions into the eigenvalue equation, and we enforce the identity
between terms of the same order, we find

\[ \begin{align*}
H^{(0)}|n\rangle^{(0)} &= E_n^{(0)}|n\rangle^{(0)}, \\
H^{(0)}|n\rangle^{(1)} + H^{(1)}|n\rangle^{(0)} &= E_n^{(0)}|n\rangle^{(1)} + E_n^{(1)}|n\rangle^{(0)}, \\
H^{(0)}|n\rangle^{(2)} + H^{(1)}|n\rangle^{(1)} &= E_n^{(0)}|n\rangle^{(2)} + E_n^{(1)}|n\rangle^{(1)} + E_n^{(2)}|n\rangle^{(0)}, \\
&\quad \ldots .
\end{align*} \]

The first equation corresponds to the unperturbed eigenvalue equation, the solutions of which, \( E_n^{(0)} \equiv E_0^n \) and \( |n\rangle^{(0)} \equiv |n0\rangle \), are assumed to be known. From the other equations, instead, we can obtain the corrections to these values produced by the perturbation \( H^{(1)} \).

In particular, if we stop to the first-order corrections for the eigenfunctions and to the second-order corrections for the eigenvalues we find

\[ \begin{align*}
|n\rangle &\approx |n0\rangle + |n\rangle^{(1)} = |n0\rangle + \sum_{m \neq n} \left( |m0\rangle \frac{\langle m0|H^{(1)}|n0\rangle}{E_0^n - E_0^m} \right), \\
E_n &\approx E_0^n + E_n^{(1)} + E_n^{(2)} = E_0^n + \langle n0|H^{(1)}|n0\rangle \\
&\quad + \sum_{m \neq n} \left( \frac{\langle n0|H^{(1)}|m0\rangle \langle m0|H^{(1)}|n0\rangle}{E_0^n - E_0^m} \right).
\end{align*} \]

When we examine degenerate unperturbed states, the expressions we have just found diverge and thus we have to modify our treatment. In particular, if the degenerate energy level \( E_0^n \) corresponds to a multiplet of degenerate states \( |na0\rangle \) (with \( a = 1, 2, \ldots, g_n \), where \( g_n \) is the degeneracy) and we have to solve the perturbed problem

\[ \begin{align*}
H|\psi\rangle &= [H^{(0)} + H^{(1)}]|\psi\rangle = E|\psi\rangle,
\end{align*} \]

we can express the new generic eigenfunction \( |\psi\rangle \) as

\[ |\psi\rangle = \sum_{a=1}^{g_n} |na\rangle \langle na|\psi\rangle, \]

where the \( |na\rangle \)'s are states which are related to the unperturbed eigenvectors \( |na0\rangle \)'s by the perturbation matrix elements between different multiplets (as we will see in eq. (23)).

If we define

\[ H_{ab}^n = \langle na|H|nb\rangle = \langle na|[H^{(0)} + H^{(1)}]|nb\rangle, \]

we can express our perturbed equation in the following way:

\[ \sum_{b=1}^{g_n} H_{ab}^n \langle nb|\psi\rangle = E \langle na|\psi\rangle. \]
Noting that the definition of the $H_{ab}^n$’s can be equivalently expressed in this way

\[ [H^{(0)} + H^{(1)}]|nb\rangle = \sum_{a=1}^{g_n} |na\rangle H_{ab}^n, \]

inserting into this equation the expansions

\[ H_{ab}^n = (H_{ab}^n)^{(0)} + (H_{ab}^n)^{(1)} + (H_{ab}^n)^{(2)} + \ldots, \]

\[ |na\rangle = |na\rangle^{(0)} + |na\rangle^{(1)} + |na\rangle^{(2)} + \ldots, \]

and enforcing the identity of the terms of the same order, we find

\[ H^{(0)}|nb\rangle^{(0)} = \sum_{a=1}^{g_n} |na\rangle^{(0)} (H_{ab}^n)^{(0)}, \]

\[ H^{(0)}|nb\rangle^{(1)} + H^{(1)}|nb\rangle^{(0)} = \sum_{a=1}^{g_n} |na\rangle^{(1)} (H_{ab}^n)^{(0)} + \sum_{a=1}^{g_n} |na\rangle^{(0)} (H_{ab}^n)^{(1)}, \]

\[ H^{(0)}|nb\rangle^{(2)} + H^{(1)}|nb\rangle^{(1)} = \sum_{a=1}^{g_n} |na\rangle^{(2)} (H_{ab}^n)^{(0)} + \sum_{a=1}^{g_n} |na\rangle^{(1)} (H_{ab}^n)^{(1)} + \sum_{a=1}^{g_n} |na\rangle^{(0)} (H_{ab}^n)^{(2)}, \]

\[ \ldots. \]

The first equation corresponds, noting that $(H_{ab}^n)^{(0)} = E_0^n \delta_{ab}$, to the unperturbed eigenvalue equation, the solutions of which, $E_0^n$ and $|na\rangle^{(0)} = |na0\rangle$, are assumed to be known. From the other equations, instead, we can obtain the corrections to these values produced by the perturbation. In particular, if we stop to the first-order corrections for the eigenstates and to the second-order corrections for the eigenvalues, we find

\[ |nb \stackrel{>}{=} |nb0\rangle + |nb\rangle^{(1)} = |nb0\rangle + \sum_{n \neq n} \sum_{c=1}^{g_n} \left( |mc0\rangle \frac{\langle mc0|H^{(1)}|nb0\rangle}{E_0^m - E_0^n} \right) \]

(choosing $\langle nc0|nb\rangle^{(1)} = 0$) and

\[ H_{cb}^n \simeq (H_{cb}^n)^{(0)} + (H_{cb}^n)^{(1)} + (H_{cb}^n)^{(2)} = E_0^n \delta_{cb} + \langle nc0|H^{(1)}|nb0\rangle + \sum_{n \neq n} \sum_{a=1}^{g_n} \left( \frac{\langle mc0|H^{(1)}|ma0\rangle \langle ma0|H^{(1)}|nb0\rangle}{E_0^m - E_0^n} \right). \]

Once the $H_{cb}^n$ have been found, we can obtain the energy levels $E$ solving the equation

\[ \sum_{b=1}^{g_n} H_{ab}^n \langle nb|\psi\rangle = E \langle na|\psi\rangle, \]
or, equivalently, finding the eigenvalues of the matrix $H^n$ (matrix $g_n \times g_n$ with elements $H^n_{ab}$) by solving

\[(26) \quad \det (H^n - EI) = 0\]

(with $I$ the $g_n \times g_n$ unit matrix). We notice that, computing also the eigenvectors $\langle na|\psi\rangle$ of such a matrix and combining such results with the $|nb\rangle$ that have been computed before up to the first order, it is also possible to know the eigenfunctions $|\psi\rangle$ of the perturbed problem.

In the case of the $k \cdot p$ Hamiltonian that we have found before [5], we can use the $u_0^n(r)$ ($u^n_k(r)$ for $k = 0$) as $|n0\rangle$ and we have that

\[(27) \quad \langle m0|H^{(1)}|n0\rangle = \langle m0| \left[ -\frac{i\hbar^2}{m_e} (k \cdot \nabla) \right]|n0\rangle + \langle m0| \frac{\hbar^2k^2}{2m_e} |n0\rangle = \frac{\hbar k}{m_e} \cdot \langle m0|(-i\hbar\nabla)|n0\rangle + \langle m0| \frac{\hbar^2k^2}{2m_e} |n0\rangle.\]

The second term clearly gives only diagonal matrix elements, because it is equal to $(\hbar^2k^2/(2m_e))\delta_{nm}$. The first term, instead, gives only non-diagonal matrix elements because it is known [68] that

\[(28) \quad \langle nk0|(-i\hbar\nabla)|nk0\rangle + \hbar k_0 = m_e v_n = \frac{m_e}{\hbar} \nabla_k E^n_k\]

(where $v_n$ is the expectation value of the velocity of the Bloch waves, and in our considerations we are assuming $k_0 = 0$) and $\nabla_k E^n_k = 0$ in the band extrema.

Then, if the unperturbed energy bands are non-degenerate, we can write that

\[(29) \quad E^n_k = E^n_0 + \frac{\hbar^2k^2}{2m_e} + \frac{\hbar^2}{m_e^2} \sum_{m \neq n} \langle m0|k \cdot (-i\hbar\nabla)|m0\rangle \langle m0|k \cdot (-i\hbar\nabla)|n0\rangle = E^n_0 + \frac{\hbar^2}{2} \sum_{\mu,\nu} k_\mu k_\nu m^{*}_{\mu\nu},\]

where $\mu, \nu = x, y, z$, while $m^{*}_{\mu\nu}$ is the effective-mass tensor defined by

\[(30) \quad \frac{1}{m^{*}_{\mu\nu}} = \frac{1}{m_e} \delta_{\mu\nu} + \frac{2}{m_e^2} \sum_{m \neq n} \frac{P^{nm}_{\mu} P^{nm}_{\nu}}{E^n_0 - E^m_0},\]

and the momentum matrix elements at the band extremum are

\[(31) \quad P^{nm}_{\mu} = \langle m0|(-i\hbar\nabla_\mu)|n0\rangle.\]
If the unperturbed energy bands are degenerate, instead, we have

$$\langle H_{cb}^{n} \rangle_{cb} = E_{0}^{n} \delta_{cb} + \frac{\hbar^{2}k^{2}}{2m_{e}} \delta_{cb} + \frac{\hbar}{m_{e}} \langle nc0|k \cdot (-i \hbar \nabla)|nb0 \rangle + \frac{\hbar^{2}}{m_{e}^{2}} \sum_{m \neq n} \sum_{a=1}^{2n} \langle nc0|k \cdot (-i \hbar \nabla)|ma0 \rangle \langle ma0|k \cdot (-i \hbar \nabla)|nb0 \rangle \frac{E_{0}^{n} - E_{0}^{m}}{E_{0}^{n} - E_{0}^{m}}$$

$$E_{0}^{n} \delta_{cb} + \frac{\hbar}{m_{e}} \sum_{\mu} k_{\mu} (P_{\mu})^{mn}_{cb} + \frac{\hbar^{2}}{2} \sum_{\mu, \nu} k_{\mu} k_{\nu} m_{cb}^{\mu \nu},$$

where \( \mu, \nu = x, y, z \), while \( m_{cb}^{\mu \nu} \) is the effective-mass tensor defined by

$$\frac{1}{m_{cb}^{\mu \nu}} = \frac{1}{m_{e}} \delta_{cb} \delta_{\mu \nu} + \frac{2}{m_{e}^{2}} \sum_{m \neq n} \sum_{a=1}^{2n} \frac{(P_{\mu})^{mn}_{ca} (P_{\nu})^{mn}_{ab}}{E_{0}^{n} - E_{0}^{m}}$$

and the momentum matrix elements at the band extremum are

$$\langle P_{\mu} \rangle^{mn}_{cb} = \langle nc0|(-i \hbar \nabla_{\mu})|mb0 \rangle.$$

In most of the cases all the \((P_{\mu})^{mn}_{cb} = 0\), and the linear term in \( k_{\mu} \) disappears. The energy levels will be found solving

$$\det (H_{cb}^{n} - EI) = 0.$$

Thus, in principle to perform a calculation of the energy bands we would have to know the \(|n0\rangle\)'s (the Bloch lattice functions at \( k = 0 \)). Since the Hamiltonian \( H^{(0)} \) and its eigenfunctions \(|n0\rangle\) have the periodicity of the lattice, the problem can be solved inside a single primitive cell, enforcing periodic boundary conditions at the surface of the cell. Most semiconductors of interest have the diamond or zincblende crystal structure; for these materials we can choose as lattice primitive cell a Wigner-Seitz cell centered around an atomic site (the one with the strongest potential in the case of the zincblende structure, characterized by atoms that are not all identical) and with, at four vertices of the cell, four other atoms forming a tetrahedron with the center coincident with the primitive cell center (fig. 1). We can use a central force model (the same results can be obtained using group theory), considering the potential inside the primitive cell as due only to the attraction of the nucleus of the central atom, shielded by its electrons [5]. We find that the Bloch lattice functions at \( k = 0 \) exhibit symmetry properties analogous to those of atomic orbitals: we have completely symmetric \( s \)-type states \( \rho_{os}(r) \), and \( p \)-type states antisymmetric with respect to a coordinate and symmetric with respect to the others, i.e. of the form \( \rho_{ox}(r)x, \rho_{oy}(r)y \), and \( \rho_{oz}(r)z \) (where \( r = \sqrt{x^{2} + y^{2} + z^{2}} \)). Then, treating the electrostatic potential of the cores at the vertices of the primitive cell as a perturbation, we see that, to first order, this potential does not change the eigenfunctions but shifts the energy levels and in particular breaks the degeneracy between each \( s \)-type state and the corresponding three \( p \)-type states (which remain mutually degenerate). As a result, we find that at \( k = 0 \) the top of the valence band can be described with three degenerate states: \(|vx0\rangle = \rho_{v}(r)x, |vy0\rangle = \rho_{v}(r)y \) and \(|vz0\rangle = \rho_{v}(r)z \), while in most cases the bottom of the conductance band is described by a non-degenerate symmetric.
Fig. 1. – Wigner-Seitz primitive cell for the diamond or zincblende structure (adapted from [5]).

state \( |c0\rangle = \rho_c(r) \) (with the important exception of silicon, where at \( k = 0 \) also the bottom of the conduction band is characterized by three states \( |cx0\rangle, |cy0\rangle \) and \( |cz0\rangle \)).

Therefore, if we treat the conduction band as a non-degenerate band, we obtain

\[
E_c^k = E_c^0 + \frac{\hbar^2}{2} \sum_{\mu,\nu} \frac{k_\mu k_\nu}{m_{\mu\nu}^*}, \tag{36}
\]

where \( \mu,\nu = x, y, z \) and

\[
\frac{1}{m_{\mu\nu}^*} = \frac{1}{m_c} \delta_{\mu\nu} + \frac{2}{m_c^2} \sum_{m \neq n} \frac{\langle c0|(-i\hbar \nabla_\mu)|m0\rangle\langle m0|(-i\hbar \nabla_\nu)|c0\rangle}{E_0^m - E_0^0}. \tag{37}
\]

The largest contribution to the sum comes from the bands \( m \) for which \( E_0^m - E_0^0 \) is smallest, i.e. from the three valence bands. If we compute the momentum matrix elements between the valence bands and the conduction band, we find that, due to the symmetry properties of the Bloch lattice functions,

\[
\langle v\mu0|(-i\hbar \nabla_\nu)|c0\rangle = -\langle c0|(-i\hbar \nabla_\nu)|v\mu0\rangle = -i\hbar P \delta_{\mu\nu}, \tag{38}
\]

with \( \mu,\nu = x, y, z \) and \( P = \langle v\mu0|\nabla_\mu|c0\rangle \) a non-zero quantity, which multiplied by \( \hbar \) has the dimensions of a momentum. Consequently, the effective mass in the conduction band that we find is isotropic and equal to

\[
\frac{1}{m_{\mu\nu}^*} = \frac{1}{m_c} \delta_{\mu\nu} = \left( \frac{1}{m_c} + \frac{2}{m_c^2} \frac{\hbar^2 P^2}{m_c^* E_0^c} \right) \delta_{\mu\nu}, \tag{39}
\]

with \( E_0^0 = E_0^c - E_0^v \).

As to the valence band, we must use the degenerate perturbation theory and, with a motivation analogous to that used in the study of the conduction band, we can consider
only the interaction between the three degenerate valence bands and the conduction band, which is the nearest energy band. Thus, using the previous results, we have that

\[(H_k^v)_{\alpha\beta} = E_0^\alpha \delta_{\alpha\beta} + \frac{\hbar^2}{2} \sum_{\mu,\nu} \frac{k_{\mu} k_{\nu}}{m_{\mu\nu}},\]

with

\[
\frac{1}{m_{\mu\nu}} \delta_{\alpha\beta} \delta_{\mu\nu} + \frac{2}{m_e^2} \sum_{m_{\neq a}=1}^{g_{m}} \left( \langle \alpha a | (-i \hbar \nabla_\mu) | ma \rangle \langle ma | (-i \hbar \nabla_\nu) | v \beta 0 \rangle \right) = \frac{1}{m_{e}} \delta_{\alpha\beta} \delta_{\mu\nu} + \frac{2}{m_e^2} \sum_{m_{\neq a}=1}^{g_{m}} \left( \langle \alpha 0 | (-i \hbar \nabla_\mu) | \epsilon \rangle \langle \epsilon | (-i \hbar \nabla_\nu) | v \beta 0 \rangle \right) = \frac{1}{m_{e}} \delta_{\alpha\beta} \delta_{\mu\nu} - \frac{2 \hbar^2 P^2}{m_e^2 E_0^\beta} \delta_{\alpha\beta} \delta_{\mu\nu},
\]

and thus the valence energy bands near the extremum can be obtained finding the eigenvalues of the matrix

\[
E_0^\beta + \frac{\hbar^2 k^2}{2 m_e} I - \frac{\hbar^4 P^2}{2 m_e E_0^\beta} \left[ \begin{array}{cccc} k_x^2 & k_y k_y & k_z k_z \\ k_y k_x & k_y^2 & k_z k_y \\ k_z k_x & k_z k_y & k_z^2 \end{array} \right].
\]

Till now we have not considered the effect of the so-called spin-orbit interaction, which often has a non-negligible influence on the energy bands. The physical phenomenon is the following [69, 70]. An electron has an intrinsic magnetic moment

\[
\mu = -\frac{\hbar}{2} \sigma = -g_e \frac{\hbar}{2} \sigma = -g_e \frac{e}{2 m_e} \sigma = -g_e \mu_B \sigma = \frac{e}{2 m_e} \sigma,
\]

where \( e \) is the modulus of the electron charge, \( \sigma \) is a vector with three components consisting of the Pauli spin matrices:

\[
\sigma_x = \left( \begin{array}{cc} 0 & 1 \\
1 & 0 \end{array} \right), \quad \sigma_y = \left( \begin{array}{cc} 0 & -i \\
i & 0 \end{array} \right), \quad \sigma_z = \left( \begin{array}{cc} 1 & 0 \\
0 & -1 \end{array} \right).
\]

\( g_e \) is the intrinsic gyromagnetic ratio of the electron, \( \gamma_L \) is its orbital gyromagnetic ratio, \( g_e = \gamma_e / \gamma_L \) is its intrinsic g-factor and \( \mu_B = e \hbar / (2 m_e) \) is the Bohr magneton. When an electron moves in a system (such as the atom) where the charge distribution (for example the nucleus charge) produces an electric field \( E \), for the theory of relativity this electric field will appear as a magnetic field in the frame of reference of the electron. In particular if the motion of the electron were uniform the equivalent magnetic field would be equal to \( B = -(v \times E) / c^2 \). The fact that the electron (and its frame of reference) is rotating halves such an equivalent magnetic field [69, 70]. Thus the Hamiltonian of the electron will have an additional part

\[
H_{SO} = \mu_B \sigma : \left( \frac{E \times v}{2 c^2} \right) = \frac{e \hbar}{4 m_e c^2} \sigma : (E \times v) = \frac{\hbar}{4 m_e c^2} \sigma : (\nabla U_L) \times v
\]
(with $U_L$ the potential energy), which in the absence of an external magnetic field can be written also as

$$H_{SO} = \frac{\hbar}{4m_e^2c^2} \sigma \cdot ((\nabla U_L) \times p).$$

However, if we insert this additional term into the original Schrödinger equation for the wave function $\psi_k^n(r) = e^{ik \cdot r} u_k^n(r)$, we obtain

$$H_{SO} \psi_k^n(r) = \frac{\hbar}{4m_e^2c^2} \sigma \cdot ((\nabla U_L) \times (-i \hbar \nabla)) e^{ik \cdot r} u_k^n(r) =$$

$$= \frac{\hbar}{4m_e^2c^2} \sigma \cdot ((\nabla U_L) \times (\hbar ke^{ik \cdot r} u_k^n(r) + e^{ik \cdot r} (-i \hbar \nabla u_k^n(r)))) =$$

$$e^{ik \cdot r} \left( \frac{\hbar^2}{4m_e^2c^2} \sigma \cdot ((\nabla U_L) \times k) + \frac{\hbar}{4m_e^2c^2} \sigma \cdot ((\nabla U_L) \times (-i \hbar \nabla)) \right) u_k^n(r).$$

If we repeat the procedure used to move from the Schrödinger equation for the wave functions $\psi_k^n(r)$ to the Schrödinger-Bloch equation for the Bloch lattice functions $u_k^n(r)$, we obtain that in the Hamiltonian of this last equation there will be two additional terms:

$$\frac{\hbar^2}{4m_e^2c^2} \sigma \cdot ((\nabla U_L) \times k) + \frac{\hbar}{4m_e^2c^2} \sigma \cdot ((\nabla U_L) \times (-i \hbar \nabla)) =$$

$$\frac{\hbar^2}{4m_e^2c^2} \sigma \cdot ((\nabla U_L) \times k) + H_{SO}.$$ 

The first term near $k = 0$ is small compared with the other term; thus only the second term is usually considered. The second term in the case of a potential energy with (locally) spherical symmetry (and thus of a radial electric field) becomes

$$H_{SO} = \frac{e\hbar}{4m_e^2c^2} \sigma \cdot (E \times p) = \frac{e\hbar}{4m_e^2c^2} \sigma \cdot \frac{E_r}{r} (r \times p) =$$

$$-i \left( \frac{e\hbar^2 E_r}{4m_e^2c^2 r} \right) \sigma \cdot (r \times \nabla) \equiv -i \frac{\Lambda}{2} \sigma \cdot (r \times \nabla).$$

In order to calculate the influence that the spin-orbit term has on the valence bands, we need to calculate the matrix elements on the basis states $|vx0\rangle$, $|vy0\rangle$, $|vz0\rangle$ and $|\rho0\rangle$. Due to the symmetry properties of such states, we see that the only non-zero elements are the non-diagonal elements between valence band states

$$\langle vy0|H_{SO}|vx0\rangle = -\langle vx0|H_{SO}|vy0\rangle = i \lambda \sigma_z,$$

$$\langle vz0|H_{SO}|vy0\rangle = -\langle vy0|H_{SO}|vz0\rangle = i \lambda \sigma_x,$$

$$\langle vx0|H_{SO}|vz0\rangle = -\langle vz0|H_{SO}|vx0\rangle = i \lambda \sigma_y,$$

with $\lambda$ a non-zero quantity given by (if $V_c$ is the volume of the lattice unit cell)

$$\lambda = \frac{\Lambda}{2V_c} \int_{V_c} x^2 \rho^2_0(r) d^2r.$$
Therefore, considering also the spin-orbit coupling, the matrix $H^v_k$ becomes

$$H^v_k = \left( E^v_0 + \frac{\hbar^2 k^2}{2m_e} \right) I - \frac{\hbar^4 P^2}{m_e^2 E_g^0} \begin{bmatrix} k_x^2 & k_x k_y & k_x k_z \\ k_y k_x & k_y^2 & k_y k_z \\ k_z k_x & k_z k_y & k_z^2 \end{bmatrix} + i \lambda \begin{bmatrix} 0 & -\sigma_z & \sigma_y \\ \sigma_z & 0 & -\sigma_x \\ -\sigma_y & \sigma_x & 0 \end{bmatrix},$$

where $\sigma_x$, $\sigma_y$, and $\sigma_z$ are the Pauli spin matrices (44), which do not commute with one another. If we consider the special case $k \parallel \hat{z}$ we can quite easily find the eigenvalues of this matrix, arriving at a third-order equation in the energy, the solutions of which represent the dispersion relations of the three valence bands, each one degenerate with respect to the spin. In particular, if we make the approximation $(\bar{\hbar}^4 P^2 k^2 / (m_e^2 E_g^0)) \ll \lambda$, we find the solutions

$$E_{hh} = E^v_0 + \lambda + \frac{\hbar^2}{2m_e} k^2,$$

$$E_{lh} = E^v_0 + \lambda + \frac{\hbar^2}{2m_e} \left( 1 - \frac{4 \hbar^2 P^2}{3m_e E_g^0} \right) k^2,$$

$$E_{\lambda h} = E^v_0 - 2\lambda + \frac{\hbar^2}{2m_e} \left( 1 - \frac{2 \hbar^2 P^2}{3m_e E_g^0} \right) k^2.$$

Thus, considering the effect of the spin-orbit interaction, we have obtained (fig. 2) two valence bands (the heavy-hole band and the light-hole band) degenerate at $k = 0$, where they have an energy $E_g = E^v_0 - (E^v_0 + \lambda) = E^v_0 - \lambda$ lower than the conduction band, and one valence band (the spin-orbit band) which for $k = 0$ has an energy $\Delta = 3\lambda$ lower than the other two valence bands. We notice that, while the light-hole band and the spin-orbit band have a negative effective mass of the same order of magnitude as the effective mass of the electrons in the conduction band, the heavy-hole band is characterized by a much larger effective mass (the fact that the obtained effective mass is positive instead disappears with a more refined treatment: obviously the effective mass of the electrons in the valence bands has to be negative, which corresponds to a positive effective mass for the holes).

This simplified model is amenable to several refinements.

As to the conduction band, we can include in the calculation the spin-orbit splitting of the valence band and the effect of the higher conduction bands. In particular, with the first change we obtain a better expression for the effective mass in the conduction band:

$$\frac{1}{m_e^*} = \frac{1}{m_e} + \frac{2}{m_e^2} \left[ \frac{2 \hbar^2 P^2}{3E_g} + \frac{\hbar^2 P^2}{3(E_g + \Delta)} \right],$$

where $E_g = E^v_0 - \lambda$. 
Also in the treatment of the valence bands we can consider the effect of the higher conduction bands; one of the effects is that the resulting valence bands lose their isotropy and exhibit a complex orientation dependence in the reciprocal space ("band warping").

It is important to notice that the expressions found for the band structure depend on a small number of parameters, for example $E_g$, $\Delta$ and $m^*_c$ (from which we can calculate the parameter $P$ using the expression found for the effective mass of the conduction band). From a practical point of view, these quantities are commonly obtained from a priori band structure calculations or, better, experimentally: in particular the bandgap values $E_g$ and $\Delta$ are accurately known from optical experiments, while $m^*_c$ is known from cyclotron resonance experiments.

The approach based on the “traditional” perturbation theory, that we have reported in this first part following the description of T. Wenckebach [5], differs from the method proposed by E. O. Kane [10-12, 37-39].

Starting from the consideration that the Bloch lattice functions can be expanded in terms of the complete, infinite set of the unperturbed Bloch lattice functions, Kane computes this expansion in an approximate way, considering only a finite set of bands. In particular he considers only the three valence bands and the conduction band (not including the effects of the other bands) and diagonalizes exactly the Hamiltonian of the Schrödinger-Bloch equation in the presence of spin-orbit interaction [38], written taking as a basis the following set, made up of a linear combination with constant coefficients of the $u_0^\sigma(r)$ considered in the absence of spin-orbit (i.e. of the functions $|c0\rangle$, $|vz0\rangle$, $|vy0\rangle$ and $|vz0\rangle$ taken with spin-up and spin-down):

\begin{align}
    i|c0\rangle|\downarrow\rangle, & \quad 1/\sqrt{2}(|vx0\rangle - i |vy0\rangle)|\uparrow\rangle, & \quad |vz0\rangle|\downarrow\rangle, & \quad -1/\sqrt{2}(|vx0\rangle + i |vy0\rangle)|\uparrow\rangle, \\
    i|c0\rangle|\uparrow\rangle, & \quad -1/\sqrt{2}(|vx0\rangle + i |vy0\rangle)|\downarrow\rangle, & \quad |vz0\rangle|\uparrow\rangle, & \quad 1/\sqrt{2}(|vx0\rangle - i |vy0\rangle)|\downarrow\rangle
\end{align}

(where $|\uparrow\rangle$ and $|\downarrow\rangle$ are, respectively, the spin-up and spin-down unit spinors).

From this diagonalization he finds, for small values of $k^2$, the following expressions for the considered bands (choosing the zero of energy at the top of the light-hole and
heavy-hole bands and defining the various quantities as before):

\[ E_c = E_g + \frac{\hbar^2}{2m_e} \left( 1 + \frac{4\hbar^2 P^2}{3m_e E_g} + \frac{2\hbar^2 P^2}{3m_e(E_g + \Delta)} \right) k^2, \]
\[ E_{hh} = \frac{\hbar^2}{2m_e} k^2, \]
\[ E_{lh} = \frac{\hbar^2}{2m_e} \left( 1 - \frac{4\hbar^2 P^2}{3m_e E_g} \right) k^2, \]
\[ E_{\lambda h} = -\Delta + \frac{\hbar^2}{2m_e} \left( 1 - \frac{2\hbar^2 P^2}{3m_e(E_g + \Delta)} \right) k^2. \]

These expressions are very similar to the expressions obtained with the previously described simplified model, but clearly show the dual effect that each reciprocal interaction has on the related couple of bands. As before, these results give an incorrect effective mass for the heavy-hole band.

From the diagonalization Kane also finds the Bloch lattice functions \( u_n(r) \) that diagonalize the Hamiltonian of the Schrödinger-Bloch equation in the presence of spin-orbit interaction (i.e. the eigenfunctions of this Hamiltonian) as linear combinations of the \( u_0(r) \) considered in the absence of spin-orbit; in particular for vanishing \( k \) they are (in the simplest case in which \( k \parallel \hat{z} \)):

\[ \begin{align*}
&\frac{i}{\sqrt{2}} |c0\rangle |\downarrow\rangle, \quad \frac{i}{\sqrt{2}} |c0\rangle |\uparrow\rangle, \\
&1/\sqrt{6} (|vx0\rangle + i |vy0\rangle) |\uparrow\rangle, \quad 1/\sqrt{2} (|vx0\rangle - i |vy0\rangle) |\downarrow\rangle, \\
&-1/\sqrt{6} (|vx0\rangle + i |vy0\rangle) |\downarrow\rangle + \sqrt{2/3} |vz0\rangle |\downarrow\rangle, \\
&1/\sqrt{3} (|vx0\rangle - i |vy0\rangle) |\downarrow\rangle - 1/\sqrt{3} |vz0\rangle |\downarrow\rangle, \\
&1/\sqrt{3} (|vx0\rangle + i |vy0\rangle) |\downarrow\rangle + 1/\sqrt{3} |vz0\rangle |\downarrow\rangle.
\end{align*} \]

In order to take into account the effect of higher and lower bands on the considered ones, Kane uses the Löwdin perturbation theory [71, 72]. Following this method, one can divide all the bands into two sets \( A \) and \( B \): \( A \) is the set we want to treat exactly and \( B \) contains all the other bands. At the lowest order of perturbation theory the coupling between the set \( A \) and the set \( B \) can be removed introducing the perturbed functions

\[ u'_i = u_i + \sum_n^B \frac{H_{ni}w_n}{(H_{ii} - H_{nn})}, \]

where \( i \) is in \( A \) and \( n \) is in \( B \). The renormalized interactions connecting \( u'_i \) and \( u'_j \) are given by

\[ H'_{ij} = H_{ij} + \sum_n^B \frac{H_{in}H_{nj}}{(H_{ii} + H_{jj} - H_{nn})}. \]
In this way we can reduce the Hamiltonian matrix, which in principle connects all the possible bands, to a Hamiltonian matrix relating only the bands of interest, but in which, however, the interactions with the non-considered bands are included. The method is accurate as long as $|H_{in}| \ll |H_{ii} - H_{nn}|$, with $i$ in $A$ and $n$ in $B$, and thus the set $A$ has to be selected in order to satisfy this relation (for example, also states degenerate with those in which we are interested have to be considered inside the set $A$). Note that the Löwdin perturbation theory reduces to the ordinary perturbation theory when only a single band is considered in the set $A$.

Kane applies this perturbation method, starting from the Bloch lattice functions (57) of the set $A$ of considered conduction and valence bands and from the unperturbed Bloch lattice functions of the set $B$ of the higher and lower bands, obtaining a better approximation of the actual dispersion relations of the considered bands.

An exact diagonalization of the Hamiltonian has also been performed (originally by M. Cardona and F. H. Pollak [28], more recently by other authors [29-32]), extending the number of considered bands (and thus the number of involved parameters) to reproduce the band structure all over the Brillouin zone to a reasonable degree of accuracy (for example, in their original paper M. Cardona and F. H. Pollak consider 15 bands, with 10 parameters, to reproduce the energy band structure of germanium and silicon).

3. – The $k \cdot p$ method in non-periodic systems: envelope function theory and application to heterostructures

Till now, we have considered the applications of the $k \cdot p$ method to periodic, homogeneous crystals, using a description of the electron wave function in terms of Bloch functions. However, in the presence of a generic external potential the periodicity of the potential inside the crystal breaks down and thus the electron wave functions are far from periodic. Since the Bloch functions $|n k\rangle = e^{ik \cdot r}u_n^k(r)/\sqrt{(2\pi)^3}$, considered as functions of $r$ and $k$, are a complete set of orthonormal functions, also in this case the generic wave function could be expanded on the basis of Bloch functions in this way

$$\psi(r) = \sum \int d|k A_n(k)\rangle|n k\rangle,$$

(where the sum over the number of bands together with the integral over the Brillouin zone corresponds to an integral over all the reciprocal space). However, in general a large number of Bloch functions, evaluated over a large range of wave vectors, would be necessary in this expansion. Therefore in this case it is convenient to replace the Bloch phase factor, involving the wave vector measured from the reference extremum point, with an envelope function, and thus to use a different formulation of the $k \cdot p$ method, based on the concept of envelope functions (1).

