A Green function approach to graphene–superconductor junctions with well-defined edges

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Abstract
This work presents a novel approach to describing spectral properties of graphene layers with well-defined edges. We microscopically analyze the boundary problem for the continuous Bogoliubov–de Gennes–Dirac equations and derive the Green functions for normal and superconducting graphene layers. Importing the idea used in tight-binding models of a microscopic hopping that couples different regions, we are able to set up and solve an algebraic Dyson equation describing a graphene–superconductor junction. For this coupled system we analytically derive the Green functions and use them to calculate the local density of states and the spatial variation of the induced pairing correlations in the normal region. Signatures of specular Andreev reflections are identified.

1. Introduction
Ideally, an interface between a graphene layer and a superconductor provides a unique opportunity to study the interplay between a relativistic-like band-structure and pairing interactions between electrons and holes. Advances in the techniques of isolation and manipulation of graphene layers together with the possibility to deposit nanoscale superconducting electrodes on top of them is bringing this idealized situation closer [1].

Several theoretical studies of the electronic and transport properties of graphene–superconductor junctions have been reported in recent years. As in the case of normal metals, a key ingredient for understanding these properties is the concept of Andreev reflection [2] by means of which an incident electron on the interface is reflected as a hole while a Cooper pair is created on the superconductor. In graphene, however, Andreev reflections may couple electrons in the conduction band with holes in the valence band, which leads to a specular reflection, as opposed to the usual retro Andreev reflection [3]. Very recently we have shown that interface bound states (IBSs) appear for energies within the superconducting gap due to the interplay of Andreev and normal reflection in graphene–superconductor junctions [4].

Within these studies various different methods and approximations have been applied. In particular, the Bogoliubov–de Gennes–Dirac equations (BdGD) have been solved under the approximation of neglecting intervalley scattering and applied to the calculation of the differential conductance and spectral properties in graphene–superconductor (GS) junctions [3, 5]. Other works have extended this method to situations including an insulator (GIS junctions [6]) or to the study of the Josephson effect in SGS junctions [7]. In spite of their interest these works are limited in the sense that they cannot provide an answer on the effect of the atomic scale properties of the interfaces or what would happen in the presence of well-defined edges in the graphene layers. This is an important issue because it is well known that the electronic spectrum of a graphene nanoribbon is strongly dependent on the direction in which its edges are defined. Armchair and zigzag cases have been the most studied but one can also envisage and study edges along arbitrary directions. From the point of view of experiments it is also becoming possible to study transport properties in graphene nanoribbons with well-defined edges at the atomic scale [8].

These type of studies typically require the use of microscopic tight-binding (TB) models and some of them have been conducted in the case of GS junctions [9, 10].
Although such methods are usually implemented numerically, much progress has been made in the derivation of analytical expressions within TB models combined with Green function techniques [9]. However, these expressions are typically more complex than those which would be obtained within the BdGD model.

The aim of the present work is to go one step beyond the existing works\(^3\) and develop a method based on the BdGD model which could deal with the presence of well-defined edges or interfaces at the atomic scale. Our method starts from the determination of the Green functions for the BdGD equations in the case of isolated graphene or superconducting layers. In order to fix the boundary conditions for these isolated regions it is, in general, necessary to mix solutions corresponding to different valleys. For the purpose of illustrating the method we would consider separately the cases of armchair and zigzag edges. For obtaining the properties of a coupled graphene–graphene or graphene–superconductor region we define a short-range coupling potential which mimics the usual hopping term in the TB models and then solves the corresponding Dyson equation analytically for several junctions. As a test we show how known results are recovered in different limits. We further use the method to study the spatial properties of the local density of states (LDOS) and the induced pairing correlations on a graphene layer. We show that, on top of an atomic scale modulation, these spatial correlations exhibit signatures of specular Andreev reflections. They also display a long-range decay due to the presence of the above mentioned IBS.

This work is organized as follows: in section 2 we implement the Green functions for graphene nanoribbons with armchair or zigzag edges. In section 3 we explain how we model the microscopic link between layers and solve the corresponding Dyson equation. Finally, section 4 covers the coupling between a normal sheet of graphene and a superconducting one. Analytical expressions for the Green functions of the coupled system are given. Profiles for the LDOS and the spatial behavior of the induced superconducting pairing correlations are presented as well. This paper is closed by some concluding remarks. Furthermore, an appendix has been added to show details of the calculations.

2. Green’s function approach for graphene layers with edges

Graphene is a single layer of carbon atoms arranged in a honeycomb structure. Its hexagonal lattice is constructed as the superposition of two triangular lattices \(A\) and \(B\). A nearest-neighbor TB model for graphene can be, in the continuum limit, represented by a linearized Hamiltonian with six Dirac points at each corner of the hexagonal Brillouin zone. Only two of these points are inequivalent which, for the orientation of the layer shown in the left panel of figure 1, can be assumed to lie in the \(x\)-axis and denoted as \(K_\pm = (\pm K, 0)\). Single-particle excitations around these points are represented by a Dirac Hamiltonian like \(H_B = h\sigma_z \cdot \mathbf{k} - E_F \delta_0 = h \{ \pm \delta_{x}, q \delta_{y} \} - E_F \delta_0\), where \(\sigma_{x,y}\) are the Pauli matrices (with \(\sigma_0\) the \(2 \times 2\) identity matrix) acting on graphene’s lattice subspace, \(E_F\) is the Fermi energy and the velocity \(v = \sqrt{M_e a/2\hbar} \approx 10^6\) m s\(^{-1}\) is proportional to the lattice constant \(a = 0.246\) nm and to the nearest-neighbor hopping energy \(t_e \approx 3\) eV on the honeycomb lattice of carbon atoms. With this choice \(K = 4\pi/3a\). The degree of freedom due to the A–B lattices defines a pseudospin \(\sigma_{\pm} = (\pm \delta_x, \delta_y)\) which points in the direction of motion of the particle and the pseudospin operator \(\sigma_{\pm} = (\pm \delta_x, q)\) is used to define the Hamiltonian on each valley. Finally, \(\mathbf{k}\) is the wavevector measured from each Dirac point \(K_\pm\).

Wavenumbers around each Dirac point satisfy the equation \(H_B \Phi_\pm(x, y) = E \Phi_\pm(x, y)\), with \(E > 0\) being the excitation energy of an electron-like quasiparticle. In the present work we consider clean samples which are infinite along the \(y\)-direction but may have edges or interfaces on the \(x\)-direction (see figure 1). Thus, momentum along the \(y\)-axis (\(\mathbf{q}\)) is conserved and the wavenumber can be written as \(\Phi_\pm(x, y) = e^{i\mathbf{q} \cdot \mathbf{R}} \Phi_\pm(x)\). With the replacement \(\mathbf{k}(q) = (-i\mathbf{q}, q)\) in Dirac’s equation, linear independent solutions for each valley are

\[
\Phi_+(x) = c_1 e^{ikx} \varphi_1 + c_2 e^{-ikx} \varphi_2
\]

\[
\Phi_-(x) = c_2 e^{ikx} \varphi_2 + c_1 e^{-ikx} \varphi_1
\]

with

\[
\varphi_1 = \begin{pmatrix} e^{-i\mathbf{q} /2} \\ e^{i\mathbf{q} /2} \end{pmatrix}, \quad \varphi_2 = \begin{pmatrix} e^{i\mathbf{q} /2} \\ -e^{-i\mathbf{q} /2} \end{pmatrix}
\]

\(c_1^\pm\) are determined by boundary conditions for the wavenumbers \(\Phi_\pm(x)\).

