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Triplet proximity effect and odd-frequency pairing in graphene

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We study the interplay between proximity-induced superconductivity and ferromagnetism in graphene by self-consistently solving the Bogoliubov de Gennes equations on the honeycomb lattice. We find that a strong triplet proximity effect is generated in graphene, leading to odd-frequency pairing correlations. These odd-frequency correlations are clearly manifested in the local density of states of the graphene sheet, which can be probed via scanning tunnel microscope measurements. Motivated by recent experiments on S|N|S graphene Josephson junctions, we also study the spectrum of Andreev bound states formed in the normal region due to the proximity effect. Our results may be useful for interpreting spectroscopic data and can also serve as a guideline for future experiments.

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I. INTRODUCTION

Graphene[1] constitutes a promising system for studying the interplay between different types of spontaneously broken internal symmetries, most notably ferromagnetism and superconductivity. The main reason for this is the unusual, relativistically invariant, low-energy electronic structure of undoped graphene. Although the intrinsic appearance of ferromagnetism and superconductivity only occurs under special circumstances in graphene (see, e.g., Refs. 2–4), they can always be induced via proximity to host materials with the desired properties. The study of how the peculiar electronic properties[5] of graphene interact with superconducting correlations has recently attracted much attention both theoretically[6–8] and experimentally.[9–11] Such studies are done by depositing two superconducting leads on graphene in order to create a graphene S|N|S Josephson junction. By also exposing the N region to a ferromagnetic host, a hybrid S|F|S junction is constructed, which then will offer an excellent platform in which to study the interplay between ferromagnetism and superconductivity. Previous work on such hybrid structures have reported on interesting effects by studying its transport properties via a scattering matrix approach.[12,13] However, this formalism does not include the full extent of the superconducting proximity effect, as it does not self-consistently solve for the superconducting order parameter inside the junction. A self-consistent solution, on the other hand, will explicitly include the Cooper pair depletion in S, and the corresponding leakage into N, near the interfaces. In addition, the scattering matrix approach neither deduces the symmetry of the induced correlations in the nonsuperconducting region nor calculate their manifestation in the local density of states (DOS). The issue of odd-frequency pairing has recently generated much activity in the field of conventional F|S junctions[14] but has not yet been addressed in the context of graphene. In particular, it remains be clarified how odd-frequency correlations[15,16] adapt to the unusual electronic environment of graphene and what their signature is in experimentally accessible quantities.

In this Rapid Communication, we present a self-consistent lattice study of the interplay between ferromagnetism and superconductivity in graphene, with focus on the behavior of the local DOS to probe this interaction. Specifically, we investigate an S|F|S junction and the concomitant manifestation of odd-frequency pairing. To make contact with the current experimental status, we also consider an S|N|S junction and identify the appearance of subgap Andreev bound states in the DOS. Our results should provide a guideline for spectroscopic measurements in graphene when superconductivity and/or ferromagnetism are induced by means of the proximity effect.