In order to introduce this concept, we can make a very approximate calculation [77,78] in the hypothesis that the external potential energy $U(r)$ (“external” here meaning “not due to the periodic structure of the lattice”) is slowly varying on an atomic scale and the $n$-th energy band that we are considering is non-degenerate (thus with unique independent Bloch lattice function $u_n^k(r)$). In this case, the Schrödinger equation (in the

\[1\] Notice that there is also an alternative approach to the envelope function theory using the definition of Wannier [73] and Slater [74], based on Wannier orbitals. See also [52,75,76].
absence of a magnetic field) for the electron wave function \( \psi(\mathbf{r}) \)

\[
\left( -\frac{\hbar^2}{2m_e} \nabla^2 + U_L(\mathbf{r}) \right) \psi(\mathbf{r}) + U(\mathbf{r})\psi(\mathbf{r}) = H^{(0)}\psi(\mathbf{r}) + U(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r})
\]

(61)

where \( U_L(\mathbf{r}) \) is the periodic lattice potential energy and \( H^{(0)} \) is the Hamiltonian in the absence of the external potential energy \( U(\mathbf{r}) \) is equivalent to the equation

\[
E_n(-i \nabla)F(\mathbf{r}) + U(\mathbf{r})F(\mathbf{r}) = EF(\mathbf{r}),
\]

(62)

where \( E_n(-i \nabla) \) represents the operator obtained replacing, in the dispersion relation \( E_n(\mathbf{k}) \) describing the \( n \)-th energy band in the absence of the external potential, each component of \( \mathbf{k} \) with the corresponding component of \(-i \nabla\), and \( F(\mathbf{r}) \) is the envelope function, a slowly varying function that, when we consider only the \( n \)-th band, multiplied by the fast varying Bloch lattice function \( u_0^{(n)}(\mathbf{r}) \) (considered in \( \mathbf{k} = 0 \) gives the electron wave function.

Indeed, if we expand \( \psi(\mathbf{r}) \) in the orthogonal basis set \( |\nu \mathbf{k}\rangle = e^{i \mathbf{k} \cdot \mathbf{r}} u_0^{(n)}(\mathbf{r})/\sqrt{V} \) (with \( V \) the crystal volume)

\[
\psi(\mathbf{r}) = \sum_{\nu, \mathbf{k}} a_{\nu}(\mathbf{k}) |\nu \mathbf{k}\rangle,
\]

(63)

we can re-write the Schrödinger equation (61) in matrix form using the basis \( |\nu \mathbf{k}\rangle \)

\[
\sum_{\nu', \mathbf{k}'} \left( \langle \nu \mathbf{k} | H^{(0)} + U(\mathbf{r}) | \nu' \mathbf{k}' \rangle a_{\nu'}(\mathbf{k}') \right) = E a_{\nu}(\mathbf{k}) \Rightarrow \\
E_n(\mathbf{k}) a_{\nu}(\mathbf{k}) + \sum_{\nu', \mathbf{k}'} \left( \langle \nu \mathbf{k} | U(\mathbf{r}) | \nu' \mathbf{k}' \rangle a_{\nu'}(\mathbf{k}') \right) = E a_{\nu}(\mathbf{k}),
\]

(64)

where we have used the fact that (being \( |\nu \mathbf{k}\rangle \) an eigenfunction of \( H^{(0)} \) with eigenvalue \( E_n(\mathbf{k}) \))

\[
\langle \nu \mathbf{k} | H^{(0)} | \nu' \mathbf{k}' \rangle = E_{\nu'}(\mathbf{k}') \langle \nu \mathbf{k} | \nu' \mathbf{k}' \rangle = E_{\nu'}(\mathbf{k}) \delta_{\nu, \nu'} \delta_{\mathbf{k}, \mathbf{k}'}.
\]

(65)

In particular, for \( \nu = n \) we have that

\[
E_n(\mathbf{k}) a_n(\mathbf{k}) + \sum_{\nu', \mathbf{k}'} \left( \langle \nu \mathbf{k} | U(\mathbf{r}) | \nu' \mathbf{k}' \rangle a_{\nu'}(\mathbf{k}') \right) = E a_n(\mathbf{k}).
\]

(66)

If instead we expand the envelope function equation in the orthogonal set of plane waves

\[
| \mathbf{k} \rangle = e^{i \mathbf{k} \cdot \mathbf{r}}/\sqrt{\mathcal{V}}
\]

\[
F(\mathbf{r}) = \sum_{\mathbf{k}} a(\mathbf{k}) | \mathbf{k} \rangle,
\]

(67)
we can re-write the envelope function equation (62) in matrix form using the basis $|k\rangle$

\begin{equation}
\sum_{k'} \langle k|E_n(-i \nabla) + U(r)|k'\rangle a(k') = E_\alpha(k) \Rightarrow
\end{equation}

\begin{equation}
E_n(k) a(k) + \sum_{k'} \langle k|U(r)|k'\rangle a(k') = E_\alpha(k),
\end{equation}

using the fact that

\begin{equation}
(-i \nabla)\delta k' k = (-i \nabla)\delta k' k = (k') e^{ik' \cdot r} \sqrt{V} = \langle k'| r \rangle e^{ik \cdot r} \sqrt{V} = \langle k'| k \rangle,
\end{equation}

with $\nu$ being $x, y, z$ and thus

\begin{equation}
\langle n k|U(r)|\nu' k'\rangle = \delta_{n \nu'} \langle k|U(r)|k'\rangle,
\end{equation}

\textit{i.e.} if the matrix elements of the external potential $U(r)$ between states from different bands are negligible. This is what happens if $U$ is slowly varying on an atomic scale. Indeed, in this case we have that

\begin{equation}
\langle n k|U(r)|\nu' k'\rangle \approx \delta_{n \nu'} \langle k|U(r)|k'\rangle,
\end{equation}

(72) \[ \langle n k|U(r)|\nu' k'\rangle = \frac{1}{V} \sum_{j=1}^{N} \int_{V_j} dr \ u^*_k(r) u^\nu_k(r) e^{i(k' - k) \cdot r} U(r) \approx \]

\[ \sum_{j=1}^{N} e^{i(k' - k) \cdot r_j} U(r_j) \frac{1}{V} \int_{V_j} dr \ u^*_k(r) u^\nu_k(r) \approx \]

\[ \sum_{j=1}^{N} e^{i(k' - k) \cdot r_j} U(r_j) \delta_{n \nu'} \frac{1}{N} \approx \delta_{n \nu'} \int_V \frac{e^{i(k' - k) \cdot r}}{V} U(r) = \delta_{n \nu'} \langle k|U(r)|k'\rangle, \]

where $V$ the crystal volume, $V_j$ the volume of the $j$-th unit cell, $r_j$ the coordinate of its center and $N$ the number of unit cells. We have assumed that $U(r)$ and $e^{i(k' - k) \cdot r}$ are approximately constant over a unit cell and $u^\nu_k(r) \approx u^\nu_k(r)$ over the range of values of $|k' - k|$ for which $\langle k|U(r)|k'\rangle$ is not negligible.

Note that usually for functions with the translation symmetry of the crystal lattice the scalar product is defined as

\begin{equation}
\langle \Psi_1|\Psi_2\rangle = \frac{1}{V_c} \int_{V_c} dr \ \Psi^*_1(r) \Psi_2(r)
\end{equation}

(with $V_c$ the volume of the unit cell); in particular $u^\nu_k(r)$ and $e^{i k \cdot r} u^\nu_k$ are normalized with respect to this scalar product.
If the two equations (66) and (68) are identical, they have the same solutions \( a_n(k) \) and \( a(k) \). Thus (assuming that \( a_n(k) \) is non-zero only for the particular band \( n \), coherently with our hypothesis that there is no mixing between the bands) we can write that

\[
\psi(r) = \sum_{\nu,k} a_{\nu}(k) |\nu k\rangle = \sum_{k} a_n(k) e^{i k \cdot r}/\sqrt{V} u_n^0(r) \simeq u_n^0(r) \sum_{k} a_n(k)|k\rangle = u_n^0(r) F(r),
\]

where we have assumed that \( u_n^0(r) \) does not vary very much with \( k \) (note that the main \( k \)'s have to be quite close to \( k_0 = 0 \) for the previous derivation to be consistent).

We notice that if we express \( E_n(k) \) as

\[
E_n(k) = E_n^0 + \frac{\hbar^2}{2} \sum_{\mu,\nu} \frac{k_\mu k_\nu}{m\mu\nu},
\]

(with \( \mu, \nu = x, y, z \)) the envelope function equation becomes

\[
-\frac{\hbar^2}{2} \sum_{\mu,\nu} \nabla_\mu \nabla_\nu F(r) + (E_n^0 + U(r)) F(r) = EF(r)
\]

and when the effective mass is isotropic ((\( 1/m^{*\mu\nu} = (1/m^*)\delta_{\mu\nu} \)) we have the well-known equation

\[
-\frac{\hbar^2}{2 m^*} \nabla^2 F(r) + (E_n^0 + U(r)) F(r) = EF(r).
\]

Luttinger and Kohn in a famous paper [40] have given an alternative derivation of the single-band envelope function equation, which has the advantage of being easily generalized to more complicated cases. The starting equation is again the Schrödinger equation \((H(0) + U)\psi = E\psi\), with \( H(0) \) being the Hamiltonian of the electron in the periodic lattice potential and \( U \) an additional potential which is assumed not to vary significantly over each unit cell. They show that the functions \( |n k\rangle = \chi_{n,k} = e^{i k \cdot r} u_n^0(r)/\sqrt{(2\pi)^3} \) (where \( u_n^0(r) \) are the Bloch lattice functions in the absence of the external potential, evaluated for \( k = 0 \)) are a complete orthonormal set, if considered as functions of \( r \) and \( k \) (exactly as the functions \( e^{i k \cdot r} u_n^0(r)/\sqrt{(2\pi)^3} \), which, contrary to the \( \chi_{n,k} \), are eigenfunctions of \( H(0) \)). This means that

\[
\langle\chi_{nk}|\chi_{n'k'}\rangle = \delta_{nn'}\delta(k - k').
\]

Therefore, they can expand the wave function \( \psi \) over the complete orthonormal set of functions \( |n k\rangle \) in this way:

\[
\psi = \sum_{n'} \int dk' A_{n'}(k') \chi_{n'k'},
\]
and, considering this basis, they can rewrite the Schrödinger equation in the following form:

\[(80) \sum_{n'} \int d\mathbf{k}' \langle n\mathbf{k}|H^{(0)} + U|n'\mathbf{k}'\rangle A_n(\mathbf{k}') = EA_n(\mathbf{k}).\]

After some calculations, they obtain that

\[(81) \langle n\mathbf{k}|H|n'\mathbf{k}'\rangle = \left( E_{n0} + \frac{\hbar^2 k^2}{2m_e} \right) \delta_{nn'} \delta(\mathbf{k} - \mathbf{k}') + \sum_{\alpha=x,y,z} \frac{\hbar k\alpha P_{\alpha n'n}}{m_e} \delta(\mathbf{k} - \mathbf{k}') \equiv \langle n\mathbf{k}|H_a|n'\mathbf{k}'\rangle + \langle n\mathbf{k}|H_b|n'\mathbf{k}'\rangle,
\]
where the momentum matrix elements at \( \mathbf{k} = 0 \)

\[(82) P_{\alpha nn'} = \frac{1}{V_c} \int_{V_c} u_{n0}^* (-ih\nabla_\alpha) u_{n'} \, d\mathbf{r}\]

are characterized by the following properties: \( P_{\alpha nn'} = 0 \) if the point \( \mathbf{k} = 0 \) around which we are working is an extremum point of the dispersion relations, and \( P_{\alpha nn'} = P_{\alpha n'n} = (P_{\alpha n'n})^* \) if a center of symmetry exists in the crystal. Moreover, if \( U \) is a “gentle” potential, with a very small variation over a unit cell,

\[(83) \langle n\mathbf{k}|U|n'\mathbf{k}'\rangle = \hat{U}(\mathbf{k} - \mathbf{k}') \delta_{nn'},\]

where \( \hat{U}(\mathbf{k}) \) is the Fourier transform of \( U \)

\[(84) \hat{U}(\mathbf{k}) = \frac{1}{(2\pi)^3} \int d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} U(\mathbf{r}).\]

As a consequence, eq. (80) becomes

\[(85) \left( E_{n0} + \frac{\hbar^2 k^2}{2m_e} \right) A_n(\mathbf{k}) + \sum_{\alpha=x,y,z} \sum_{n' \neq n} \frac{\hbar k\alpha P_{\alpha nn'}}{m_e} A_{n'}(\mathbf{k}) + \int d\mathbf{k}' \hat{U}(\mathbf{k} - \mathbf{k}') A_n(\mathbf{k}') = EA_n(\mathbf{k}).\]

In order to decouple the equation corresponding to the band \( n \) from the other bands, the terms involving \( P_{\alpha nn'} \), which couple the bands, have to be removed to the first order. Luttinger and Kohn obtain this result applying a proper canonical transformation \( T \):

\[(86) A_n(\mathbf{k}) = \sum_{n'} \int d\mathbf{k}' \langle n\mathbf{k}|T|n'\mathbf{k}'\rangle B_{n'}(\mathbf{k}'),\]

which corresponds, more abstractly, to \( A = TB \). Writing \( T = e^S \) and applying this transformation to the equation (85), which can be rewritten as \( H A = EA \), with \( H = H_a + H_b + U \), we obtain \( (e^{-S}HE^S)B = EB \). After some calculations, it can be proved.
that, choosing $S$ in such a way that $H_b + [H_a, S] = 0$ (the square brackets denoting the commutator), i.e.

$$\langle nk|S|n'k'\rangle = \begin{cases} \frac{\hbar k \cdot P^{nn'} \delta(k-k')}{m_e(E_n^0 - E_{n'}^0)}, & \text{if } n \neq n', \\ 0, & \text{if } n = n', \end{cases}$$

and neglecting the terms of order $k^3$ and higher and the terms which assume very small values for a “gentle” potential $U$, this equation becomes

$$\left( E_n^0 + \frac{\hbar^2 k^2}{2m_e} + \frac{\hbar^2}{m_e^2} \sum_{\alpha,\beta=x,y,z} k_\alpha k_\beta \sum_{n'' \neq n} \frac{P^{nn''} P^{n''n}_a}{E_n^0 - E_0^{n''}} \right) B_n(k) + \int U(k-k')B_n(k')dk' = E B_n(k),$$

which can be written more briefly in this form:

$$E_n(k)B_n(k) + \int U(k-k')B_n(k')dk' = E B_n(k),$$

where $E_n(k)$ is the dispersion relation in the absence of $U(r)$ expanded to second order in $k$.

Converting eq. (89) from the momentum space to the position space and defining the envelope function in this way

$$F_n(r) = \frac{1}{\sqrt{(2\pi)^3}} \int e^{ik \cdot r} B_n(k)dk,$$

the single band envelope function equation is obtained

$$(E_n(-i \nabla) + U(r))F_n(r) = EF_n(r),$$

with $E_n(-i \nabla)$ obtained expanding $E_n(k)$ (the dispersion relation in the absence of $U(r)$) to second order in $k$ around $k = 0$ with non-degenerate perturbation theory and substituting each component of $k$ with the corresponding component of $-i \nabla$. Being $F_n(r)$ a smooth function, it has significant Fourier components only for small values of $k$. Since for small values of $k$ also $S$ is small, for these components $A_n(k) = e^S B_n(k) \simeq B_n(k)$ and thus, exploiting the eqs. (79) and (90), we have

$$\psi \simeq \sum_n \int dk B_n(k)e^{i k \cdot r} \frac{u_n^0(r)}{\sqrt{(2\pi)^3}} = \sum_n F_n(r)u_n^0(r)$$

and, noting that eq. (91) contains no interband coupling,

$$\psi = F_n(r)u_n^0(r)$$
(as already seen). If locally the external potential changes considerably within a cell, in such a region the equation we have derived is no longer valid, but it continues to be valid in regions of space sufficiently distant from it.

Then Luttinger e Kohn adopt an analogous procedure starting from the Schrödinger equation written in the presence of an external magnetic field. In this way, they demonstrate that in such a case the envelope function satisfies an equation similar to the one in the absence of a magnetic field, the only difference being that the new Hamiltonian is obtained replacing, in the expansion of $E_n(k)$ to quadratic terms, each $k_\alpha$ by the operator $-i\mathbf{\nabla}_\alpha + eA_\alpha/h$ (using the MKS system of units) with $A_\alpha$ the $\alpha$-th component of the vector potential. Moreover in the expansion of $E_n(k)$ to the second order any arising product of non-commuting factors has to be interpreted as the symmetrized product.

In the case in which the extremum is at $k = k_0 \neq 0$, the demonstrations (both with and without an external magnetic field) can be repeated by just replacing $u^\alpha_0(r)$ (the eigenfunctions of the Hamiltonian for $k = 0$ in the absence of $U(r)$ and of an external magnetic field) with $\varphi_{n\kappa_0} \equiv e^{ik_0 r} u^\kappa_0(r)$ (the eigenfunctions of the Hamiltonian for $k = k_0$ in the absence of $U(r)$ and of an external magnetic field). Indeed, it can be seen that the functions $\varphi_{n\kappa} \equiv e^{ik\kappa r} (e^{ik_0 r} u^\kappa_0 (r))/\sqrt{(2\pi)^3}$ have properties analogous to those previously seen for the $\chi_{n\kappa} = e^{ik\kappa r} u^\kappa_0(r)/\sqrt{(2\pi)^3}$ considered as functions of $r$ and $\kappa$, they are a complete orthonormal set of functions (such that $\langle \varphi_{n\kappa} | \varphi_{n'\kappa'} \rangle = \delta_{nn'} \delta(\kappa - \kappa')$) and the momentum matrix elements computed in $k_0$, defined as

$$P^{\alpha\alpha'}_{nn'} = \frac{1}{V_c} \int_{V_c} u^\alpha_{k_0 \alpha} (\hbar k_0 - ih \mathbf{\nabla}_\alpha) u^{\alpha'}_{k_0 \alpha'} dr,$$

have properties analogous to those seen in the case in which $k_0 = 0$. In this case the relation between the wave function and the envelope function is

$$\psi = F_n(r) (e^{ik_0 r} u^n_{k_0}(r))$$

and the envelope function equation is

$$[E_n(k_0 - i\mathbf{\nabla}) + U] F_n = EF_n,$$

in the absence of magnetic field, and

$$\left[ E_n \left( k_0 - i\mathbf{\nabla} + \frac{eA}{h} \right) + U \right] F_n = EF_n,$$

in the presence of magnetic field. As before, in these expressions an expansion of $E_n$ around $k_0$ to second-order terms in $-i\mathbf{\nabla}$ and in $-i\mathbf{\nabla} + eA/h$, respectively, is meant.

If there are extrema at several different values of $k_0$ within the band, we obtain an envelope function equation for each of them; if the solutions corresponding to the different $k_0$ values have different energies, the corresponding wave functions represent independent solutions of the Schrödinger equation; otherwise the correct wave function will be a linear combination of those from the different extrema associated with the same energy.

When the band of interest is degenerate, Luttinger and Kohn, using a similar calculation, arrive at a set of coupled second-order equations which correspond to the effective
mass equation found in the case of non-degenerate bands. In particular (assuming for simplicity that the degeneracy occurs at $k = 0$) they assume to have, at $k = 0$, $r$ unperturbed degenerate Bloch lattice functions corresponding to the same unperturbed energy $E^0_j$ (where “unperturbed” means for $k = 0$ and in the absence of $U(r)$ and of an external magnetic field) and they define them as $\phi_j$ (with $j = 1, \ldots, r$, where $r$ is the degeneracy), i.e.

\begin{equation}
H^{(0)} \phi_j = E^0_j \phi_j
\end{equation}

(notice that the $\phi_j$’s, i.e. the $u_0^n$’s, can be seen as Bloch functions $e^{i k \cdot r} u_0^n$ for $k = 0$ and thus they have to satisfy the Schrödinger equation for $k = 0$). They instead indicate as $\phi_i$ (with $i \neq 1, \ldots, r$) the unperturbed Bloch lattice functions at $k = 0$ corresponding to the other bands, that are not degenerate with the $\phi_j$’s. If the crystal has a center of symmetry, it can be proved that the momentum matrix elements between different $\phi_j$’s vanish, i.e. $P_{ji}^{(0)} = 0$. Luttinger and Kohn introduce the complete set of functions $|n k\rangle = \phi_n k = e^{i k \cdot r} \phi_n / \sqrt{(2\pi)^3}$ (where $\phi_n$ indicates both the $\phi_j$’s and the $\phi_i$’s). Using this basis, they can expand the wave function in this way:

\begin{equation}
\psi = \sum \int dk A_n(k) \phi_{nk}
\end{equation}

and rewrite the Schrödinger equation as

\begin{equation}
\sum \int dk' \langle nk|H^{(0)} + U|n'k'\rangle A_{n'}(k') = EA_n(k),
\end{equation}

thus obtaining:

\begin{equation}
\left( E^0_j + \frac{\hbar^2 k^2}{2 m_c} \right) A_j(k) + \sum_{\alpha=x,y,z} \sum_i \frac{\hbar k_\alpha P_{ji}^{\alpha}}{m_c} A_i(k)
+ \int dk' \delta(k-k') A_j(k') = EA_j(k)
\end{equation}

(writing only the equations corresponding to the degenerate states $j$). In order to decouple the equations corresponding to the states $j$ from those of the states $i$, a proper canonical transformation $A = TB = e^S B$ is again applied, with

\begin{equation}
\langle nk|S|n'k'\rangle = \left\{ \begin{array}{ll}
\frac{\hbar k \cdot P_{nn'} \delta(k-k')}{m_c (E^0_n - E^0_{n'})}, & \text{if } n \text{ or } n' \notin [1, r], \\
0, & \text{if } n \text{ and } n' \in [1, r].
\end{array} \right.
\end{equation}

In this way Luttinger and Kohn obtain, to second-order terms in $k$, the following set of
equations for the $r$ degenerate states:

$$
\sum_{j'=1}^{r} \left( E_0^j \delta_{jj'} + \sum_{\alpha,\beta=x,y,z} \left( D_{jj'}^{\alpha\beta} k_{\alpha} k_{\beta} \right) \right) B_{j'}(k) + \int U(k-k') B_j(k') dk' = E B_j(k),
$$

with

$$
D_{jj'}^{\alpha\beta} = \frac{\hbar^2}{2 m_e} \delta_{jj'} \delta_{\alpha\beta} + \frac{\hbar^2}{m^*} \sum_i \frac{P_{\alpha i} P_{i j'}^*}{(E_0^j - E_0^i)}.
$$

Therefore, introducing again the envelope functions

$$
F_j(r) = \frac{1}{\sqrt{(2\pi)^3}} \int e^{ik \cdot r} B_j(k) dk,
$$

Luttinger and Kohn arrive at the conclusion that the $r$ envelope functions $F_j(r)$ corresponding to the originally degenerate energy bands satisfy the $r$ coupled differential equations

$$
\sum_{j'=1}^{r} \left( E_0^j \delta_{jj'} + \sum_{\alpha,\beta=x,y,z} \left( D_{jj'}^{\alpha\beta} (i\nabla_{\alpha} - i\nabla_{\beta}) \right) \right) F_{j'}(r) = E F_j(r)
$$

(if the energy zero is set at $E_0^j$ the term $E_0^j \delta_{jj'}$ disappears).

Analogously to what happens in the non-degenerate case, for small values of $k$, $A_n(k) \approx B_n(k)$ and thus

$$
\psi \approx \sum_n \int dk B_n(k) e^{ik \cdot r} \frac{\phi_n(r)}{\sqrt{(2\pi)^3}} = \sum_n F_n(r) \phi_n(r) \approx \sum_{j=1}^{r} F_j(r) \phi_j(r),
$$

since in eq. (106) no coupling remains between the states $j$ and the states $i$. The numbers $D_{jj'}^{\alpha\beta}$ play the same role in the case of degenerate bands as $\hbar^2/(2 m^* \delta_{\alpha\beta})$ for a non-degenerate band.

As before, in the presence of a magnetic field the components of $-i \nabla$ appearing in the envelope function equations will be replaced with the corresponding components of $-i \nabla + eA/\hbar$.

In the presence of spin-orbit coupling, Luttinger and Kohn adopt the same treatment, considering the spin-orbit contribution as part of the unperturbed Hamiltonian (therefore the total unperturbed Hamiltonian will be $H^{(0)} + H_{SO}$) and assuming the Bloch lattice functions and the corresponding energies for $k = 0$ of $H^{(0)} + H_{SO}$ as known quantities. Thus the $u_n^0$ are replaced with the $\pi_n^0$ (the spinorial Bloch lattice functions for $k = 0$ in the presence of spin-orbit interaction), $E_n(k)$ by $E_n^0(k)$ (the dispersion relations in the
presence of spin-orbit interaction) and the $P^{n,n'}_\alpha$ by

\begin{equation}
(\pi_\alpha)^{n,n'}_\alpha = \langle \varphi_0^\alpha | \left( -i \hbar \nabla_\alpha + \frac{\hbar}{4 m_e c^2} (\sigma \times \nabla V)_\alpha \right) | \varphi_0^{n'} \rangle,
\end{equation}

where the extra term arises from the fact that the spin-orbit coupling contains the differential operator $p$. When we treat energy bands which are degenerate in the absence of spin-orbit interaction, we have to remember that (as seen previously) the spin-orbit coupling can lift, at least partially, the degeneracy. In such a case, we have to consider that the validity of the adopted theory rests on the assumption that the interband separations are large compared with the energies involved in the solution of the envelope function equation. Thus we have to evaluate if the external potential $U$ or the magnetic field are sufficiently small to produce no appreciable mixing of the bands, the degeneracy of which has been lifted by the spin-orbit coupling. If they are sufficiently small, we can obtain a different set of coupled envelope function equations for each set of bands that have remained degenerate; otherwise we will have to deal with the full set of coupled equations for all the bands that are degenerate in the absence of spin-orbit.

We can introduce a matrix $D$, the elements of which are

\begin{equation}
D_{jj'} = \sum_{\alpha,\beta} D^{\alpha\beta}_{j} k_\alpha k_\beta.
\end{equation}

If in these matrix elements we replace each component of the vector $k$ with the corresponding component of the operator $-i \nabla + eA/\hbar$, we obtain the terms which appear in the envelope function coupled equations. In particular, the envelope function coupled equations written in the absence of an external perturbation read (if we set the energy zero at $E_{0}^{j}$)

\begin{equation}
\sum_{j'=1}^{r} \sum_{\alpha,\beta} (D^{\alpha\beta}_{jj'}(-i\nabla_\alpha)(-i\nabla_\beta))F_{j'}(r) = EF_{j}(r).
\end{equation}

If we convert them from the position representation to the momentum representation, we obtain

\begin{equation}
\sum_{j'=1}^{r} \sum_{\alpha,\beta} (D^{\alpha\beta}_{jj'}k_\alpha k_\beta)B_{j'}(k) = EB_{j}(k) \Rightarrow \sum_{j'=1}^{r} D_{jj'}B_{j'}(k) = EB_{j}(k) \Rightarrow DB = EB,
\end{equation}

from which it is evident that the dispersion relations $E(k)$ near the extremum can be obtained by finding the eigenvalues of the matrix $D$. We notice that this clearly corresponds to what happens in the case of non-degeneracy, in which (as we have seen) the envelope function equation contains $E_{0}(\nabla)$ (the dispersion relation in the absence of external potential energy or magnetic field, where each component of $k$ is replaced with the corresponding component of $-i \nabla$).

In order to determine the number of independent parameters which appear in the matrix $D$, the symmetry properties of the considered lattices are exploited.
In [41] Luttinger proposes a different way to obtain an explicit expression for $D$, based only on symmetry arguments. He writes this matrix for diamond-type semiconductors using group theory, in particular considering that the Hamiltonian $D$ should be invariant under the operations of the cubic group (so that the Hamiltonian will give us results which transform correctly with respect to the transformations of the cubic group, which is the symmetry group of $k$) and thus writing $D$ as a linear combination of the invariants obtained combining angular momentum matrices and components of $k$. The elements of such a matrix are polynomials in the components of $k$, at most of the second order, and involve parameters characteristic of the materials, which have been experimentally found and are available for most common semiconductors [79]. For example, in the case of the $4 \times 4$ matrix $D$ corresponding to the light-hole and heavy-hole bands (the extra factor of 2 coming from spin) they are $\gamma_1, \gamma_2, \gamma_3, \kappa$ (which is useful in the presence of an external magnetic field) and $q$ (which approaches zero as the spin-orbit coupling does).

Bir and Pikus [14] have shown that in uniformly strained semiconductors, such that the periodicity of the structure is preserved, the strain introduces in the dispersion relation of non-degenerate bands an extra term of the kind

$$(112) \quad a_c (\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz})$$

and in the Hamiltonian of degenerate bands additional terms of the form

$$(113) \quad \sum_{\alpha,\beta} \hat{D}_{j\beta}^{\alpha\beta} \epsilon_{\alpha\beta},$$

where $\alpha, \beta = x, y, z$ and $\epsilon_{\alpha\beta}$ is the generic component of the strain matrix.

Bastard [42-44] uses the envelope function method to study heterostructures, for example made up of two materials $A$ and $B$ (fig. 3). In particular, he assumes that the two materials are perfectly lattice-matched and crystallize with the same crystallographic structure, so that the functions $u_{n}^{A}(r)$ in the two materials can be considered identical. With this hypothesis, if in each material the wave functions are written as

$$(114) \quad \psi^{(A,B)} = \sum_{n} F_{n}^{(A,B)}(r) u_{n}^{n}(r),$$

Fig. 3. – Heterojunction between two semiconductors $A$ and $B$. 
it is evident that, since the $u_{n}^0$ are linearly independent and the wave function has to be continuous at the interface, also the envelope functions have to be continuous at the interface. For the derivative of the envelope functions, Bastard finds, enforcing the continuity of the probability current density at the interface, a general condition [80], which, in the simple case of two materials that are both characterized by non-degenerate parabolic and isotropic bands but with different effective masses $m^*_{(A)}$ and $m^*_{(B)}$, reduces to enforcing the continuity of

$$\frac{1}{m^*} \frac{\partial F_n}{\partial z}$$

(where we have assumed the $\hat{z}$ axis orthogonal to the interface). This can be easily obtained enforcing in this case the continuity of the $z$ component of the probability current density, which is equal to

$$j_z = -\frac{i}{2m} \left( \psi^* \frac{\partial \psi}{\partial z} - \psi \frac{\partial \psi^*}{\partial z} \right)$$

and noting that the continuity of the envelope function has already been enforced. As to the asymptotic behavior of the envelope functions far from the interface, it depends on the heterostructure under consideration. For example, for superlattices the $z$-dependent part of the envelope function will be a Bloch wave, due to the periodicity of the structure in that direction, while for the bound states of a quantum well it should tend to zero for large $z$. Thus the envelope functions in the overall structure can be found solving the envelope function equations in the different materials, knowing the asymptotic behavior far from the interface and enforcing the correct boundary conditions at the interface. Bastard has also made an extensive analysis of the applications of this method [81].

Also M. Altarelli has given important contributions to the development of the envelope function method [82] and to its applications to the study of heterostructures [45-47].

M. G. Burt [48-52] has pointed out the errors deriving from the assumption, normally made in the application of the envelope function method to heterostructures, that the $u_{n}^0(r)$ in the two materials are the same and from the boundary condition enforced on the derivative of the envelope function at the interface. In a series of interesting and detailed articles he has developed an alternative envelope function theory expanding the wave function in the overall structure on the same periodic basis functions $U_{n}(r)$ throughout, even though they are not necessarily eigenstates of the constituent crystals, without making any hypothesis about the real eigenstates $u_{n}^0(r)$

$$\psi(r) = \sum_{n} F_n(r) U_{n}(r).$$

The envelope functions $F_n(r)$ univocally defined in this way and all their derivatives are certainly continuous everywhere, including at the interface. Using this approach, he has first derived exact envelope function equations, then, for local potentials and slowly varying envelope functions (but without any assumption on the rate of variation of the composition), he has formulated approximate envelope function equations, and finally, with the assumption of the dominance of one envelope function, he has arrived at an effective-mass equation that includes also the effect of the differences in the $u_{n}^0(r)$
between the two materials. At each step the associated approximations are accurately described, so that it is possible to estimate the error.

A more detailed description of the applications of the \( \mathbf{k} \cdot \mathbf{p} \) method to materials with a diamond, zincblende and wurtzite lattice, both in the periodic and in the non-periodic case, can be found (besides in the other books and in the original publications reported in the list of references of this review) in the recent book by L. C. Lew Yan Voon and M. Willatzen [4].

4. – Application of the \( \mathbf{k} \cdot \mathbf{p} \) method to graphene

In the last years the \( \mathbf{k} \cdot \mathbf{p} \) method, and in particular the formulation (described in the last section) based on the envelope functions, has been successfully applied to the analysis of the electronic properties of graphene and graphene-related structures, such as carbon nanotubes and graphene nanoribbons.

In this section we will begin the description of this particular application deriving the \( \mathbf{k} \cdot \mathbf{p} \) relations for a simple sheet of graphene.