A complete description of the low energy electron excitations on a graphene layer is reached by superposing solutions on both valleys. Each solution \(\Phi_{\pm}\) is modulated by

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\(^3\) A notably exception is the work by Tkachov [11], where the Green functions for normal graphene layers with zigzag edges have been derived.
a rapidly varying plane wave from each valley $e^{iK_x x}$ [12] thus giving
\[
\Phi(x, y) = e^{i\eta y} \psi(x) = e^{i\eta y}[e^{iK_x x} \phi_+ (x) + e^{-iK_x x} \phi_- (x)].
\] (4)

This wavefunction is the solution of Schrödinger’s equation for a Hamiltonian that combines both valleys. However, it is useful in order to calculate the full Green function of the system, including both valley and pseudospin degrees of freedom. The four-dimensional spinor obeys the equation
\[
\mathit{H} \psi(x) = E \psi(x),
\]
where
\[
\mathit{H} = \begin{pmatrix} \mathit{H}_+ & 0 \\ 0 & \mathit{H}_- \end{pmatrix}
\] (5)
is the Dirac Hamiltonian in sublattice and valley spaces. We are using the notation $\cdot \cdot$ for $4 \times 4$ matrices and $\cdot \cdot$ for $2 \times 2$ matrices. The Green function associated to $\psi(x, y) = e^{i\eta y} \psi(x)$ is $\tilde{G}_\phi(x, x', y) = \int \tilde{G}_\phi(x, x', y; q) e^{i q y} dq$, where $\tilde{G}_\phi(x, x'; q)$ satisfies the $4 \times 4$ matrix equation
\[
[H(q) - E \mathit{I}]\tilde{G}_\phi(x, x'; q) = \delta(x - x') \mathit{I},
\] (6)
with $\mathit{I}$ the four-dimensional identity matrix. Hereafter we implicitly assume that $E$ stands for $E + i\eta$ and that the limit $\eta \to 0$ has been taken to obtain the retarded component of the Green function. From the elements of the full Green function $\tilde{G}_\phi$ we can define a valley superson Green function $\tilde{G}_\phi$, associated with the wavefunction of (4), as
\[
\tilde{G}_\phi(x, x', y, y') = \int dq' \ e^{i\eta y'} \psi_
u \left( \sum_{\mu,\nu} \ e^{i(K_x x - K_y y')} \tilde{G}_\phi^{\mu\nu}(x, x'; q) \right.
\]
\[
\times \left. \sum_{\mu,\nu} \ e^{iK_x x'} \tilde{G}_\phi^{\mu\nu}(x, x'; q) \right).
\] (7)

Besides allowing valley mixing, this Green function includes the phase factors $\exp i(K_{\mu} \cdot r - K_{\nu} \cdot r')$ which are crucial to describe the presence of well-defined edges or interfaces at the atomic scale. This valley superson Green function is derived in the next sections for armchair and zigzag edges.

The method that we implement to calculate the Green function is based in using the asymptotic solutions of the differential equation (6). Basically, we extend the method used in [14] to the relativistic Bogoliubov–de Gennes equations. Thus, the full Green function in pseudospin and valley spaces can be written as
\[
\tilde{G}_\phi(x, x'; q) = \begin{cases} 
\sum_{\mu,\nu = +1, -1} A_{\mu\nu} \psi^\mu_{\nu}(x) \cdot \tilde{\psi}_{\nu}^{\mu T}(x') \cdot \tilde{\gamma}; & x < x' \\
\sum_{\mu,\nu = +1, -1} A_{\mu\nu}^* \psi^\mu_{\nu}(x) \cdot \tilde{\psi}_{\nu}^{\mu T}(x') \cdot \tilde{\gamma}; & x > x',
\end{cases}
\] (8)

where the indexes $\mu$ and $\nu$ represent different valley projections of the wavefunctions. We build the Green function using tensor products as $\tilde{G}_\phi(x \leq x') \propto \psi^\mu_{\nu}(x) \cdot \tilde{\psi}_{\nu}^{\mu T}(x')$. Where $\psi^\mu_{\nu}(x)$ and $\tilde{\psi}_{\nu}^{\mu T}(x)$ are the asymptotic solutions that fulfil the boundary conditions to the left and right edges of the system, respectively. In figure 2(a) the possible processes for an armchair edge are shown. The labels $\mu$ and $\nu$ are always determined by the valley index of the incident particle. On the other hand, $\tilde{\psi}_{\nu}^{\mu T}(x)$ represent asymptotic solutions for the transposed Dirac equation with the same boundary conditions and opposite wavenumber $\tilde{\psi}_{\nu}^{\mu T}(x) = \exp(-i\eta q) \psi^\mu_{\nu}(x)$. Since $\mathit{H}^T(-\eta) = \mathit{H}(\eta)$, the wavefunctions $\tilde{\psi}_{\nu}^{\mu T}(x)$ fulfill the same differential equation than $\psi^\mu_{\nu}(x)$.

\[
-\frac{1}{h v} \tilde{\gamma} \otimes \tilde{\sigma}_z = \sum_{\mu,\nu = +1, -1} A_{\mu\nu} \psi^\mu_{\nu}(x) \cdot \tilde{\psi}_{\nu}^{\mu T}(x) \cdot \tilde{\gamma} = \sum_{\mu,\nu = +1, -1} A_{\mu\nu}^* \psi^\mu_{\nu}(x) \cdot \tilde{\psi}_{\nu}^{\mu T}(x) \cdot \tilde{\gamma},
\] (9)
which is obtained integrating (6) around $x = x'$. 

![Figure 2](image-url)
In our definition of the Green functions in (8) we have introduced the parity matrix \( \tilde{\gamma} \) in order to make the scalar product \( \hat{\psi}\hat{G}\hat{\psi} \) invariant under Lorentz transformations and spatial inversion (parity transformation). Here \( \hat{\psi} \) is the adjoint Dirac spinor defined as \( \hat{\psi} = \psi^{\dagger}\tilde{\gamma} \). The transformation rule for Dirac spinors is \( \psi \rightarrow \psi' = \tilde{S}\psi \), where \( \tilde{S} \) is a 4 \( \times \) 4 matrix that fulfills \( \tilde{S}\tilde{S} = \gamma \). With this rule, the product \( \langle \hat{\psi}\hat{G}\hat{\psi} \rangle = \psi^{\dagger}\tilde{G}\tilde{\gamma}\tilde{S}\psi = \psi'\tilde{\gamma}\tilde{G}\tilde{\gamma}\tilde{S}\psi' = \psi\tilde{\gamma}\tilde{G}\tilde{\gamma}\tilde{S}\psi' = \hat{\psi}\hat{G}\hat{\psi} \) is Lorentz invariant (for a complete description of the symmetry fermions see [13]). Now, since \( \hat{G} \propto \psi^{\dagger}\tilde{\gamma} \), we have that \( \hat{G} \rightarrow \hat{G}' = \tilde{S}\hat{G}\tilde{\gamma}\tilde{S} \) and the product \( \langle \hat{\psi}\hat{G}\hat{\psi} \rangle = \psi^{\dagger}\tilde{G}\tilde{\gamma}\tilde{S}\psi = \psi'\tilde{\gamma}\tilde{G}\tilde{\gamma}\tilde{S}\psi' = \hat{\psi}\hat{G}\hat{\psi} \) is also Lorentz invariant. The matrix \( \gamma \) in reciprocal space changes both valley and pseudospin indexes. Then, since the spinor is in the basis \( (A_{+}, B_{+}, A_{-}, B_{-}) \) the matrix \( \gamma \) can be written as \( \gamma = \tilde{\tau}_{z} \otimes \tilde{\sigma}_{x} \) and we can check that the Hamiltonian \( \hat{H} \) is transformed with \( \gamma \) as \( \gamma \hat{H}(p) \gamma = \hat{H}(-p) \). In section 2.1, where the armchair edge is studied, we use this form of the matrix \( \gamma \). A simplified form of matrix \( \gamma \) for one valley is derived in appendix A and is used for zigzag edges.