II. THEORY

We start out with the following tight-binding lattice Hamiltonian for graphene: $\mathcal{H}=-t\Sigma_{\langle \mathbf{i},\mathbf{j}\rangle,\sigma}(f^{\dagger}_{\mathbf{i}\sigma}g_{\mathbf{j}\sigma}+g^{\dagger}_{\mathbf{i}\sigma}f_{\mathbf{j}\sigma})-\Sigma_{\mathbf{i}\sigma}\mu_{\mathbf{i}\sigma}(f^{\dagger}_{\mathbf{i}\sigma}f_{\mathbf{i}\sigma}+g^{\dagger}_{\mathbf{i}\sigma}g_{\mathbf{i}\sigma})-\Sigma_{\mathbf{i}}U_{\mathbf{i}}(f^{\dagger}_{\mathbf{i}\uparrow}f_{\mathbf{i}\uparrow}f^{\dagger}_{\mathbf{i}\downarrow}f_{\mathbf{i}\downarrow}+g^{\dagger}_{\mathbf{i}\uparrow}g_{\mathbf{i}\uparrow}g^{\dagger}_{\mathbf{i}\downarrow}g_{\mathbf{i}\downarrow})$, and largely employ the notation and methods of Ref. 17. Here $f^{\dagger}_{\mathbf{i}\sigma}(g^{\dagger}_{\mathbf{i}\sigma})$ is the creation operator on the A (B) site of the honeycomb lattice, $t\sim 2.5$ eV is the nearest-neighbor hopping parameter, $\langle \mathbf{i},\mathbf{j}\rangle$ denotes summation over nearest neighbors, and σ is the spin index. Moreover, $\mu_{\mathbf{i}\sigma}=\mu_{\mathbf{i}}+\sigma h_{\mathbf{i}}$ is the spin-dependent chemical potential. We will assume that the native chemical potential $\mu_{\mathbf{i}}$ is a constant within each region of the junction (S or N/F). Experimentally, an overall chemical potential can be set in the whole sample by applying a backgate voltage. In addition, it is expected that some charge transfer takes place between graphene and the superconducting leads and, therefore, μ_{S} can sometimes be higher than $\mu_{\mathrm{N/F}}$. $h_{\mathbf{i}}$ is the site-dependent exchange field, which regulates the ferromagnetic order induced by proximity to the ferromagnetic host material. Thus, $h_{\mathbf{i}}$ is only nonzero in the region between the two superconducting leads. The last term in the above Hamiltonian models the influence of the superconducting leads on graphene. The attractive on-site interaction $U_{\mathbf{i}}$ gives rise to s-wave superconductivity and this parameter is only nonzero in the S regions of the junctions.

We perform a mean-field approximation, with the superconducting order parameter defined by

$$\Delta_{\mathbf{i}}=-U_{\mathbf{i}}[\langle f_{\mathbf{i}\downarrow}f_{\mathbf{i}\uparrow}\rangle+\langle g_{\mathbf{i}\downarrow}g_{\mathbf{i}\uparrow}\rangle]/2. \quad (1)$$

We have ignored spatial variations within one unit cell since the order parameter varies smoothly and only over much

longer length scales. Such variations can be neglected since the order parameter varies smoothly over much longer length scales. We further consider a geometry with translational invariance along the interfaces, i.e., orthogonal to the direction of the junction, and thus the effective width of our system in this direction is infinite. For concreteness, we focus on a zigzag interface and Fourier transform the eigenvectors in the y direction. Note that for an s-wave symmetry, the specific direction of the interface will not matter. By a standard procedure, we arrive at the tight-binding Bogoliubov de Gennes equations for graphene,

$$\sum_m \begin{pmatrix} \hat{H}_\uparrow(n,m) & \hat{\Delta}(n,m) \\ \hat{\Delta}^\dagger(n,m) & -\hat{H}_\downarrow(n,m) \end{pmatrix} \psi_n^\nu = E^\nu(k_y)\psi_n^\nu. \tag{2}$$

Here n is the lattice site index along the junction and $k_y = 2\pi l/(N_y a)$, where l is an integer such that $k_y \in]-\pi/a, \pi/a]$ and a is the lattice constant. Moreover, $\psi_n^\nu = [u_n^\nu(k_y), y_n^\nu(k_y), v_n^\nu(k_y), z_n^\nu(k_y)]^{\mathrm{T}}$ is generated by two copies (one for each sublattice) of the standard canonical Bogoliubov transformation. We have also introduced the following matrices: $\hat{H}_\sigma(n,m) = -(\mu_n + \sigma h_n)\delta_{nm}\hat{1} - t\delta_{nm}\hat{\sigma}_x + \zeta_{n+1,m}(\hat{\sigma}_x + i\hat{\sigma}_y) + \zeta_{n-1,m}(\hat{\sigma}_x - i\hat{\sigma}_y)$ with $\hat{\Delta}(n,m) = \Delta_n\delta_{nm}\hat{1}$ and $\zeta_{nm} = -t\delta_{nm}\cos(k_y a/2)$. For a self-consistent solution of the above equations, we first guess an initial Δ_n, then find the corresponding eigenvalues and eigenvectors to Eq. (2), followed by a recalculation of Δ_n using the self-consistency criteria in Eq. (1). This process is iterated until Δ_n no longer changes between subsequent iterations. We note in passing that for the case of a zero exchange field, Eq. (2) is particle-hole symmetric and it is then enough to solve for only the negative eigenvalues. However, this is not the case for a nonzero h, and we are therefore forced to calculate all the eigenvalues. We will fix $U/t = 1.36$ in the S regions and set $U = 0$ otherwise. This gives rise to a bulk gap of order $\Delta_0/t = 0.04$ and thus a coherence length ξ of around 25 lattice sites, which allows for simulations of junctions with $L \sim \xi$. The validity of this setup has been verified by its good agreement with previous analytical work employing parameter values closer to the experimental range.[17,18]