A graphene sheet is a hexagonal lattice of carbon atoms. In fig. 4(a) we show its structure in the real space and, in particular, its unit cell as a dashed rhombus, containing two inequivalent carbon atoms \( A \) and \( B \), while in fig. 4(b) we show the lattice in the reciprocal space with the Brillouin zone as a shaded hexagon. The lattice unit vectors are \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \) in the real space, and \( \mathbf{b}_1 \) and \( \mathbf{b}_2 \) in the reciprocal space. If we define 
\[
\mathbf{a} = |\mathbf{a}_1| = |\mathbf{a}_2| = a_{C-C} \sqrt{3} \quad \text{(with } a_{C-C} \text{ the distance between nearest-neighbor carbon atoms)},
\]
the coordinates of these vectors in the right-hand reference frame \( \Sigma' = (\hat{\mathbf{x}}', \hat{\mathbf{y}}', \hat{\mathbf{z}}') \) are (observe that we have taken \( \hat{\mathbf{z}}' \) along the vector \( \mathbf{a}_1 + \mathbf{a}_2 \))

\[
\begin{align*}
\mathbf{a}_1 & \equiv \Sigma' \begin{bmatrix} \frac{\sqrt{3}}{2}a \\ \frac{a}{2} \\ 0 \end{bmatrix}, & \mathbf{a}_2 & \equiv \Sigma' \begin{bmatrix} \frac{\sqrt{3}}{2}a \\ \frac{a}{2} \\ 0 \end{bmatrix}, & \mathbf{b}_1 & \equiv \Sigma' \begin{bmatrix} 2\pi \frac{\sqrt{3}a}{\sqrt{3}a} \\ 2\pi \frac{a}{\sqrt{3}a} \\ 0 \end{bmatrix}, & \mathbf{b}_2 & \equiv \Sigma' \begin{bmatrix} 2\pi \frac{\sqrt{3}a}{\sqrt{3}a} \\ 2\pi \frac{a}{\sqrt{3}a} \\ 0 \end{bmatrix}
\end{align*}
\]

(following the conventions used by R. Saito, G. Dresselhaus and M. S. Dresselhaus [83]), which (being \( \mathbf{b}_1 = 2\pi(\mathbf{a}_2 \times \hat{\mathbf{z}}')/(\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \hat{\mathbf{z}}')) \) and \( \mathbf{b}_2 = 2\pi(\hat{\mathbf{z}}' \times \mathbf{a}_1)/(\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \hat{\mathbf{z}}')) \)) fulfill the well-know relation \( \mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij} \) between lattice unit vectors in the real space and in the reciprocal space. Note that the letter written under the symbol “\( \equiv \)” indicates the
adopted reference frame. The most relevant graphene dispersion relations for transport and other solid-state properties are the two $\pi$-bands (an upper anti-bonding band and a lower bonding band), which are degenerate at the points (considering the point $\Gamma$ at the center of the hexagonal Brillouin zone of graphene as the origin of the reciprocal space)

$$K = \frac{1}{3} (b_2 - b_1) \equiv \frac{4\pi}{3\alpha} \begin{bmatrix} 0 & -1 \\ -1 & 0 \end{bmatrix} \quad \text{and} \quad K' = \frac{1}{3} (b_1 - b_2) \equiv \frac{4\pi}{3\alpha} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$

and obviously at their equivalents in the reciprocal space (as we can see from fig. 5, which has been obtained with a nearest-neighbor tight-binding approach limited to the $2p^z$ atomic orbitals, with nonzero nearest-neighbor overlap integral).

Thus we can use the $\mathbf{k} \cdot \mathbf{p}$ method to find the dispersion relations of graphene near these extrema points (called Dirac points), following T. Ando’s approach [54–56]. However, in our description we will continue to use the conventions of ref. [83] and we will consider the pair (119) of Dirac points (which will simplify the treatment of zigzag and armchair graphene nanoribbons in the last section of this review). Other articles where a $\mathbf{k} \cdot \mathbf{p}$ treatment of graphene is introduced are refs. [84–89].

We start by using a simple tight-binding model, in which we use as basis functions the $2p^z$ orbitals of all the carbon atoms of the graphene sheet, which are the orbitals leading to the $\pi$-bonds and thus to the above-mentioned two $\pi$-bands. The generic eigenfunction in the material can be expressed [55,56] as a linear combination (with coefficients $\psi_A(\mathbf{R}_A)$ and $\psi_B(\mathbf{R}_B)$) of these atomic orbitals $\varphi(\mathbf{r} - \mathbf{R}_A)$ and $\varphi(\mathbf{r} - \mathbf{R}_B)$ (centered on atoms of type $A$ and $B$, respectively)

$$\psi(\mathbf{r}) = \sum_{\mathbf{R}_A} \psi_A(\mathbf{R}_A) \varphi(\mathbf{r} - \mathbf{R}_A) + \sum_{\mathbf{R}_B} \psi_B(\mathbf{R}_B) \varphi(\mathbf{r} - \mathbf{R}_B),$$

where the first (second) sum spans over all the positions of the atoms of type $A$ ($B$) in the lattice.
Using the definition of the Hamiltonian operator

\[ H |\psi\rangle = E |\psi\rangle, \]

we have that [83]

\[ \langle \psi | H |\psi\rangle = E \langle \psi |\psi\rangle \]

and thus (using \( j \) and \( j' \) to indicate the type of the atoms and \( n \) and \( m \) to specify the particular atoms)

\[ E = \frac{\langle \psi | H |\psi\rangle}{\langle \psi |\psi\rangle} = \frac{\sum_{j,j'=A,B} \sum_{R_{jn}, R_{j'm}} \psi_j^*(R_{jn}) \varphi(r - R_{jn}) \sum_{j''=A,B} \sum_{R_{jn}, R_{j''m}} \psi_{j''}(R_{j''m}) \varphi(r - R_{j''m})}{\sum_{j,j'=A,B} \sum_{R_{jn}, R_{j'm}} \psi_j^*(R_{jn}) \varphi(r - R_{jn}) \sum_{j''=A,B} \sum_{R_{jn}, R_{j''m}} \psi_{j''}(R_{j''m}) \varphi(r - R_{j''m})} = \]

\[ \frac{\sum_{j,j'=A,B} \sum_{R_{jn}, R_{j'm}} \psi_j^*(R_{jn}) \psi_{j'}(R_{j'm}) \langle \varphi(r - R_{jn}) | H |\varphi(r - R_{j'm})\rangle}{\sum_{j,j'=A,B} \sum_{R_{jn}, R_{j'm}} \psi_j^*(R_{jn}) \psi_{j'}(R_{j'm}) \langle \varphi(r - R_{jn}) | \varphi(r - R_{j'm}) \rangle} = \]

\[ \frac{\sum_{j,j'=A,B} \sum_{R_{jn}, R_{j'm}} \psi_j^*(R_{jn}) \psi_{j'}(R_{j'm}) \varphi(r - R_{jn}) | H |\varphi(r - R_{j'm})}{\sum_{j,j'=A,B} \sum_{R_{jn}, R_{j'm}} \psi_j^*(R_{jn}) \psi_{j'}(R_{j'm}) \varphi(r - R_{jn}) | \varphi(r - R_{j'm}) \rangle} = \]

where we have introduced the transfer integrals \( h_{R_{jn}, R_{j'm}} \) and the overlap integrals \( s_{R_{jn}, R_{j'm}} \) between atomic orbitals. Now we can minimize \( E \) to obtain the actual physical state (for each coefficient, and thus for each atom)

\[ \frac{\partial E}{\partial \psi_j^*(R_{jn})} = \frac{\sum_{j'', j'=A,B} \sum_{R_{jn}, R_{j'm}} \psi_{j''}(R_{jn}) \psi_{j'}(R_{j'm}) h_{R_{jn}, R_{j'm}}}{\sum_{j'', j'=A,B} \sum_{R_{jn}, R_{j'm}} \psi_{j''}(R_{jn}) \psi_{j'}(R_{j'm}) s_{R_{jn}, R_{j'm}}} - \]

\[ \left( \frac{\sum_{j'', j'=A,B} \sum_{R_{jn}, R_{j'm}} \psi_{j''}(R_{jn}) \psi_{j'}(R_{j'm}) h_{R_{jn}, R_{j'm}}}{\sum_{j'', j'=A,B} \sum_{R_{jn}, R_{j'm}} \psi_{j''}(R_{jn}) \psi_{j'}(R_{j'm}) s_{R_{jn}, R_{j'm}}} \right)^2 \]

\[ \cdot \sum_{j'', j'=A,B} \sum_{R_{jn}, R_{j'm}} \psi_{j''}(R_{jn}) s_{R_{jn}, R_{j'm}} = 0. \]
Multiplying both members by the denominator of eq. (123) and rearranging, we find:

\[
\sum_{j' = A, B} \sum_{R_{j'm}} \psi_j' (R_{j'm})^A_R h_{R_{j'm}, R_{j'm}} = \\
\sum_{j, j' = A, B} \sum_{R_{j'n}} \sum_{R_{j'm}} \psi_j (R_{j'n}) \psi_j' (R_{j'm})^B_R h_{R_{j'n}, R_{j'm}} \\
\sum_{j, j' = A, B} \sum_{R_{j'n}} \sum_{R_{j'm}} \psi_j (R_{j'n}) \psi_j' (R_{j'm})^A_R s_{R_{j'n}, R_{j'm}} + \sum_{j' = A, B} \sum_{R_{j'm}} \psi_j' (R_{j'm})^B_R s_{R_{j'm}, R_{j'm}}.
\]

and recognizing that the fraction in the right-hand side is the expression of \( E \), we have

\[
\sum_{j' = A, B} \sum_{R_{j'm}} \psi_j' (R_{j'm})^A_R h_{R_{j'm}, R_{j'm}} = E \sum_{j' = A, B} \sum_{R_{j'm}} \psi_j' (R_{j'm})^B_R s_{R_{j'm}, R_{j'm}}.
\]

Let us expand this result for the coefficients (and thus for the atoms) with \( j = A \) and for those with \( j = B \)

\[
\begin{align*}
\sum_{R_{Am}} & \psi_A (R_{Am})^A_R h_{R_{Am}, R_{Am}} + \sum_{R_{Bm}} \psi_B (R_{Bm})^B_R h_{R_{Bm}, R_{Bm}} = \\
& E \left( \sum_{R_{Am}} \psi_A (R_{Am})^A_R s_{R_{Am}, R_{Am}} + \sum_{R_{Bm}} \psi_B (R_{Bm})^B_R s_{R_{Bm}, R_{Bm}} \right); \\
\sum_{R_{Am}} & \psi_A (R_{Am})^A_R h_{R_{Bm}, R_{Am}} + \sum_{R_{Bm}} \psi_B (R_{Bm})^B_R h_{R_{Bm}, R_{Am}} = \\
& E \left( \sum_{R_{Am}} \psi_A (R_{Am})^A_R s_{R_{Bm}, R_{Am}} + \sum_{R_{Bm}} \psi_B (R_{Bm})^B_R s_{R_{Bm}, R_{Am}} \right).
\end{align*}
\]

We consider non-negligible only the integrals between each atom and itself and between each atom and its nearest neighbors (which are the nearest three \( B \) atoms for an \( A \) atom, while they are the nearest three \( A \) atoms for a \( B \) atom). Therefore, if (in order to simplify the notation) we rename \( R_{Am} \) as \( R_A \) and \( R_{Bm} \) as \( R_B \) and we use the index \( l \) to indicate the nearest three atoms, we can rewrite these equations in the following way:

\[
\begin{align*}
\psi_A (R_A)^A_R h_{R_A, R_A} + & \sum_{l=1}^3 \psi_B (R_{Bl})^B_R h_{R_A, R_{Bl}} = \\
& E \left( \psi_A (R_A)^A_R s_{R_A, R_A} + \sum_{l=1}^3 \psi_B (R_{Bl})^B_R s_{R_A, R_{Bl}} \right), \\
& \sum_{l=1}^3 \psi_A (R_{Al})^A_R h_{R_{Bl}, R_A} + \psi_B (R_B)^B_R h_{R_{Bl}, R_B} = \\
& E \left( \sum_{l=1}^3 \psi_A (R_{Al})^A_R s_{R_{Bl}, R_A} + \psi_B (R_B)^B_R s_{R_{Bl}, R_B} \right).
\end{align*}
\]
In particular, we consider

\[
\begin{align*}
\epsilon_{R_{jn}} = u(R_{jn}) & \quad \text{if } R_{jn} = R_{j'm}, \\
-\gamma_0 & \quad \text{if } R_{jn} \neq R_{j'm} \text{ and } R_{jn} \text{ and } R_{j'm} \text{ are nearest neighbors,} \\
0 & \quad \text{otherwise,}
\end{align*}
\]

\[
\begin{cases}
1 & \text{if } R_{jn} = R_{j'm}, \\
0 & \text{if } R_{jn} \neq R_{j'm}.
\end{cases}
\]

Here \(\gamma_0\) is the modulus of the nearest-neighbor transfer integral. Instead \(\epsilon_{R_{jn}}\) is the onsite energy, that we take as zero of the energy in the absence of an external (i.e. not due to the periodic structure of the lattice) potential energy; if the external potential energy is not zero, we have to consider the term \(u(R_{jn})\), which represents the value of this external potential energy in the position \(R_{jn}\).

Note that the reason for the values of the overlap integrals reported in eq. (129) is that we consider atomic orbitals orthonormalized using the Löwdin procedure [90-92].

Thus the tight-binding relations become

\[
\begin{align*}
-\gamma_0 \sum_{i=1}^{3} \psi_B(R_{B_i}) &= (E - u(R_A)) \psi_A(R_A), \\
-\gamma_0 \sum_{i=1}^{3} \psi_A(R_{A_i}) &= (E - u(R_B)) \psi_B(R_B).
\end{align*}
\]

If we introduce the vectors (fig. 4(a))

\[
\begin{align*}
\tau_1 & \equiv \frac{a}{\sqrt{3}} \begin{bmatrix} -1 \\ 0 \\ 0 \end{bmatrix}, \\
\tau_2 & \equiv \frac{a}{\sqrt{3}} \begin{bmatrix} \frac{1}{2} \\ \frac{1}{2} \sqrt{3} \\ 0 \end{bmatrix}, \\
\tau_3 & \equiv \frac{a}{\sqrt{3}} \begin{bmatrix} \frac{1}{2} \\ 0 \\ \frac{1}{2} \sqrt{3} \end{bmatrix}
\end{align*}
\]

(with respect to the frame \(\Sigma' = (\hat{x}', \hat{y}', \hat{z}')\)), we can write the positions of the nearest-neighbor atoms in this way:

\[
\begin{align*}
R_{B_1} &= R_A - \tau_1, \\
R_{B_2} &= R_A - \tau_2, \\
R_{B_3} &= R_A - \tau_3, \\
R_{A_1} &= R_B + \tau_1, \\
R_{A_2} &= R_B + \tau_2, \\
R_{A_3} &= R_B + \tau_3.
\end{align*}
\]
and thus we can rewrite the tight-binding relations in the following form:

\[
\begin{align*}
-\gamma_0 \sum_{l=1}^{3} \psi_B(R_A - \tau_i) &= (E - u(R_A)) \psi_A(R_A), \\
-\gamma_0 \sum_{l=1}^{3} \psi_A(R_B + \tau_i) &= (E - u(R_B)) \psi_B(R_B).
\end{align*}
\]

(133)

Now let us consider what happens near the points \( K \) and \( K' \).

Let us assume that we can write

\[
\begin{align*}
\psi_A(R_A) &= e^{iK \cdot F_A^K(R_A)} - i e^{i\theta'} e^{iK' \cdot F_A^{K'}(R_A)}, \\
\psi_B(R_B) &= i e^{i\theta'} e^{iK \cdot F_B^K(R_B)} + e^{iK' \cdot F_B^{K'}(R_B)}
\end{align*}
\]

(134)

(the angle \( \theta' \) will be properly chosen later). If \( k \) is the wave vector of \( \psi_A \) and \( \psi_B \), the functions \( F_A^K \) and \( F_B^K \) have a wave vector \( \kappa = k - K \) and thus are slowly-varying functions (with small \( \alpha \) and \( \alpha' \)).

Near the point

\[
\begin{align*}
\psi_A(R_A) &= e^{iK \cdot F_A^K(R_A)} - i e^{i\theta'} e^{iK' \cdot F_A^{K'}(R_A)}, \\
\psi_B(R_B) &= i e^{i\theta'} e^{iK \cdot F_B^K(R_B)} + e^{iK' \cdot F_B^{K'}(R_B)}
\end{align*}
\]

(135)

where we have substituted \( F_i^{Kj}(r) \) to \( F_i^{Kj}(R_i) \) using the fact that \( F_i^{Kj} \) is a slowly varying function of \( r \) near \( K_j \), while the atomic orbital \( \varphi \) has significant values only near the corresponding atom. The quantity between square brackets (that we have called here \( \tilde{u}_{Kj}^{i} \)) is periodic with the periodicity of the lattice, since, if \( a_\ell \) is a lattice unit vector (and thus, if \( R_i \) is the position of a lattice point, also \( R_i^0 = R_i - a_\ell \) is the position of
a lattice point), then

$$\tilde{u}_k^{K_j}(r + a_l) = \alpha_k^{K_j} \sum_{R_i} \varphi((r + a_l) - R_i) e^{-iK_j \cdot ((r + a_l) - R_i)} =$$

$$\alpha_k^{K_j} \sum_{R_i} \varphi(r - (R_i - a_l)) e^{-iK_j \cdot (r - (R_i - a_l))} =$$

$$\alpha_k^{K_j} \sum_{R_i} \varphi(r - R_i^0) e^{-iK_j \cdot (r - R_i^0)} = \tilde{u}_k^{K_j}(r).$$

Therefore, since \(\tilde{u}_k^{K_j}\) has the lattice periodicity and \(K_j\) is an extremum point (different from 0) of the dispersion relations, from the relation between \(\psi(r)\), \(\tilde{u}_k^{K_j}(r)\) and \(F_i^{K_j}(r)\) we conclude that the 4 functions \(F_i^{K_j}(r)\) can be seen as the electron envelope functions corresponding to the 2 extremum points \(K_j\) where the 2 considered bands of graphene are degenerate (see eq. (95), the related discussion, and eq. (107)).

Let us point out that this whole procedure does not need a particular choice of scalar product and of normalization: these have just to be chosen coherently with each other. However, one could find desirable to normalize the periodic function \(\tilde{u}_k^{K_j}\) according to the scalar product defined in (73), as is generally done in the envelope function theory. Following this particular criterion, one should have (if \(\Omega_0\) is the area of a graphene unit cell, while \(\Omega\) is the area of the overall graphene sheet)

$$\frac{1}{\Omega} \int_{\Omega} |\tilde{u}_k^{K_j}(r)|^2 dr = \frac{1}{\Omega} \int_{\Omega} |\tilde{u}_k^{K_j}(r)|^2 dr =$$

$$\frac{1}{\Omega} \int_{\Omega} \left( \sum_{R_i} \varphi(r - R_i) e^{-iK_j \cdot (r - R_i)} \right)^* \left( \sum_{R_i} \varphi(r - R_i^0) e^{-iK_j \cdot (r - R_i^0)} \right) dr =$$

$$\frac{1}{\Omega} \sum_{R_i} |\varphi(r - R_i)|^2 dr + \frac{1}{\Omega} \sum_{R_i, R_i', R_i \neq R_i'} \int_{\Omega} \varphi^*(r - R_i) \varphi(r - R_i') dr e^{iK_j \cdot (R_i' - R_i)} =$$

$$\frac{1}{\Omega} \sum_{R_i} |\varphi(r - R_i)|^2 dr = \frac{1}{\Omega_0} \sum_{R_i} |\varphi(r - R_i)|^2 dr \simeq$$

$$\frac{1}{\Omega_0} \int_{\Omega} |\varphi(r - R_i)|^2 dr = \frac{1}{\Omega_0} \int_{\Omega} |\varphi(r - R_i)|^2 dr.$$

Here we have exploited the following properties of the involved functions. First of all, integrating a function with the lattice periodicity over the whole graphene sheet and dividing the result by its area is equivalent to integrating it over the lattice unit cell and dividing by the corresponding area. Moreover, each atomic orbital \(\varphi\) (orthonormalized using the Löwdin procedure) has a non-zero overlap only with itself. Finally, since each
atomic orbital has significative values only near the corresponding atom, the integral of the square modulus over the whole graphene sheet is nearly the same for all the considered atomic orbitals, and thus the sum of all the integrals is approximately equal to a single integral multiplied by the number \( \Omega/\Omega_0 \) of orbitals.

Therefore, adopting this particular normalization for \( \tilde{u}_{\mathbf{K}}^1 \), the atomic orbital \( \varphi \) should be normalized in such a way that

\[
(138) \quad \frac{1}{\Omega_0} \int_\Omega |\varphi(\mathbf{r} - \mathbf{R}_i)|^2 \, d\mathbf{r} = 1 \Rightarrow \int_\Omega |\varphi(\mathbf{r} - \mathbf{R}_i)|^2 \, d\mathbf{r} = \Omega_0,
\]

and thus we should consider atomic orbitals \( \sqrt{\Omega_0} \) times greater than those deriving from the usual normalization over the whole graphene sheet.

The corresponding scalar product

\[
(139) \quad \langle \varphi_1 | \varphi_2 \rangle = \frac{1}{\Omega_0} \int_\Omega \varphi_1^*(\mathbf{r}) \varphi_2(\mathbf{r}) \, d\mathbf{r}
\]

should be used in all the calculations involving atomic orbitals.

If we introduce the assumptions (134) into the tight-binding equations (133), we obtain

\[
(140) \quad \begin{cases}
(E - u(\mathbf{R}_A)) \left[ e^{i\mathbf{K} \mathbf{R}_A} F_A^\mathbf{K}(\mathbf{R}_A) - i e^{i\theta} e^{i\mathbf{K}' \mathbf{R}_A} F_A^{\mathbf{K}'}(\mathbf{R}_A) \right] = \\
-\gamma_0 \sum_{l=1}^3 \left[ i e^{i\theta} e^{i\mathbf{K} (\mathbf{R}_A - \mathbf{\tau}_l)} F_B^{\mathbf{K}}(\mathbf{R}_A - \mathbf{\tau}_l) + e^{i\mathbf{K}' (\mathbf{R}_A - \mathbf{\tau}_l)} F_B^{\mathbf{K}'}(\mathbf{R}_A - \mathbf{\tau}_l) \right] = \\
(E - u(\mathbf{R}_B)) \left[ i e^{i\theta} e^{i\mathbf{K} \mathbf{R}_B} F_B^\mathbf{K}(\mathbf{R}_B) + e^{i\mathbf{K}' \mathbf{R}_B} F_B^{\mathbf{K}'}(\mathbf{R}_B) \right] = \\
-\gamma_0 \sum_{l=1}^3 \left[ e^{i\mathbf{K} (\mathbf{R}_B + \mathbf{\tau}_l)} F_A^\mathbf{K}(\mathbf{R}_B + \mathbf{\tau}_l) - i e^{i\theta} e^{i\mathbf{K}' (\mathbf{R}_B + \mathbf{\tau}_l)} F_A^{\mathbf{K}'}(\mathbf{R}_B + \mathbf{\tau}_l) \right].
\]

It is useful to introduce [55, 56] a smoothing function \( g(\mathbf{r}) \), i.e. a real function which varies smoothly around the point around which it is centered, has non-negligible values only in a range of a few lattice constants around the center, and then decays rapidly for larger distances. This function (point-symmetric around its center) is chosen in such a way as to satisfy the conditions

\[
(141) \quad \sum_{\mathbf{R}_A} g(\mathbf{r} - \mathbf{R}_A) = \sum_{\mathbf{R}_B} g(\mathbf{r} - \mathbf{R}_B) = 1
\]

and

\[
(142) \quad \int_\Omega d\mathbf{r} g(\mathbf{r} - \mathbf{R}_A) = \int_\Omega d\mathbf{r} g(\mathbf{r} - \mathbf{R}_B) = \Omega_0
\]

(where \( \Omega_0 = \sqrt{3}a^2/2 \) is the area of a graphene unit cell, while \( \Omega \) is the area of the overall graphene sheet); moreover it has to satisfy the relations

\[
(143) \quad \sum_{\mathbf{R}_A} g(\mathbf{r} - \mathbf{R}_A) e^{i(\mathbf{K}' - \mathbf{K}) \cdot \mathbf{R}_A} = \sum_{\mathbf{R}_B} g(\mathbf{r} - \mathbf{R}_B) e^{i(\mathbf{K}' - \mathbf{K}) \cdot \mathbf{R}_B} \simeq 0.
\]
Due to its locality, when this function is multiplied by a generic smooth function \( f(r) \) (such as the envelope functions \( F \) we have defined), we clearly have that

\[
(144) \quad f(r)g(r - R) \simeq f(R)g(r - R)
\]

(for positions \( r \) for which \( g(r - R) \) is not negligible, the smooth function \( f(r) \) is approximately equal to \( f(R) \), while for positions \( r \), further away from \( R \), for which \( f(r) \) significantly differs from \( f(R) \), the function \( g(r - R) \) is null). In fig. 6 we show a possible smoothing function \( g(r) \), which approximately satisfies all the previous relations \(^2\).

If we multiply the first of the tight-binding equations (140) by \( g(r - R_A) e^{-iK \cdot R_A} \) and we sum it over \( R_A \), we find

\[
(145) \quad E \sum_{R_A} g(r - R_A) F_A^{K}(R_A) =
\]

\[
- E i e^{i\theta} \sum_{R_A} g(r - R_A) e^{i(K' - K) \cdot R_A} F_A^{K'}(R_A)
\]

\[
- \sum_{R_A} g(r - R_A) u(R_A) F_A^{K}(R_A)
\]

\[
+ i e^{i\theta} \sum_{R_A} g(r - R_A) e^{i(K' - K) \cdot R_A} u(R_A) F_A^{K'}(R_A) =
\]

\[
- \gamma_0 i e^{i\theta} \sum_{l=1}^{3} e^{-iK \cdot \tau_l} \sum_{R_A} g(r - R_A) F_B^{K}(R_A - \tau_l)
\]

\[
- \gamma_0 \sum_{l=1}^{3} e^{-iK' \cdot \tau_l} \sum_{R_A} g(r - R_A) e^{i(K' - K) \cdot R_A} F_B^{K'}(R_A - \tau_l);
\]

\(^2\) In detail, we have represented the function defined as \( 106.5307 \exp(-0.5767(\frac{1}{1.5 - |r|/0.355 \text{ nm}})^2) \) for \(|r| < 0.355 \text{ nm} \), and \( 0 \) for \(|r| \geq 0.355 \text{ nm} \), but better approximations for the smoothing function \( g(r) \) can be found.
Exploiting the property (144) it becomes

\[ (146) \quad E \left[ \sum_{R_A} g(r - R_A) F_A^K(r) - E \, i \, e^{i\theta'} \left[ \sum_{R_A} g(r - R_A) e^{i(K' - K)R_A} \right] F_A^{K'}(r) \right] \\
- \left[ \sum_{R_A} g(r - R_A)u(R_A) \right] F_A^K(r) \\
+ i \, e^{i\theta'} \left[ \sum_{R_A} g(r - R_A) e^{i(K' - K)R_A} u(R_A) \right] F_A^{K'}(r) = \\
- \gamma_0 \, i \, e^{i\theta'} \sum_{l=1}^{3} e^{-iK' \tau_l} \left[ \sum_{R_A} g(r - R_A) e^{i(K' - K)R_A} \right] F_B^{K'}(r - \tau_l). \]

For the quantities in the square brackets, we can use the properties (141) and (143), together with the definitions

\[ (147) \quad u_A(r) = \sum_{R_A} g(r - R_A)u(R_A), \quad u'_A(r) = \sum_{R_A} g(r - R_A) e^{i(K' - K)R_A} u(R_A), \]

obtaining

\[ (148) \quad E F_A^K(r) - u_A(r) F_A^K(r) + i \, e^{i\theta'} u'_A(r) F_A^{K'}(r) = \\
- \gamma_0 \, i \, e^{i\theta'} \sum_{l=1}^{3} e^{-iK' \tau_l} F_B^{K'}(r - \tau_l). \]

Expanding the smooth quantity \( F_B^K(r - \tau_l) \) to the first order in \( \tau_l \), we have that

\[ (149) \quad \sum_{l=1}^{3} e^{-iK' \tau_l} F_B^K(r - \tau_l) \approx \sum_{l=1}^{3} e^{-iK' \tau_l} \left[ F_B^K(r) - \left( \tau_l \frac{\partial}{\partial r} \right) F_B^K(r) \right] = \\
\left\{ \sum_{l=1}^{3} e^{-iK' \tau_l} F_B^K(r) - \sum_{l=1}^{3} e^{-iK' \tau_l} \left( \tau_l \frac{\partial}{\partial r} \right) F_B^K(r) \right\}. \]

Let us now calculate the value of the sums which appear in the previous expression

\[ (150) \quad \sum_{l=1}^{3} e^{-iK' \tau_l} = 1 + e^{-i\frac{2\pi}{3}} + e^{i\frac{2\pi}{3}} = 0; \]

\[ \sum_{l=1}^{3} e^{-iK' \tau_l} \left( \tau_l \frac{\partial}{\partial r} \right) = \frac{a}{\sqrt{3}} \left( -\frac{\partial}{\partial x'} \right) \]

\[ + e^{-i\frac{2\pi}{3}} \frac{a}{\sqrt{3}} \left( \frac{1}{2} \frac{\partial}{\partial x'} - \frac{\sqrt{3}}{2} \frac{\partial}{\partial y'} \right) + e^{i\frac{2\pi}{3}} \frac{a}{\sqrt{3}} \left( \frac{1}{2} \frac{\partial}{\partial x'} + \frac{\sqrt{3}}{2} \frac{\partial}{\partial y'} \right) = \\
\frac{a}{\sqrt{3}} \left( -1 + \frac{1}{2} e^{-i\frac{2\pi}{3}} + \frac{1}{2} e^{i\frac{2\pi}{3}} \right) \frac{\partial}{\partial x'} + \left( \frac{\sqrt{3}}{2} e^{-i\frac{2\pi}{3}} + \frac{\sqrt{3}}{2} e^{i\frac{2\pi}{3}} \right) \frac{\partial}{\partial y'} \right). \]
\[
\sum_{l=1}^{3} e^{-iK \cdot \tau_l} \left( \tau_l \cdot \frac{\partial}{\partial r} \right) = -\frac{a}{\sqrt{3}} \left( \frac{\partial}{\partial x'} - i \frac{\partial}{\partial y'} \right) = -\frac{\sqrt{3}}{2} a(\hat{k}_{x'} + \hat{k}_{y'}) = -\frac{i\sqrt{3}}{2} a(\hat{k}_{x'} - i\hat{k}_{y'}),
\]

where we have defined \( \hat{k} = -i \nabla \) and thus

\[
\hat{k}_{x'} = -i \frac{\partial}{\partial x'} \quad \text{and} \quad \hat{k}_{y'} = -i \frac{\partial}{\partial y'}.
\]

Substituting these results, eq. (148) becomes

\[
E F_A^K(r) = u_A(r) F_A^K(r) + i e^{i\theta'} u'_A(r) F_A^K(r) = -\gamma_0 a e^{i\theta'} \left( \frac{\sqrt{3}}{2} a(\hat{k}_{x'} - i\hat{k}_{y'}) F_B^K(r) \right) = \\
\sqrt{3} \gamma_0 a e^{i\theta'} (\hat{k}_{x'} - i\hat{k}_{y'}) F_B^K(r) = \gamma(\hat{k}_x - i\hat{k}_y) F_B^K(r),
\]

where we have passed from the original reference frame \( \Sigma' = (\hat{x}', \hat{y}', \hat{z}') \) to a new frame \( \Sigma = (\hat{x}, \hat{y}, \hat{z}) \), rotated, in the plane \( (\hat{x}', \hat{y}') \), around the origin by an angle \( \theta' \) (positive in the counterclockwise direction) with respect to the original one (fig. 7) and we have used the fact that

\[
e^{i\theta'} (\hat{k}_{x'} - i\hat{k}_{y'}) = (\cos \theta' + i \sin \theta')(\hat{k}_{x'} - i\hat{k}_{y'}) = \\
(\cos \theta' \hat{k}_{x'} + \sin \theta' \hat{k}_{y'}) - i(\cos \theta' \hat{k}_{y'} - \sin \theta' \hat{k}_{x'}) = \hat{k}_x - i\hat{k}_y
\]

(due to the relations between old and new coordinates), with

\[
\hat{k}_x = -i \frac{\partial}{\partial x} \quad \text{and} \quad \hat{k}_y = -i \frac{\partial}{\partial y}.
\]

Indeed, it is a well-known result that, for a rotation by \( \theta' \) of the reference frame, the relations between the new and the old coordinates are \( x = x' \cos \theta' + y' \sin \theta' \) and \( y = y' \cos \theta' - x' \sin \theta' \). Therefore we have that

\[
\frac{\partial F(x, y)}{\partial x'} = \frac{\partial F(x, y)}{\partial x} \frac{\partial x}{\partial x'} + \frac{\partial F(x, y)}{\partial y} \frac{\partial y}{\partial x'} = \frac{\partial F(x, y)}{\partial x} \cos \theta' - \frac{\partial F(x, y)}{\partial y} \sin \theta'
\]

and that

\[
\frac{\partial F(x, y)}{\partial y'} = \frac{\partial F(x, y)}{\partial x} \frac{\partial x}{\partial y'} + \frac{\partial F(x, y)}{\partial y} \frac{\partial y}{\partial y'} = \frac{\partial F(x, y)}{\partial x} \sin \theta' + \frac{\partial F(x, y)}{\partial y} \cos \theta'.
\]
As a consequence, we have that

\[ (\cos \theta \hat{\kappa}_x + \sin \theta \hat{\kappa}_y) F(x, y) = \cos \theta \left( -i \frac{\partial F(x, y)}{\partial x'} + \sin \theta \frac{\partial F(x, y)}{\partial y'} \right) = \]
\[ -i \left[ \frac{\partial F(x, y)}{\partial x} \cos^2 \theta' - \frac{\partial F(x, y)}{\partial y} \cos \theta' \sin \theta' \right. \]
\[ + \frac{\partial F(x, y)}{\partial x} \sin^2 \theta' + \frac{\partial F(x, y)}{\partial y} \sin \theta' \cos \theta' \bigg] = \]
\[ -i \frac{\partial F(x, y)}{\partial x} (\cos^2 \theta' + \sin^2 \theta') = -i \frac{\partial F(x, y)}{\partial x} = \hat{\kappa}_x F(x, y) \]

and that

\[ (\cos \theta' \hat{\kappa}_y - \sin \theta' \hat{\kappa}_x) F(x, y) = \cos \theta' \left( -i \frac{\partial F(x, y)}{\partial y'} - \sin \theta' \frac{\partial F(x, y)}{\partial x'} \right) = \]
\[ -i \left[ \frac{\partial F(x, y)}{\partial x} \sin \theta' \cos \theta' + \frac{\partial F(x, y)}{\partial y} \cos^2 \theta' - \right. \]
\[ \left. - \frac{\partial F(x, y)}{\partial x} \cos \theta' \sin \theta' + \frac{\partial F(x, y)}{\partial y} \sin^2 \theta' \right] = \]
\[ -i \frac{\partial F(x, y)}{\partial y} (\cos^2 \theta' + \sin^2 \theta') = -i \frac{\partial F(x, y)}{\partial y} = \hat{\kappa}_y F(x, y), \]

from which we obtain eq. (154).