### 2.1. Armchair edges

We can now apply this method to derive the Green functions for a layer of graphene with armchair edges. Within the geometry depicted in the left panel of figure 1, the direction perpendicular to the edge may be infinite or have a finite size \( W \). In this later case, we have two edges at positions \( x_{L} \) and \( x_{R} \). The main characteristic of an armchair edge is that scattering at the edges changes the valley index. This is a direct result of vanishing either the wavefunction (equation (4)) or its derivative on both lattices at the armchair edge. Asymptotic solutions for this system correspond to incoming waves from one valley that are reflected on the other valley. All possible processes are illustrated in figure 2(a). The index \( \pm \) symbolizes an incoming wave around the Dirac point \( K_{\pm} \) that is reflected at the interface. For incident waves reflected at the left \((<)\) or at the right \((>)\) edge we have the four-dimensional spinors in valley and lattice spaces

\[
\psi_{<}(x) = e^{i\pm kx} \begin{pmatrix} 0 \\ \varphi_{2}(1) \end{pmatrix} + r_{L/R} e^{i \pm kx} \begin{pmatrix} 0 \\ \varphi_{2}(1) \end{pmatrix}.
\]

\[
\psi_{>}(x) = e^{i \mp kx} \begin{pmatrix} 0 \\ \varphi_{1}(2) \end{pmatrix} + r_{L/R} e^{i \mp kx} \begin{pmatrix} 0 \\ \varphi_{1}(2) \end{pmatrix}.
\]

The reflection amplitudes \( r_{L/R} \) are calculated imposing boundary conditions to the two-dimensional wavefunction of (4) at the edge \( x_{L/R} \). This is \( \phi(x_{L}) = \phi(x_{R}) = 0 \) or \( \partial_{x} \phi(x_{L}) = \partial_{x} \phi(x_{R}) = 0 \), which yields

\[
r_{L/R} = s e^{i 2\pi K_{\pm} k_{x} L} e^{-i 2\pi K_{\pm} k_{x} R},
\]

where \( s = \pm \) corresponds to the case in which the wavefunction \((-)\) or its derivative \((+)\) vanishes at the interface. The main differences between both cases are studied in the next section. For simplicity we have chosen that \( x_{L} \in (-\infty, 0) \) and \( x_{R} \in [0, \infty) \). Combining the asymptotic solutions, as has been explained in the previous section, we obtain a general expression for the full Green function with armchair edges \( \hat{G}^{arm} \) equivalent to (8). The constants \( A^{(\pm)}_{<\rightarrow} \) in this equation correspond to processes in which the excitation changes its valley projection when it propagates from one edge to the other. Therefore, these processes have zero probability and, from (9), one explicitly obtains \( A^{(\pm)}_{<\rightarrow} = A^{(\pm)}_{\rightarrow<} = 0 \). Combining the asymptotic solutions, as has been explained in the previous section, we obtain a general expression for the full Green function with armchair edges \( \hat{G}^{arm} \) equivalent to (8). The constants \( A^{(\pm)}_{<\rightarrow} \) in this equation correspond to processes in which the excitation changes its valley projection when it propagates from one edge to the other. Therefore, these processes have zero probability and, from (9), one explicitly obtains \( A^{(\pm)}_{<\rightarrow} = A^{(\pm)}_{\rightarrow<} = 0 \). Combining the asymptotic solutions, as has been explained in the previous section, we obtain a general expression for the full Green function with armchair edges \( \hat{G}^{arm} \) equivalent to (8). The constants \( A^{(\pm)}_{<\rightarrow} \) in this equation correspond to processes in which the excitation changes its valley projection when it propagates from one edge to the other. Therefore, these processes have zero probability and, from (9), one explicitly obtains \( A^{(\pm)}_{<\rightarrow} = A^{(\pm)}_{\rightarrow<} = 0 \). Combining the asymptotic solutions, as has been explained in the previous section, we obtain a general expression for the full Green function with armchair edges \( \hat{G}^{arm} \) equivalent to (8). The constants \( A^{(\pm)}_{<\rightarrow} \) in this equation correspond to processes in which the excitation changes its valley projection when it propagates from one edge to the other. Therefore, these processes have zero probability and, from (9), one explicitly obtains \( A^{(\pm)}_{<\rightarrow} = A^{(\pm)}_{\rightarrow<} = 0 \). Combining the asymptotic solutions, as has been explained in the previous section, we obtain a general expression for the full Green function with armchair edges \( \hat{G}^{arm} \) equivalent to (8). The constants \( A^{(\pm)}_{<\rightarrow} \) in this equation correspond to processes in which the excitation changes its valley projection when it propagates from one edge to the other. Therefore, these processes have zero probability and, from (9), one explicitly obtains \( A^{(\pm)}_{<\rightarrow} = A^{(\pm)}_{\rightarrow<} = 0 \).
In order to study a semi-infinite superconducting graphene region with an armchair edge extending from $x_L = 0$ to $x_R \to \infty$, we define a finite and constant pair potential $\Delta (x) = \Theta (x) \Delta$. Reflection amplitudes are then fixed to $r_L^0 = r_L = +1 \equiv r$ and $r_R^0 = r_R = 0$. The asymptotic solutions are

$$\psi_\infty^{(\pm)}(x) = \begin{cases} e^{\mp ik_{\alpha\beta} x} \left( \varphi_{2e}(1) \right) & \text{if } x R \to \infty \\ \cos \left( \varphi_{1e}(2) \right) & \text{if } x L \to \infty \end{cases}$$

(15)

$$\psi_\infty^{(\pm)}(x) = \begin{cases} e^{\mp ik_{\alpha\beta} x} \left( \varphi_{1e}(2) \right) & \text{if } x R \to \infty \\ \cos \left( \varphi_{2e}(1) \right) & \text{if } x L \to \infty \end{cases}$$

(16)

$$\psi_\infty^{(\pm)}(x) = \begin{cases} e^{\mp ik_{\alpha\beta} x} \left( \varphi_{1e}(2) \right) & \text{if } x R \to \infty \\ \cos \left( \varphi_{2e}(1) \right) & \text{if } x L \to \infty \end{cases}$$

(17)

$$\psi_\infty^{(\pm)}(x) = \begin{cases} e^{\mp ik_{\alpha\beta} x} \left( \varphi_{2e}(1) \right) & \text{if } x R \to \infty \\ \cos \left( \varphi_{1e}(2) \right) & \text{if } x L \to \infty \end{cases}$$

(18)

where $\varphi_{1e}(0)$, with $i = 1, 2$, is obtained from (3) making $\alpha \to \alpha_{1e}^i$ and defining $e_{\alpha_{1e}^i} = h v (k_{\alpha_{1e}^i}^{(1)} + i q)/|E|^2 \pm |E|$ and $u^2 (v^2) = (1 \pm \Omega/|E|)/2$. The function $\psi_\infty^{(\pm)}$ describes an incoming electron-like (hole-like) quasiparticle with energy $E > E_F \left( E < E_F \right)$ and valley index $\pm$ that is reflected at $x_L$ into an electron-like (hole-like) quasiparticle with valley index $\mp$.

The $8 \times 8$ matrix Green function can be written as the superposition of all possible quasi-electron and quasi-hole injection processes depicted in figures 2(b) and (c). The resulting Green function, written in full in the Nambu, valley, and pseudospin spaces, has the form where $\tau_{x,y,z}$ and $\tau_0$ are Pauli matrices in Nambu space. The parity matrix $\hat{\gamma}$ is diagonal in this space and only acts on graphene’s valley and pseudospin degrees of freedom.