We are particularly interested in investigating the appearance of spin-triplet correlations in the system when the exchange field h_i is nonzero. These triplet correlations are necessarily of an unusual nature since the spatial symmetry of the superconducting order parameter is isotropic (s-wave). According to the Pauli principle, it is possible to have superconducting correlations which are both isotropic and spin-triplet simultaneously as long as these have an *odd-frequency symmetry*. The frequency dependence is obtained by Fourier transforming the relative time coordinate $(\tau - \tau')$, and it thus follows that such an odd triplet amplitude must be antisymmetric with respect to $(\tau - \tau')$. In effect, this amounts to a strong retardation effect since the correlator vanishes at equal times. The study of proximity-induced odd-frequency pairing has recently generated much interest in conventional metallic S|F systems but has not yet been explored in graphene. To investigate the presence of odd-frequency pairing, we introduce[19]

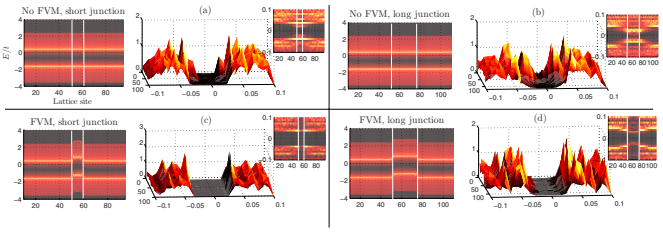

FIG. 1. (Color online) Local DOS on a large energy scale (left panel) and near the gapped region (right panels) in an S|N|S graphene junction for a variety of lengths and CPMs. Large values of the DOS are indicated by a bright color while small values are given by a dark color. We have fixed $L_S = 50$ sites and $\mu_S/t = 0.6$, as well as set the superconducting phase difference to zero, $\phi = 0$. (a) $\mu_N = \mu_S$ and $L_N = 8$ sites ($\xi \sim 25$ sites). (b) $\mu_N = \mu_S$ and $L_N = 24$ sites. (c) $\mu_N/t = 0.2$ and $L_N = 8$ sites. (d) $\mu_N/t = 0.2$ and $L_N = 24$ sites. As seen, in-gap bound states, below the gap edge, are formed and persist even in the long-junction regime. The DOS is in general not symmetric around $E = 0$ since there is a finite chemical potential in each region. Note that the value of the LDOS is determined by the height, and not the colors, in the middle three-dimensional surface plot of (a)–(d).

$$\mathcal{F}^t_{f,\mathbf{i}} = \langle f_{\mathbf{i}\uparrow}(\tau) f_{\mathbf{i}\downarrow}(0) + f_{\mathbf{i}\downarrow}(\tau) f_{\mathbf{i}\uparrow}(0) \rangle. \tag{3}$$

A similar correlation function may be written down for the g sublattice. As with the order parameter in Eq. (1), we define the effective odd-frequency correlator $\mathcal{F}^t_{\mathbf{i}}$ as the average between the expectation values on the two sublattices described by the f- and g-fermion operators, i.e., $\mathcal{F}^t_{\mathbf{i}} = (\mathcal{F}^t_{f,\mathbf{i}} + \mathcal{F}^t_{g,\mathbf{i}})/2$. We will also calculate with the local DOS $\mathcal{N}_{\mathbf{i}}(E)$, which in the low-temperature limit is obtained via the charge density ρ as follows:

$$\rho_{\mathbf{i}} = \int_{-\infty}^{0} \mathcal{N}_{\mathbf{i}}(E) dE = \sum_\sigma \langle f^\dagger_{\mathbf{i}\sigma} f_{\mathbf{i}\sigma} + g^\dagger_{\mathbf{i}\sigma} g_{\mathbf{i}\sigma} \rangle. \tag{4}$$