\( \theta' \) is the angle, taken counterclockwise, from the vector \( \mathbf{a}_1 + \mathbf{a}_2 \) to the axis \( \hat{x} \) of the new frame. We have also defined the quantity \( \gamma = (\sqrt{3}/2)\gamma_0 a \).
Note that in the new reference frame $\Sigma = (\hat{x}, \hat{y}, \hat{z})$

\begin{align}
(160) \quad & a_1 \equiv \frac{\alpha}{2} \begin{bmatrix} \sqrt{3} \cos \theta' + \sin \theta' \\ \cos \theta' - \sqrt{3} \sin \theta' \\ 0 \end{bmatrix}, \quad a_2 \equiv \frac{\alpha}{2} \begin{bmatrix} \sqrt{3} \cos \theta' - \sin \theta' \\ - \cos \theta' - \sqrt{3} \sin \theta' \\ 0 \end{bmatrix}, \\
& b_1 \equiv \frac{2\pi}{\sqrt{3}a} \begin{bmatrix} \cos \theta' + \sqrt{3} \sin \theta' \\ \sqrt{3} \cos \theta' - \sin \theta' \\ 0 \end{bmatrix}, \quad b_2 \equiv \frac{2\pi}{\sqrt{3}a} \begin{bmatrix} \cos \theta' - \sqrt{3} \sin \theta' \\ - \sqrt{3} \cos \theta' - \sin \theta' \\ 0 \end{bmatrix}, \\
& K \equiv \frac{4\pi}{3a} \begin{bmatrix} - \sin \theta' \\ - \cos \theta' \\ 0 \end{bmatrix}, \quad K' \equiv \frac{4\pi}{3a} \begin{bmatrix} \sin \theta' \\ \cos \theta' \\ 0 \end{bmatrix}.
\end{align}

Analogously, if we multiply the second of the tight-binding equations (140) by $g(r - R_B)(-i e^{-i\theta'} e^{iK'R_B})$ and we sum it over $R_B$, using again the properties (144), (141) and (143), together with the definitions

\begin{align}
(161) \quad & u_B(r) = \sum_{R_B} g(r - R_B)u(R_B), \quad u'_B(r) = \sum_{R_B} g(r - R_B)\varepsilon_i(K' - K)R_B u(R_B),
\end{align}

we obtain [93]

\begin{align}
(162) \quad & E F^K_B(r) - u_B(r) F^K_B(r) + i e^{-i\theta'} u'_B(r) F^K_B'(r) = \\
& \gamma_0 \varepsilon_i e^{-i\theta'} \sum_{l=1}^3 e^{iK' \tau_l} F^K_A(r + \tau_l).
\end{align}

Expanding the smooth quantity $F^K_A(r + \tau_l)$ to the first order in $\tau_l$, we have that

\begin{align}
(163) \quad & \sum_{l=1}^3 e^{iK' \tau_l} F^K_A(r + \tau_l) \simeq \sum_{l=1}^3 e^{iK' \tau_l} \left[ F^K_A(r) + \left( \tau_l \cdot \frac{\partial}{\partial r} \right) F^K_A(r) \right] = \\
& \left( \sum_{l=1}^3 e^{iK' \tau_l} \right) F^K_A(r) + \left[ \sum_{l=1}^3 e^{iK' \tau_l} \tau_l \cdot \frac{\partial}{\partial r} \right] F^K_A(r).
\end{align}

Since

\begin{align}
(164) \quad & \sum_{l=1}^3 e^{iK' \tau_l} = 0 \quad \text{and} \quad \sum_{l=1}^3 e^{iK' \tau_l} \tau_l \cdot \frac{\partial}{\partial r} = -i \frac{\sqrt{3}}{2} u(\kappa_{x'} + i\kappa_{y'}),
\end{align}

eq. (162) becomes

\begin{align}
(165) \quad & E F^K_B(r) - u_B(r) F^K_B(r) + i e^{-i\theta'} u'_B(r) F^K_B'(r) \simeq \\
& \gamma_0 \varepsilon_i e^{-i\theta'} \left( -i \frac{\sqrt{3}}{2} u(\kappa_{x'} + i\kappa_{y'}) \right) F^K_A(r) = \\
& \frac{\sqrt{3}}{2} \gamma_0 \varepsilon_i e^{-i\theta'} (\kappa_{x'} + i\kappa_{y'}) F^K_A(r) = \gamma (\kappa_x + i\kappa_y) F^K_A(r),
\end{align}

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where we have made use of the relation
\begin{equation}
(166) \quad e^{-i\theta'}(\hat{k}_{x'} + i\hat{k}_{y'}) = (\cos\theta' - i\sin\theta')(\hat{k}_{x'} + i\hat{k}_{y'}) =
(\cos\theta'\hat{k}_{x'} + \sin\theta'\hat{k}_{y'}) + i(\cos\theta'\hat{k}_{y'} - \sin\theta'\hat{k}_{x'}) = \hat{k}_x + i\hat{k}_y.
\end{equation}

Instead, if we multiply the first of the tight-binding equations (140) by \( g(r - R_A) \times (i e^{-i\theta'} e^{-iK' \cdot R_A}) \) and we sum it over \( R_A \), we obtain (exploiting the properties (144), (141) and (143)) [93]
\begin{equation}
(167) \quad E F_A^{K'}(r) - i e^{-i\theta'} u_A^*(r) F_A^K(r) - u_A(r) F_A^{K'}(r) =
-\gamma_0 i e^{-i\theta'} \sum_{l=1}^{3} e^{-iK' \cdot \tau_l} F_B^{K'}(r - \tau_l).
\end{equation}

Expanding the smooth quantity \( F_B^{K'}(r - \tau_l) \) to the first order in \( \tau_l \), we have that
\begin{equation}
(168) \quad \sum_{l=1}^{3} e^{-iK' \cdot \tau_l} F_B^{K'}(r - \tau_l) \simeq 
\sum_{l=1}^{3} e^{-iK' \cdot \tau_l} \left[ F_B^{K'}(r) - \left( \tau_l \cdot \frac{\partial}{\partial r} \right) F_B^{K'}(r) \right] =
\left( \sum_{l=1}^{3} e^{-iK' \cdot \tau_l} \right) F_B^{K'}(r) - \sum_{l=1}^{3} e^{-iK' \cdot \tau_l} \left( \tau_l \cdot \frac{\partial}{\partial r} \right) F_B^{K'}(r),
\end{equation}
with
\begin{equation}
(169) \quad \sum_{l=1}^{3} e^{-iK' \cdot \tau_l} = 0 \quad \text{and} \quad \sum_{l=1}^{3} e^{-iK' \cdot \tau_l} \left( \tau_l \cdot \frac{\partial}{\partial r} \right) = -i\sqrt{3}a(\hat{k}_{x'} + i\hat{k}_{y'}).
\end{equation}

Therefore eq. (167) becomes
\begin{equation}
(170) \quad E F_A^{K'}(r) - i e^{-i\theta'} u_A^*(r) F_A^K(r) - u_A(r) F_A^{K'}(r) \simeq
-\gamma_0 i e^{-i\theta'} \left( \frac{\sqrt{3}}{2}a(\hat{k}_{x'} + i\hat{k}_{y'}) F_B^{K'}(r) \right) =
\frac{\sqrt{3}}{2} \gamma_0 a e^{-i\theta'}(\hat{k}_{x'} + i\hat{k}_{y'}) F_B^{K'}(r) = \gamma(\hat{k}_x + i\hat{k}_y) F_B^{K'}(r),
\end{equation}
where we have exploited the relation (166).

Finally, if we multiply the second of the tight-binding equations (140) by \( g(r - R_B) \times e^{-iK' \cdot R_B} \) and we sum it over \( R_B \), we obtain (using the properties (144), (141) and (143)) [93]
\begin{equation}
(171) \quad E F_B^{K'}(r) - i e^{i\theta'} u_B^*(r) F_B^K(r) - u_B(r) F_B^{K'}(r) =
\gamma_0 i e^{i\theta'} \sum_{l=1}^{3} e^{iK' \cdot \tau_l} F_A^{K'}(r + \tau_l).
\end{equation}
Expanding the smooth quantity \( F^K_A(r + \tau) \) to the first order in \( \tau \), we have that

\[
(172) \quad \sum_{l=1}^{3} e^{iK' \cdot \tau_l} F^K_A(r + \tau_l) \approx \sum_{l=1}^{3} e^{iK' \cdot \tau_l} \left[ F^K_A(r) + \left( \tau_l \cdot \frac{\partial}{\partial r} \right) F^K_A(r) \right] = \\
\left( \sum_{l=1}^{3} e^{iK' \cdot \tau_l} \right) F^K_A(r) + \left[ \sum_{l=1}^{3} e^{iK' \cdot \tau_l} \left( \tau_l \cdot \frac{\partial}{\partial r} \right) \right] F^K_A(r).
\]

Since

\[
(173) \quad \sum_{l=1}^{3} e^{iK' \cdot \tau_l} = 0 \quad \text{and} \quad \sum_{l=1}^{3} e^{iK' \cdot \tau_l} \left( \tau_l \cdot \frac{\partial}{\partial r} \right) = -\frac{\sqrt{3}}{2} \gamma \left( \hat{k}_x - i\hat{k}_y \right),
\]

eq. (171) becomes

\[
(174) \quad E F^K_B(r) - i \epsilon^{i\theta'} u'_B(r) F^K_A(r) - \frac{\sqrt{3}}{2} \gamma \left( \hat{k}_x - i\hat{k}_y \right) F^K_A(r) = \\
\gamma_0 \epsilon^{i\theta'} \left( -i \frac{\sqrt{3}}{2} \gamma \left( \hat{k}_x - i\hat{k}_y \right) \right) F^K_A(r) = \\
\frac{\sqrt{3}}{2} \gamma_0 \epsilon^{i\theta'} \left( \hat{k}_x - i\hat{k}_y \right) F^K_A(r) = \gamma \left( \hat{k}_x - i\hat{k}_y \right) F^K_A(r),
\]

where the relation (154) has been used.

In this way, we have obtained the four equations (153), (165), (170) and (174), that we can summarize

\[
(175) \quad \begin{cases}
  u_A(r) F^K_A(r) + \gamma(\hat{k}_x - i\hat{k}_y) F^K_B(r) - i \epsilon^{i\theta'} u'_A(r) F^K_A(r) = E F^K_B(r), \\
  \gamma(\hat{k}_x + i\hat{k}_y) F^K_A(r) + u_B(r) F^K_B(r) - i \epsilon^{-i\theta'} u'_B(r) F^K_A(r) = E F^K_B(r), \\
  i \epsilon^{-i\theta'} u'_A(r) F^K_A(r) + u_A(r) F^K_A(r) + \gamma(\hat{k}_x + i\hat{k}_y) F^K_B(r) = E F^K_A(r), \\
  i \epsilon^{i\theta'} u'_B(r) F^K_B(r) + \gamma(\hat{k}_x - i\hat{k}_y) F^K_A(r) + u_B(r) F^K_B(r) = E F^K_A(r),
\end{cases}
\]

and write in matrix form

\[
(176) \quad \begin{bmatrix}
  u_A(r) & \gamma(\hat{k}_x - i\hat{k}_y) & -i \epsilon^{i\theta'} u'_A(r) & 0 \\
  \gamma(\hat{k}_x + i\hat{k}_y) & u_B(r) & 0 & -i \epsilon^{-i\theta'} u'_B(r) \\
  i \epsilon^{-i\theta'} u'_A(r) & 0 & u_A(r) & \gamma(\hat{k}_x + i\hat{k}_y) \\
  0 & i \epsilon^{i\theta'} u'_B(r) & \gamma(\hat{k}_x - i\hat{k}_y) & u_B(r)
\end{bmatrix}
\begin{bmatrix}
  F^K_A(r) \\
  F^K_B(r) \\
  F^K_A(r) \\
  F^K_B(r)
\end{bmatrix} = \\
\begin{bmatrix}
  E F^K_A(r) \\
  E F^K_B(r) \\
  E F^K_A(r) \\
  E F^K_B(r)
\end{bmatrix},
\]

which is the \( k \cdot p \) equation of graphene.
Incidentally, if we repeat all the previous calculations considering the following different pair of reference Dirac points:

\[ K = \begin{bmatrix} 2\pi \\ 2\pi \\ 0 \end{bmatrix} \frac{1}{\sqrt{3a}}, \quad K' = \begin{bmatrix} 2\pi \\ 2\pi \\ 0 \end{bmatrix} \frac{1}{3a} \]

(equivalent, in the reciprocal space, to the pair (119) of Dirac points), we have to replace (134) with

\[
\left\{ \begin{array}{l}
\psi_A(R_A) = e^{iK\cdot R_A} F_A^K (R_A) + e^{i\eta} e^{iK'\cdot R_A} F_A^{K'} (R_A), \\
\psi_B(R_B) = -e^{i\frac{2\pi}{3\eta}} e^{iK\cdot R_B} F_B^K (R_B) + e^{iK'\cdot R_B} F_B^{K'} (R_B),
\end{array} \right.
\]

where \( \eta = \pi/6 + \theta' \), and we obtain (instead of eq. (176))

\[
\begin{bmatrix}
\gamma(\hat{p}_z - i\hat{p}_y) & e^{i\eta} u'_A(r) & 0 \\
\gamma(\hat{p}_z + i\hat{p}_y) & u_B(r) & 0 \\
e^{-i\eta} u'_A(r) & 0 & \gamma(\hat{p}_z - i\hat{p}_y)
\end{bmatrix}
\begin{bmatrix}
F_A^K (r) \\
F_B^K (r) \\
F_A^{K'} (r)
\end{bmatrix}
= \begin{bmatrix}
F_A^K (r) \\
F_B^K (r) \\
F_A^{K'} (r)
\end{bmatrix}
\]

as found by Ando \[55, 56\].

Summarizing, we have that the overall wave function is given by (see (120))

\[
\psi(r) = \sum_{R_A} \psi_A(R_A) \varphi(r - R_A) + \sum_{R_B} \psi_B(R_B) \varphi(r - R_B),
\]

with (see (134))

\[
\left\{ \begin{array}{l}
\psi_A(r) = e^{iK\cdot r} F_A^K (r) - i e^{i\theta} e^{iK'\cdot r} F_A^{K'} (r), \\
\psi_B(r) = i e^{i\theta} e^{iK\cdot r} F_B^K (r) + e^{iK'\cdot r} F_B^{K'} (r),
\end{array} \right.
\]

where the envelope functions \( F \) satisfy eq. (176).

We can treat two limiting cases for the external potential, depending on its range \[94, 95\].

If the potential range is much smaller than the lattice constant (short-range case), we can consider the external potential as different from zero only on one carbon atom.

If it is non-zero only on an atom of type A (in position \( R_{A_0} \)), \textit{i.e.} \( u(R_{A_0}) \neq 0 \), \( u(R_A) = 0 \) for \( R_A \neq R_{A_0} \) and \( u(R_B) = 0 \) for every \( R_B \), recalling eq. (147) and (161),
we have that

\begin{align}
(182) \quad u_A(r) &= \sum_{R_A} g(r - R_A)u(R_A) = g(r - R_{A_0})u(R_{A_0}), \\
        u'_A(r) &= \sum_{R_A} g(r - R_A)e^{i(K' - K) \cdot R_A}u(R_A) = \\
                 &= g(r - R_{A_0})e^{i(K' - K) \cdot R_{A_0}}u(R_{A_0}) = u_A(r)e^{i(K' - K) \cdot R_{A_0}}, \\
        u_B(r) &= \sum_{R_B} g(r - R_B)u(R_B) = 0, \\
        u'_B(r) &= \sum_{R_B} g(r - R_B)e^{i(K' - K) \cdot R_B}u(R_B) = \\
                 &= g(r - R_{B_0})e^{i(K' - K) \cdot R_{B_0}}u(R_{B_0}) = u_B(r)e^{i(K' - K) \cdot R_{B_0}}.
\end{align}

Instead, if it is nonzero only on an atom of type B (in position \( R_{B_0} \), i.e. \( u(R_{B_0}) \neq 0 \), \( u(R_B) = 0 \) for \( R_B \neq R_{B_0} \) and \( u(R_A) = 0 \) for every \( R_A \), we have that

\begin{align}
(183) \quad u_A(r) &= \sum_{R_A} g(r - R_A)u(R_A) = 0, \\
        u'_A(r) &= \sum_{R_A} g(r - R_A)e^{i(K' - K) \cdot R_A}u(R_A) = 0, \\
        u_B(r) &= \sum_{R_B} g(r - R_B)u(R_B) = g(r - R_{B_0})u(R_{B_0}), \\
        u'_B(r) &= \sum_{R_B} g(r - R_B)e^{i(K' - K) \cdot R_B}u(R_B) = \\
                 &= g(r - R_{B_0})e^{i(K' - K) \cdot R_{B_0}}u(R_{B_0}) = u_B(r)e^{i(K' - K) \cdot R_{B_0}}.
\end{align}

If instead the potential range is much larger than the lattice constant (long-range case), using eq. (141), (143) and (144), we have that

\begin{align}
(184) \quad u_A(r) &= \sum_{R_A} g(r - R_A)u(R_A) \approx \sum_{R_A} g(r - R_A)u(r) = \left[ \sum_{R_A} g(r - R_A) \right]u(r) = u(r), \\
        u'_A(r) &= \sum_{R_A} g(r - R_A)e^{i(K' - K) \cdot R_A}u(R_A) \approx \sum_{R_A} g(r - R_A)e^{i(K' - K) \cdot R_A}u(r) = \\
                 &= \left[ \sum_{R_A} g(r - R_A)e^{i(K' - K) \cdot R_A} \right]u(r) = 0, \\
        u_B(r) &= \sum_{R_B} g(r - R_B)u(R_B) \approx \\
                 &= \left[ \sum_{R_B} g(r - R_B) \right]u(r) = u(r) = u_A(r), \\
        u'_B(r) &= \sum_{R_B} g(r - R_B)e^{i(K' - K) \cdot R_B}u(R_B) \approx \sum_{R_B} g(r - R_B)e^{i(K' - K) \cdot R_B}u(r) = \\
                 &= \left[ \sum_{R_B} g(r - R_B)e^{i(K' - K) \cdot R_B} \right]u(r) = 0.
\end{align}
Here we have used first (exploiting the hypothesis that the external potential is a very smooth function in comparison with \( g(r) \)) the property (144) and then (for the quantities inside the square brackets) the properties (141) and (143) of the function \( g(r) \). In this last case the effect of the external potential on the Hamiltonian matrix is only to sum the same quantity, \( u(r) \), to all the diagonal elements of the matrix, as expected from the \( k \cdot p \) theory (see eq. (106), where the external potential was assumed slowly variable).

\[
E = \begin{bmatrix}
   u(r) & \gamma(\hat{k}_x - i\hat{k}_y) & 0 & 0 \\
   \gamma(\hat{k}_x + i\hat{k}_y) & u(r) & 0 & 0 \\
   0 & 0 & u(r) & \gamma(\hat{k}_x + i\hat{k}_y) \\
   0 & 0 & \gamma(\hat{k}_x - i\hat{k}_y) & u(r)
\end{bmatrix} \begin{bmatrix}
   F_A^K(r) \\
   F_B^K(r) \\
   F_A'^K(r) \\
   F_B'^K(r)
\end{bmatrix} = \begin{bmatrix}
   F_A^K(r) \\
   F_B^K(r) \\
   F_A'^K(r) \\
   F_B'^K(r)
\end{bmatrix}
\]

Let us note that by reordering the elements of the envelope function vector, we can rewrite this equation in the form

\[
E = \begin{bmatrix}
   u(r) & 0 & 0 & \gamma(\hat{k}_x - i\hat{k}_y) \\
   0 & u(r) & \gamma(\hat{k}_x + i\hat{k}_y) & 0 \\
   0 & \gamma(\hat{k}_x - i\hat{k}_y) & u(r) & 0 \\
   \gamma(\hat{k}_x + i\hat{k}_y) & 0 & 0 & u(r)
\end{bmatrix} \begin{bmatrix}
   F_A^K(r) \\
   F_A'^K(r) \\
   F_B^K(r) \\
   F_B'^K(r)
\end{bmatrix} = \begin{bmatrix}
   F_A^K(r) \\
   F_A'^K(r) \\
   F_B^K(r) \\
   F_B'^K(r)
\end{bmatrix}
\]

which can be more compactly written as

\[
(187) \quad \begin{bmatrix}
   u(r) & \gamma \sigma \cdot \hat{k} \\
   \gamma \sigma \cdot \hat{k} & u(r)
\end{bmatrix} \begin{bmatrix}
   F_A^K(r) \\
   F_B^K(r) \\
   F_A'^K(r) \\
   F_B'^K(r)
\end{bmatrix} = E \begin{bmatrix}
   F_A^K(r) \\
   F_A'^K(r) \\
   F_B^K(r) \\
   F_B'^K(r)
\end{bmatrix}
\]

(where \( I \) is the 2 × 2 identity matrix and \( \sigma \) is the vector having as components the Pauli spin matrices \( \sigma_x \) and \( \sigma_y \)). This equation is analytically equivalent to the Dirac
equation for massless particles (Weyl’s equation) of relativistic quantum mechanics \(^{(3)}\); therefore eq. (185) is commonly called the Dirac equation for graphene. Since charge carriers in graphene obey a relation identical to that describing the relativistic behavior of elementary massless spin-(1/2) particles, transport in graphene exhibits many phenomena, such as Klein’s tunneling, analogous to those predicted in relativistic quantum mechanics [57-61].

Note that in the presence of a magnetic field the operator \( \hat{\kappa} = -i \nabla \) which appears in the equation has to be replaced by \(-i \nabla + eA/\hbar\), as we have shown in the general introduction on the \( \mathbf{k} \cdot \mathbf{p} \) method.

In the absence of an external potential, the quantities \( u_A, u'_A, u_B \) and \( u'_B \) are null and thus the matrix equation becomes

\[
\begin{bmatrix}
0 & \gamma(\hat{\kappa}_x - i\hat{\kappa}_y) & 0 & 0 \\
\gamma(\hat{\kappa}_x + i\hat{\kappa}_y) & 0 & 0 & 0 \\
0 & 0 & 0 & \gamma(\hat{\kappa}_x + i\hat{\kappa}_y) \\
0 & 0 & \gamma(\hat{\kappa}_x - i\hat{\kappa}_y) & 0 \\
\end{bmatrix}
\begin{bmatrix}
F^K_A(r) \\
F^K_B(r) \\
F'^K_A(r) \\
F'^K_B(r) \\
\end{bmatrix}
= E
\begin{bmatrix}
F^K_A(r) \\
F^K_B(r) \\
\end{bmatrix}.
\]

Since in this case the part of equation corresponding to the point \( \mathbf{K} \) is decoupled from that corresponding to the point \( \mathbf{K}' \), we can consider the two parts separately.

In particular, the part of equation corresponding to the point \( \mathbf{K} \) is

\[
\begin{bmatrix}
0 & \gamma(\hat{\kappa}_x - i\hat{\kappa}_y) \\
\gamma(\hat{\kappa}_x + i\hat{\kappa}_y) & 0 \\
\end{bmatrix}
\begin{bmatrix}
F^K_A(r) \\
F^K_B(r) \\
\end{bmatrix}
= E
\begin{bmatrix}
F^K_A(r) \\
F^K_B(r) \\
\end{bmatrix},
\]

or (using the Pauli spin matrices (44))

\[
\gamma(\hat{\kappa}_x \sigma_x + \hat{\kappa}_y \sigma_y) F^K(r) = \gamma(\hat{\kappa} \cdot \sigma) F^K(r) = E F^K(r).
\]

This \( \mathbf{k} \cdot \mathbf{p} \) Hamiltonian matrix, converted into the momentum representation (see eq. (111)), has as eigenvalues the dispersion relations of the two degenerate energy bands \( E^K(\kappa) \) and as eigenvectors the corresponding electron envelope functions \( F^K(r) \).

In particular, if we set

\[
\text{det} \left\{ \begin{bmatrix} 0 & \gamma(\kappa_x - i\kappa_y) \\ \gamma(\kappa_x + i\kappa_y) & 0 \end{bmatrix} - E \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \right\} = 0,
\]

\(^{(3)}\) For example, compare this equation with eq. (3.62) of ref. [96], with \( m = 0, \ A = 0, \ eA_0 = u(r) \), \( c \) substituted by \( v_F = \gamma/\hbar \), \( \psi_A \) substituted by \([F^K_A, F^K_A]^T \), and \( \psi_B \) substituted by \([F'^K_B, F'^K_B]^T \).
we find the dispersion relations

\[ E^K_s(\mathbf{\kappa}) = s\gamma \sqrt{\kappa_x^2 + \kappa_y^2} = s\gamma |\mathbf{\kappa}|, \]

where \( s \) can assume the values +1 or -1.

If we define the angle \( \alpha \) in such a way that

\[ \kappa_x + i\kappa_y = |\mathbf{\kappa}|e^{i(\frac{\pi}{2} + \alpha)} = i|\mathbf{\kappa}|e^{i\alpha} \]

and thus

\[ \kappa_x - i\kappa_y = (\kappa_x + i\kappa_y)^* = |\mathbf{\kappa}|e^{i(-\frac{\pi}{2} - \alpha)} = -i|\mathbf{\kappa}|e^{-i\alpha}, \]

we have that the corresponding envelope functions (properly normalized, as we will see), are

\[ F^K_{s\kappa}(r) = \frac{1}{\sqrt{2\Omega}} e^{i\mathbf{\kappa} \cdot \mathbf{r}} e^{i\phi_s(\mathbf{\kappa})} R(-\alpha(\mathbf{\kappa})) |s\rangle, \]

with

\[ |s\rangle = \frac{1}{\sqrt{2}} \begin{bmatrix} -is \\ 1 \end{bmatrix}, \]

where \( \Omega \) is the considered surface area, \( \phi_s(\mathbf{\kappa}) \) is an arbitrary phase factor and \( R(\alpha) \) is a spin-rotation operator, given by

\[ R(\alpha) = \begin{bmatrix} e^{i\frac{\alpha}{2}} & 0 \\ 0 & e^{-i\frac{\alpha}{2}} \end{bmatrix}. \]

This can be easily verified noting that

\[ \gamma \begin{bmatrix} 0 & \frac{\kappa_x - i\kappa_y}{\sqrt{\kappa_x^2 + \kappa_y^2}} \\ \frac{\kappa_x + i\kappa_y}{\sqrt{\kappa_x^2 + \kappa_y^2}} & 0 \end{bmatrix} F^K_{s\kappa}(r) = \]

\[ \gamma \begin{bmatrix} 0 & \frac{\kappa_x - i\kappa_y}{\sqrt{\kappa_x^2 + \kappa_y^2}} \\ \frac{\kappa_x + i\kappa_y}{\sqrt{\kappa_x^2 + \kappa_y^2}} & 0 \end{bmatrix} \frac{1}{\sqrt{2\Omega}} e^{i\mathbf{\kappa} \cdot \mathbf{r}} e^{i\phi_s(\mathbf{\kappa})} R(-\alpha(\mathbf{\kappa})) |s\rangle = \]

\[ \frac{1}{\sqrt{2\Omega}} e^{i\mathbf{\kappa} \cdot \mathbf{r}} e^{i\phi_s(\mathbf{\kappa})} \left( \frac{1}{\sqrt{2\Omega}} e^{i\mathbf{\kappa} \cdot \mathbf{r}} e^{i\phi_s(\mathbf{\kappa})} \right) \left( \begin{bmatrix} e^{i\frac{\alpha}{2}} & 0 \\ 0 & e^{-i\frac{\alpha}{2}} \end{bmatrix} \frac{1}{\sqrt{2}} \begin{bmatrix} -is \\ 1 \end{bmatrix} \right) = \]

\[ \frac{1}{\sqrt{2\Omega}} e^{i\mathbf{\kappa} \cdot \mathbf{r}} e^{i\phi_s(\mathbf{\kappa})} \left( \begin{bmatrix} 0 & -i|\mathbf{\kappa}|e^{-i\phi_s} \\ -i|\mathbf{\kappa}|e^{i\phi_s} & 0 \end{bmatrix} \frac{1}{|\mathbf{\kappa}|e^{i\phi_s}} \right) \left( \begin{bmatrix} 0 \\ -is \end{bmatrix} \right) = \]

\[ \frac{1}{\sqrt{2\Omega}} e^{i(\mathbf{\kappa} \cdot \mathbf{r} + \phi_s)} \left( \begin{bmatrix} 0 \\ -i|\mathbf{\kappa}|e^{-i\phi_s} \end{bmatrix} \right) \left( \begin{bmatrix} 0 \\ |\mathbf{\kappa}|e^{i\phi_s} \end{bmatrix} \right) = \]

\[ \frac{1}{\sqrt{2\Omega}} e^{i\mathbf{\kappa} \cdot \mathbf{r} + \phi_s} \left( \begin{bmatrix} 0 \\ -i|\mathbf{\kappa}|e^{-i\phi_s} \end{bmatrix} \right) \left( \begin{bmatrix} 0 \\ |\mathbf{\kappa}|e^{i\phi_s} \end{bmatrix} \right) = \]
and also

\[
E^K_s F^K_s(r) = s \gamma |\kappa| \left( \frac{1}{\sqrt{2\Omega}} e^{i\kappa \cdot r} e^{i\phi_s} \begin{bmatrix} e^{-i\frac{\phi_s}{2}} & 0 \\ 0 & e^{i\frac{\phi_s}{2}} \end{bmatrix} \begin{bmatrix} -i s \\ 1 \end{bmatrix} \right) = 
\]

\[
\begin{bmatrix} 0 \\ \gamma(e^{i(\kappa \cdot r + \phi_s)} - i s e^{-i\frac{\phi_s}{2}}) \end{bmatrix} = \frac{1}{2\sqrt{\Omega}} \gamma e^{i(\kappa \cdot r + \phi_s)} \begin{bmatrix} -i s |\kappa| e^{-i\frac{\phi_s}{2}} \\ |\kappa| e^{i\frac{\phi_s}{2}} \end{bmatrix} = 
\]

(199) (200)

\[
E^K'_{s}\tilde{F}^K'_{s}\kappa(r) = \frac{1}{2\sqrt{\Omega}} \gamma e^{i(\kappa \cdot r + \phi_s)} \begin{bmatrix} 0 \\ \gamma(\kappa_x + i\kappa_y) \end{bmatrix} \begin{bmatrix} F^K_A'_{s}(r) \\ F^K_B'_{s}(r) \end{bmatrix} = E \begin{bmatrix} F^K_A'_{s}(r) \\ F^K_B'_{s}(r) \end{bmatrix}, 
\]

or equivalently (using the Pauli spin matrices (44))

\[
\gamma (\kappa_x \sigma - \kappa_y \sigma) F^K'_{s}(r) = \gamma \left( \begin{bmatrix} \kappa_x \\ -\kappa_y \end{bmatrix} \cdot \sigma \right) F^K'_{s}(r) = E F^K'_{s}(r). 
\]

If we move to the momentum representation (see eq. (111)) and enforce

\[
\det \left\{ \begin{bmatrix} 0 \\ \gamma(\kappa_x - i\kappa_y) \end{bmatrix} - E \begin{bmatrix} 1 \\ 0 \\ 0 \\ 1 \end{bmatrix} \right\} = 0, 
\]

we find the dispersion relations

\[
E^K'_{s}(\kappa) = s \gamma \sqrt{\kappa_x^2 + \kappa_y^2} = s \gamma |\kappa|, 
\]

(202)

where \( s \) can assume the values +1 or −1.

The corresponding envelope functions are

\[
E^K'_{s}(r) = \frac{1}{\sqrt{2\Omega}} e^{i\kappa \cdot r} e^{i\tilde{\phi}_s(\kappa)} R(\alpha(\kappa)|\tilde{s}), 
\]

(204)

with \( \tilde{\phi}_s(\kappa) \) an arbitrary phase factor and

\[
|\tilde{s} = \frac{1}{\sqrt{2}} \begin{bmatrix} is \\ 1 \end{bmatrix}. 
\]

(205)

This result is easily verified in a way completely analogous to eqs. (198)-(199) [93].

From these functions \( E^K_{sA}, E^K_{sB}, F^K_{sA} \) and \( F^K_{sB} \), we can find the functions \( \psi_A \) and \( \psi_B \) and thus the electron wave function \( \psi \) in the absence of an external potential, using the relations (134) and (120).
We notice that the energy dispersion relations that we have found in this way near $K$ and $K'$ are identical to those one can obtain by first computing the dispersion relations in the absence of an external potential by using the nearest-neighbor tight-binding technique, and then expanding them near the extrema points.

Let us now find an expression for the probability density and for the probability current density in graphene.