As in the normal case, the coefficients $A_{\mu,\nu}^{(ij)}$ with $\mu = \nu$ vanish as they correspond to processes which change the valley polarization without reflection at the edges. Additionally, the processes that couple quasi-electron with quasi-hole and vice versa have zero probability. This can be explicitly found from the condition given by (9) where $A_{\mu,\nu}^{(ij)} = 0$, $A_{\nu,-(\nu)}^{(i,-i)} = (\cos (2\hbar \Omega/|E|) \cos (\omega_0))$, and $A_{\nu,+(\nu)}^{(i,+i)} = (\cos (2\hbar \Omega/|E|) \cos (\omega_0))$. Thus, after applying boundary conditions and solving (9), the valley superposed Green function in Nambu space for a superconducting region with an armchair edge is

$$\hat{G}_{\phi}^S (x, x') = \begin{cases} -\frac{1}{2h\nu} \left( A_{\phi}^x + A_{\phi}^y \right) \left( E \Omega \tau_0 + \frac{\Delta}{\Omega} \hat{\sigma}_x \right) & \text{if } x R \to \infty \\ -\frac{1}{2h\nu} \left( A_{\phi}^x + A_{\phi}^y \right) \left( E \Omega \tau_0 + \frac{\Delta}{\Omega} \hat{\sigma}_x \right) & \text{if } x L \to \infty \end{cases}$$

(19)

with the following definitions

$$A_{\phi}^{(i)} = f_{\phi}^{(i)} \cos (1 - \alpha_{\phi}^{(i)} \hat{\sigma}_0 + \tan \alpha_{\phi}^{(i)} \hat{\sigma}_y) \pm i g_{\phi}^{(i)} \hat{\sigma}_x$$

$$f_{\phi}^{(i)} = \cos (K (x' - x)) e^{i k_{\alpha_{\phi}^{(i)} \hat{\sigma}_y}} + r \cos (K (x' + x)) e^{i k_{\alpha_{\phi}^{(i)} \hat{\sigma}_x}} + r \sin (K (x' - x)) e^{i k_{\alpha_{\phi}^{(i)} \hat{\sigma}_y}}$$

$$g_{\phi}^{(i)} = \sinh (x' - x) \sin (K (x' - x)) e^{i k_{\alpha_{\phi}^{(i)} \hat{\sigma}_y}} + r \sin (K (x' + x)) e^{i k_{\alpha_{\phi}^{(i)} \hat{\sigma}_x}}$$

(20)

It is interesting to take this expression to the heavily doped limit in which $E_F^2 \gg E, \Delta, \hbar v q$ and thus $\cos^2 \alpha_{\phi}^{(i)} \hat{\sigma}_x \to 1$ and $\sin \alpha_{\phi}^{(i)} \hat{\sigma}_y \to 0$. Within this approximation, for a microscopic distance $x_0 \sim a$ from the interface we have

$$\hat{G}_{\phi}^S (x_0, x) \approx \frac{i}{\hbar v} \left[ 1 + r \cos 2K x_0 \hat{\sigma}_0 \otimes \left( \frac{E}{\Omega} \tau_0 + \frac{\Delta}{\Omega} \hat{\sigma}_x \right) \right]$$

$$+ i r \sin 2K x_0 \hat{\sigma}_x \otimes \hat{\sigma}_x$$

(21)

which corresponds to the momentum independent BCS Green function without sublattice structure [9]. Then, $2/\hbar v$ corresponds to an averaged Fermi energy DOS per unit length for the superconductor.

On the other hand, for the boundary condition over the wavefunction ($r = -1$) the Green function vanishes at $x_0 = 0$. For finite $x_0$, the Green function can exhibit a structure in pseudospin space given by the last term in (20). This expression is used in the following sections when we microscopically couple normal and superconducting regions.

2.2. Zigzag edges

The geometry of the graphene sheet is now set to have a zigzag edge along the $y$-axis. With this new orientation of the layer the Brillouin zone rotates as illustrated in the upper part of the right panel of figure 1, which allows to select the Dirac points at $K_{\pm} = (0, \pm k)$. We still call $h q$ the conserved momentum along the $y$ direction. We consider either a finite layer with edges at positions $x_L$ and $x_R$ or a semi-infinite one in which $x_L$ or $x_R$ goes to infinity. Zigzag edges are formed by a line of atoms all pertaining to one sublattice. These edges do not mix valleys so we can treat them separately and use a Dirac Hamiltonian of just one valley, $\tilde{H} = h v (\hat{\sigma}_x + q \hat{\sigma}_y) - E_F \hat{\sigma}_0$. Thus, the asymptotic wavefunctions including a reflection at the edge are

$$\phi_<(x) = e^{-ikx} \varphi_2 + r \cos kx \varphi_1$$

(22)

$$\phi_>(x) = e^{ikx} \varphi_1 + r \cos kx \varphi_2$$

(23)

The reflection amplitudes depend on the atoms chosen to form the zigzag edge. Thus, if we choose the border at $x_L$ to be formed by atoms of $A$ ($B$) lattice, the one at $x_R$ is formed by atoms pertaining to $B$ ($A$) lattice (see right panel of figure 1). Imposing the boundary conditions $\phi_<(x_L)|_{A(B)} = 0$ we obtain the reflection amplitudes:

$$r_A^L = -e^{ikx} e^{2ikx}|x_L|$$

$$r_B^R = e^{-ikx} e^{2ikx}|x_R|$$

(24)

When combining the asymptotic solutions to build the Green functions, as it was done in section 2.1, the elements of the full Green function that mix valleys $(+, -)$ are zero. In what follows the full Green function is understood to represent
only a projection over one valley (i.e. $\hat{G}_\alpha^{z,z'}$). Following the steps given in the previous sections we can write

$$
\hat{G}_\alpha^{z,z'}(x,x') = \begin{cases} 
\alpha \phi_\alpha(x) \cdot \phi^\dagger_\alpha(x') \cdot \gamma; & x < x' \\
A' \phi_\alpha(x) \cdot \phi^\dagger_\alpha(x') \cdot \gamma; & x > x'.
\end{cases}
$$

(25)

When restricted to a single valley, the parity matrix $\gamma$ is equivalent to $\hat{\gamma}$ (see appendix A for a detailed discussion). For a ribbon of graphene with the left zigzag edge of type $B$ (and thus the right one of type $A$) we have

$$
\hat{G}_\alpha^{z,z'}(x,x') = \frac{-i}{2\hbar v} \left[ e^{ik(x-x')} \psi_2 \psi_2^\dagger + r_L^B r_A^B e^{-ik(x-x')} \psi_1 \psi_1^\dagger \right]
$$

$$
\times \left[ e^{ik(x-x')} \psi_1 \psi_1^\dagger + r_L^B r_A^B e^{-ik(x-x')} \psi_2 \psi_2^\dagger \right] e^{ik(x-x)} \psi_1 \psi_1^\dagger + r_L^B r_A^B e^{-ik(x-x')} \psi_2 \psi_2^\dagger,
$$

$$
x < x',
$$

$$
\frac{-i}{2\hbar v} \left[ e^{ik(x-x')} \psi_2 \psi_2^\dagger + r_L^B r_A^B e^{-ik(x-x')} \psi_1 \psi_1^\dagger \right]
$$

$$
\times \left[ e^{ik(x-x')} \psi_1 \psi_1^\dagger + r_L^B r_A^B e^{-ik(x-x')} \psi_2 \psi_2^\dagger \right] e^{ik(x-x)} \psi_2 \psi_2^\dagger + r_L^B r_A^B e^{-ik(x-x')} \psi_2 \psi_2^\dagger,
$$

(26)

For the other valley we obtain the same result with the change $\psi_{1,2} \leftrightarrow \psi_{2,1}$. As it was explained in the previous section, $\cos \alpha = 0$ gives the bulk dispersion relation. Furthermore, if the layer has a finite width which is set to $W = x_R - x_L$, the condition $1 - r^B_L r^A = 0$ transforms into

$$
e^{2ikW} = q + ik
$$

(27)

whose solutions correspond to surface states, at $E = E_F$, localized along the edges of the ribbon [15].