III. RESULTS AND DISCUSSION

In what follows, we present a numerical and self-consistent solution of the above equations. Let us first consider the S|N|S case, shown in Fig. 1. To model experimentally relevant scenarios, we consider both short and long junctions in addition to the presence or absence of a chemical-potential mismatch (CPM) at the interface. It may be instructive to start with a reminder of the analytical result for the Andreev bound-state energy inside a junction, obtainable in the ultrashort-junction regime where $L \ll \xi$, with ξ being the superconducting coherence length. This relation reads $E = \Delta_0[1 - D\sin^2(\phi/2)]^{1/2}$, where D denotes the interface transparency and ϕ the superconducting phase difference between the two leads. For $\phi = 0$, it is seen that the bound state lies right at the gap edge, irrespective of the interface transparency. As a consistency check, we have verified that we also obtain this result numerically when using a nonself-consistent step-function profile of the superconducting order parameter. Let us now turn to the self-consistent treatment in Fig. 1, where we consider four scenarios for a junction. In (a), we have no CPM (i.e., $\mu_S = \mu_N$) and a short

junction, $L_N=8$ sites to be compared with $\xi\sim 25$ sites. The superconducting regions are chosen to be large, $L_S=45$ sites so that they act as superconducting reservoirs. We find that the self-consistent solution for the order parameter only slightly shifts the bound states inside the gap. This can be understood as a consequence of the proximity-effect suppression of the order parameter near the interface. In (b), we increase the length of the normal region to $L_N=24$ sites. In this case, the bound states now reside well within the superconducting gap, in contrast to the analytical prediction for ultrashort junctions. Note that the large value of L_N ensures that these states do not pertain to some surface effect but that they penetrate into the entire N region. When turning on a CPM ($\mu_S > \mu_N$) in (c) and (d), the magnitude of the in-gap bound states in the N region is strongly reduced, due to the reduced normal-state DOS in the N region. Nonetheless, the general energy dependence is seen to be similar as in (a) and (b).

We now turn to the case where the region between the superconducting leads is ferromagnetic via a proximity to a ferromagnetic host material. The ground state of an S|F|S junction can occur for a superconducting phase difference ϕ of either 0 or π,[14] whence it becomes necessary to consider the free energy of the junction to correctly identify the ground state. In Fig. 2, we consider a short junction with $L_F=8$ sites and no CPM. Our results remain qualitatively the same also when including a moderate CPM (e.g., $\mu_F/\mu_S=0.8$). For a sufficiently low chemical potential in the F region, the DOS becomes too small to sustain any appreciable in-gap electron density, as was also seen in Fig. 1. In the experimentally relevant scenario, it is reasonable to expect that μ_F is doped away from the Dirac point to support the presence of ferromagnetism, which is precisely the case considered here. In Fig. 2(a), we show the spatial self-consistent profile of the superconducting order parameter and the generation of odd-frequency correlations in the F region (inset). The magnitude of the corresponding anomalous Green's function peaks in the middle of the ferromagnetic region, and penetrates a short distance into the S regions. We have chosen to plot the imaginary part of $\mathcal{F}^t$ since this is the quantity that directly relates to the DOS.[20] The experimental manifestation of such odd-frequency correlations have previously been discussed in conventional metals in which case one expects an enhancement of the DOS at the Fermi level.[20] In Fig. 2(b), we demonstrate that the same signature applies for graphene. Namely, a zero-energy peak emerges and it is also flanked by additional in-gap bound states. The ground state for the parameters used in Fig. 2 was numerically found to be the 0 phase.

It is well known that the superconducting phase difference ϕ can be tuned actively via an external flux or current flowing through the system. We investigate in Fig. 3 how the local DOS in a S|F|S junction changes when the length of the F region is increased ($L_F=24$ sites) and compare specifically the 0 and π phases. As seen in Fig. 3(a), the odd-frequency pairing correlations are clearly manifested for the 0 phase as a strong zero-energy peak when there is no CPM. Going to the π phase in (b), it is seen that this peak is suppressed whereas the nonzero bound states inside the gap are instead more pronounced. Upon introducing a strong CPM in (c) and