The probability to find an electron in a region of area $S$ is equal to

$$\int_S |\psi(r)|^2 dr = \int_S \psi^*(r) \psi(r) dr =$$

$$\int_S \left[ \sum_{R_A} \psi_A^*(R_A) \varphi^*(r - R_A) + \sum_{R_B} \psi_B^*(R_B) \varphi^*(r - R_B) \right] dr =$$

$$\sum_{R_A \in S} |\psi_A(R_A)|^2 \int_S |\varphi(r - R_A)|^2 dr + \sum_{R_B \in S} |\psi_B(R_B)|^2 \int_S |\varphi(r - R_B)|^2 dr \simeq$$

$$\sum_{R_A \in S} |\psi_A(R_A)|^2 \int_S |\varphi(r - R_A)|^2 dr + \sum_{R_B \in S} |\psi_B(R_B)|^2 \int_{\Omega} |\varphi(r - R_B)|^2 dr$$

($\Omega$ is the area of the whole graphene sheet), where we have exploited the fact that each atomic orbital $\varphi$ has a non-zero overlap only with itself (since we use Löwdin orthonormalized atomic orbitals) and has significant values only near the atom on which it is centered. If the atomic orbital $\varphi$ is normalized according to (138), the integral of its square modulus on $\Omega$ is equal to the unit cell area $\Omega_0$ (otherwise, if the usual normalization for $\varphi$ is adopted, this integral is equal to 1 and the following results just have to be divided by the constant $\Omega_0$). Therefore, in this case we have that

$$\int_S |\psi(r)|^2 dr \simeq \Omega_0 \sum_{R_A \in S} |\psi_A(R_A)|^2 + \Omega_0 \sum_{R_B \in S} |\psi_B(R_B)|^2.$$

Using the relations (134), we have that

$$\sum_{R_A} |\psi_A(R_A)|^2 = \sum_{R_A} \psi_A^*(R_A) \psi_A(R_A) =$$

$$\sum_{R_A} \left\{ \left[ e^{-iK \cdot R_A} F_A^{K*} (R_A) + i e^{-i\theta'} e^{-iK' \cdot R_A} F_A^{K'*} (R_A) \right] \right\} =$$

$$\sum_{R_A} \left[ |F_A^K (R_A)|^2 + \sum_{R_A} |F_A^{K'} (R_A)|^2 \right]$$

$$-i e^{i\theta'} \sum_{R_A} \left[ e^{i(K' - K) \cdot R_A} F_A^{K*} (R_A) F_A^{K'} (R_A) \right]$$

$$+ i e^{-i\theta'} \sum_{R_A} \left[ e^{-i(K' - K) \cdot R_A} F_A^{K*} (R_A) F_A^K (R_A) \right].$$
and that

\begin{equation}
\sum_{R_B} |\psi_B(R_B)|^2 = \sum_{R_B} \psi_B^*(R_B)\psi_B(R_B) =
\end{equation}

\begin{align*}
&\sum_{R_B} \left\{ -ie^{-i\theta'}e^{-iK \cdot R_B}F_B^K(R_B) + e^{-iK' \cdot R_B}F_B^{K'}(R_B) \right\} \\
&\left[ ie^{i\theta'}e^{iK \cdot R_B}F_B^K(R_B) + e^{iK' \cdot R_B}F_B^{K'}(R_B) \right] = \\
&\sum_{R_B} |F_B^K(R_B)|^2 + \sum_{R_B} |F_B^{K'}(R_B)|^2 \\
&-ie^{-i\theta'}\sum_{R_B} [e^{i(K'-K) \cdot R_B}F_B^{K'}(R_B)F_B^{K'}(R_B)] \\
&+ie^{i\theta'}\sum_{R_B} [e^{-i(K'-K) \cdot R_B}F_B^{K'}(R_B)F_B^{K'}(R_B)].
\end{align*}

However the terms containing the phase factors $e^{i(K'-K) \cdot R_A}$, $e^{i(K'-K) \cdot R_B}$, or their complex conjugates are negligible with respect to the others.

Indeed, using the smoothing function $g(r)$, we know from the property (141) with $r = R_A$ that $\sum_{R_A} g(R_A - R'_A) = 1$. Therefore we can insert this sum into the term

\begin{equation}
\sum_{R_A} \left[ e^{i(K'-K) \cdot R_A}F_A^{K'}(R_A)F_A^K(R_A) \right],
\end{equation}

obtaining

\begin{equation}
\sum_{R_A} \left\{ \sum_{R'_A} g(R_A - R'_A) \right\} e^{i(K'-K) \cdot R_A}F_A^{K'}(R_A)F_A^K(R_A)
\end{equation},

that can be rewritten, as a result of the point-symmetry of the function $g$ with respect to its center and thus of the fact that $g(R_A - R'_A) = g(-(R_A - R'_A))$, in this way:

\begin{equation}
\sum_{R_A} \sum_{R'_A} g(R'_A - R_A)e^{i(K'-K) \cdot R_A}F_A^{K'}(R_A)F_A^K(R_A).
\end{equation}

If then we use the property (144) with $r = R'_A$ and in particular the fact that

\begin{equation}
g(R'_A - R_A)F_A^{K'}(R_A)F_A^K(R_A) = g(R'_A - R_A)F_A^{K'}(R'_A)F_A^K(R_A)
\end{equation}

(due to the smoothness of the envelope functions), the term becomes

\begin{equation}
\sum_{R'_A} \sum_{R_A} g(R'_A - R_A)e^{i(K'-K) \cdot R_A}F_A^{K'}(R'_A)F_A^K(R_A)
\end{equation}

and, by way of the property (143) with $r = R'_A$, we conclude that the quantities between square brackets, and thus the overall term, are very small.
Analogously, we can see that the terms
\[
\sum_{R_A} e^{-i(K'-K)\cdot R_A} F_A^{K'}(R_A) F_A^K(R_A),
\]
\[
\sum_{R_B} e^{i(K'-K)\cdot R_B} F_B^{K'}(R_B) F_B^K(R_B)
\]
and
\[
\sum_{R_B} e^{-i(K'-K)\cdot R_B} F_B^{K'}(R_B) F_B^K(R_B)
\]
are negligible [93]. Since \(g(r)\) has non-negligible values only within a few lattice constants from its center, the previous considerations are approximately valid also if we limit the sums to the atoms contained in the area \(S\).

We conclude that
\[
\int_S |\psi(r)|^2 dr \simeq \Omega_0 \sum_{R_A \in S} |\psi_A(R_A)|^2 + \Omega_0 \sum_{R_B \in S} |\psi_B(R_B)|^2 \simeq
\]
\[
\Omega_0 \sum_{R_A \in S} |F_A^K(R_A)|^2 + \Omega_0 \sum_{R_B \in S} |F_B^K(R_A)|^2 + \Omega_0 \sum_{R_B \in S} |F_B^K(R_B)|^2 \simeq
\]
\[
\int_S \left[ |F_A^K(r)|^2 + |F_A^{K'}(r)|^2 + |F_B^K(r)|^2 + |F_B^{K'}(r)|^2 \right] dr,
\]
where we have exploited the fact that the envelope functions \(F\) are smooth functions, which are nearly constant over a unit cell. Therefore we can consider
\[
P = |F_A^K(r)|^2 + |F_A^{K'}(r)|^2 + |F_B^K(r)|^2 + |F_B^{K'}(r)|^2
\]
as a probability density, and the correct normalization condition is
\[
\int_{\Omega} \left( |F_A^K(r)|^2 + |F_A^{K'}(r)|^2 + |F_B^K(r)|^2 + |F_B^{K'}(r)|^2 \right) dr = 1.
\]

We now follow a procedure similar to that used in relativistic quantum mechanics [96] to find the expression of the probability current density. Let us consider the envelope function equation in the case of long-range external potential (eq. (185)), writing explicitly the operators \(\hat{\kappa}_x\) and \(\hat{\kappa}_y\) (see eq. (155)). Let us consider the time-dependent wave function \(\psi(r, t)\) and thus the time-dependent envelope functions \(\mathbf{F}(r, t)\) (\(\mathbf{F}\) will be the column vector \([F_A^K, F_B^K, F_A^{K'}, F_B^{K'}]^T\)). We now convert the time-independent envelope function equation into a time-dependent envelope function equation, substituting in the r.h.s. of eq.(185) the quantity \(\hat{E}\mathbf{F}(r)\) with \(i\hbar(\partial \mathbf{F}(r, t)/\partial t)\) (for stationary states \(\psi(r, t) = \psi(r)e^{-iEt/\hbar}\), \(\mathbf{F}(r, t) = \mathbf{F}(r)e^{-iEt/\hbar}\), and thus the time-dependent equation is
clearly equivalent to the time-independent one). Therefore we can write

\[
\gamma \begin{bmatrix}
0 & -i \frac{\partial}{\partial x} - \frac{\partial}{\partial y} & 0 & 0 \\
-i \frac{\partial}{\partial x} + \frac{\partial}{\partial y} & 0 & 0 & 0 \\
0 & 0 & 0 & -i \frac{\partial}{\partial x} + \frac{\partial}{\partial y} \\
0 & 0 & -i \frac{\partial}{\partial x} - \frac{\partial}{\partial y} & 0
\end{bmatrix} \begin{bmatrix}
F^K_A \\
F^K_B \\
F^K_A' \\
F^K_B'
\end{bmatrix} + u(r) \begin{bmatrix}
F^K_A \\
F^K_B \\
F^K_A' \\
F^K_B'
\end{bmatrix} = \hbar \gamma \begin{bmatrix}
I & 0 & 0 & I \\
0 & -i \sigma_x & 0 & i \sigma_x \\
0 & 0 & 0 & -i \sigma_y \\
I & 0 & 0 & I
\end{bmatrix} \begin{bmatrix}
\frac{\partial F}{\partial x} \\
\frac{\partial F}{\partial y} \\
\frac{\partial F}{\partial t} \\
F\gamma
\end{bmatrix} = 0.
\]

Dividing by \( \gamma \) and using the Pauli matrices (44), we can rewrite the equation in this form (in the following we will indicate with \( I \) the 2 \( \times \) 2 identity matrix):

\[
\begin{bmatrix}
-i \sigma_x & 0 \\
0 & -i \sigma_x
\end{bmatrix} \left( \frac{\partial F}{\partial x} \right) + \begin{bmatrix}
-i \sigma_y & 0 \\
0 & i \sigma_y
\end{bmatrix} \left( \frac{\partial F}{\partial y} \right) + \frac{i \hbar}{\gamma} \begin{bmatrix}
I & 0 & 0 & I \\
0 & -i \sigma_x & 0 & i \sigma_x \\
0 & 0 & 0 & -i \sigma_y \\
I & 0 & 0 & I
\end{bmatrix} \begin{bmatrix}
\frac{\partial F}{\partial t} \\
F\gamma
\end{bmatrix} = 0
\]

that, if we define

\[
A = \begin{bmatrix}
i \sigma_x & 0 \\
0 & i \sigma_x
\end{bmatrix}, \quad B = \begin{bmatrix}
i \sigma_y & 0 \\
0 & -i \sigma_y
\end{bmatrix},
\]

we can rewrite in this compact way:

\[
-A \left( \frac{\partial F}{\partial x} \right) - B \left( \frac{\partial F}{\partial y} \right) - \frac{i \hbar}{\gamma} \left( \frac{\partial F}{\partial t} \right) + \frac{u(r)}{\gamma} F = 0.
\]

If we left-multiply this equation by the row vector \( F^\dagger \) (the conjugate transpose of \( F \)), we obtain:

\[
-F^\dagger A \left( \frac{\partial F}{\partial x} \right) - F^\dagger B \left( \frac{\partial F}{\partial y} \right) - \frac{i \hbar}{\gamma} \left( \frac{\partial F}{\partial t} \right) + \frac{u(r)}{\gamma} F^\dagger F = 0.
\]

Instead, if we consider the conjugate transpose of eq. (219) we obtain

\[
\left( \frac{\partial F^\dagger}{\partial x} \right) \begin{bmatrix}
i \sigma_x^\dagger & 0 \\
0 & i \sigma_x^\dagger
\end{bmatrix} + \left( \frac{\partial F^\dagger}{\partial y} \right) \begin{bmatrix}
i \sigma_y^\dagger & 0 \\
0 & -i \sigma_y^\dagger
\end{bmatrix} + \frac{i \hbar}{\gamma} \left( \frac{\partial F^\dagger}{\partial t} \right) \begin{bmatrix}
I & 0 \\
0 & I
\end{bmatrix} + \frac{u(r)}{\gamma} F^\dagger F = 0.
\]

Instead, if we consider the conjugate transpose of eq. (219) we obtain

\[
\left( \frac{\partial F^\dagger}{\partial x} \right) \begin{bmatrix}
i \sigma_x^\dagger & 0 \\
0 & i \sigma_x^\dagger
\end{bmatrix} + \left( \frac{\partial F^\dagger}{\partial y} \right) \begin{bmatrix}
i \sigma_y^\dagger & 0 \\
0 & -i \sigma_y^\dagger
\end{bmatrix} + \frac{i \hbar}{\gamma} \left( \frac{\partial F^\dagger}{\partial t} \right) \begin{bmatrix}
I & 0 \\
0 & I
\end{bmatrix} + \frac{u(r)}{\gamma} F^\dagger F = 0,
\]
which, since $\sigma_x^1 = \sigma_x$ and $\sigma_y^1 = \sigma_y$, is equal to

\[
(224) \quad \left( \frac{\partial}{\partial x} F^\dagger \right) A + \left( \frac{\partial}{\partial y} F^\dagger \right) B + \frac{i\hbar}{\gamma} \left( \frac{\partial}{\partial t} F^\dagger \right) + \frac{u(r)}{\gamma} F^\dagger = 0.
\]

If we right-multiply this equation by the column vector $F$, we obtain

\[
(225) \quad \left( \frac{\partial}{\partial x} F^\dagger \right) A F + \left( \frac{\partial}{\partial y} F^\dagger \right) B F + \frac{i\hbar}{\gamma} \left( \frac{\partial}{\partial t} F^\dagger \right) F + \frac{u(r)}{\gamma} F^\dagger F = 0.
\]

Subtracting (222) from (225), we find

\[
(226) \quad \left[ \left( \frac{\partial}{\partial x} F^\dagger \right) A F + F^\dagger A \left( \frac{\partial}{\partial x} F \right) \right] + \left[ \left( \frac{\partial}{\partial y} F^\dagger \right) B F + F^\dagger B \left( \frac{\partial}{\partial y} F \right) \right] + \frac{i\hbar}{\gamma} \left[ \left( \frac{\partial}{\partial t} F^\dagger \right) F + F^\dagger \left( \frac{\partial}{\partial t} F \right) \right] = 0 \Rightarrow \\
\frac{\partial}{\partial x} (F^\dagger AF) + \frac{\partial}{\partial y} (F^\dagger BF) + \frac{i\hbar}{\gamma} \frac{\partial}{\partial t} (F^\dagger F) = 0.
\]

Since $F^\dagger F = P$ (probability density), we have that (defining $v_F = \gamma/h$)

\[
(227) \quad -\frac{\partial}{\partial t} P = -\frac{\partial}{\partial t} (F^\dagger F) = -i \left( \frac{\gamma}{h} \right) \nabla \cdot \left[ (F^\dagger AF) \hat{x} + (F^\dagger BF) \hat{y} \right] = \\
\nabla \cdot \left[ (-i v_F F^\dagger AF) \hat{x} + (-i v_F F^\dagger BF) \hat{y} \right] = \nabla \cdot J,
\]

which is the well-known continuity equation, if we define as probability current density the vector

\[
(228) \quad J = \begin{bmatrix} J_x \\ J_y \end{bmatrix} = \begin{bmatrix} -i v_F F^\dagger AF \\ -i v_F F^\dagger BF \end{bmatrix}.
\]

In particular, we have that

\[
(229) \quad J_x = -i v_F F^\dagger AF = \\
- i v_F \begin{bmatrix} F^K_A & F^{K^*}_A & F^{K^*_A} & F^{K^*_B} \end{bmatrix} \begin{bmatrix} 0 & 0 & 0 & 0 & i \\ 0 & 0 & 0 & 0 & 0 & i \\ 0 & 0 & 0 & 0 & 0 & i \end{bmatrix} = \\
F^K_A + F^{K^*_A} + F^{K^*_B} + F^{K^*} = \\
v_F \begin{bmatrix} F^K_A & F^K_B & F^{K^*}_A & F^{K^*}_B \end{bmatrix} \begin{bmatrix} 0 & 0 & 0 & i \\ 0 & 0 & 0 & i \\ 0 & 0 & 0 & i \end{bmatrix} = \\
v_F \left( F^K_A + F^{K^*_A} + F^{K^*_B} + F^{K^*} \right)
\]
and that

\( J_y = -i v_F \mathbf{F}^\dagger \mathbf{B} \mathbf{F} = \)

\[
- i v_F \begin{pmatrix}
  F_{K_A}^* & F_{K_B}^* & F_{K_A'}^* & F_{K_B'}^*
\end{pmatrix}
\begin{pmatrix}
  0 & 1 & 0 & 0 \\
  -1 & 0 & 0 & 0 \\
  0 & 0 & 0 & -1 \\
  0 & 0 & 1 & 0
\end{pmatrix}
\begin{pmatrix}
  F_{K_A} \\
  F_{K_B} \\
  F_{K_A'} \\
  F_{K_B'}
\end{pmatrix}
= \]

\[
- i v_F \begin{pmatrix}
  F_{K_B}^* & F_{K_B'}^* & F_{K_A} & F_{K_A'}
\end{pmatrix}
\begin{pmatrix}
  F_{K_B} \\
  F_{K_B'} \\
  -F_{K_A} \\
  F_{K_A'}
\end{pmatrix}
= \]

\[
- i v_F \left( F_{K_A}^* F_{K_B} - F_{K_B}^* F_{K_A} - F_{K_A'}^* F_{K_B} + F_{K_B'}^* F_{K_A} \right).
\]

We note that a different ordering of the elements inside the envelope function vector is often used \([62, 61]\), in which, instead of \( \mathbf{F} \), the vector \( \tilde{\mathbf{F}} = [ F_{K_A}(r), F_{K_B}(r), F_{K_B'}(r), F_{K_A'}(r) ]^T \) is considered. Consequently, the \( \mathbf{k} \cdot \mathbf{p} \) equation in the case of long-range external potential (185) can be rewritten in this way:

\[
(231) \quad J_y = -i v_F \tilde{\mathbf{F}}^\dagger \tilde{\mathbf{F}} =
\]

\[
\begin{bmatrix}
  u(r) & \gamma(\tilde{\kappa}_x - i \tilde{\kappa}_y) & 0 & 0 \\
  \gamma(\tilde{\kappa}_x + i \tilde{\kappa}_y) & u(r) & 0 & 0 \\
  0 & 0 & u(r) & \gamma(\tilde{\kappa}_x - i \tilde{\kappa}_y) \\
  0 & 0 & \gamma(\tilde{\kappa}_x + i \tilde{\kappa}_y) & u(r)
\end{bmatrix}
\begin{pmatrix}
  F_{K_A}(r) \\
  F_{K_B}(r) \\
  F_{K_B'}(r) \\
  F_{K_A'}(r)
\end{pmatrix}
= \]

\[
E
\begin{bmatrix}
  F_{K_A}(r) \\
  F_{K_B}(r) \\
  F_{K_B'}(r) \\
  F_{K_A'}(r)
\end{bmatrix},
\]

which is the so-called valley-isotropic representation of the Dirac equation, characterized by two identical \( 2 \times 2 \) submatrices corresponding to the two valleys \( K \) and \( K' \).

Following this representation, the previously obtained expressions for the probability current density can be compactly restated in this form:

\[
\mathbf{J} = v_F \tilde{\mathbf{F}}^\dagger (I \otimes \boldsymbol{\sigma}) \tilde{\mathbf{F}},
\]

where \( I \otimes \boldsymbol{\sigma} \) is the Kronecker product between the \( 2 \times 2 \) identity matrix \( I \) and the vector
The wave functions \( \psi(r) \) and \( \psi_1(r) \) corresponding to the envelope functions \( F(r) \) and \( F_1(r) \) therefore have opposite energies and thus, being (see eq. (121)) eigenfunctions of the Hermitian operator \( H \) corresponding to different eigenvalues, are orthogonal. But,
due to the form of \( F(r) \) and \( F_1(r) \) and to eq. (181), we see that \( \psi(r) \) and \( \psi_1(r) \) have the same \( \psi_A(r) \) but opposite \( \psi_B(r) \). Therefore, if we write the orthogonality relation between \( \psi(r) \) and \( \psi_1(r) \), we have that

\[
0 = \int_{\Omega} \psi^*(r) \psi_1(r) dr = \\
\int_{\Omega} \left[ \sum_{R_A} \psi_A(R_A) \varphi(r - R_A) + \sum_{R_B} \psi_B(R_B) \varphi(r - R_B) \right]^* \\
\cdot \left[ \sum_{R_A} \psi_A(R_A) \varphi(r - R_A) - \sum_{R_B} \psi_B(R_B) \varphi(r - R_B) \right] dr = \\
\sum_{R_A} |\psi_A(R_A)|^2 \int_{\Omega} |\varphi(r - R_A)|^2 dr - \sum_{R_B} |\psi_B(R_B)|^2 \int_{\Omega} |\varphi(r - R_B)|^2 dr = \\
\sum_{R_A} |\psi_A(R_A)|^2 \Omega_0 - \sum_{R_B} |\psi_B(R_B)|^2 \Omega_0 \\
\Omega_0 \sum_{R_A} |\psi_A(R_A)|^2 = \Omega_0 \sum_{R_B} |\psi_B(R_B)|^2,
\]

where we have exploited the fact that each atomic wave function \( \varphi \) has a non-zero overlap only with itself and has been normalized according to (138). Since (as we have seen)

\[
0 \leq \int_{\Omega} \left( |F^K_A(r)|^2 + |F^{K'}_A(r)|^2 \right) dr
\]

\[
0 \leq \int_{\Omega} \left( |F^K_B(r)|^2 + |F^{K'}_B(r)|^2 \right) dr
\]

we conclude that

\[
\int_{\Omega} \left( |F^K_A(r)|^2 + |F^{K'}_A(r)|^2 \right) dr = \int_{\Omega} \left( |F^K_B(r)|^2 + |F^{K'}_B(r)|^2 \right) dr
\]

and this means that in the absence of an external potential the normalization (217) is equivalent to

\[
\left\{ \begin{array}{l}
\int_{\Omega} \left( |F^K_A(r)|^2 + |F^{K'}_A(r)|^2 \right) dr = \frac{1}{2}, \\
\int_{\Omega} \left( |F^K_B(r)|^2 + |F^{K'}_B(r)|^2 \right) dr = \frac{1}{2}
\end{array} \right.
\]

(the expressions of the envelope functions previously written for graphene in the absence of an external potential satisfy this normalization criterion).
5. – Application of the \(k \cdot p\) method to carbon nanotubes

A single-wall carbon nanotube can be described as a graphite sheet rolled, along one of its lattice translational vectors (the vector \(C_h\) shown in fig. 7), into a cylindrical shape [83]. In particular, it is completely specified by the so-called chiral vector \(C_h\), which corresponds to a section of the nanotube perpendicular to the nanotube axis and thus has a length equal to the nanotube circumference and connects two points of the graphene sheet which coincide in the nanotube. This vector can be expressed as a linear combination of the real space unit vectors of graphene with integer coefficients \(n\) and \(m\)

\[
C_h = na_1 + ma_2 \equiv na_{\Sigma'} + ma_{\Sigma'} = a \begin{pmatrix} \frac{\sqrt{3}}{2} \\ \frac{1}{2} \\ 0 \end{pmatrix} + \begin{pmatrix} \frac{\sqrt{3}}{2} \\ -\frac{1}{2} \\ 0 \end{pmatrix} = a \begin{pmatrix} \frac{\sqrt{3}}{2} (n + m) \\ \frac{1}{2} (n - m) \end{pmatrix}.
\]

The corresponding carbon nanotube will be indicated as \((n,m)\).

If we define the chiral angle of the nanotube \(\theta\) (with \(-\pi/6 < \theta \leq \pi/6\), due to the hexagonal symmetry of graphene lattice) as the angle (positive in the clockwise direction) between \(a_1\) and \(C_h\) (see fig. 7) or, equivalently, as the tilt angle of the edges of the hexagons constituting the graphene sheet with respect to the direction of the nanotube axis, such an angle can be found from the values of \(n\) and \(m\) noting that

\[
\cos \theta = \frac{C_h \cdot a_1}{|C_h| |a_1|} = \frac{2n + m}{2\sqrt{n^2 + m^2 + nm}}
\]

and

\[
\sin \theta = \frac{(C_h \times a_1) \cdot \mathbf{\hat{z}'}}{|C_h| |a_1|} = \frac{\sqrt{3}m}{2\sqrt{n^2 + m^2 + nm}},
\]

where the right-hand reference frame \(\Sigma' = (\mathbf{\hat{x}'}, \mathbf{\hat{y}'}, \mathbf{\hat{z}'})\) is that already used in the calculations on graphene. In the successive expressions we will identify the previously introduced angle \(\theta'\) with \(\theta' = (\pi/6) - \theta\) (the angle between \(C_h\) and the axis \(\mathbf{\hat{x}'}\)), as shown in fig. 7, and thus we will take the axis \(\mathbf{\hat{x}}\) along \(C_h\).

Following Ando’s approach [55, 56], the dispersion relations and the electron wave functions of a carbon nanotube can be obtained from those of graphene, enforcing for the electron wave function the following periodic boundary condition in the circumferential direction:

\[
\psi(r + C_h) = \psi(r)
\]

(in the calculations we will not consider the curvature effects \((^4)\)). Remembering that

\(^4\) For the effects of the finite curvature on the electronic properties of carbon nanotubes see, for example, ref. [97] and the references therein.
using the tight-binding technique the electron wave function can be expressed as

\[
\psi(r) = \sum_{R_A} \psi_A(R_A) \varphi(r - R_A) + \sum_{R_B} \psi_B(R_B) \varphi(r - R_B),
\]

the boundary condition can be written as

\[
\psi(r + C_h) = \sum_{R_A} \psi_A(R_A) \varphi((r + C_h) - R_A) + \sum_{R_B} \psi_B(R_B) \varphi((r + C_h) - R_B) = \\
\sum_{R_A} \psi_A(R_A) \varphi(r - (R_A - C_h)) + \sum_{R_B} \psi_B(R_B) \varphi(r - (R_B - C_h)) = \\
\sum_{R_A} \psi_A((R_A - C_h) + C_h) \varphi(r - (R_A - C_h)) + \sum_{R_B} \psi_B((R_B - C_h) + C_h) \varphi(r - (R_B - C_h)) = \\
\psi(r) = \sum_{R_A} \psi_A(R_A^*) \varphi(r - R_A^*) + \sum_{R_B} \psi_B(R_B^*) \varphi(r - R_B^*)
\]

(where we have used the fact that, being \(C_h\) a linear combination with integer coefficients of the real space lattice unit vectors, also \(R_A - C_h\) and \(R_B - C_h\) are atomic positions, defined \(R_A^*\) and \(R_B^*\). Thus the boundary condition is equivalent to the two conditions

\[
\left\{ \begin{array}{l}
\psi_A(R_A^* + C_h) = \psi_A(R_A^*), \\
\psi_B(R_B^* + C_h) = \psi_B(R_B^*).
\end{array} \right.
\]

If we use the expressions \((134)\) for \(\psi_A(r)\) and \(\psi_B(r)\) (and we define again the generic atomic position \(R_A\) and \(R_B\), instead of \(R_A^*\) and \(R_B^*\)), these conditions can be rewritten in the following form:

\[
\left\{ \begin{array}{l}
e^{iK \cdot (R_A + C_h)} F_A^K (R_A + C_h) - i e^{i\theta'} e^{iK' \cdot (R_A + C_h)} F_A^{K'} (R_A + C_h) = \\
e^{iK \cdot R_A} F_A^K (R_A) - i e^{i\theta'} e^{iK' \cdot R_A} F_A^{K'} (R_A), \\
 i e^{i\theta'} e^{iK \cdot (R_B + C_h)} F_B^K (R_B + C_h) + e^{iK' \cdot (R_B + C_h)} F_B^{K'} (R_B + C_h) = \\
i e^{i\theta'} e^{iK \cdot R_B} F_B^K (R_B) + e^{iK' \cdot R_B} F_B^{K'} (R_B).
\end{array} \right.
\]

Multiplying the first equation of \((245)\) by \(g(r - R_A)e^{-iK \cdot R_A}\), summing it over \(R_A\) and
then using the properties of the function \( g \) (defined in eqs. (141), (143) and (144)), we find

\[
\begin{align*}
\sum_{\mathbf{R}_A} g(\mathbf{r} - \mathbf{R}_A) F^{\mathbf{K}}_{\mathbf{A}}(\mathbf{R}_A + \mathbf{C}_h) &= e^{i\mathbf{K} \cdot \mathbf{C}_h} \sum_{\mathbf{R}_A} g(\mathbf{r} - \mathbf{R}_A) e^{i(\mathbf{K}' - \mathbf{K}) \cdot \mathbf{R}_A} F^{\mathbf{K}'}_{\mathbf{A}}(\mathbf{R}_A + \mathbf{C}_h) \\
- i e^{i\theta'} e^{i\mathbf{K}' \cdot \mathbf{C}_h} \sum_{\mathbf{R}_A} g(\mathbf{r} - \mathbf{R}_A) e^{i(\mathbf{K}' - \mathbf{K}) \cdot \mathbf{R}_A} F^{\mathbf{K}'}_{\mathbf{A}}(\mathbf{R}_A) &= e^{i\mathbf{K} \cdot \mathbf{C}_h} \sum_{\mathbf{R}_A} g(\mathbf{r} - \mathbf{R}_A) F^{\mathbf{K}}_{\mathbf{A}}(\mathbf{r} + \mathbf{C}_h) \\
- i e^{i\theta'} e^{i\mathbf{K}' \cdot \mathbf{C}_h} \sum_{\mathbf{R}_A} g(\mathbf{r} - \mathbf{R}_A) e^{i(\mathbf{K}' - \mathbf{K}) \cdot \mathbf{R}_A} F^{\mathbf{K}'}_{\mathbf{A}}(\mathbf{r} + \mathbf{C}_h) &= F^{\mathbf{K}}_{\mathbf{A}}(\mathbf{r} + \mathbf{C}_h).
\end{align*}
\]

If we calculate the scalar product between \( \mathbf{K} \) and \( \mathbf{C}_h \) we obtain

\[
\mathbf{K} \cdot \mathbf{C}_h = 2\pi \left( \frac{m - n}{3} \right) = 2\pi \tilde{N} + \frac{2\pi \nu}{3},
\]

where \( m - n = 3\tilde{N} + \nu \), with \( \nu = 0 \) or \( \pm 1 \) and \( \tilde{N} \) a proper integer. Therefore we have that

\[
e^{i\mathbf{K} \cdot \mathbf{C}_h} = e^{i2\pi \tilde{N}} e^{i\frac{2\pi \nu}{3}} = e^{i\frac{2\pi \nu}{3}}
\]

and thus the first boundary condition near \( \mathbf{K} \) is

\[
e^{i2\pi \nu \mathbf{C}_h} F^{\mathbf{K}}_{\mathbf{A}}(\mathbf{r} + \mathbf{C}_h) = F^{\mathbf{K}}_{\mathbf{A}}(\mathbf{r}),
\]

or equivalently

\[
F^{\mathbf{K}}_{\mathbf{A}}(\mathbf{r} + \mathbf{C}_h) = e^{-i\frac{2\pi \nu}{3}} F^{\mathbf{K}}_{\mathbf{A}}(\mathbf{r}).
\]

Multiplying the second equation of (245) by \( g(\mathbf{r} - \mathbf{R}_B)(-ie^{-i\theta} e^{-i\mathbf{K} \cdot \mathbf{R}_B}) \), summing it over \( \mathbf{R}_B \) and then using the properties of the function \( g \), we find analogously [93]

\[
e^{i\mathbf{K} \cdot \mathbf{C}_h} F^{\mathbf{K}}_{\mathbf{B}}(\mathbf{r} + \mathbf{C}_h) = F^{\mathbf{K}}_{\mathbf{B}}(\mathbf{r}).
\]

Substituting the value of \( e^{i\mathbf{K} \cdot \mathbf{C}_h} \), we can rewrite this boundary condition in the form

\[
e^{i\frac{2\pi \nu}{3}} F^{\mathbf{K}}_{\mathbf{B}}(\mathbf{r} + \mathbf{C}_h) = F^{\mathbf{K}}_{\mathbf{B}}(\mathbf{r}),
\]
or, equivalently

\begin{equation}
F_B^K(r + C_h) = e^{-i\frac{2\pi}{3}} F_B^K(r).
\end{equation}

Thus the periodic boundary condition near \( K \) is

\begin{equation}
\begin{bmatrix}
F_A^K(r + C_h) \\
F_B^K(r + C_h)
\end{bmatrix} = e^{-i\frac{2\pi}{3}}
\begin{bmatrix}
F_A^K(r) \\
F_B^K(r)
\end{bmatrix},
\end{equation}

which can be written in this compact way:

\begin{equation}
F^K(r + C_h) = e^{-i\frac{2\pi}{3}} F^K(r).
\end{equation}

However, as we have previously seen (eq. (195)), in the absence of an external potential the envelope functions have the following form:

\begin{equation}
F_{\kappa s}^K(r) = \frac{1}{\sqrt{2L\ell}} e^{i\kappa x \cdot r} e^{i\phi_s(\kappa)} R(-\alpha(\kappa)) |s\rangle = \frac{1}{\sqrt{2L\ell}} e^{i(\kappa x x + \kappa y y)} e^{i\phi_s(\kappa)} R(-\alpha(\kappa)) |s\rangle,
\end{equation}

with the surface area \( \Omega = L\ell \), where \( L = |C_h| \) and \( \ell \) is the length of the nanotube. Thus the periodic boundary condition becomes

\begin{equation}
\frac{1}{\sqrt{2L\ell}} e^{i\kappa x (r + C_h)} e^{i\phi_s(\kappa)} R(-\alpha(\kappa)) |s\rangle = e^{-i\frac{2\pi}{3}} \frac{1}{\sqrt{2L\ell}} e^{i\kappa x \cdot r} e^{i\phi_s(\kappa)} R(-\alpha(\kappa)) |s\rangle,
\end{equation}

or equivalently

\begin{equation}
e^{i\kappa x C_h} = e^{-i\frac{2\pi}{3}}.
\end{equation}

This condition can be written also in the following way:

\begin{equation}
e^{i\kappa x L} = e^{-i\frac{2\pi}{3}} 1 = e^{-i\frac{2\pi}{3}} e^{i2\pi \tilde{n}},
\end{equation}

or, equivalently

\begin{equation}
\kappa x L = \frac{2\pi \nu}{3} + 2\pi \tilde{n},
\end{equation}

and thus

\begin{equation}
\kappa x = \frac{2\pi}{L} \left( \tilde{n} - \frac{\nu}{3} \right) = \kappa_{\nu}(\tilde{n}),
\end{equation}

with \( \tilde{n} \) integer.

This condition on \( \kappa x \) can be obtained also in a different way, enforcing the boundary condition on the overall wave vector \( k \). In order to do this, we have to observe that, considering only the periodic lattice potential inside the graphene sheet, the wave function
ψ(r) has to be a Bloch function $u(k,r)e^{ik\cdot r}$, where $u(k,r)$ has the periodicity of the lattice.