Analogously to the armchair case, we now consider a superconducting region spread over the $x > 0$ infinite half-plane with a zigzag edge at $x = 0$. If we couple electronic excitations with $\mathbf{k}_\perp$ index to hole-like quasiparticles with the other valley index, (14) is reduced to a $4 \times 4$ matrix equation in Nambu and pseudospin spaces

$$
\begin{pmatrix} 
\hat{H}_+ - E_F^z \\
\hat{H}_- - E_F^z
\end{pmatrix}
\begin{pmatrix} 
\phi^z_1 \\
\phi^z_2
\end{pmatrix} = E
\begin{pmatrix} 
\phi^z_1 \\
\phi^z_2
\end{pmatrix}.
$$

(29)

The asymptotic wavefunctions for quasi-electron and quasi-hole injection are written in Nambu and pseudospin space as

$$
\psi^\text{eh}_e(x) = \left[ e^{i\mathbf{k}_\perp \mathbf{x}} \psi_{2e(1h)}^\text{eh} + r^B e^{i\mathbf{k}_\perp \mathbf{x}} \psi_{1e(2h)}^\text{eh} \right] \left( \frac{u(v)}{v(u)} \right)
$$

(30)

$$
\psi^\text{eh}_o(x) = e^{i\mathbf{k}_\perp \mathbf{x}} \psi_{1e(2h)}^\text{eh} \left( \frac{u(v)}{v(u)} \right),
$$

(31)

where the edge has been chosen to be formed by atoms from sublattice $B$. Boundary conditions for the wavefunction at the zigzag edge determine the reflection amplitudes. Thus, for electronic excitations we substitute $\alpha \rightarrow \alpha_+^z$ in (24), while we change $\alpha \rightarrow -\alpha_+^z$ for hole excitations. The resulting Green function for a semi-infinite superconducting region reads

$$
\hat{G}_{\text{FS},z}(x,x') = \frac{-i}{2\hbar v} \left\{ [\hat{Z}^z + \hat{Z}^{\dagger z}] \otimes \frac{1}{\Omega} \left( \hat{E} t_0 + \Delta \hat{t}_x \right) \right. \\
+ \left. [\hat{Z}^z - \hat{Z}^{\dagger z}] \otimes \hat{t}_x \right\},
$$

(32)

where

$$
\hat{Z}^{\text{eh}}_{(\text{eh})} = \frac{e^{i\mathbf{k}_\perp \mathbf{x}}}{2\cos \alpha^z_{(\text{eh})}} \left( \left[ \psi_{2e(1h)} \right] \left( \psi_{2e(1h)} \right) + \left[ \psi_{1e(2h)} \right] \left( \psi_{1e(2h)} \right) \right),
$$

(33)

When (32) is evaluated at the edge of the graphene layer it reduces to

$$
\hat{G}_{\text{FS},z}(0,0) = \frac{-i}{2\hbar v} \left\{ \begin{pmatrix} e^{-ikz} + e^{ikz} & 0 \\
0 & 0 \end{pmatrix} \right\}
$$

$$
\otimes \frac{1}{\Omega} \left( \hat{E} t_0 + \Delta \hat{t}_x \right) + \left\{ \begin{pmatrix} e^{-ikz} & e^{ikz} \\
0 & 0 \end{pmatrix} \right\}
$$

$$
\otimes \hat{t}_x \otimes \hat{t}_x,
$$

(34)

Furthermore, in the heavily doped limit ($E_F^z \gg E, \Delta, \hbar \nu q$), the previous expression reduces to

$$
\hat{G}_{\text{FS},z}(0,0) = \frac{-i}{2\hbar v} \left\{ \begin{pmatrix} \hat{\sigma}_z + \hat{\sigma}_z & 0 \\
0 & 0 \end{pmatrix} \right\}
$$

$$
\otimes \frac{1}{\Omega} \left( \hat{E} t_0 + \Delta \hat{t}_x \right) + \left\{ \begin{pmatrix} 0 & 0 \\
0 & 0 \end{pmatrix} \right\}
$$

$$
\otimes \hat{t}_x \otimes \hat{t}_x,
$$

(35)

where the sign identifies the cases with $x < x'$ or $x > x'$. Thus, in this limit we roughly have a BCS Green function projected to the site $A$.

3. The Dyson equation for coupling separate regions

Once the expressions for bulk, armchair and zigzag graphene sheets, as well as for the semi-infinite superconducting regions have been obtained, we concentrate in the determination of the Green functions for the coupled system. This amounts, in principle, to solve the integral Dyson equation

$$
\hat{G}_\phi(x,x') = \hat{g}_\phi(x,x') + \int dx \psi^*_2(x) \hat{V}(x_1, x_2) \hat{G}_\phi(x_2, x'),
$$

(36)

where now $\hat{G}_\phi$ denotes the valley superposed Green function of the coupled system, $\hat{g}_\phi$ corresponds to the uncoupled ones and $\hat{V}$ is an appropriate perturbation describing the coupling between the two regions. In general, we must use valley superposed Green functions in Dyson’s equation to have a microscopic description of the coupling between graphene layers. In order to simplify the model while still keeping the possibility to describe interfaces of arbitrary transparency we
shall assume that the perturbation only connect points on an atomic scale close to the interface. We thus define a general perturbation
\[ \hat{V}(x_1, x_2) = \beta t_x a_{eff} \delta(x_1 - x_0) \delta(x_2 + x_0) \hat{\sigma}_z, \]
where \( \beta \in [0, 1] \) is a dimensionless parameter that controls the transparency of the interface and \( x_0 \) is a microscopic distance from the interface. The effective hopping matrix \( t_x a_{eff} \hat{\sigma}_z \) has a structure dictated by the change of sublattice associated with the hopping between the two graphene sheets at the interface.

In this expression \( a_{eff} \) represents an ‘effective distance’ which we determine from the condition that the bulk graphene result is recovered when coupling two semi-infinite regions with \( \beta = 1 \).

We first discuss the case of two semi-infinite graphene sheets with armchair edges. The simplest possible choice would be \( x_0 \to 0^+ \), which can be applied when the condition of vanishing the derivative of the wavefunction at the edge has been taken. In this way one may convert (36) into an algebraic equation, which for the local Green functions at the interface can be written as
\[ \hat{G}_{R(L)} = \left( \hat{\sigma}_+ \phi_{R(L)}^{\dagger} \hat{\sigma}_- \phi_{R(L)} \right)^{-1}, \]
where \( R, L \) denotes \((x, x') \to (0^+, 0^-) \) and \( \hat{\sigma}_- \phi_{R(L)} \) are given by
\[ \hat{\sigma}_- \phi_{R(L)} = \frac{-2i}{h \nu} (\cos^{-1} a \hat{\sigma}_0 + \tan a \hat{\sigma}_y) \hat{\sigma}_z. \]

One can check that the bulk Green function is recovered for \( a_{eff} = \sqrt{3} \alpha / 4 \), which therefore sets the condition of perfect transparency for this case. The reader is directed to appendix B for more details about the bulk results for a normal or superconducting graphene sheet.

A slightly more cumbersome matching condition has to be introduced if one would like to reproduce the limiting results of the TB model for such an interface [9]. This requires using the Green functions obtained by vanishing the wavefunction at the edges of the graphene sheet and take \( x_0 = a / 4 \). One obtains then a Dyson equation like (38) with \( R, L \) denoting \((x, x') \to (\pm a / 4, \pm a / 4) \) and \( \hat{G}_{R(L)} \) given by
\[ \hat{G}_{R(L)} = \frac{-\sqrt{3i}}{2h \nu} \sqrt{3} (\cos^{-1} a \hat{\sigma}_0 + \tan a \hat{\sigma}_y) - i \hat{\sigma}_z \]

These expressions exactly reproduce the TB results in the continuum limit, this is \( a \to 0 \) but with \( K_a \to 4\pi / 3 \) [4]. One can further check that for this case the bulk graphene result is recovered for \( a_{eff} = a / 2 \) which is the distance between lines of atoms along the \( x \) direction in an armchair edge.

We now focus on zigzag edges. In this case one can disregard the valley mixing but care should be taken due to the discontinuity of the Green functions at \( x = x' \). As discussed in section 2, we select the condition of vanishing one of the wavefunction components at the interface and take \( x_0 \to 0^+ \). The precise value of \( x_0 = a \) is here irrelevant because the Dirac points lie along the \( y \) direction.