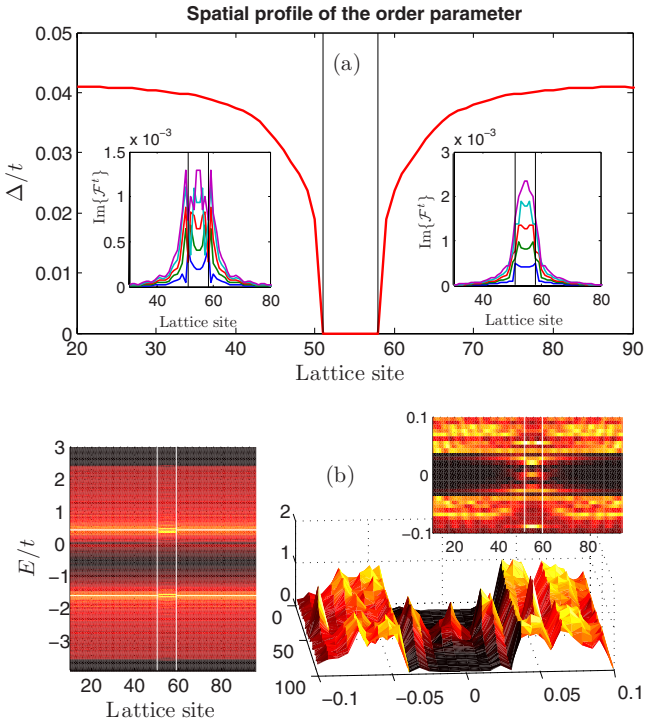

FIG. 2. (Color online) Local DOS in an S|F|S graphene junction with $L_S=50$ sites, $L_F=8$ sites, $h/t=0.05$, and $\mu_S/t=\mu_F/t=0.6$. (a) Spatial profile for the superconducting order parameter. The position of the interfaces is marked with black vertical lines. The right inset shows the imaginary part of the induced odd-frequency correlations, which from bottom to top correspond to times $t\tau=1,2,3,4,5$. The left inset shows the same thing for $h/t=0.06$ and $\mu_F/t=0.2$. (b) Local DOS on a large energy scale (left panel) and near the gapped region (right panels). Large values of the DOS are indicated by a bright color while small values are given by a dark color. In (b), the value of the LDOS is given by the height of the curve similarly to Fig. 1. As seen, odd-frequency correlations give rise to a zero-energy peak in the DOS.

(d), we see again how the magnitude of the proximity effect in the F region is severely suppressed, although some signs of the odd-frequency correlations are still visible in (c) and (d). In this case, the even-frequency correlations dominate since the DOS is mainly gapped in the low-energy region.

The presence of significant in-gap DOS in the whole F region, even for long junctions ($L_F=24$ sites), rules out the possibility of these being caused by surface states at the S|F interfaces. We have performed numerical calculations for several sets of parameters to investigate the robustness of the odd-frequency peak, and find that it in general competes with the singlet correlations which instead induce a standard minigap in the electronic spectrum inside the junction. In spite of this coexistence, these results demonstrate that the odd-frequency amplitude can be read out from spectroscopic information in a feasible parameter regime.

Compared to its conventional metallic S|F|S counterpart, the graphene system under consideration displays two distinctive features. One distinct property of graphene is the possibility to tune the local Fermi level by a local gate potential, in contrast to conventional metallic systems. In this way, one can modify the strength of the odd-frequency pair-