Thus the boundary condition

\begin{equation}
\psi(r + C_h) = \psi(r)
\end{equation}

is equivalent to

\begin{equation}
\psi(r + C_h) = \psi(r) \quad \text{is equivalent to}
\end{equation}

\begin{equation}
u(k, r + C_h) e^{ik\cdot (r + C_h)} = u(k, r) e^{ik\cdot r}.
\end{equation}

Since we know that $u(k, r)$ has the lattice periodicity and thus $u(k, r + C_h) = u(k, r)$ ($C_h$ being a linear combination with integer coefficients of the lattice unit vectors) the boundary condition can also be written as

\begin{equation}
\text{or, equivalently}
\end{equation}

\begin{equation}e^{ik\cdot C_h} = 1,
\end{equation}

or, equivalently

\begin{equation}
k \cdot C_h = 2\pi\tilde{m}.
\end{equation}

Thus the boundary condition is (being $\hat{C}_h = C_h/|C_h| = C_h/L$)

\begin{equation}
k \cdot \hat{C}_h = k \cdot \hat{x} = k_x = (K)_x + \kappa_x = \frac{2\pi}{L} \tilde{m}
\end{equation}

and (using eq. (247))

\begin{equation}
\kappa_x = \frac{2\pi}{L} \tilde{m} - (K)_x = \frac{2\pi}{L} \tilde{m} - \frac{K \cdot C_h}{L} = \frac{2\pi}{L} \tilde{m} - \frac{2\pi}{L} \tilde{N} - \frac{2\pi}{3L'} = \frac{2\pi}{L} \left( \tilde{m} - \tilde{N} - \frac{\nu}{3} \right) = \frac{2\pi}{L} \left( \tilde{n} - \frac{\nu}{3} \right) = \kappa_y(\tilde{n})
\end{equation}

(with $\tilde{n} \equiv \tilde{m} - \tilde{N}$), which is equal to the previously found expression.

If we substitute this condition on $\kappa_x$ in the dispersion relations of graphene, we find

\begin{equation}
E^K_{s,\tilde{n}}(\kappa_y) = s\gamma |\kappa| = s\gamma \sqrt{\kappa_x^2 + \kappa_y^2} = s\gamma \sqrt{\kappa_y(\tilde{n})^2 + \kappa_y^2},
\end{equation}

where $s = +1$ and $s = -1$ indicate the conduction and valence bands, respectively.

We notice that now $k_y$ is the wave vector $k$ of the nanotube, which, being a substantially unidimensional material, has a one-dimensional Brillouin zone with width $2\pi/T$ (where $T$ is the length of the unit cell of the nanotube, along its axis, which can be easily found from the numbers $n$ and $m$ characterizing the nanotube [83]). Correspondingly, $\kappa_y$ is the difference between the wave vector $k$ of the nanotube and the component of $K$ along $y$. 
As to the envelope functions near \( K \), if, starting from eq. (195), we choose as value of the arbitrary phase \( \phi_s = -\alpha/2 \) and then we enforce the condition on \( \kappa_x \), we can write

\[
F_{Ks}^x(r) = \frac{1}{\sqrt{2L_e}} e^{ik_xr} e^{i\phi_s} \begin{bmatrix} e^{-i\frac{\kappa_x}{2}} & 0 \\ 0 & e^{i\frac{\kappa_x}{2}} \end{bmatrix} \frac{1}{\sqrt{2}} \begin{bmatrix} -i \kappa_x \\ 1 \end{bmatrix} = \\
\frac{1}{2\sqrt{L_e}} e^{i(\kappa_x x + \kappa_y y)} e^{i\phi_s} \begin{bmatrix} -i e^{-i\frac{\kappa_x}{2}} e^{i\frac{\kappa_x}{2}} \\ 1 \end{bmatrix} = \\
\frac{1}{2\sqrt{L_e}} \begin{bmatrix} se^{-i(\frac{\kappa_x}{2} + \alpha)} \\ 1 \end{bmatrix} e^{i\kappa_x x + i\kappa_y y} = \\
\frac{1}{2\sqrt{L_e}} \begin{bmatrix} sb_{\nu}(\bar{n}, \kappa_y) \\ 1 \end{bmatrix} e^{i\kappa_x (\bar{n}) x + i\kappa_y y} = F_{Ks}^{x\nu}(r).
\]

The function \( b_{\nu}(\bar{n}, \kappa_y) = e^{-i(\frac{\kappa_x}{2} + \alpha)} \) can be found noting that \( \alpha \) has been defined (see eq. (193)) in such a way that

\[
(273) \quad e^{i(\frac{\kappa_x}{2} + \alpha)} = \frac{\kappa_x + i\kappa_y}{\sqrt{\kappa_x^2 + \kappa_y^2}}
\]

and thus

\[
(272) \quad b_{\nu}(\bar{n}, \kappa_y) = e^{-i(\frac{\kappa_x}{2} + \alpha)} = \left( e^{i(\frac{\kappa_x}{2} + \alpha)} \right)^* = \\
\frac{e^{i\kappa_x (\bar{n}) x + i\kappa_y y}}{\sqrt{\kappa_x^2 + \kappa_y^2}} = \frac{\kappa_x - i\kappa_y}{\sqrt{\kappa_x^2 + \kappa_y^2}}.
\]

We can proceed analogously for the boundary conditions near \( K' \).

Indeed, multiplying the first equation of (245) by \( g(r - R_A)(ie^{-i\theta'}e^{-iK' \cdot R_A}) \), summing it over \( R_A \) and then using the properties of the function \( g \), we find [93]

\[
(273) \quad e^{iK' \cdot C_h} F_A^{K'}(r + C_h) = F_A^{K'}(r).
\]

The scalar product between \( K' \) and \( C_h \) is equal to

\[
(274) \quad K' \cdot C_h = -\frac{2\pi}{3} (m - n) = -2\pi \tilde{N} - \frac{2\pi \nu}{3},
\]

where we have used the previously introduced relation \( m - n = 3\tilde{N} + \nu \) with \( \nu = 0 \) or \( \pm 1 \) and \( \tilde{N} \) a proper integer. Thus we have that

\[
e^{iK' \cdot C_h} = e^{-i2\pi \tilde{N}} e^{-i\frac{2\pi \nu}{3}} = e^{-i\frac{2\pi \nu}{3}}
\]
and consequently the boundary condition near $K'$ is

\[(275)\quad e^{-\frac{2\pi\nu}{3}} F_A^{K'}(r + C_h) = F_A^{K'}(r),\]

or, equivalently

\[(276)\quad F_A^{K'}(r + C_h) = e^{\frac{2\pi\nu}{3}} F_A^{K'}(r).\]

On the other hand, multiplying the second equation of (245) by $g(r - R_B)e^{-iK'R_h}$, summing it over $R_B$ and then using the properties of the function $g$, we find [93]

\[(277)\quad e^{iK'C_h} F_B^{K'}(r + C_h) = F_B^{K'}(r).\]

Substituting the value of $e^{iK'C_h}$, we can rewrite this second boundary condition near $K'$ in the form

\[(278)\quad e^{-\frac{2\pi\nu}{3}} F_B^{K'}(r + C_h) = F_B^{K'}(r),\]

or, equivalently

\[(279)\quad F_B^{K'}(r + C_h) = e^{\frac{2\pi\nu}{3}} F_B^{K'}(r).\]

Thus the overall periodic boundary condition near $K'$ is

\[(280)\quad \begin{bmatrix} F_A^{K'}(r + C_h) \\ F_B^{K'}(r + C_h) \end{bmatrix} = e^{\frac{2\pi\nu}{3}} \begin{bmatrix} F_A^{K'}(r) \\ F_B^{K'}(r) \end{bmatrix},\]

which can be written in a compact form

\[(281)\quad F^{K'}(r + C_h) = e^{\frac{2\pi\nu}{3}} F^{K'}(r).\]

Substituting the form that, in the absence of an external potential, the envelope functions have near $K'$ (eq. (204))

\[(282)\quad F_{s\kappa}^{K'}(r) = \frac{1}{\sqrt{2L}} e^{i\kappa \cdot r} e^{i\tilde{\phi}_s(\kappa)} R(\alpha(\kappa))|\tilde{s}\rangle = \frac{1}{\sqrt{2L}} e^{i(k_x x + k_y y)} e^{i\tilde{\phi}_s(\kappa)} R(\alpha(\kappa))|\tilde{s}\rangle,
\]

the periodic boundary condition becomes

\[(283)\quad \frac{1}{\sqrt{2L}} e^{i\kappa \cdot (r + C_h)} e^{i\tilde{\phi}_s(\kappa)} R(\alpha(\kappa))|\tilde{s}\rangle = \frac{1}{\sqrt{2L}} e^{i\kappa \cdot r} e^{i\tilde{\phi}_s(\kappa)} R(\alpha(\kappa))|\tilde{s}\rangle,
\]

or, equivalently

\[(284)\quad e^{i\kappa \cdot C_h} = e^{\frac{2\pi\nu}{3}}.
\]

This can be rewritten in the form

\[(285)\quad e^{i\kappa \cdot L} = e^{\frac{2\pi\nu}{3}} 1 = e^{\frac{2\pi\nu}{3}} e^{i\frac{2\pi\nu}{3} \pi},\]
or, equivalently

\begin{equation}
\kappa_x L = \frac{2\pi\nu}{3} + 2\pi\bar{\pi}
\end{equation}

and thus

\begin{equation}
\kappa_x = \frac{2\pi}{L} (\bar{\pi} + \frac{\nu}{3}) = \tilde{\kappa}_\nu(\bar{\pi}),
\end{equation}

with \(\bar{\pi}\) integer.

Analogously to what we have done near \(K\), this condition on \(\kappa_x\) can be found \([93]\) also setting \(e^{ik\cdot C_h} = 1\).

If we substitute this condition on \(\kappa_x\) in the dispersion relations of graphene, we find

\begin{equation}
E_s(K') = s\gamma|\kappa| = s\gamma\sqrt{\kappa_x^2 + \kappa_y^2} = s\gamma\sqrt{\tilde{\kappa}_\nu(\bar{\pi})^2 + \kappa_y^2},
\end{equation}

where \(\kappa_y\) now is the wave vector \(k\) of the nanotube and \(\kappa_y\) is the difference between the wave vector \(k\) of the nanotube and the component of \(K'\) along \(y\).

On the other hand, if, starting from eq. (204), we choose as arbitrary phase \(\tilde{\phi}_s = \alpha/2\) and then we enforce the condition on \(\kappa_x\), we find \([93]\) as envelope functions in the carbon nanotube near \(K'\)

\begin{equation}
F^K_s(r) = \frac{1}{2\sqrt{L}} \left[ \frac{\tilde{\delta}_\nu(\bar{\pi},\kappa_y)}{1} \right] e^{i\tilde{\kappa}_\nu(\bar{\pi})x + i\kappa_y y} = F^K_{s\kappa_y}(r),
\end{equation}

where (using the definition of the angle \(\alpha\): see eq. (193))

\begin{equation}
\tilde{\delta}_\nu(\bar{\pi},\kappa_y) = e^{i(\frac{\pi}{2} + \alpha)} = \frac{\kappa_x + i\kappa_y}{\sqrt{\kappa_x^2 + \kappa_y^2}} = \frac{\tilde{\kappa}_\nu(\bar{\pi}) + i\kappa_y}{\sqrt{\tilde{\kappa}_\nu(\bar{\pi})^2 + \kappa_y^2}}.
\end{equation}

If \(m - n\) is a multiple of 3 and thus \(\nu = 0\), for \(\tilde{n} = 0\) and \(\bar{\pi} = 0\) we have that \(\kappa_x(\tilde{n}) = 0\) and \(\tilde{\kappa}_\nu(\bar{\pi}) = 0\), and consequently \(E_s = s\gamma|\kappa_y|\), which vanishes for \(\kappa_y = 0\), so that \(E_s = E_s = 0\). This means that when \(m - n\) is a multiple of 3 the points \(K\) and \(K'\), where the upper and lower bands of graphene are degenerate, are among the values of \(k\) allowed by the periodic boundary condition, and thus the nanotube is metallic.

Instead, if \(m - n\) is not a multiple of 3 and thus \(\nu = \pm 1\), the allowed \(k\)'s nearest to \(K\) and \(K'\) correspond to \(\tilde{n} = 0\) and \(\bar{\pi} = 0\), for which \(\kappa_x(\tilde{n}) = \pm 2\pi/(3L)\) and \(\tilde{\kappa}_\nu(\bar{\pi}) = \pm 2\pi/(3L)\), and consequently

\begin{equation}
E_s = s\gamma \sqrt{\left(\frac{2\pi}{3L}\right)^2 + \kappa_y^2}.
\end{equation}

In particular, the minimum and maximum values of the nanotube bands are obtained with the further position \(\kappa_y = 0\) and therefore are equal to

\begin{equation}
E_s = \frac{2\pi}{3L};
\end{equation}
Fig. 8. – The nanotube (10,0) and its dispersion relations, obtained both by means of the tight-binding method (solid lines) and (for the bands corresponding to the smallest values of $|\kappa_\nu(\tilde{n})|$ and $|\tilde{\kappa}_\nu(\pi)|$) by means of the $k \cdot p$ method (dashed lines).

Fig. 9. – The density of states per unit length of the nanotube (10,0), obtained both by means of the tight-binding method (solid lines) and (in a smaller region around $E = 0$) by means of the $k \cdot p$ method (dashed lines).

thus the bandgap of the nanotube is

$$E_g = E_+ - E_- = 2\gamma = \frac{2\pi}{3L} = \frac{4\pi \gamma}{3L} = \frac{4\pi \sqrt{3}a\gamma_0}{3L} = \frac{2\pi}{L} \frac{a}{\sqrt{3}} \gamma_0 = \frac{2\gamma_0 a_{C-C}}{d_t},$$

where $d_t = L/\pi$ is the nanotube diameter. Therefore we have that the bandgap of the nanotube depends on the reciprocal nanotube diameter.

We can observe that the approximate approach for the computation of the density of states in carbon nanotubes proposed by J. W. Mintmire and C. T. White [98], being based on a linear approximation of the dispersion relations of graphene near the extrema points, can be seen as a consequence of a $k \cdot p$ study of the nanotube energy bands.

In fig. 8 we compare the dispersion relations that we have obtained for the same carbon nanotube using the nearest-neighbor tight-binding method and the $k \cdot p$ method (without considering curvature effects) [27,99-101]. We see that the $k \cdot p$ method gives a good approximation for the portions of energy bands of the nanotube deriving from the graphene dispersion relations around $K$ and $K'$. In fig. 9, instead, for the same nanotube we show both the density of states that we
have obtained by properly differentiating the tight-binding dispersion relations, and the
density of states deriving from the Mintmire-White approach [27,99]. We see that this
last approximation gives good results near \( E = 0 \), thus in the region corresponding to
the graphene dispersion relations around \( K \) and \( K' \).

6. – Application of the \( k \cdot p \) method to graphene nanoribbons

A graphene sheet can be laterally confined (along the \( y \)-direction) to form a graphene
nanoribbon (extending in the \( x \)-direction). The properties of the nanoribbon strongly
depend on the characteristics of the boundary. Here we will consider nanoribbons with
perfect zigzag and armchair edges, that can be easily studied using the Dirac equation and
enforcing the correct boundary conditions [63,64,102-106]. An analysis of the boundary
conditions that have to be enforced in nanoribbons with more general terminations can
be found in ref. [107]. In particular, we will perform the analytical calculations in the
absence of an external potential following Brey and Fertig’s approach [63,64], but using
the representation adopted in the previous sections. While inside the nanoribbon each
atom has 3 nearest-neighbor atoms, for the atoms on the edges of the ribbon some of
the nearest-neighbor lattice sites are outside the ribbon and thus are not occupied by
a carbon atom. These lattice sites are instead occupied by passivation atoms (such as
hydrogen atoms), which saturate the dangling bonds. The correct boundary condition
to be enforced in our calculations is the vanishing of the wave function in correspondence
of these lattice sites (let us call them “boundary lattice sites”).

6.1. Zigzag nanoribbons. – In the case of zigzag nanoribbons (fig. 10), the graphene
sheet has been cut at an angle of 30° with respect to the nearest-neighbor carbon bonds,
and therefore the edges have a zigzag shape. In order to simplify the following calcula-
tions, we can choose (see fig. 10) the graphene lattice vectors in the real space \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \)
(and consequently those in the reciprocal space \( \mathbf{b}_1 \) and \( \mathbf{b}_2 \)) in this way (we express them

Fig. 10. – Sketch of a zigzag nanoribbon with \( N \) zigzag lines (the black atoms are carbon atoms,
while the grey atoms are passivation atoms).
in the reference frame $\Sigma = (\hat{x}, \hat{y}, \hat{z})$:

\[
\begin{align*}
\mathbf{a}_1 &\equiv \Sigma \begin{bmatrix}
\frac{a}{2} \\
-\frac{\sqrt{3}}{2} a \\
0
\end{bmatrix}, & \mathbf{a}_2 &\equiv \Sigma \begin{bmatrix}
\frac{a}{2} \\
\frac{\sqrt{3}}{2} a \\
0
\end{bmatrix}, \\
\mathbf{b}_1 &\equiv \Sigma \begin{bmatrix}
\frac{2\pi}{a} \\
\frac{2\pi}{\sqrt{3}a} \\
0
\end{bmatrix}, & \mathbf{b}_2 &\equiv \Sigma \begin{bmatrix}
-\frac{2\pi}{a} \\
-\frac{2\pi}{\sqrt{3}a} \\
0
\end{bmatrix},
\end{align*}
\]

(294)

(which, being $\mathbf{b}_1 = 2\pi(a_2 \times \hat{z})/(a_1 \cdot (a_2 \times \hat{z}))$ and $\mathbf{b}_2 = 2\pi(\hat{z} \times a_1)/(a_1 \cdot (a_2 \times \hat{z}))$, fulfill the relation $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{ij}$). Consequently we have that

\[
\begin{align*}
K &= \frac{1}{3}(\mathbf{b}_2 - \mathbf{b}_1) \equiv \Sigma \frac{4\pi}{3a} \begin{bmatrix}
-1 \\
0 \\
0
\end{bmatrix} = \begin{bmatrix}
-K \\
0 \\
0
\end{bmatrix}, \\
K' &= \frac{1}{3}(\mathbf{b}_1 - \mathbf{b}_2) \equiv \Sigma \frac{4\pi}{3a} \begin{bmatrix}
1 \\
0 \\
0
\end{bmatrix} = \begin{bmatrix}
K \\
0 \\
0
\end{bmatrix},
\end{align*}
\]

(295)

where we have defined $K = 4\pi/(3a)$. For our choice of $a_1$ and $a_2$, the angle $\theta'$ from the vector $a_1 + a_2$ (i.e. from the axis $\hat{x}'$ used in previous calculations) to the axis $\hat{x}$ (taken in the longitudinal direction) is equal to $\pi/2$.

Therefore the total wave function is given by (eq. (120))

\[
\psi(r) = \sum_{R_A} \psi_A(R_A) \varphi(r - R_A) + \sum_{R_B} \psi_B(R_B) \varphi(r - R_B).
\]

(296)

with (eq. (181) with $\theta' = \pi/2$)

\[
\begin{align*}
\psi_A(r) &= e^{iK \cdot r} F_A^K(r) + e^{iK' \cdot r} F_A^{K'}(r), \\
\psi_B(r) &= -e^{iK \cdot r} F_B^K(r) + e^{iK' \cdot r} F_B^{K'}(r),
\end{align*}
\]

(297)

where (using eq. (295)), if we write $r \equiv \Sigma [x, y, 0]^T$ we have that $K \cdot r = -Kx$ and that $K' \cdot r = Kx$. In the absence of an external potential, the envelope functions satisfy the
usual Dirac equation (eq. (188))

\[
\gamma \left[ \begin{array}{cccc}
0 & -i \frac{\partial}{\partial x} - \frac{\partial}{\partial y} & 0 & 0 \\
-i \frac{\partial}{\partial x} + \frac{\partial}{\partial y} & 0 & 0 & 0 \\
0 & 0 & -i \frac{\partial}{\partial x} - \frac{\partial}{\partial y} & 0 \\
0 & 0 & 0 & -i \frac{\partial}{\partial x} + \frac{\partial}{\partial y}
\end{array} \right] \begin{array}{c}
F^K_A(r) \\
F^K_B(r) \\
F^K'_A(r) \\
F^K'_B(r)
\end{array} = 0
\]

(298)

Due to the translational invariance along the \( x \)-direction, we can write the envelope functions as the product of a propagating part along the longitudinal direction \( x \) and of a confined part along the transverse direction \( y \). Therefore we can assume that

\[
\begin{align*}
F^K_A(r) &= e^{i\kappa x} \phi^K_A(y), \\
F^K_B(r) &= e^{i\kappa x} \phi^K_B(y), \\
F^K'_A(r) &= e^{i\kappa' x} \phi^K'_A(y), \\
F^K'_B(r) &= e^{i\kappa' x} \phi^K'_B(y)
\end{align*}
\]

(299)

We have to enforce that the overall wave function vanishes in correspondence with the “boundary lattice sites” on the lower and upper edges of the ribbon. Let us define as \( W \) the real width of the nanoribbon, i.e. the distance between the lowest row of carbon atoms (all of type \( A \)) and the highest row of carbon atoms (all of type \( B \)); if the ribbon has \( N \) zigzag lines across its width, we have that \( W = (3N - 2)a_{C-C}/2 \). If we take \( y = 0 \) in correspondence of the row of “boundary lattice sites” on the lower edge, the row of “boundary lattice sites” on the upper edge will be for \( y = W = W + 2a_{C-C} = (3N + 2)a_{C-C}/2 \). The proper boundary condition thus implies that, for every \( x \), \( \psi(x, y = 0) = \psi(x, y = W) = 0 \). Since in the zigzag nanoribbon all the “boundary lattice sites” on the lower edge belong to the \( B \) sublattice, while all those on the upper edge belong to the \( A \) sublattice, looking at eq. (296) and observing that the atomic orbitals \( \varphi \) are strongly localized around the atom on which they are centered, the boundary condition on the wave function is equivalent to setting, for every \( x \), \( \psi_B(x, y = 0) = \psi_A(x, y = W) = 0 \).

Using eq. (297), we have that

\[
\psi_B(x, y = 0) = 0 \quad \forall x \Rightarrow -e^{-iKx}F^K_B(x, y = 0) + e^{iKx}F^K'_B(x, y = 0) = 0 \\
\Rightarrow F^K_B(0) = 0, \quad F^K'_B(0) = 0
\]

(300)

and that

\[
\psi_A(x, y = W) = 0 \quad \forall x \Rightarrow e^{-iKx}F^K_A(x, y = W) + e^{iKx}F^K'_A(x, y = W) = 0 \\
\Rightarrow F^K_A(W) = 0, \quad F^K'_A(W) = 0
\]

(301)
As we can see, in zigzag nanoribbons the boundary conditions do not couple the envelope functions relative to the Dirac points \( \mathbf{K} \) and \( \mathbf{K}' \).

First let us make the calculation around the point \( \mathbf{K} \). The corresponding part of the Dirac equation is:

\[
\gamma \left[ \begin{array}{ccc}
0 & -i \frac{\partial}{\partial x} & -\frac{\partial}{\partial y} \\
-\frac{\partial}{\partial x} + \frac{\partial}{\partial y} & 0 & 0 \\
-\frac{\partial}{\partial x} + \frac{\partial}{\partial y} & 0 & 0 \\
\end{array} \right] \left[ \begin{array}{c}
F^K_A(r) \\
F^K_B(r) \\
\Phi^K_A(y)e^{i\kappa_x x} \\
\Phi^K_B(y)e^{i\kappa_x x} \\
\end{array} \right] = E \left[ \begin{array}{c}
F^K_A(r) \\
F^K_B(r) \\
\Phi^K_A(y)e^{i\kappa_x x} \\
\Phi^K_B(y)e^{i\kappa_x x} \\
\end{array} \right]
\]

\[
\gamma \left[ \begin{array}{ccc}
0 & -i \frac{\partial}{\partial x} & -\frac{\partial}{\partial y} \\
-\frac{\partial}{\partial x} + \frac{\partial}{\partial y} & 0 & 0 \\
-\frac{\partial}{\partial x} + \frac{\partial}{\partial y} & 0 & 0 \\
\end{array} \right] \left[ \begin{array}{c}
\Phi^K_A(y) \\
\Phi^K_B(y) \\
\Phi^K_A(y) \\
\Phi^K_B(y) \\
\end{array} \right] = \gamma \frac{\kappa_x}{\gamma} \left[ \begin{array}{c}
\Phi^K_A(y) \\
\Phi^K_B(y) \\
\Phi^K_A(y) \\
\Phi^K_B(y) \\
\end{array} \right] e^{i\kappa_x x} =
\]

\[
E \left[ \begin{array}{c}
F^K_A(r) \\
F^K_B(r) \\
\Phi^K_A(y) \\
\Phi^K_B(y) \\
\end{array} \right] = \frac{E}{\gamma} \left[ \begin{array}{c}
\Phi^K_A(y) \\
\Phi^K_B(y) \\
\Phi^K_A(y) \\
\Phi^K_B(y) \\
\end{array} \right] e^{i\kappa_x x} \Rightarrow
\]

\[
\left[ \begin{array}{ccc}
0 & \kappa_x - \frac{d}{dy} & 0 \\
\kappa_x + \frac{d}{dy} & 0 & 0 \\
\end{array} \right] \left[ \begin{array}{c}
\Phi^K_A(y) \\
\Phi^K_B(y) \\
\end{array} \right] = \frac{E}{\gamma} \left[ \begin{array}{c}
\Phi^K_A(y) \\
\Phi^K_B(y) \\
\end{array} \right],
\]

which can be rewritten as

\[
\left\{ \begin{array}{c}
\left( \kappa_x - \frac{d}{dy} \right) \Phi^K_B(y) = \frac{E}{\gamma} \Phi^K_A(y), \\
\left( \kappa_x + \frac{d}{dy} \right) \Phi^K_A(y) = \frac{E}{\gamma} \Phi^K_B(y).
\end{array} \right.
\]

Obtaining \( \Phi^K_B(y) \) from the second of (303) and then substituting \( \Phi^K_A(y) \) from the first of (303), we find:

\[
\Phi^K_B(y) = \frac{\gamma}{E} \left( \kappa_x + \frac{d}{dy} \right) \Phi^K_A(y) = \left( \frac{\gamma}{E} \right)^2 \left( \kappa_x + \frac{d}{dy} \right) \left( \kappa_x - \frac{d}{dy} \right) \Phi^K_B(y) =
\]

\[
\left( \frac{\gamma}{E} \right)^2 \left( \kappa_x^2 - \kappa_x \frac{d}{dy} + \kappa_x \frac{d}{dy} - \frac{d^2}{dy^2} \right) \Phi^K_B(y) =
\]

\[
\left( \frac{\gamma}{E} \right)^2 \left( \kappa_x^2 - \frac{d}{dy} \right) \right) \Phi^K_B(y) \Rightarrow
\]

\[
\left( \frac{\gamma}{E} \right)^2 \left( \kappa_x^2 - \frac{d}{dy} \right) \Phi^K_B(y) = \left( \frac{E}{\gamma} \right)^2 \Phi^K_B(y),
\]
the solution of which is

\[ \Phi_K^B(y) = Ae^{zy} + Be^{-zy}, \]

with \( z = \sqrt{\kappa_x^2 - \left( \frac{E}{\gamma} \right)^2} \) (and thus \( E = \pm \gamma \sqrt{\kappa_x^2 - z^2} \)).

Substituting \( \Phi_K^B(y) \) back into the first of (303), we obtain that

\[ \Phi_K^A(y) = \frac{\gamma}{E} \left( \kappa_x - \frac{d}{dy} \right) \Phi_K^B(y) = \frac{\gamma}{E} \left( \kappa_x Ae^{zy} + \kappa_x Be^{-zy} - zAe^{zy} + zBe^{-zy} \right) = \frac{\gamma}{E} \left( (\kappa_x - z)Ae^{zy} + (\kappa_x + z)Be^{-zy} \right). \]

Let us now enforce the boundary conditions on \( \Phi_K^B(y) \) and \( \Phi_K^A(y) \)

\[ \Phi_K^B(0) = 0 \Rightarrow A + B = 0 \Rightarrow B = -A; \]
\[ \Phi_K^A(\tilde{W}) = 0 \Rightarrow \frac{\gamma}{E} \left( (\kappa_x - z)Ae^{z\tilde{W}} + (\kappa_x + z)Be^{-z\tilde{W}} \right) = 0 \Rightarrow \]
\[ (\kappa_x - z)Ae^{z\tilde{W}} - (\kappa_x + z)Be^{-z\tilde{W}} = 0 \Rightarrow \]
\[ (\kappa_x - z)Ae^{z\tilde{W}} = (\kappa_x + z)Be^{-z\tilde{W}} \Rightarrow \]
\[ e^{-2z\tilde{W}} = \frac{\kappa_x - z}{\kappa_x + z}. \]

As we can see, in zigzag nanoribbons the longitudinal and the transverse wave vectors are coupled.

Incidentally, note that, instead of eq. (307), an equivalent equation can be used [106]; indeed, being \( E = \pm \gamma \sqrt{\kappa_x^2 - z^2} \) and thus \( (E/\gamma)^2 = \kappa_x^2 - z^2 \), we have that

\[ e^{-2z\tilde{W}} = \frac{\kappa_x - z}{\kappa_x + z} \Rightarrow \]
\[ \frac{E}{\gamma} = \pm (\kappa_x + z)e^{-z\tilde{W}}. \]

Here we consider real values of \( \kappa_x \).

If we graphically represent (fig. 11) the two functions \( f_1(z) = e^{-2z\tilde{W}} \) and \( f_2(z) = (\kappa_x - z)/(\kappa_x + z) \), we see that (apart from \( z = 0 \), which corresponds to identically null \( \Phi \)'s) there is an intersection between \( f_1 \) and \( f_2 \) for a real value of \( z \) (and thus eq. (307)
Fig. 11. – Graphical solution (in the real domain) of eq. (307) (the dotted lines are the asymptotes of $f_2(z)$).

has a real solution $z$ only if $\kappa_x > 0$ and if $f_1(z)$ is steeper than $f_2(z)$ in $z = 0$, i.e. if

$$\left| \frac{d}{dz} f_1(z) \right|_{z=0} > \left| \frac{d}{dz} f_2(z) \right|_{z=0} \Rightarrow$$

$$\left| -2W e^{-2z\tilde{W}} \right|_{z=0} > \left| -\frac{1}{\kappa_x + z} \frac{\kappa_x - z}{(\kappa_x + z)^2} \right|_{z=0} =$$

$$\left| \frac{\kappa_x + z + \kappa_x - z}{(\kappa_x + z)^2} \right|_{z=0} = \left| -\frac{2\kappa_x}{(\kappa_x + z)^2} \right|_{z=0} \Rightarrow 2\tilde{W} > \frac{2\kappa_x}{W} \Rightarrow W > \frac{1}{W} \Rightarrow \kappa_x > \frac{1}{W}.$$  

If instead $\kappa_x < 1/W$, eq. (307) does not have real solutions $z$ (apart from $z = 0$). In the case of real $z$, from eq. (307) we can find that

$$e^{-2z\tilde{W}} = \frac{\kappa_x - z}{\kappa_x + z} \Rightarrow$$

$$\kappa_x e^{-2z\tilde{W}} + ze^{-2z\tilde{W}} = \kappa_x - z \Rightarrow \kappa_x (1 - e^{-2z\tilde{W}}) = z(1 + e^{-2z\tilde{W}}) \Rightarrow$$

$$\kappa_x = z \frac{1 + e^{-2z\tilde{W}}}{1 - e^{-2z\tilde{W}}} = z \frac{e^{2z\tilde{W}} + e^{-z\tilde{W}}}{e^{2z\tilde{W}} - e^{-z\tilde{W}}} = \frac{z}{\tanh(z\tilde{W})}$$

($z = 0$ does not have to be considered) and thus

$$\left( \frac{E}{\gamma} \right)^2 = \kappa_x^2 - z^2 = \frac{z^2}{\tanh^2(z\tilde{W})} - z^2 = z^2 \left( \frac{\cosh^2(z\tilde{W}) - \sinh^2(z\tilde{W})}{\sinh^2(z\tilde{W})} \right) =$$

$$z^2 \left( \frac{\cosh^2(z\tilde{W}) - \sinh^2(z\tilde{W})}{\sinh^2(z\tilde{W})} \right) = \frac{z^2}{\sinh^2(z\tilde{W})} \Rightarrow \left| \frac{E}{\gamma} \right| = \left| \frac{z}{\sinh(z\tilde{W})} \right|.$$  

Since (for the properties of the hyperbolic sine function) $|\sinh(z\tilde{W})| > |z\tilde{W}| = |z|\tilde{W}$, we see that in this case

$$\left| \frac{E}{\gamma} \right| < \frac{|z|}{|z|\tilde{W}} = \frac{1}{\tilde{W}}.$$
We can write (exploiting what we have found from the boundary conditions) that

\[ \Phi^K_A(y) = \frac{\gamma}{E} ((\kappa_x - z)Ae^{zy} + (\kappa_x + z)Be^{-zy}) = \]

\[ \frac{\gamma}{E} ((\kappa_x - z)Ae^{zy} - (\kappa_x + z)Ae^{-zy}) = \]

\[ \frac{\gamma}{E} A (\kappa_x (e^{zy} - e^{-zy}) - z(e^{zy} + e^{-zy})) = \]

\[ \frac{\gamma}{E} 2A (\kappa_x \sinh(zy) - z \cosh(zy)) = \]

\[ 2A \frac{\gamma}{E} \left( \frac{z}{\tanh(zW)} \sinh(zy) - z \cosh(zy) \right) = \]

\[ 2A \frac{\gamma}{E} \cosh(z\bar{W}) \sinh(zy) - \sinh(z\bar{W}) \cosh(zy) = \]

\[ -2A \frac{\gamma}{E} z \cosh(z\bar{W}) \sinh(-zy) + \sinh(z\bar{W}) \cosh(-zy) = \]

\[ -2A \left( \frac{\gamma}{E} \frac{z}{\sinh(zW)} \right) \sinh(z(\bar{W} - y)) = \]

\[ -2A \text{sign} \left( \frac{E}{\gamma} \frac{z}{\sinh(zW)} \right) \sinh(z(\bar{W} - y)), \]

where in the last step we have taken advantage of the fact that, due to eq. (311), the product between \( \gamma/E \) and \( z/\sinh(z\bar{W}) \) can only be equal to +1 (if the two quantities have the same sign) or -1 (if they have opposite signs).