When we evaluate (26) at the edge of each region we get
\[ \hat{g}_L = -\frac{i}{h \nu} \left( \begin{array}{cc} 0 & -1 \\ 0 & e^{-i \nu} \end{array} \right) \hat{\sigma}_z^L; \quad x < x' \to 0^- \]
\[ \hat{g}_R = \frac{i}{h \nu} \left( \begin{array}{cc} e^{-i \nu} & 0 \\ 0 & 1 \end{array} \right) \hat{\sigma}_z^R; \quad x' < x \to 0^- \]
\[ \hat{g}_L = -\frac{i}{h \nu} \left( \begin{array}{cc} -1 & 0 \\ 0 & e^{-i \nu} \end{array} \right) \hat{\sigma}_z^L; \quad x < x' \to 0^+ \]
\[ \hat{g}_R = \frac{i}{h \nu} \left( \begin{array}{cc} e^{i \nu} & 0 \\ 0 & 1 \end{array} \right) \hat{\sigma}_z^R; \quad x' < x \to 0^+. \]

We have implicitly assumed a \( A(B) \) termination for the \( L(R) \) graphene sheet. The Green function of the coupled system must be constructed including the discontinuity of the uncoupled Green functions at the edges, i.e. for \( x, x' < 0 \)
\[ \hat{G}_L(x, x') = \hat{g}_L(x', x) + (t_x a_{eff})^2 \hat{g}_L(0, 0^-) \hat{\sigma}_z \]
\[ \times \left[ 1 - (t_x a_{eff})^2 \hat{\sigma}_z^L \hat{\sigma}_z^L \right]^{-1} \hat{g}_R^\dagger(0^-, x'), \]
where \( \hat{g}_L(0, 0^-) = \exp(-i \nu) \hat{g}_L^\dagger(0^-, x) = \exp(-i \nu) \hat{g}_L(0^-, 0) = \hat{g}_L(0^-, 0) \) and \( \hat{g}_L(0^-, 0) \) corresponds to (26) with \( t_x = 0 \). When \( x < x' \), and using that for this case \( t_x = -r_A \), this results in
\[ \hat{G}_L(x, x') = \frac{-i}{2h \nu \cos \alpha} \left[ e^{ik(x-x') \nu} \varphi_2^\dagger + e^{-ik(x+x') \nu} \varphi_1^\dagger \right] \left( 1 - \frac{\beta^2 (1 + e^{-2i \alpha})}{2h \nu \cos \alpha + \beta e^{-2i \alpha}} \right). \]

where we have replaced \( t_x = 2h \nu / (\sqrt{3} a) \). The bulk result is recovered at perfect transparency (\( \beta = 1 \)) for \( a_{eff} = \sqrt{3} a / 2 \), which corresponds to the horizontal separation between atoms of the same sublattice. This result corresponds to the projection over the point \( \varphi_2 \). For the other valley, the same result with \( \varphi_1 \leftrightarrow \varphi_2 \) is reached and the bulk result is recovered for perfect transparency superposing both valleys.

4. Graphene–superconductor junction

All the ingredients necessary to analyze the graphene–superconductor coupling have been already introduced. In the present section, we analytically derive the Green function of the coupled system both for armchair and zigzag edges. We locate the interface at \( x = 0 \), parallel to the \( y \) axis, with the normal region covering the \( x < 0 \) infinite half-plane. Since the superconducting region is represented in Nambu space, in order to use Dyson’s equation as has been explained in section 3, the Green functions of the normal region are written as
\[ \hat{\varphi}_L = \left( \begin{array}{cc} \varphi_0 & 0 \\ 0 & \varphi_h \end{array} \right). \]

Electron excitations are states above the Fermi energy. Then, \( \varphi_0 \) corresponds to (13) for armchair edges or (26) for zigzag edges if we set \( \alpha = \alpha_0 \), with \( h \nu \epsilon \equiv \sqrt{(E_F + E)^2 - (h \nu \sigma)^2} \). On the other hand, hole excitations have energies below \( E_F \). Thus, \( \varphi_h \) corresponds to the same equations but with the change \( \alpha_0 = \arcsin h \nu \sigma / (E_F - E), \) with \( h \nu \epsilon_h = \sqrt{(E_F - E)^2 - (h \nu \sigma)^2} \). For the superconducting region (R),
for armchair edges or (32) for zigzag edges, evaluated at the interface, stand for \( \hat{g}_k \) in Dyson’s equation.

The coupling with the superconductor appears in the Green function as a perturbation of the semi-infinite result \( \hat{g}_L \) given by (13) and (26). Thus we can write

\[
\hat{G}_L(x, x') = \hat{g}_L(x, x') + \delta \hat{G}(x, x'),
\]

where \( \delta \hat{G} \) is the correction with respect to the uncoupled case. Our formalism allows in principle to obtain analytical results for \( \delta \hat{G} \) in the case of arbitrary effective hopping and coordinates \( x \) and \( x' \).

For the case of an armchair interface, using the boundary conditions of vanishing the derivative of the wavefunction and setting \( \beta = 1 \), for \( x = x' \) we obtain

\[
\delta \hat{G}_{ee}^{arm}(x = x') = \frac{i}{\hbar v} \frac{e^{-2ik_x x}}{\cos \alpha_e} \left[ \left( \frac{\cos 2K x}{\cos 2K x + \alpha_e} \right) - i \frac{\sin(2K x + \alpha_e)}{\sin(2K x - \alpha_e)} \right] + \frac{N_{arm}}{D_{arm}} \left( \frac{\sin \alpha_e}{\sin \alpha_e} - i \frac{\sin \alpha_h}{\sin \alpha_h} \right),
\]

where we have defined the auxiliary quantities

\[
N_{arm} = 2 \sin \alpha_e \left( 1 + \frac{E}{\Omega} \cos \theta_h \right) + \frac{\Delta^2}{\Omega^2} (\sin \alpha_e - \sin \alpha_h),
\]

\[
D_{arm} = 2 \left( 1 + 2 \cos \alpha_e \cos \alpha_h + \frac{E}{\Omega} (\cos \alpha_e + \cos \alpha_h) \right) + \Delta^2 \left( 1 + \cos \alpha_e + \alpha_h \right).
\]

The denominator \( D_{arm} \) contains information on the spectral properties of the coupled system. In particular, the condition \( D_{arm} = 0 \) is satisfied by states with energy given by

\[
E = \frac{\pm \sqrt{(\lambda_e + \lambda_h)^2 - \text{sign}(E^2 - E_F^2) \sin(\lambda_e + \lambda_h)}}{2 \cosh \lambda_e \cosh \lambda_h},
\]

where we define \( \lambda_{e,h} = \text{sign}(q) \arcsinh(h v q / |E \pm E_F|) \) for evanescent electron or hole states with \( |h v q| > |E \pm E_F| \). As demonstrated in [4], these states correspond to interface bound states (IBSs) arising from the interplay between normal and Andreev reflection at the junction region. The decay of these states into the normal region is given by \( e^{\xi_h x} / \cos \theta_h \), which can be clearly much larger than the BCS superconducting coherence length \( \xi = \hbar v / \Delta \) when \( E_F \ll \Delta \). In the opposite limit, \( E_F \gg \Delta \), the states are confined to the interface.

On the other hand, for the calculation of the LDOS it is necessary to obtain the diagonal components of the local Green’s function ([ee, AA] and [ee, BB]). Whenever \( K x = n \pi \), they simplify to

\[
G_{\text{arm}, \text{EE}, \text{AA}}^{\text{arm}}(x, x) = G_{\text{arm}, \text{EE}, \text{BB}}^{\text{arm}}(x, x) \equiv -\frac{i}{\hbar v} \frac{1 - e^{-2ik_x x}}{\cos \alpha_e} \frac{N_{arm}}{D_{arm}} \tan \alpha_e.
\]

Furthermore, for analyzing the induced pairing correlations in the normal graphene layer, the electron–hole elements of \( \delta \hat{G} \) are needed. Within the same conditions of the previous result, but for any values of \( x \) and \( x' \), these elements reduce to

\[
\delta \hat{G}_{\text{arm}, \text{EE}, \text{AA}}^{\text{arm}}(x, x') = \frac{-i e^{-2ik_x x} e^{ih_x x'} \Delta}{\hbar v D_{arm}} \left[ \frac{\cos(K x - x')}{\Omega} \right] \times \left[ 1 + \cos(\alpha_e - \alpha_h) + \frac{E}{\Omega} (\cos \alpha_e + \cos \alpha_h) \right] + \frac{1}{2} \left[ \sin(K x - x') \right] \frac{\cos \alpha_e - \cos \alpha_h}{\cos \alpha_e \cos \alpha_h} \times \left[ \sin \alpha_e + \sin \alpha_h + \frac{E}{\Omega} \sin(\alpha_e - \alpha_h) \right].
\]

We now analyze a normal–superconductor graphene junction with a zigzag edge at \( x = 0 \). As it was explained at the beginning of this section, we have chosen the normal (superconducting) region to be at \( x < 0 \) (\( x > 0 \)) and to have the edge formed by \( A (B) \) atoms. For these conditions we obtain the following correction

\[
\delta \hat{G}_{\text{ee}}^{\text{arm}}(x, x') = -\frac{i e^{2i\alpha_{x}(x+x')}}{\hbar v D_{zz}} \left[ \frac{E}{\Omega} + \frac{\beta^2 e^{i\alpha_{x}}}{\cos \theta_h} \right] \times \left[ 1 - \frac{-i e^{-i\alpha_{x}}}{e^{-i\alpha_{x}} - e^{-i\alpha_{x}}} \right],
\]

with \( D_{zz} = 1 + \frac{\beta^2 E}{\Omega} (\epsilon_{x} + \epsilon_{x'}) + \frac{\beta^2 e^{-i\alpha_{x}}}{\cos \theta_h \cos \theta_h} + \frac{\beta^2 e^{i\alpha_{x}}}{\cos \theta_h \cos \theta_h} \). Again, when this denominator is set to zero one obtains the dispersion relation for the IBSs along this edge,

\[
E = \frac{\pm \sqrt{(\epsilon_{x} + \epsilon_{x'})^{2} - \beta^2 \text{sign}(E^2 - E_{F}^2) \sin(\lambda_e + \lambda_h)^2}}{2 \sqrt{(\epsilon_{x} + \epsilon_{x'}) (\epsilon_{x} + \epsilon_{x'})}},
\]

which is in agreement with the result of [4].

On the other hand, the electron–hole component of the Green function is given by

\[
\delta \hat{G}_{\text{ee}}^{\text{arm}}(x, x') = \frac{i e^{2i\alpha_{x} x'} e^{i\alpha_{x} x}}{\hbar v D_{zz}} \left[ \frac{\Delta}{\Omega} \left( -\frac{1}{e^{-i\alpha_{x}} - e^{-i\alpha_{x}}} \right) \right].
\]

4.1. LDOS for armchair and zigzag edges

As a test of the method we analyze in this section the LDOS for a graphene–superconductor junction. The electronic LDOS per unit length for a distance \( x = x' \equiv d \) is defined as

\[
\rho(E, d) = -\frac{1}{\pi} \int_{-\infty}^{\infty} dq \text{Tr} \left[ \text{Im} \{ \hat{G}_{\text{ee}}(q, E; d, d) \} \right].
\]

Hereafter, for the numerical calculations, we set \( \Delta / \epsilon_{F} = 10^{-2} \) which corresponds to \( \xi / a = 100 \) and we also include a finite relaxation rate \( \eta = 0.005 \Delta \).

The left panel of figure 3 shows the LDOS for an armchair edge close to the interface \( (d = -0.1\xi) \) obtained using the boundary conditions of vanishing the wavefunction or its derivative. For comparison we also show in this figure the results obtained for the TB model calculations of [9]. The results of figure 3 are normalized to the density of a bulk graphene layer with zero doping at \( E = \Delta, \rho_0 = 2 \Delta / h^2 v^2 \) (see appendix B). The discrepancies between the different matching conditions tend to disappear when we move away
Figure 3. LDOS in the normal region with $E_F = 0$ for a semi-infinite layer of graphene with armchair edges coupled to a superconducting region (left panel). Profiles for both boundary conditions (full blue line when vanishing the wavefunction and dotted red line for the derivative) are equivalent to the TB results (dashed line). The right panel shows the oscillating behavior of the LDOS for $E = 2\Delta$ along the direction transversal to the interface. The transversal distance $d$ is normalized to the BCS superconducting coherence length $\xi$. All the results show the same oscillating behavior around the bulk value. The oscillatory behavior at the atomic scale is shown in the inset for the boundary condition of vanishing the wavefunction.

Figure 4. LDOS profiles, at a distance $d = -0.41\xi$ inside the normal region with $E_F = 0$, for different transparencies of the zigzag (left panel) and armchair (right panel) interface. In the zigzag case, the edge state splits and evolves into a band inside the superconducting gap when the transparency $\beta$ goes from 0 (uncoupled case represented by a dashed black line) to 1 (perfect transparency, solid black line). For the armchair case the superconducting proximity effect is manifested by the appearance of sharp peaks in the LDOS for energies $E \sim \Delta$. This panel also illustrates the oscillatory behavior of the LDOS inside the normal region of graphene around the bulk value (indicated by the dashed line). The period of the oscillation is given roughly by $\hbar v/E$ and the amplitude decreases with the distance to the interface. When studying the spatial evolution of the LDOS of an armchair layer of graphene, it is well known that there is an oscillatory behavior at the atomic scale [15, 9]. This is a direct result of the valley mixing that happens at an armchair edge. For the sake of clarity, the evolution of the LDOS with the direction transversal to the interface shown in the right panel of figure 3 has been calculated for values $|x|/a = 3n$, with $n$ a positive integer. Similar profiles are reached for different multiplicities of the coordinate $x$. The oscillatory behavior at the atomic scale is shown in the inset of this panel for the boundary conditions of vanishing the wavefunction.

On the other hand, the left panel of figure 4 shows the LDOS for a zigzag edge at a distance inside the normal region $d' = -0.4\xi$. The results correspond to different values of the parameter $\beta$ controlling the interface transparency. For the uncoupled case with $\beta = 0$, a localized edge state appears at $E = E_F$ (dashed line in figure 4). However, for a non-zero transparency the edge state splits and evolves into a band inside the superconducting gap. As it was demonstrated in [4], this band is formed by the IBSs which give rise to the peaks in the DOS for energies around $E \sim \Delta$ when $\beta = 1$.

It is important to emphasize that although the surface state at $E = E_F$ for zigzag edges has been thoroughly studied, our results demonstrate that the superconducting proximity effect splits this state and produces a shift that depends on the transparency between the normal and superconducting regions.

The LDOS for the armchair case with the same set of parameters is illustrated in the right panel of figure 4. As
by the proximity effect. We can map the spatial variation of these correlations using the Green function of the coupled system. The element $\tilde{G}_{(\text{ch}, A)}(x, x', y)\, y'$ corresponds to the injection of electron excitations at the point $x'$ on the $y = 0$ axis and its propagation as a hole excitation to the rest of the plane $(x, y)$ after an electron–hole conversion at the interface. The probability $P_{e\rightarrow h}$ that an electron injected at $(x', 0)$ would be converted into a hole at $(x, y)$ is proportional to

$$P_{e\rightarrow h}(E; x, x', y) \propto \int_{-\infty}^{\infty} dq \, e^{i\xi y} \tilde{G}_{(\text{ch}, SS')}(q, E; x, x')^2,$$

with $S, S' = A, B$.

In our study of the spatial variation of the superconducting correlations we set $x' = -\xi$. We find it interesting to explore the change in the induced pair correlations for electrons injected within the gap ($E < \Delta$) when the doping level varies from $E_F \gg \Delta$ (left panel of figure 5) to $E_F \ll \Delta$ (right panel). As it was demonstrated in [3], these two limiting cases correspond to the regimes in which Andreev reflection exhibits respectively a retro or a specular character. In these limits and in the case of perfect transparency, the main difference between an armchair edge and a zigzag one is that the atomic oscillations happen along the $x$ or $y$ axis, respectively. Thus, we only analyze the results for an armchair edge with a fixed multiplicity.