Moreover we have that

\[ \Phi^K_B(y) = Ae^{zy} + Be^{-zy} = Ae^{zy} - Ae^{-zy} = A(e^{zy} - e^{-zy}) = 2A \sinh(zy). \]

These are edge states, each one exponentially localized on one edge of the ribbon.

These edge states correspond to bands flattened towards \( E = 0 \), as we can see both from the graphical solution of eq. (307) (where we observe that we have an intersection between \( f_1 \) and \( f_2 \) for a \( z \) coordinate very close to \( \kappa_x \) and thus the energy \( E = \pm \gamma \sqrt{\kappa_x^2 - z^2} \) has a very small value), and from our previous analytical conclusion that \( |E/\gamma| < 1/\bar{W} \) in this case. Since the Dirac point \( \mathbf{K} \), folded into the Brillouin zone \((-\pi/a, \pi/a)\) of the zigzag nanoribbon (the unit cell of which is of length \( a \)), corresponds to \( k_x = -4\pi/(3a) + 2\pi/a = 2\pi/(3a) \), the condition \( \kappa_x > 1/\bar{W} \) (under which we have a real solution and thus the edge states) is equivalent to \( k_x = K_x + \kappa_x > 2\pi/(3a) + 1/\bar{W} \) (note the difference between the total wave vectors \( k \) and the wave vectors \( \kappa \) measured from the Dirac points). Therefore in the region \( 2\pi/(3a) + 1/\bar{W} < k_x < \pi/a \) we have two bands flattened towards \( E = 0 \); this means that the zigzag nanoribbons are always metallic [108]. However, further studies [109-111] have shown that actual zigzag nanoribbons have a non-zero gap deriving from a staggered sublattice potential due to edge magnetization.

Let us now instead consider the imaginary solutions \( z = i\kappa_n \) (with \( \kappa_n \) real) of eq. (307). In this case the dispersion relation \( E = \pm \gamma \sqrt{\kappa_x^2 - z^2} \) becomes \( E = \pm \gamma \sqrt{\kappa_x^2 + \kappa_n^2} \), from which we see more clearly that \( \kappa_x \) and \( \kappa_n = -iz \) have the meaning
of longitudinal and transverse components of the wave vector, measured from the Dirac point. The solutions are given by

\[
\begin{align*}
& e^{-2i\kappa_n \tilde{W}} = \frac{\kappa_x - z}{\kappa_x + z} \\
& e^{-i2\kappa_n \tilde{W}} = \frac{\kappa_x - i\kappa_n}{\kappa_x + i\kappa_n} = \sqrt{\frac{\kappa_x^2 + \kappa_n^2}{\kappa_x^2 + \kappa_n^2}} e^{-i\sqrt{\kappa_x^2 + \kappa_n^2}} = e^{-i\sqrt{\kappa_x^2 + \kappa_n^2}} \quad (315) \\
& e^{-i2\kappa_n \tilde{W}} = e^{-i2\sqrt{\kappa_x^2 + \kappa_n^2}} e^{i2\pi m} \Rightarrow \\
& \kappa_n \tilde{W} = \pi (\kappa_x + i\kappa_n) - \pi m \Rightarrow \tan(\kappa_n \tilde{W}) = \frac{\kappa_n}{\kappa_x} \Rightarrow \kappa_x = \frac{\kappa_n}{\tan(\kappa_n \tilde{W})}
\end{align*}
\]

(with \(m\) integer); \(\kappa_n = 0\) corresponds to identically null \(\Phi\)'s and thus does not have to be considered. We have that

\[
\begin{align*}
& \left(\frac{E}{\gamma}\right)^2 = \kappa_n^2 + \kappa_n^2 = \left(\frac{\kappa_n}{\tan(\kappa_n \tilde{W})}\right)^2 + \kappa_n^2 = \left(\frac{\cos^2(\kappa_n \tilde{W})}{\sin^2(\kappa_n \tilde{W})} + 1\right) \kappa_n^2 = \\
& \frac{\cos^2(\kappa_n \tilde{W}) + \sin^2(\kappa_n \tilde{W})}{\sin^2(\kappa_n \tilde{W})} \Rightarrow \left| \frac{E}{\gamma} \right| = \left| \frac{\kappa_n}{\sin(\kappa_n \tilde{W})} \right| ;
\end{align*}
\]

since (for the properties of the sin function) \(|\sin(\kappa_n \tilde{W})| < |\kappa_n \tilde{W}| = |\kappa_n| \tilde{W}|\), we see that in this case

\[
\left| \frac{E}{\gamma} \right| > \left| \frac{\kappa_n}{\sin(\kappa_n \tilde{W})} \right| = \frac{1}{\tilde{W}}
\]

We can write (exploiting what we have found from the boundary conditions) that

\[
\begin{align*}
& \Phi^K_A(y) = \frac{\gamma}{E} \left( (\kappa_x - i\kappa_n) A e^{i\kappa_n y} + (\kappa_x + i\kappa_n) B e^{-i\kappa_n y} \right) = \\
& \frac{\gamma}{E} \left( (\kappa_x - i\kappa_n) A e^{i\kappa_n y} - (\kappa_x + i\kappa_n) B e^{-i\kappa_n y} \right) = \\
& \frac{\gamma}{E} A \left( e^{i\kappa_n y} - e^{-i\kappa_n y} \right) \Rightarrow \kappa_n = \frac{\cos(\kappa_n \tilde{W})}{\sin(\kappa_n \tilde{W})} \\
& 2iA \left( \frac{\kappa_n}{\tan(\kappa_n \tilde{W})} \sin(\kappa_n y) - \kappa_n \cos(\kappa_n y) \right) \\
& 2iA \left( \cos(\kappa_n y) \sin(\kappa_n \tilde{W}) - \sin(\kappa_n \tilde{W}) \cos(\kappa_n y) \right) \\
& -2iA \left( \frac{\gamma}{E} \frac{\kappa_n}{\sin(\kappa_n \tilde{W})} \right) \sin(\kappa_n (\tilde{W} - y)) \\
& -2iA \left( \frac{\gamma}{E} \frac{\kappa_n}{\sin(\kappa_n \tilde{W})} \right) \sin(\kappa_n (\tilde{W} - y))
\end{align*}
\]

where in the last step we have taken advantage of the fact that, due to eq. (316), the product between \(\gamma/E\) and \(\kappa_n/\sin(\kappa_n \tilde{W})\) can only be equal to +1 (if the two quantities have the same sign) or −1 (if they have opposite signs).
Moreover we have that

\[ \Phi^K_B (y) = Ae^{i\kappa_0 y} + Be^{-i\kappa_0 y} = Ae^{i\kappa_0 y} - Ae^{-i\kappa_0 y} = A(e^{i\kappa_0 y} - e^{-i\kappa_0 y}) = A2i \sin(\kappa_0 y). \]

These are clearly confined states extending all over the ribbon.

The calculations around the point \( \mathbf{K'} \) are completely analogous. The corresponding part of the Dirac equation is

\[
\gamma \begin{bmatrix}
- \frac{i}{\hbar} \frac{\partial}{\partial x} - \frac{\partial}{\partial y} & 0 \\
- \frac{i}{\hbar} \frac{\partial}{\partial x} - \frac{\partial}{\partial y} & 0
\end{bmatrix}
\begin{bmatrix}
F^K_A' (r) \\
F^K_B' (r)
\end{bmatrix}
= E \begin{bmatrix}
F^K_A' (r) \\
F^K_B' (r)
\end{bmatrix} \Rightarrow
\]

\[
\gamma \begin{bmatrix}
\kappa_x' \Phi^K_A'(y) e^{i\kappa'_x x} + \kappa'_x \Phi^K_A'(y) e^{i\kappa'_x x} \\
\kappa'_x \Phi^K_A'(y) e^{i\kappa'_x x} - \kappa'_x \Phi^K_A'(y)
\end{bmatrix}
= E \begin{bmatrix}
\Phi^K_A'(y) \\
\Phi^K_B'(y)
\end{bmatrix} e^{i\kappa'_x x} = E \begin{bmatrix}
\Phi^K_A'(y) \\
\Phi^K_B'(y)
\end{bmatrix} \Rightarrow
\]

\[
\begin{bmatrix}
0 & \kappa_x' + \frac{d}{dy} \\
\kappa'_x - \frac{d}{dy} & 0
\end{bmatrix}
\begin{bmatrix}
\Phi^K_A'(y) \\
\Phi^K_B'(y)
\end{bmatrix}
= \frac{E}{\gamma} \begin{bmatrix}
\Phi^K_A'(y) \\
\Phi^K_B'(y)
\end{bmatrix},
\]

which can be rewritten as

\[
\begin{align*}
\left\{ \begin{array}{l}
\kappa_x' + \frac{d}{dy} & \Phi^K_B'(y) = \frac{E}{\gamma} \Phi^K_A'(y), \\
\kappa_x' - \frac{d}{dy} & \Phi^K_A'(y) = \frac{E}{\gamma} \Phi^K_B'(y).
\end{array} \right.
\end{align*}
\]

Obtaining \( \Phi^K_B'(y) \) from the second of (321) and then substituting \( \Phi^K_A'(y) \) from the first of (321), we find

\[
\Phi^K_B'(y) = \frac{\gamma}{E} \left( \kappa_x' - \frac{d}{dy} \right) \Phi^K_A'(y) = \left( \frac{\gamma}{E} \right)^2 \left( \kappa_x' - \frac{d}{dy} \right) \left( \kappa_x' + \frac{d}{dy} \right) \Phi^K_B'(y) =
\]

\[
\left( \frac{\gamma}{E} \right)^2 \left( \kappa_x'^2 + \kappa_x' \frac{d}{dy} - \kappa_x' \frac{d}{dy} - \frac{d^2}{dy^2} \right) \Phi^K_B'(y) =
\]

\[
\left( \frac{\gamma}{E} \right)^2 \left( \kappa_x'^2 - \frac{d^2}{dy^2} \right) \Phi^K_B'(y) \Rightarrow
\]

\[
\left( - \frac{d^2}{dy^2} + \kappa_x'^2 \right) \Phi^K_B'(y) = \left( \frac{E}{\gamma} \right)^2 \Phi^K_B'(y),
\]
the solution of which is

\[ \Phi_K'(y) = Ce^{z'y} + De^{-z'y}, \]

with \[ z' = \sqrt{k'_x^2 - \left(\frac{E}{\gamma}\right)^2} \quad \text{(and thus} \; E = \pm \gamma \sqrt{k'_x^2 - z'^2}. \]

Substituting \( \Phi_K'(y) \) back into the first of (321), we obtain that

\[ \Phi_K'(y) = \gamma \left( \kappa'_x + \frac{d}{dy} \right) \Phi_K'(y) = \gamma \left( \kappa'_x + z' \right)Ce^{z'y} + \kappa'_x De^{-z'y} = 0 \]

\[ e^{-2z'W} = \frac{\kappa'_x + z'}{-\kappa'_x - z'} \]

which is equal to eq. (307) if we substitute \( \kappa_x \) with \( -\kappa'_x \). Therefore the calculations are completely analogous to those seen around the point \( K \).

We consider again real values of \( \kappa'_x \).

We conclude [93] that (apart from \( z' = 0 \), which corresponds to identically null \( \Phi \)'s) eq. (325) has a real solution \( z' \) only if \( -\kappa'_x > 1/W \), i.e. if \( \kappa'_x < -1/W \).

If instead \( \kappa'_x > -1/W \), eq. (325) does not have real solutions \( z' \) (apart from \( z' = 0 \)).

In the case of real \( z' \), from eq. (325) we can find that [93]

\[ \kappa'_x = -\frac{z'}{\tanh(z'W)} \]

\( z' = 0 \) does not have to be considered) and thus [93]

\[ \left( \frac{E}{\gamma} \right)^2 = \kappa_x^2 - z'^2 = \frac{z'^2}{\sinh^2(z'W)} \quad \Rightarrow \quad \left| \frac{E}{\gamma} \right| = \frac{|z'|}{\sinh(z'W)} < \frac{|z'|}{|z'|W} = \frac{1}{W}. \]
The corresponding $\Phi$ functions are [93]

$$\Phi_A^C(y) = \frac{\gamma}{E} \left( (\kappa'_x + z')Ce^{z'y} + (\kappa'_x - z')De^{-z'y} \right) =$$

$$2C \text{sign} \left( \frac{E}{\gamma \sinh(z'W)} \right) \sinh(z'(W - y));$$

$$\Phi_B^C(y) = Ce^{z'y} + De^{-z'y} = 2C \sinh(z'y).$$

These are edge states, each one exponentially localized on one edge of the ribbon.

Also in this case, these edge states correspond to bands flattened towards $E = 0$. Since the Dirac point $K'$, folded into the Brillouin zone ($-\pi/a, \pi/a$) of the zigzag nanoribbon, corresponds to $k_x = 4\pi/(3a) - 2\pi/a = -2\pi/(3a)$, the condition $\kappa'_x < -1/W$ is equivalent to $k_x = K'_x + \kappa'_x < -2\pi/(3a) - 1/W$. Therefore also in the region $-\pi/a < k_x < -2\pi/(3a) - 1/W$ we have two bands flattened towards $E = 0$, which confirms the metallic nature of zigzag nanoribbons.

Let us now instead consider the imaginary solutions $z' = i\kappa'_n$ (with $\kappa'_n$ real) of eq. (325). The dispersion relation $E = \pm \gamma \sqrt{\kappa'_x^2 - z'^2}$ becomes $E = \pm \gamma \sqrt{\kappa'_x^2 + \kappa'_n^2}$. The solutions are given by [93]

$$\kappa'_x = -\frac{\kappa'_n}{\tan(\kappa'_nW)}$$

($\kappa'_n = 0$ corresponds to identically null $\Phi$’s and thus does not have to be considered) and thus [93]

$$\left( \frac{E}{\gamma} \right)^2 = \kappa'_x^2 + \kappa'_n^2 = \frac{\kappa'_n^2}{\sin^2(\kappa'_nW)} \Rightarrow \frac{E}{\gamma} = \left| \frac{\kappa'_n}{\sin(\kappa'_nW)} \right| > \frac{|\kappa'_n|}{|\kappa'_nW|} = \frac{1}{W}.$$}

The corresponding $\Phi$ functions are [93]

$$\Phi_A^C(y) = \frac{\gamma}{E} \left( (\kappa'_x + i\kappa'_n)Ce^{i\kappa'_n y} + (\kappa'_x - i\kappa'_n)De^{-i\kappa'_n y} \right) =$$

$$2iC \text{sign} \left( \frac{E}{\gamma \sin(\kappa'_nW)} \right) \sin(\kappa'_n(W - y));$$

$$\Phi_B^C(y) = Ce^{i\kappa'_n y} + De^{-i\kappa'_n y} = C2i \sin(\kappa'_n y).$$

These are confined states extending all over the ribbon.

Obviously, once the expressions of the functions $\Phi$ have been obtained, the overall wave function is given by the equations (296), (297) and (299).

In fig. 12 we show the bands of a zigzag nanoribbon with $N = 45$ zigzag lines and of a zigzag nanoribbon with $N = 50$ zigzag lines, that we have computed both with a simple tight-binding model not including edge magnetization effects (thick dotted lines) and with the $k \cdot p$ (Dirac equation) method (thin solid lines). For low energy values and for not too narrow ribbons the results obtained with the two techniques are very similar. In both cases, the presence of the two bands flattened towards zero and corresponding to the edge states can be clearly seen.
Fig. 12. – Bands of a zigzag nanoribbon with $N = 45$ zigzag lines (a) and with $N = 50$ zigzag lines (b), computed both with a simple tight-binding model not including edge magnetization effects (thick dotted lines) and with the $k \cdot p$ method (thin solid lines). The two dashed lines correspond to the energy values $\pm \gamma / \tilde{W}$; the dispersion relations in the region between the two dashed lines are obtained for real values of $z$, while those outside this region correspond to purely imaginary values of $z$.

6.2. Armchair nanoribbons. – Instead, in the case of armchair nanoribbons (fig. 13), the graphene sheet has been cut along the direction of the nearest-neighbor carbon bonds, and therefore the edges have an armchair shape. In order to simplify the following calculations, we can choose (see fig. 13) the graphene lattice vectors in the real space $\mathbf{a}_1$ and $\mathbf{a}_2$ (and consequently those in the reciprocal space $\mathbf{b}_1$ and $\mathbf{b}_2$) in this way (we express them in the reference frame $\Sigma = (\hat{x}, \hat{y}, \hat{z})$):

\begin{align}
\mathbf{a}_1 & \equiv \Sigma \begin{bmatrix} \sqrt{3}a/2 \\ \sqrt{3}a/2 \\ 0 \end{bmatrix}, \\
\mathbf{a}_2 & \equiv \Sigma \begin{bmatrix} \sqrt{3}a/2 \\ -\sqrt{3}a/2 \\ 0 \end{bmatrix}, \\
\mathbf{b}_1 & \equiv \Sigma \begin{bmatrix} 2\pi/\sqrt{3}a \\ 2\pi/\sqrt{3}a \\ 0 \end{bmatrix}, \\
\mathbf{b}_2 & \equiv \Sigma \begin{bmatrix} 2\pi/3a \\ 2\pi/3a \\ 0 \end{bmatrix},
\end{align}

Fig. 13. – Sketch of an armchair nanoribbon with $N$ dimer lines (the black atoms are carbon atoms, while the grey atoms are passivation atoms).
(which, being \( \mathbf{b}_1 = 2\pi(\mathbf{a}_2 \times \hat{z})/(\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \hat{z})) \) and \( \mathbf{b}_2 = 2\pi(\hat{z} \times \mathbf{a}_1)/(\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \hat{z})) \), fulfill the relation \( \mathbf{a}_1 \cdot \mathbf{b}_2 = 2\pi\delta_{ij} \). Consequently we have that

\[
K = \frac{1}{3}(\mathbf{b}_2 - \mathbf{b}_1) \equiv \frac{4\pi}{3a} \begin{bmatrix} 0 \\ -1 \\ 0 \end{bmatrix} = \begin{bmatrix} 0 \\ -K \\ 0 \end{bmatrix},
\]

and

\[
K' = \frac{1}{3}(\mathbf{b}_1 - \mathbf{b}_2) \equiv \frac{4\pi}{3a} \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} = \begin{bmatrix} K \\ 0 \\ 0 \end{bmatrix},
\]

with \( K = 4\pi/(3a) \). For our choice of \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \), the angle \( \theta' \) from the vector \( \mathbf{a}_1 + \mathbf{a}_2 \) (i.e. from the axis \( \hat{z}' \) used in previous calculations) to the axis \( \hat{x} \) (taken in the longitudinal direction) is equal to 0.

Therefore the total wave function is given by (eq. 120)

\[
\psi(r) = \sum_{\mathbf{R}_A} \psi_A(\mathbf{R}_A) \varphi(r - \mathbf{R}_A) + \sum_{\mathbf{R}_B} \psi_B(\mathbf{R}_B) \varphi(r - \mathbf{R}_B),
\]

with (eq. (181) with \( \theta' = 0 \))

\[
\begin{cases}
\psi_A(r) = e^{iK \cdot r} F_A^K(r) - ie^{iK' \cdot r} F_A^{K'}(r), \\
\psi_B(r) = ie^{iK \cdot r} F_B^K(r) + e^{iK' \cdot r} F_B^{K'}(r),
\end{cases}
\]

where (using eq. (333)), if we write \( r \equiv [x, y, 0]^T \) we have that \( \mathbf{K} \cdot \mathbf{r} = -K'y \) and that \( \mathbf{K}' \cdot \mathbf{r} = Ky \). In the absence of an external potential the envelope functions satisfy the usual Dirac equation (eq. (188))

\[
\gamma\begin{bmatrix}
0 & -i \frac{\partial}{\partial x} - \frac{\partial}{\partial y} & 0 & 0 \\
-i \frac{\partial}{\partial x} + \frac{\partial}{\partial y} & 0 & 0 & 0 \\
0 & 0 & 0 & -i \frac{\partial}{\partial x} + \frac{\partial}{\partial y} \\
0 & 0 & -i \frac{\partial}{\partial x} - \frac{\partial}{\partial y} & 0
\end{bmatrix}\begin{bmatrix}
F_A^K(r) \\
F_B^K(r) \\
F_A^{K'}(r) \\
F_B^{K'}(r)
\end{bmatrix} = 0.
\]

Due to the translational invariance along the \( x \)-direction, we can write the envelope functions as the product of a propagating part along the longitudinal direction \( x \) and of a confined part along the transverse direction \( y \). Here we have to consider the same
longitudinal component $\kappa_x$ for the wave vector measured from $K$ and $K'$ because in this case if we consider $\kappa'_x \neq \kappa_x$ the boundary conditions are satisfied for every $x$ only by the identically null wave function. Therefore we can assume that

$$
(337) \begin{bmatrix}
F_A^K(r) \\
F_B^K(r)
\end{bmatrix} = e^{i\kappa_x} \begin{bmatrix}
\Phi_A^K(y) \\
\Phi_B^K(y)
\end{bmatrix}
$$

and that

$$
(338) \begin{bmatrix}
F_A^{K'}(r) \\
F_B^{K'}(r)
\end{bmatrix} = e^{i\kappa_x} \begin{bmatrix}
\Phi_A^{K'}(y) \\
\Phi_B^{K'}(y)
\end{bmatrix}.
$$

We have to enforce that the overall wave function vanishes in correspondence with the “boundary lattice sites” on the lower and upper edges of the ribbon. Let us define as $W$ the real width of the nanoribbon, i.e. the distance between the bottom row and the top row of carbon atoms of the ribbon; if the ribbon has $N$ dimer lines across the ribbon width, we have that $W = (N - 1)a/2$. If we take $y = 0$ in correspondence of the row of “boundary lattice sites” on the lower edge of the ribbon, the row of “boundary lattice sites” on the upper edge of the ribbon will be at $y = W = W + 2a/2 = W + a = (N + 1)a/2$. Therefore, for every $x$, we must have $\psi(x, y = 0) = \psi(x, y = W) = 0$. We notice that in an armchair nanoribbon the “boundary lattice sites” on the lower and upper edges belong to both the $A$ and the $B$ sublattices. Therefore, looking at eq. (334) and observing that the atomic orbitals $\varphi$ are strongly localized around the atom on which they are centered, the boundary condition on the wave function is equivalent to setting, for every $x$, $\psi_A(x, y = 0) = \psi_B(x, y = 0) = \psi_A(x, y = W) = \psi_B(x, y = W) = 0$. Using eq. (335) we obtain the following 4 boundary conditions:

$$
(338) \begin{align*}
\psi_A(x, y = 0) &= 0 \forall x \Rightarrow e^{-iK_0}F_A^K(x, y = 0) - ie^{iK_0}F_A^{K'}(x, y = 0) = \\
F_A^K(x, y = 0) - iF_A^{K'}(x, y = 0) &= e^{i\kappa_x} \Phi_A^K(0) - ie^{i\kappa_x} \Phi_A^{K'}(0) = 0 \forall x \Rightarrow \\
\Phi_A^K(0) - i\Phi_A^{K'}(0) &= 0;
\end{align*}
$$

$$
(339) \begin{align*}
\psi_B(x, y = 0) &= 0 \forall x \Rightarrow ie^{-iK_0}F_B^K(x, y = 0) + e^{iK_0}F_B^{K'}(x, y = 0) = \\
iF_B^K(x, y = 0) + iF_B^{K'}(x, y = 0) &= ie^{i\kappa_x} \Phi_B^K(0) + ie^{i\kappa_x} \Phi_B^{K'}(0) = 0 \forall x \Rightarrow \\
i\Phi_B^K(0) + \Phi_B^{K'}(0) &= 0;
\end{align*}
$$

$$
(340) \begin{align*}
\psi_A(x, y = W) &= 0 \forall x \Rightarrow e^{-iKW}F_A^K(x, y = W) - ie^{iKW}F_A^{K'}(x, y = W) = \\
e^{-iKW}e^{i\kappa_x} \Phi_A^K(W) - ie^{iKW}e^{i\kappa_x} \Phi_A^{K'}(W) &= 0 \forall x \Rightarrow \\
e^{-iKW} \Phi_A^K(W) - ie^{iKW} \Phi_A^{K'}(W) &= 0;
\end{align*}
$$

$$
(341) \begin{align*}
\psi_B(x, y = W) &= 0 \forall x \Rightarrow ie^{-iKW}F_B^K(x, y = W) + e^{iKW}F_B^{K'}(x, y = W) = \\
ie^{-iKW}e^{i\kappa_x} \Phi_B^K(W) + e^{iKW}e^{i\kappa_x} \Phi_B^{K'}(W) &= 0 \forall x \Rightarrow \\
ie^{-iKW} \Phi_B^K(W) + e^{iKW} \Phi_B^{K'}(W) &= 0.
\end{align*}
$$

As we can see, in armchair nanoribbons the boundary conditions couple the envelope functions relative to the Dirac points $K$ and $K'$. 
We can solve the part of the Dirac equation around the point \( \mathbf{K} \), that is

\[
\gamma \left[ \begin{array}{cc}
0 & -i \frac{\partial}{\partial x} - \frac{\partial}{\partial y} \\
-i \frac{\partial}{\partial x} + \frac{\partial}{\partial y} & 0
\end{array} \right] \left[ \begin{array}{c}
F^K_A(r) \\
F^K_B(r)
\end{array} \right] = E \left[ \begin{array}{c}
F^K_A(r) \\
F^K_B(r)
\end{array} \right],
\]

repeating the calculations made for zigzag nanoribbons (eqs. (302)-(306)) and obtaining that

\[
\Phi^K_A(y) = \frac{\gamma}{E} \left( (\kappa_x - z) A e^{z y} + (\kappa_x + z) B e^{-z y} \right),
\]

\[
\Phi^K_B(y) = A e^{z y} + B e^{-z y},
\]

with \( z = \sqrt{\kappa_x^2 - \left( \frac{E}{\gamma} \right)^2} \) and thus \( E = \pm \gamma \sqrt{\kappa_x^2 - z^2} \).

Analogously, we can solve the part of the Dirac equation around the point \( \mathbf{K}' \), that is

\[
\gamma \left[ \begin{array}{cc}
0 & -i \frac{\partial}{\partial x} + \frac{\partial}{\partial y} \\
-i \frac{\partial}{\partial x} - \frac{\partial}{\partial y} & 0
\end{array} \right] \left[ \begin{array}{c}
F'^K_A(r) \\
F'^K_B(r)
\end{array} \right] = E \left[ \begin{array}{c}
F'^K_A(r) \\
F'^K_B(r)
\end{array} \right],
\]

repeating the calculations made for zigzag nanoribbons (eqs. (320)-(324), with the difference that \( \kappa'_x \) and \( z' \) here have to be replaced by \( \kappa_x \) and \( z \)) and obtaining that

\[
\Phi'^K_A(y) = \frac{\gamma}{E} \left( (\kappa_x + z) C e^{z y} + (\kappa_x - z) D e^{-z y} \right),
\]

\[
\Phi'^K_B(y) = C e^{z y} + D e^{-z y},
\]

with (as written before) \( z = \sqrt{\kappa_x^2 - \left( \frac{E}{\gamma} \right)^2} \) and thus \( E = \pm \gamma \sqrt{\kappa_x^2 - z^2} \).

Let us define \( z = i \kappa_n \). In this case the dispersion relation becomes \( E = \pm \gamma \sqrt{\kappa_x^2 + \kappa_n^2} \); therefore \( \kappa_x \) and \( \kappa_n = -iz \) are the longitudinal and transverse components of the wave vector, measured from the Dirac point.

The functions \( \Phi \) become

\[
\left\{ \begin{array}{l}
\Phi^K_A(y) = \frac{\gamma}{E} \left( (\kappa_x - i \kappa_n) A e^{i \kappa_n y} + (\kappa_x + i \kappa_n) B e^{-i \kappa_n y} \right), \\
\Phi^K_B(y) = A e^{i \kappa_n y} + B e^{-i \kappa_n y}, \\
\Phi'^K_A(y) = \frac{\gamma}{E} \left( (\kappa_x + i \kappa_n) C e^{i \kappa_n y} + (\kappa_x - i \kappa_n) D e^{-i \kappa_n y} \right), \\
\Phi'^K_B(y) = C e^{i \kappa_n y} + D e^{-i \kappa_n y}.
\end{array} \right.
\]
Now we can enforce the 4 boundary conditions (338)-(341), obtaining:

\[(347) \quad \Phi^K_A(0) - i\Phi^K_A'(0) = 0 \Rightarrow \]
\[(\kappa_x - i\kappa_n)A + (\kappa_x + i\kappa_n)B - i(\kappa_x + i\kappa_n)C - i(\kappa_x - i\kappa_n)D = 0 \Rightarrow \]
\[\kappa_x (A + B - iC - iD) + i\kappa_n (-A + B + iC + iD) = 0; \]
\[(348) \quad i\Phi^K_B(0) + \Phi^K_B'(0) = 0 \Rightarrow i(A + B) + (C + D) = 0 \Rightarrow \]
\[A + B - iC - iD = 0; \]
\[(349) \quad e^{-iK\hat{W}} \Phi^K_A(\hat{W}) - ie^{iK\hat{W}} \Phi^K_A'(\hat{W}) = 0 \Rightarrow \]
\[e^{-iK\hat{W}} (\kappa_x - i\kappa_n)Ae^{i\kappa_n\hat{W}} + e^{-iK\hat{W}} (\kappa_x + i\kappa_n)Be^{-i\kappa_n\hat{W}} \]
\[-ie^{iK\hat{W}} (\kappa_x + i\kappa_n)Ce^{i\kappa_n\hat{W}} - ie^{iK\hat{W}} (\kappa_x - i\kappa_n)De^{-i\kappa_n\hat{W}} = \]
\[\kappa_x \left( Ae^{i(\kappa_n-K)\hat{W}} + Be^{-i(\kappa_n+K)\hat{W}} - iCe^{i(\kappa_n+K)\hat{W}} - iDe^{-i(\kappa_n-K)\hat{W}} \right) \]
\[+i\kappa_n \left( -Ae^{i(\kappa_n-K)\hat{W}} - Be^{-i(\kappa_n+K)\hat{W}} - iCe^{i(\kappa_n+K)\hat{W}} + iDe^{-i(\kappa_n-K)\hat{W}} \right) = 0; \]
\[(350) \quad ie^{-iK\hat{W}} \Phi^K_B(\hat{W}) + e^{iK\hat{W}} \Phi^K_B'(\hat{W}) = 0 \Rightarrow \]
\[ie^{-iK\hat{W}} (Ae^{i\kappa_n\hat{W}} + Be^{-i\kappa_n\hat{W}}) + e^{iK\hat{W}} (C e^{i\kappa_n\hat{W}} + D e^{-i\kappa_n\hat{W}}) = 0 \Rightarrow \]
\[iAe^{i(\kappa_n-K)\hat{W}} + iBe^{-i(\kappa_n+K)\hat{W}} + iCe^{i(\kappa_n+K)\hat{W}} + iDe^{-i(\kappa_n-K)\hat{W}} = 0 \Rightarrow \]
\[Ae^{i(\kappa_n-K)\hat{W}} + Be^{-i(\kappa_n+K)\hat{W}} + iCe^{i(\kappa_n+K)\hat{W}} + iDe^{-i(\kappa_n-K)\hat{W}} = 0. \]

In the following we examine the different cases in which all of these 4 boundary conditions are satisfied.

**Case I**
If \(\kappa_n = 0\) the condition (347) is equivalent to the condition (348), and the condition (349) is equivalent to the condition (350).

But the condition (348) is satisfied if

\[(351) \quad A + B - iC - iD = 0 \Rightarrow A + B = iC + iD \Rightarrow \begin{cases} A + B = G \\ C + D = -iG \end{cases} \]

(where we have defined \(A + B \equiv G\).

The condition (350) instead is satisfied if (exploiting the fact that \(\kappa_n = 0\))

\[(352) \quad Ae^{i(\kappa_n-K)\hat{W}} + Be^{-i(\kappa_n+K)\hat{W}} - iCe^{i(\kappa_n+K)\hat{W}} - iDe^{-i(\kappa_n-K)\hat{W}} = 0 \Rightarrow \]
\[Ae^{-iK\hat{W}} + Be^{-iK\hat{W}} - iCe^{iK\hat{W}} - iDe^{iK\hat{W}} = 0 \Rightarrow \]
\[(A + B)e^{-iK\hat{W}} - i(C + D)e^{iK\hat{W}} = 0 \Rightarrow Ge^{-iK\hat{W}} - Ge^{iK\hat{W}} = 0 \Rightarrow \]
\[-G(e^{iK\hat{W}} - e^{-iK\hat{W}}) = 0 \Rightarrow -G2i \sin(K\hat{W}) = 0. \]
Since in this case ($\kappa_n = 0$) for $G = 0$ all the $\Phi$ functions (346) would become identically null and thus we have to consider $G \neq 0$, this equation can be satisfied only if $\sin(K\tilde{W}) = 0$. But, since $K = 4\pi/(3a)$ and $\tilde{W} = (N + 1)a/2$, we have that

\[
\sin(K\tilde{W}) = 0 \Rightarrow \sin \left( \frac{4\pi}{3a} (N + 1) \frac{a}{2} \right) = 0 \Rightarrow \sin \left( \frac{2\pi}{3} (N + 1) \right) = 0
\]

and this is true only if $N + 1$ is a multiple of 3, i.e. if $N + 1 = 3M$ (with $M$ integer) and thus $N = 3M - 1$. In this case we have that

\[
K\tilde{W} = \frac{2\pi}{3} (N + 1) = \frac{2\pi}{3} (3M) = 2\pi M \Rightarrow K = 2M \frac{\pi}{\tilde{W}} \Rightarrow 2M \frac{\pi}{\tilde{W}} - K = 0 (= \kappa_n)
\]

and the nanoribbon is metallic (as we will see). Being $\kappa_n = 0$, the $\Phi$ functions (346) are equal to

\[
\begin{align*}
\Phi^K_A(y) &= \frac{\gamma}{E}(\kappa_x A + \kappa_z B) = \frac{\gamma}{E}\kappa_x(A + B) = \frac{\gamma}{E}\kappa_x G, \\
\Phi^K_B(y) &= A + B = G, \\
\Phi^K_A(y) &= \frac{\gamma}{E}(\kappa_x C + \kappa_z D) = \frac{\gamma}{E}\kappa_x(C + D) = -\frac{\gamma}{E}\kappa_x iG, \\
\Phi^K_B(y) &= C + D = -iG.
\end{align*}
\]

**Case II**

The other possibility is to satisfy the conditions (347)-(348) in this way:

\[
\begin{cases}
A + B - iC - iD = 0 \\
- A + B - iC + iD = 0
\end{cases} \Rightarrow \begin{cases}
2B - 2iC = 0 \\
2A - 2iD = 0 \Rightarrow \begin{cases}
C = -iB \\
D = -iA
\end{cases}
\end{cases}
\]

(where in the first step we have summed and subtracted the two equations of the system), and to satisfy the conditions (349)-(350) enforcing

\[
\begin{cases}
A e^{i(\kappa_n - K)\tilde{W}} + B e^{-i(\kappa_n + K)\tilde{W}} - iC e^{i(\kappa_n + K)\tilde{W}} - iD e^{-i(\kappa_n - K)\tilde{W}} = 0, \\
- A e^{i(\kappa_n - K)\tilde{W}} + B e^{-i(\kappa_n + K)\tilde{W}} - iC e^{i(\kappa_n + K)\tilde{W}} + iD e^{-i(\kappa_n - K)\tilde{W}} = 0.
\end{cases}
\]

Using (356), we can write these equations in the following form:

\[
\begin{cases}
A e^{i(\kappa_n - K)\tilde{W}} + B e^{-i(\kappa_n + K)\tilde{W}} - B e^{i(\kappa_n + K)\tilde{W}} - A e^{-i(\kappa_n - K)\tilde{W}} = 0, \\
- A e^{i(\kappa_n - K)\tilde{W}} + B e^{-i(\kappa_n + K)\tilde{W}} - B e^{i(\kappa_n + K)\tilde{W}} + A e^{-i(\kappa_n - K)\tilde{W}} = 0.
\end{cases}
\]
If now we separate the real and imaginary part of $\kappa_n$ (i.e. we write $\kappa_n$ as $\kappa_{nr} + i\kappa_{ni}$) we have that

\begin{equation}
\begin{cases}
A e^{-\kappa_{ni} \tilde{w}} e^{i(\kappa_{nr} - K) \tilde{w}} + B e^{\kappa_{ni} \tilde{w}} e^{-i(\kappa_{nr} + K) \tilde{w}} \\
-B e^{-\kappa_{ni} \tilde{w}} e^{i(\kappa_{nr} + K) \tilde{w}} - A e^{\kappa_{ni} \tilde{w}} e^{-i(\kappa_{nr} - K) \tilde{w}} = 0,
\end{cases}
\end{equation}

\begin{equation}
\begin{cases}
-A e^{-\kappa_{ni} \tilde{w}} e^{i(\kappa_{nr} - K) \tilde{w}} + B e^{\kappa_{ni} \tilde{w}} e^{-i(\kappa_{nr} + K) \tilde{w}} \\
-B e^{-\kappa_{ni} \tilde{w}} e^{i(\kappa_{nr} + K) \tilde{w}} + A e^{\kappa_{ni} \tilde{w}} e^{-i(\kappa_{nr} - K) \tilde{w}} = 0,
\end{cases}
\end{equation}

\begin{equation}
\begin{cases}
[A e^{-\kappa_{ni} \tilde{w}} \cos((\kappa_{nr} - K) \tilde{w}) + B e^{\kappa_{ni} \tilde{w}} \cos((\kappa_{nr} + K) \tilde{w})] \\
-B e^{-\kappa_{ni} \tilde{w}} \sin((\kappa_{nr} - K) \tilde{w}) + B e^{\kappa_{ni} \tilde{w}} \sin((\kappa_{nr} + K) \tilde{w}) = 0,
\end{cases}
\end{equation}

\begin{equation}
\begin{cases}
-A e^{-\kappa_{ni} \tilde{w}} \cos((\kappa_{nr} - K) \tilde{w}) + B e^{\kappa_{ni} \tilde{w}} \cos((\kappa_{nr} + K) \tilde{w}) \\
-B e^{-\kappa_{ni} \tilde{w}} \sin((\kappa_{nr} - K) \tilde{w}) + A e^{\kappa_{ni} \tilde{w}} \sin((\kappa_{nr} + K) \tilde{w}) = 0,
\end{cases}
\end{equation}

\begin{equation}
\begin{cases}
-A e^{-\kappa_{ni} \tilde{w}} \cos((\kappa_{nr} - K) \tilde{w}) - B e^{\kappa_{ni} \tilde{w}} \cos((\kappa_{nr} + K) \tilde{w}) \\
-B e^{-\kappa_{ni} \tilde{w}} \sin((\kappa_{nr} - K) \tilde{w}) - A e^{\kappa_{ni} \tilde{w}} \sin((\kappa_{nr} + K) \tilde{w}) = 0,
\end{cases}
\end{equation}

If we sum and subtract the two equations, we obtain

\begin{equation}
\begin{cases}
4 \sinh(\kappa_{ni} \tilde{w}) B \cos((\kappa_{nr} + K) \tilde{w}) \\
-i4 \cosh(\kappa_{ni} \tilde{w}) B \sin((\kappa_{nr} + K) \tilde{w}) = 0,
\end{cases}
\end{equation}

\begin{equation}
\begin{cases}
4 \sinh(\kappa_{ni} \tilde{w}) A \cos((\kappa_{nr} - K) \tilde{w}) \\
+i4 \cosh(\kappa_{ni} \tilde{w}) A \sin((\kappa_{nr} - K) \tilde{w}) = 0,
\end{cases}
\end{equation}

\begin{equation}
\begin{cases}
B \left[ \sinh(\kappa_{ni} \tilde{w}) \cos((\kappa_{nr} + K) \tilde{w}) - i \cosh(\kappa_{ni} \tilde{w}) \sin((\kappa_{nr} + K) \tilde{w}) \right] = 0, \\
A \left[ \sinh(\kappa_{ni} \tilde{w}) \cos((\kappa_{nr} - K) \tilde{w}) - i \cosh(\kappa_{ni} \tilde{w}) \sin((\kappa_{nr} - K) \tilde{w}) \right] = 0.
\end{cases}
\end{equation}

Apart from the case $A = B = 0$, which (being also $C = -i B$ and $D = -i A$) gives identically null functions $\Phi$, both of these two equations are satisfied in 3 cases, that we will indicate with II-A, II-B and II-C.
Case II-A

The eqs. (360) are satisfied if

\begin{equation}
\begin{aligned}
\sinh(k_n W) \cos((k_n - K)W) - i \cosh(k_n W) \sin((k_n + K)W) &= 0, \\
\sinh(k_n W) \cos((k_n + K)W) - i \cosh(k_n W) \sin((k_n + K)W) &= 0.
\end{aligned}
\end{equation}

If we separately equate to zero the real and imaginary parts, we find

\begin{equation}
\begin{aligned}
\sinh(k_n W) \cos((k_n + K)W) &= 0, \\
\cosh(k_n W) \sin((k_n + K)W) &= 0, \\
\sinh(k_n W) \cos((k_n - K)W) &= 0, \\
\cosh(k_n W) \sin((k_n - K)W) &= 0.
\end{aligned}
\end{equation}

Since the hyperbolic cosine is never equal to zero, these become

\begin{equation}
\begin{aligned}
\sinh(k_n W) \cos((k_n + K)W) &= 0, \\
\sin((k_n + K)W) &= 0, \\
\sinh(k_n W) \cos((k_n - K)W) &= 0, \\
\sin((k_n - K)W) &= 0.
\end{aligned}
\end{equation}

However, when the sine of an angle is equal to zero, the cosine of that angle is certainly different from zero; therefore the previous equations become

\begin{equation}
\begin{aligned}
\sinh(k_n W) &= 0, \\
\sin((k_n + K)W) &= 0, \\
\sin((k_n - K)W) &= 0.
\end{aligned}
\end{equation}

Since the hyperbolic sine is null only when its argument is null, we conclude that in this case:

\begin{equation}
\begin{aligned}
k_n &= 0, \\
\sin((k_n + K)W) &= 0, \\
\sin((k_n - K)W) &= 0.
\end{aligned}
\end{equation}

From the condition on \( \sin((k_n + K)W) \) it follows that

\begin{equation}
\begin{aligned}
\sin((k_n + K)W) &= 0 \Rightarrow (k_n + K)W = n\pi \Rightarrow \\
k_n + K &= n\frac{\pi}{W} \Rightarrow k_n = n\frac{\pi}{W} - K
\end{aligned}
\end{equation}
(with \( n \) integer). Then from the condition on \( \sin((\kappa_n - K)\tilde{W}) \), substituting what we have just found and then remembering that \( K = 4\pi/(3a) \) and that \( \tilde{W} = (N + 1)a/2 \), we obtain that

\[
\sin((\kappa_n - K)\tilde{W}) = 0 \Rightarrow \sin\left(\left(n\frac{\pi}{\tilde{W}} - K - K\right)\tilde{W}\right) = \sin\left(n\pi - 2K\tilde{W}\right) = \\
\sin\left(n\pi - 2\frac{4\pi}{3a}(N + 1)\frac{a}{2}\right) = \sin\left(n\pi - 4\frac{N + 1}{3}\right) = 0 \Rightarrow \\
\frac{n - 4}{3}\frac{N + 1}{3} \text{ is an integer.}
\]

This is true only if \( N + 1 \) is a multiple of 3, \textit{i.e.} if \( N + 1 = 3M \) (with \( M \) integer), \textit{i.e.} if \( N = 3M - 1 \); this means that the nanoribbon is metallic (as we will see). In this case the \( \Phi \) functions (346) are equal to

\[
\begin{align*}
\Phi_A^K(y) &= \frac{\gamma}{E}(\kappa_x - i\kappa_n)Ae^{i\kappa_n y} + (\kappa_x + i\kappa_n)Be^{-i\kappa_n y}, \\
\Phi_B^K(y) &= Ae^{i\kappa_n y} + Be^{-i\kappa_n y}, \\
\Phi_A^{K'}(y) &= \frac{\gamma}{E}(\kappa_x + i\kappa_n)Ce^{i\kappa_n y} + (\kappa_x - i\kappa_n)De^{-i\kappa_n y}, \\
\Phi_B^{K'}(y) &= Ce^{i\kappa_n y} + De^{-i\kappa_n y} = -i(\kappa_x Be^{i\kappa_n y} + Ae^{-i\kappa_n y}),
\end{align*}
\]

that can be written as a superposition of the modes

\[
\begin{align*}
\Phi_A^K(y) &= \frac{\gamma}{E}(\kappa_x + i\tilde{\kappa}_n)Ae^{-i\tilde{\kappa}_n y}, \\
\Phi_B^K(y) &= Ae^{-i\tilde{\kappa}_n y}, \\
\Phi_A^{K'}(y) &= \frac{\gamma}{E}(\kappa_x + i\tilde{\kappa}_n)iAe^{i\tilde{\kappa}_n y}, \\
\Phi_B^{K'}(y) &= -iAe^{i\tilde{\kappa}_n y},
\end{align*}
\]

\[
\begin{align*}
\Phi_A^K(y) &= \frac{\gamma}{E}(\kappa_x + i\kappa_n)Be^{-i\kappa_n y}, \\
\Phi_B^K(y) &= Be^{-i\kappa_n y}, \\
\Phi_A^{K'}(y) &= \frac{\gamma}{E}(\kappa_x + i\kappa_n)iBe^{i\kappa_n y}, \\
\Phi_B^{K'}(y) &= -iBe^{i\kappa_n y},
\end{align*}
\]

with \( \kappa_n = (n\pi/\tilde{W}) - K \) and \( \tilde{\kappa}_n = -\kappa_n \). We notice that, since in this case \( N + 1 = 3M \), we have that

\[
K\tilde{W} = \frac{4\pi}{3a}(N + 1)\frac{a}{2} = \frac{2\pi}{3}(N + 1) = \frac{2\pi}{3}(3M) = 2\pi M \Rightarrow K = 2M\frac{\pi}{\tilde{W}}
\]

and therefore \( \tilde{\kappa}_n \) can be written as

\[
\tilde{\kappa}_n = -\kappa_n = -\left(n\frac{\pi}{\tilde{W}} - K\right) = \left(-n\frac{\pi}{\tilde{W}} + 2K\right) - K = \\
\left(-n\frac{\pi}{\tilde{W}} + 4M\frac{\pi}{\tilde{W}}\right) - K = (4M - n)\frac{\pi}{\tilde{W}} - K = \tilde{n}\frac{\pi}{\tilde{W}} - K,
\]

with \( \tilde{n} = 4M - n \) integer. Clearly, if \( \kappa_n \) satisfies \( E = \pm\gamma\sqrt{\kappa_n^2 + \kappa_n^2} \), also \( \tilde{\kappa}_n = -\kappa_n \) satisfies \( E = \pm\gamma\sqrt{\kappa_n^2 + \kappa_n^2} \).
It can be observed that in the particular case in which $\kappa_n = 0$ we find again Case I.

**Case II-B**

Equations (360) are satisfied also if

$$\begin{align*}
\sinh(\kappa_n \tilde{W}) \cos((\kappa_{nr} + K) \tilde{W}) - i \cosh(\kappa_n \tilde{W}) \sin((\kappa_{nr} + K) \tilde{W}) &= 0, \\
A &= 0.
\end{align*}$$

If we separately equate to zero the real and imaginary parts of the first equation, we find

$$\begin{align*}
\sinh(\kappa_n \tilde{W}) \cos((\kappa_{nr} + K) \tilde{W}) &= 0, \\
\cosh(\kappa_n \tilde{W}) \sin((\kappa_{nr} + K) \tilde{W}) &= 0, \\
A &= 0.
\end{align*}$$

Since the hyperbolic cosine is never equal to zero, these become

$$\begin{align*}
\sinh(\kappa_n \tilde{W}) \cos((\kappa_{nr} + K) \tilde{W}) &= 0, \\
\sin((\kappa_{nr} + K) \tilde{W}) &= 0, \\
A &= 0.
\end{align*}$$

But when the sine of an angle is equal to zero, surely the cosine of that angle is different from zero; therefore the previous equations become

$$\begin{align*}
\sinh(\kappa_n \tilde{W}) &= 0, \\
\sin((\kappa_{nr} + K) \tilde{W}) &= 0, \\
A &= 0.
\end{align*}$$

Since the hyperbolic sine is null only when its argument is null, we conclude that in this case:

$$\begin{align*}
\kappa_n &= 0, \\
\sin((\kappa_{nr} + K) \tilde{W}) &= 0, \\
A &= 0,
\end{align*}$$

$$\Rightarrow \begin{align*}
\kappa_n &\text{ real,} \\
\sin((\kappa_n + K) \tilde{W}) &= 0, \\
A &= 0.
\end{align*}$$

Due to the fact that $A = 0$, also $D = -iA = 0$ (while $C = -iB$).

Instead the consequence of the condition on $\sin((\kappa_n + K) \tilde{W})$ is

$$\begin{align*}
\sin((\kappa_n + K) \tilde{W}) &= 0 \Rightarrow (\kappa_n + K) \tilde{W} = n\pi \Rightarrow \\
\kappa_n + K &= n \frac{\pi}{\tilde{W}} \Rightarrow \kappa_n &= n \frac{\pi}{\tilde{W}} - K.
\end{align*}$$
In this case the \( \Phi \) functions (346) are equal to

\[
\begin{align*}
\Phi^K_A(y) &= \frac{\gamma}{E} ((\kappa_x - i\kappa_n)Ae^{i\kappa_ny} + (\kappa_x + i\kappa_n)Be^{-i\kappa_ny}) = \\
&= \frac{\gamma}{E}(\kappa_x + i\kappa_n)Be^{-i\kappa_ny}, \\
\Phi^K_B(y) &= Ae^{i\kappa_ny} + Be^{-i\kappa_ny} = Be^{-i\kappa_ny}, \\
\Phi^K_A'(y) &= \frac{\gamma}{E} ((\kappa_x + i\kappa_n)Ce^{i\kappa_ny} + (\kappa_x - i\kappa_n)De^{-i\kappa_ny}) = \\
&= -\frac{\gamma}{E}(\kappa_x + i\kappa_n)iBe^{i\kappa_ny}, \\
\Phi^K_B'(y) &= Ce^{i\kappa_ny} + De^{-i\kappa_ny} = -iBe^{i\kappa_ny}.
\end{align*}
\]

Case II-C

Finally, eqs. (360) are satisfied also if

\[
\begin{align*}
B &= 0, \\
\sinh(\kappa_n\tilde{W}) \cos((\kappa_n - K)\tilde{W}) - i\cosh(\kappa_n\tilde{W}) \sin((\kappa_n - K)\tilde{W}) &= 0.
\end{align*}
\]

With calculations analogous to Case II-B, we conclude [93] that in this case:

\[
\begin{align*}
B &= 0, \\
\kappa_n &\text{ real}, \\
\sin((\kappa_n - K)\tilde{W}) &= 0.
\end{align*}
\]

Due to the fact that \( B = 0 \), also \( C = -iB = 0 \) (while \( D = -iA \)).

Instead the consequence of the condition on \( \sin((\kappa_n - K)\tilde{W}) \) is

\[
\begin{align*}
\sin((\kappa_n - K)\tilde{W}) = 0 &\Rightarrow (\kappa_n - K)\tilde{W} = n\pi \Rightarrow \\
\kappa_n - K &= n\frac{\pi}{\tilde{W}} \Rightarrow \kappa_n = n\frac{\pi}{\tilde{W}} + K.
\end{align*}
\]

In this case the \( \Phi \) functions (346) are equal to

\[
\begin{align*}
\Phi^K_A(y) &= \frac{\gamma}{E} ((\kappa_x - i\kappa_n)Ae^{i\kappa_ny} + (\kappa_x + i\kappa_n)Be^{-i\kappa_ny}) = \\
&= \frac{\gamma}{E}(\kappa_x - i\kappa_n)Ae^{i\kappa_ny} = \frac{\gamma}{E}(\kappa_x + i\kappa_n)Be^{-i\kappa_ny}, \\
\Phi^K_B(y) &= Ae^{i\kappa_ny} + Be^{-i\kappa_ny} = Ae^{i\kappa_ny} = Ae^{-i\kappa_ny}, \\
\Phi^K_A'(y) &= \frac{\gamma}{E} ((\kappa_x + i\kappa_n)Ce^{i\kappa_ny} + (\kappa_x - i\kappa_n)De^{-i\kappa_ny}) = \\
&= -\frac{\gamma}{E}(\kappa_x + i\kappa_n)iCe^{-i\kappa_ny} = \frac{\gamma}{E}(\kappa_x + i\kappa_n)iCe^{i\kappa_ny}, \\
\Phi^K_B'(y) &= Ce^{i\kappa_ny} + De^{-i\kappa_ny} = -iAe^{-i\kappa_ny} = -iAe^{i\kappa_ny}.
\end{align*}
\]
with

\( \tilde{\kappa}_n = -\kappa_n = -\left( n \frac{\pi}{W} + K \right) = -n \frac{\pi}{W} - K = \tilde{n} \frac{\pi}{W} - K \)

(383)

(where \( \tilde{n} = -n \) is an integer). Clearly, if \( \kappa_n \) satisfies \( E = \pm \gamma \sqrt{\kappa_n^2 + \kappa_n^2} \), also \( \tilde{\kappa}_n = -\kappa_n \) satisfies \( E = \pm \gamma \sqrt{\kappa_n^2 + \kappa_n^2} \).

In conclusion, in all the cases we have that

\[
\begin{aligned}
\Phi^K_A(y) &= \frac{\gamma}{E} (\kappa_x + i\kappa_n) A e^{-i\kappa_n y}, \\
\Phi^K_B(y) &= A e^{-i\kappa_n y}, \\
\Phi^{K'}_A(y) &= -\frac{\gamma}{E} (\kappa_x + i\kappa_n) i A e^{i\kappa_n y}, \\
\Phi^{K'}_B(y) &= -iA e^{i\kappa_n y},
\end{aligned}
\]

(384)

with \( A \) being a proper normalization constant, \( \kappa_n = (n \pi/W) - K \) and \( E = \pm \gamma \sqrt{\kappa_n^2 + \kappa_n^2} \).

Consequently, for eq. (335) we have that

\[
\begin{aligned}
\psi_A(r) &= e^{iK \cdot r} F^K_A(r) - i e^{iK' \cdot r} F^{K'}_A(r) = \\
e^{-iK y} \Phi^K_A(y) e^{i\kappa_n x} - i e^{iK y} \Phi^{K'}_A(y) e^{i\kappa_n x} = \\
\left( e^{-iK y} \Phi^K_A(y) - i e^{iK y} \Phi^{K'}_A(y) \right) e^{i\kappa_n x} = \\
\frac{\gamma}{E} \left( e^{-iK y} (\kappa_x + i\kappa_n) A e^{-i\kappa_n y} + i e^{iK y} (\kappa_x + i\kappa_n) i A e^{i\kappa_n y} \right) e^{i\kappa_n x} = \\
-\frac{\gamma}{E} (\kappa_x + i\kappa_n) A \left( e^{i(\kappa_n + K) y} - e^{-i(\kappa_n + K) y} \right) e^{i\kappa_n x} = \\
-\frac{\gamma}{E} (\kappa_x + i\kappa_n) A 2i \sin \left( (\kappa_n + K) y \right) e^{i\kappa_n x}
\end{aligned}
\]

and that

\[
\begin{aligned}
\psi_B(r) &= i e^{iK \cdot r} F^K_B(r) + e^{iK' \cdot r} F^{K'}_B(r) = \\
i e^{-iK y} \Phi^K_B(y) e^{i\kappa_n x} + e^{iK y} \Phi^{K'}_B(y) e^{i\kappa_n x} = \\
\left( i e^{-iK y} \Phi^K_B(y) + e^{iK y} \Phi^{K'}_B(y) \right) e^{i\kappa_n x} = \\
\left( i e^{-iK y} A e^{-i\kappa_n y} - e^{iK y} A e^{i\kappa_n y} \right) e^{i\kappa_n x} = \\
- iA \left( e^{i(\kappa_n + K) y} - e^{-i(\kappa_n + K) y} \right) e^{i\kappa_n x} = \\
- iA 2i \sin \left( (\kappa_n + K) y \right) e^{i\kappa_n x} = \\
2A \sin \left( (\kappa_n + K) y \right) e^{i\kappa_n x}.
\end{aligned}
\]

We observe that in large ribbons the lowest-energy modes will have values of \( \kappa_n \) much smaller than \( K \) and thus their wave functions will be characterized by a transverse
wave vector approximately equal to \( K \) and by a transverse wave length about equal to 
\[ 2\pi/K = 2\pi (3a/(4\pi)) = 3a/2, \text{ i.e. of the order of the lattice constant.} \]

No edge state exists in armchair nanoribbons.

Using the relations \( K = 4\pi/(3a) \) and \( \tilde{W} = (N+1)a/2 \), we have that

\[ \kappa_n = n\pi \frac{W}{W} - K = \frac{n2\pi}{(N+1)a} - \frac{4\pi}{3a} = \frac{2\pi(3a - 2(N + 1))}{3(N+1)a}. \] (387)

Since \( E_n = \pm\gamma\sqrt{\kappa_x^2 + \kappa_n^2} \), we have a double band degeneracy if, for any integer \( n \), another integer \( n' \) exists such that \( \kappa_{n'} = -\kappa_n \) and thus \( E_{n'} = E_n \). This happens if

\[ 3n' - 2(N + 1) = -(3n - 2(N + 1)) \Rightarrow 3n' = -3n + 4(N + 1) \Rightarrow n' = -n + 4(N + 1)/3, \] (388)

with \( n \) and \( n' \) integer, which means that \( N + 1 \) has to be a multiple of 3, \text{i.e.} \( N + 1 = 3M \) with \( M \) integer, or equivalently \( N = 3M - 1 \) (so that \( n' = -n + 4M \)).

We also observe that among the allowed \( \kappa_n \)'s (given by eq. (387)) we have \( \kappa_n = 0 \) if an integer \( n \) exists, such that

\[ 3n - 2(N + 1) = 0 \Rightarrow n = \frac{2(N + 1)}{3}, \] (389)

which again means that \( N + 1 \) has to be a multiple of 3, \text{i.e.} \( N + 1 = 3M \) with \( M \) integer, or equivalently \( N = 3M - 1 \) (so that \( n = 2M \)).

Therefore an armchair nanoribbon has a double band degeneracy and has \( \kappa_n = 0 \) among the allowed values of \( \kappa_n \) only if it has a number of dimer lines \( N = 3M - 1 \) (with \( M \) an integer). In this case for \( \kappa_n = 0 \) we have \( E = \pm\gamma|\kappa_x| \) which vanishes for \( \kappa_x \to 0 \) and thus the nanoribbon is metallic. Instead for \( N \neq 3M - 1 \) the armchair nanoribbon is not metallic and has non-degenerate bands.

This conclusion is coherent with the fact that the dispersion relations of an armchair nanoribbon can be obtained from those of graphene enforcing the Dirichlet boundary conditions at \( y = 0 \) and \( y = \tilde{W} \); this means that there has to be an integer number of transverse half-wavelengths \( \lambda_y/2 \) inside \( \tilde{W} \); thus it must happen that

\[ \tilde{W} = n\frac{\lambda_y}{2} \Rightarrow k_y = \frac{2\pi}{\lambda_y} = n\pi/\tilde{W}. \] (390)

(where \( k_y \) is the transverse component of the total wave vector, measured from the origin of the reciprocal space). Therefore the bands of the ribbon can be obtained by cross-sectioning those of graphene along the parallel lines \( k_y = n\pi/\tilde{W} \), and then folding them into the Brillouin zone \((-\pi/(\sqrt{3}a), \pi/(\sqrt{3}a))\) of the armchair nanoribbon (the unit cell of which has a length \( 3a_{C-C} = \sqrt{3}a \)). There are bands of the nanoribbon with a zero gap, and thus the nanoribbon is metallic, only if some of the lines with \( k_y = n\pi/\tilde{W} \) pass through a Dirac point of graphene (where the graphene dispersion relations have a zero gap). But, since

\[ \tilde{W} = (N + 1)\frac{a}{2} \Rightarrow a = \frac{2\tilde{W}}{N + 1} \Rightarrow K = \frac{4\pi}{3a} = \frac{4\pi}{3} \frac{N + 1}{2\tilde{W}} = \frac{2}{3} \frac{N + 1}{\tilde{W}}, \] (391)
Fig. 14. – Bands of an armchair nanoribbon with $N = 98$ dimer lines (a) and with $N = 99$ dimer lines (b), computed both with a tight-binding method not including the reduction of the bond lengths at the edges (thick dotted lines) and with the $\mathbf{k} \cdot \mathbf{p}$ method (thin solid lines).

This is possible only if $N + 1$ is a multiple of 3, i.e. $N + 1 = 3M$ with $M$ integer, or equivalently $N = 3M - 1$.

A more exact tight-binding analysis (taking into consideration the reduction of the carbon-carbon bond lengths parallel to dimer lines at the edges with respect to the bond lengths in the core of the ribbon) leads to the appearance of a small gap also in this subset of armchair nanoribbons, that have to be more correctly considered as quasi-metallic ones [109-111].

In fig. 14 we show the bands of an armchair nanoribbon with $N = 98$ dimer lines (metallic) and of an armchair nanoribbon with $N = 99$ dimer lines (semiconductor), that we have computed both with a tight-binding method not including the reduction of the bond lengths at the edges (thick dotted lines) and with the $\mathbf{k} \cdot \mathbf{p}$ (Dirac equation) method (thin solid lines). As we see, for low energy values and for not too narrow ribbons they are nearly coincident.

All previous considerations are valid both for real values of $\kappa_x$ (propagating modes), and for purely imaginary values of $\kappa_x$ (evanescent modes).

As an application of the relations (229) and (230) to the case of an armchair nanoribbon in the absence of an external potential, we can observe, using the (384) (with $\kappa_n$ real and $\kappa_x$ real or purely imaginary), that

$$ J_x = v_F \frac{\gamma}{E} \left( (\kappa_x^* - i\kappa_n) A^* e^{i\kappa_n y} e^{-i\kappa_x^* z} A e^{-i\kappa_n y} e^{i\kappa_x x} ight. $$

$$ + A^* e^{i\kappa_n y} e^{-i\kappa_x^* z} (\kappa_x + i\kappa_n) A e^{-i\kappa_n y} e^{i\kappa_x x} $$

$$ + (\kappa_x^* - i\kappa_n) i A^* e^{-i\kappa_n y} e^{-i\kappa_x^* z} (-i) A e^{i\kappa_n y} e^{i\kappa_x x} $$

$$ + i A^* e^{-i\kappa_n y} e^{-i\kappa_x^* z} (\kappa_x + i\kappa_n) (-i) A e^{i\kappa_n y} e^{i\kappa_x x} \right) =

$$ v_F \frac{\gamma}{E} |A|^2 e^{i(\kappa_x^* - \kappa_n) z} (\kappa_x^* - i\kappa_n + \kappa_x + i\kappa_n + \kappa_x^* - i\kappa_n + \kappa_x + i\kappa_n) =

$$ 2v_F \frac{\gamma}{E} |A|^2 e^{i(\kappa_x^* - \kappa_n) z} (\kappa_x + \kappa_n^*), $$
which if \( \kappa_x \) is real (and thus \( \kappa_x^* = \kappa_x \)) is equal to (remembering that \( v_F = \gamma/\hbar \))

\[
J_x = 4v_F \frac{\gamma}{E} |A|^2 \kappa_x = 4|A|^2 \frac{\gamma^2}{\hbar E} \kappa_x,
\]

while if \( \kappa_x \) is purely imaginary (and thus \( \kappa_x^* = -\kappa_x \)) is null.

Note that (using (216) and (384)) if \( \kappa_x \) is real the probability density is equal to

\[
P = |F_A^K(r)|^2 + |F_A^{K'}(r)|^2 + |F_B^K(r)|^2 + |F_B^{K'}(r)|^2 = \left( \frac{\gamma}{E} \right)^2 |\kappa_x + i\kappa_n|^2 |A|^2 + |A| + \left( \frac{\gamma}{E} \right)^2 |\kappa_x + i\kappa_n|^2 |A|^2 + |A| = 2|A|^2 \left( 1 + \frac{\gamma^2(\kappa_x^2 + \kappa_n^2)}{E^2} \right) = 2|A|^2 \left( 1 + \frac{\kappa_x}{\hbar \sqrt{\kappa_x^2 + \kappa_n^2}} \right)^2 = 4|A|^2.
\]

Moreover, since in this case the energy dispersion relations are \( E = \pm \gamma \sqrt{\kappa_x^2 + \kappa_n^2} \), the mean velocity of the electrons is

\[
v_x = \frac{1}{\hbar} \frac{\partial E}{\partial k_x} = \frac{1}{\hbar} \left( \frac{\gamma}{\hbar} \frac{\kappa_x}{\sqrt{\kappa_x^2 + \kappa_n^2}} \right) = \frac{\gamma}{\hbar} \frac{\kappa_x}{\sqrt{\kappa_x^2 + \kappa_n^2}} = \frac{\gamma}{\hbar} \frac{\kappa_x}{\sqrt{\kappa_x^2 + \kappa_n^2}} = \frac{\gamma}{\hbar} \kappa_x.
\]

Therefore if \( \kappa_x \) is real we have that \( J_x = P v_x \), as expected.

As to the transversal part of the probability current density, we have that

\[
J_y = -iv_F \left( F_A^{K+} F_B^{K'} - F_B^{K+} F_A^{K'} - F_A^{K'} F_B^{K'} + F_B^{K'} F_A^{K'} \right) = -iv_F \frac{\gamma}{E} \left( \kappa_x - i\kappa_n \right) A^* e^{ik_n y} e^{-ik_n x} A e^{-ik_n y} e^{ik_n x} - A^* e^{ik_n y} e^{-ik_n x} \left( \kappa_x + i\kappa_n \right) A e^{-ik_n y} e^{ik_n x} - \left( \kappa_x - i\kappa_n \right) iA^* e^{-ik_n y} e^{ik_n x} \left( -i \right) e^{ik_n y} e^{ik_n x} + iA^* e^{-ik_n y} e^{-ik_n x} \left( \kappa_x + i\kappa_n \right) \left( -i \right) e^{ik_n y} e^{ik_n x} = -iv_F \frac{\gamma}{E} \left( |A|^2 \delta^{(\kappa_x - \kappa_n)^2} (\kappa_x - i\kappa_n - \kappa_x - i\kappa_n + \kappa_x + i\kappa_n) = 0, \right.
\]

as expected (at least at the edges) in a transversally confined structure.

7. Conclusion

The \( \mathbf{k} \cdot \mathbf{p} \) method and the related envelope function method are widely used to study the physical properties of materials within a continuum approach, without having to resort to an atomic analysis, which requires (in the case of large structures) a prohibitive computational effort. These methods have been developed in many and sometimes quite different ways by several authors and have been successfully applied to a multitude of different problems. This explains the great variety and inhomogeneity of the related
literature. In this review, we have briefly described the basics of these methodologies, dwelling upon the treatments that we have considered more useful for an easy comprehension. For a detailed explanation of the different approaches, the interested reader can resort to the many papers and books on the topic, some of which are listed in the references. In particular, we have focused on the application of the $k \cdot p$ method to graphene and graphene-related materials, where it results in a description of the electronic properties in terms of the Dirac equation. We have compared the different formulations adopted in the literature and we have shown how this continuum approach allows to quickly obtain the most relevant electrical properties of graphene, carbon nanotubes and graphene nanoribbons.

∗ ∗ ∗

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