In figures 5(a) and (b), these two cases are shown for an incident energy $E = 0.75\Delta$. In the case $E_F > \Delta$, shown in figure 5(a), electron–hole conversion occurs mainly for $y \simeq 0$ decaying fast for $y \gtrsim \xi$. This confinement of the spatial variation of the superconducting correlations along the $y$ axis is a consequence of the underlying diffraction pattern for the injected electrons at one point which has a spatial extension of the order of $\hbar v/F E_F$. This behavior is drastically different in the limit $E_F < E < \Delta$ for which specular reflection is enhanced (figure 5(b)). In addition to the electron–hole conversion for normal incidence, the results exhibit the presence of long-range superconducting correlations along the $x$ axis, provided that $x \sim \xi$. In order to more clearly appreciate the difference in the spatial decay of the correlations in these two regimes we plot in figure 5(c) the probability as a function of $y$ in both cases when $x = x' = -\xi$. As can be observed while the correlation decays very strongly in the retro-reflection regime, with an approximate scaling of the type $e^{-y/\xi}/(y/\xi)^3$ which is characteristic of a 2D s-wave superconductor [16]; in the specular reflection regime the probability does not decay even for $y \gtrsim 5\xi$. For this large $y$-range we find a decay of the type $e^{-y/\xi^\alpha}$ where $\alpha$ is a very small $\sim 7 \times 10^{-2}$ parameter which appears in these numerical calculations due to the presence of a small but finite relaxation rate $\eta$, which we fixed to $\eta = 5 \times 10^{-3}\Delta$ (see the inset in figure 5(c)). These long-range correlations can be directly associated with the presence of IBSs which in this regime have a spatial extension inside the normal region which is much larger than $\xi$. At the same time, the extended correlations can be interpreted as a signature of divergent Andreev reflection trajectories characteristic of the regime $E_F \ll \Delta$.

![Figure 5](image-url)

Figure 5. (a), (b) Spatial mapping of the induced pairing correlations $P_{e\rightarrow h}(x, y)$ in the graphene normal region for an incident energy $E = 0.75\Delta$ and $x' = -\xi$ for two values of the doping level: $E_F = 2.1\Delta$ (a) and $E_F = 0.1\Delta$ (b). $P_{e\rightarrow h}(x, y)$ is normalized to its value at $x = x' = -\xi$ and $y = 0$. In (c) we plot the normalized probability as a function of $y$ for $x = x' = -\xi$. The approximate asymptotic behavior is indicated by the dotted lines in the inset of the figure for $E_F = 0.1\Delta$.
5. Conclusions

In this paper we have developed a method that allows the Green function in inhomogeneous graphene systems with well-defined edges to be obtained, such as nanoribbons and graphene–superconductor interfaces. In this approach the asymptotic solutions of the Bogoliubov–de Gennes–Dirac equations satisfying the appropriate boundary conditions are used to analytically build the Green functions associated to the quasiparticles in the system.

Within this formalism we have analyzed the LDOS of a normal-superconducting graphene junction and showed how it is affected by the type of edge and the interface transparency. In particular, for the zigzag case, when the parameter β (which controls the transparency of the junction) increases, the localized edge state appearing at $E = E_F$ splits and evolves into symmetric bands within the superconducting gap. These bands correspond to the interface bound states already described in a previous work [4].

Furthermore, we have studied the spatial distribution of the induced pairing correlations inside the normal region. This correlations illustrate the crossover between retro and specular Andreev reflection. We indicate the appearance of long-range correlations between distant points on the graphene layer close to the interface due to the presence of IBSs. These superconducting correlations are enhanced in the regime corresponding to specular Andreev reflection.

We would like to conclude stressing that the analytical results obtained in the present work could be very useful for the study of transport properties in more complex hybrid systems which combine finite normal and superconducting graphene regions. Work along these lines is under progress.

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Appendix A. Green’s functions for zigzag edges. One valley description

For the case of a graphene sheet with zigzag edges, we have set the Dirac points to be at $K_{\pm} = (0, \pm K)$. Thus, the Hamiltonian on each valley is given by $\hat{H}_{\pm} = \hbar v [\hat{k} \vec{\delta} \pm q \vec{\delta} \hat{\sigma}_3] - E_F \hat{\sigma}_0$. The Hamiltonian of the full system is related with the one given in (5) by $\hat{H}_{zz} = \hat{T} \hat{H} \hat{T}$, with

$$\hat{T} = \hat{T}^{-1} = \begin{pmatrix} 1 & 0 \\ 0 & \hat{\sigma}_z \end{pmatrix}. \quad (A.1)$$

The matrix $\hat{\gamma} = \hat{T} \hat{T} \hat{\sigma} \hat{T}^{-1}$ is then transformed as $\hat{\gamma}_{zz} = \hat{T} \hat{T} \hat{\sigma} \hat{T}^{-1}$. When we apply this matrix to $\hat{H}_{zz}$ we have $\hat{\gamma}_{zz}(\hat{H}_{zz}(k)) \hat{\gamma}_{zz}^{-1} = \hat{H}_{zz}(-k)$, which corresponds to a parity transformation.

Since the zigzag boundary conditions do not mix valleys we can work only with one valley ($K_+$) using Hamiltonian $\hat{H}^z_{zz} = \hat{H}_{zz}$. For this Hamiltonian the effect of the parity transformation, restricted to the sublattice subspace, is equivalent to set $\hat{\gamma} = \hat{\sigma}_z$.

Appendix B. Bulk Green’s functions

If we set all the reflection amplitudes to zero in (13) we obtain the bulk solution for an infinite graphene layer

$$\tilde{G}_{\phi}^\text{bulk}(x, x') = \frac{-i}{2 \hbar v \cos \alpha} \left\{ e^{i(K-k)|x-x'|} \hat{\varphi}_1 \hat{\varphi}_1^\dagger + e^{-i(K-k)|x-x'|} \hat{\varphi}_2 \hat{\varphi}_2^\dagger, \quad x < x' \right\} \left\{ e^{i(K+k)|x-x'|} \hat{\varphi}_2 \hat{\varphi}_2^\dagger + e^{-i(K+k)|x-x'|} \hat{\varphi}_1 \hat{\varphi}_1^\dagger, \quad x > x' \right\}. \quad (B.1)$$

Thus, the local propagator for a bulk of graphene is

$$\tilde{G}_{\phi}^\text{bulk}(x = x') = \frac{-i}{2 \hbar v \cos \alpha} \left\{ \hat{\varphi}_1 \hat{\varphi}_1^\dagger + \hat{\varphi}_2 \hat{\varphi}_2^\dagger \right\}. \quad (B.2)$$

Furthermore, the bulk LDOS is obtained integrating this simple result, thus giving $\rho_{\text{bulk}}(E) = 2(E + E_F)/\hbar^2 v^2$.

On the other hand, vanishing the reflection coefficient ($\Gamma$) in (19) we reach the bulk solution for an infinite superconducting region. The local valley superposed Green function is then written as

$$\tilde{G}_{\phi}^\text{S,bulk}(x = x') = \frac{-i}{2 \hbar v} \left\{ \cos^{-1} \alpha \hat{\sigma}_0 + \tan \alpha \hat{\sigma}_y \right\} \hat{T} \left( E \hat{\tau}_0 + \Delta \hat{\tau}_x + \hat{\tau}_z \right) \hat{T} \left( E \hat{\tau}_0 + \Delta \hat{\tau}_x - \hat{\tau}_z \right) \left\{ \cos^{-1} \alpha \hat{\sigma}_0 + \tan \alpha \hat{\sigma}_y \right\} \hat{T}^{-1}. \quad (B.3)$$

In the heavily doped limit, the Green function loses all structure in sublattice space,

$$\tilde{G}_{\phi}^\text{S,bulk}(x = x') \approx \frac{-i}{\hbar v} \left( E \hat{\tau}_0 + \Delta \hat{\tau}_x \right). \quad (B.4)$$

and is equivalent to the bulk BCS Green function.

References

[1] Heersche H B, Jarillo-Herrero P, Oostinga J B, Vandervondek L M K and Morpurgo A 2007 Nature 446 56
[2] Shabti A, Natyel W, Kasumov A, Collet C, Ferrier M, Gueron S, Debloch R and Bouchiat H 2007 Europhys. Lett. 79 57008
[3] Miao F, Wijeratne S, Zhang Y, Coskun U C, Bao W and Lau C N 2007 Phys. Rev. Lett. 100 147001
[4] Buset P, Herrera W and Yeyati A L 2009 Phys. Rev. B 80 041402(R)
[5] Ossipov A, Titov M and Beenakker C W J 2007 Phys. Rev. B 75 241401(R)
[6] Linder J and Sudbo A 2007 Phys. Rev. Lett. 99 147001
[7] Tchakov G 2007 Phys. Rev. B 76 235409
[8] Cayssol J 2008 Phys. Rev. Lett. 100 147001