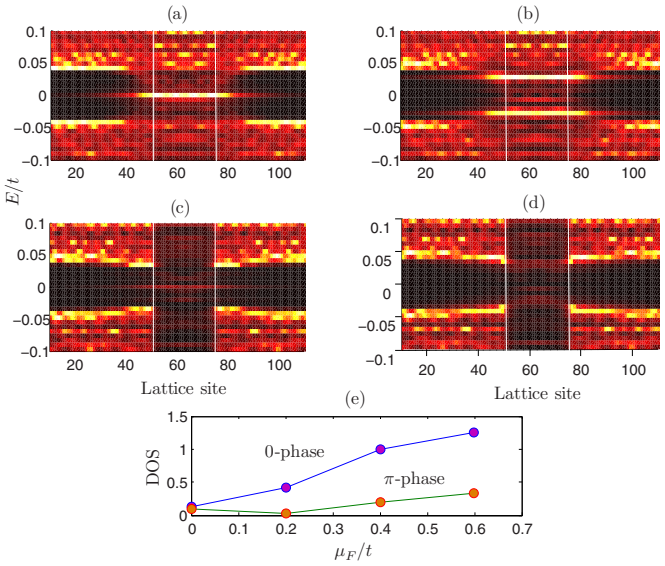

FIG. 3. (Color online) Local DOS in an S|F|S graphene junction with $L_S=50$ sites, $L_F=24$ sites, $\mu_S/t=0.6$, and $h/t=0.06$. (a) 0 phase, $\mu_F/t=0.6$. (b) π phase, $\mu_F/t=0.6$. (c) 0 phase, $\mu_F/t=0.2$. (d) π phase, $\mu_F/t=0.2$. Large values of the DOS are indicated by a bright color while small values are given by a dark color. As seen, the odd-frequency pairing amplitude is most pronounced in the 0 phase, both with and without a CPM. This is illustrated directly in (e), where the zero-energy peak value is plotted against μ_F/t.

ing amplitude induced in the normal region, both in absolute value and relative the standard even-frequency singlet amplitude, as can be inferred from Fig. 3. In fact, the magnitude of the DOS is seen to play a crucial role for the appearance of odd-frequency correlations. At low doping levels, these correlations are strongly suppressed whereas they gradually appear upon increasing the chemical potential in the ferromagnetic region. In addition, the signature of the odd-frequency state in graphene appears to be quite sensitive to whether the system is in the 0 or π phase, also shown in Fig. 3(e). This has not been reported in conventional S|F|S junctions, and thus seems to pertain specifically to graphene. A natural extension of this work would be to consider in more detail how the competition between even- and odd-frequency pairing is manifested for a variety of parameter regimes, including the 0 and π phase and intermediate length and doping regimes between the short-junction/long-junction case and heavily doped/undoped case. These issues are left for forthcoming work.

IV. SUMMARY

In summary, we have investigated in a self-consistent manner the proximity effect and its implications for the local DOS in both magnetic and nonmagnetic graphene Josephson junctions. We have considered several experimentally relevant ranges of doping levels and junction lengths. It is found that a considerable triplet proximity effect can be induced in an S|F|S graphene junction, giving rise to so-called odd-frequency correlations. These are manifested clearly as zero-energy peaks in the DOS, which may be probed by STM measurements. We have also identified the appearance of Andreev bound states in a S|N|S graphene Josephson junction. They appear as in-gap resonances in the DOS, in contrast to nonself-consistent results positioning them at the gap edge. Our results should be helpful for the interpretation of spectroscopic data and will hopefully serve as a guideline for future experimental activity.

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[1] K. S. Novoselov *et al.*, Science **306**, 666 (2004).
[2] H. Ohldag, T. Tyliszczak, R. Höhne, D. Spemann, P. Esquinazi, M. Ungureanu, and T. Butz, Phys. Rev. Lett. **98**, 187204 (2007).
[3] J. Červenka *et al.*, Nat. Phys. **5**, 840 (2009).
[4] P. Esquinazi, N. García, J. Barzola-Quiquia, P. Rödiger, K. Schindler, J.-L. Yao, and M. Ziese, Phys. Rev. B **78**, 134516 (2008).
[5] A. H. Castro Neto *et al.*, Rev. Mod. Phys. **81**, 109 (2009).
[6] C. W. J. Beenakker, Phys. Rev. Lett. **97**, 067007 (2006).
[7] M. Titov and C. W. J. Beenakker, Phys. Rev. B **74**, 041401 (2006).
[8] C. W. Beenakker, Rev. Mod. Phys. **80**, 1337 (2008).
[9] H. B. Heersche *et al.*, Nature (London) **446**, 56 (2007).
[10] X. Du, I. Skachko, and E. Y. Andrei, Phys. Rev. B **77**, 184507 (2008).
[11] C. Ojeda-Aristizabal, M. Ferrier, S. Guéron, and H. Bouchiat, Phys. Rev. B **79**, 165436 (2009).
[12] J. Linder, T. Yokoyama, D. Huertas-Hernando, and A. Sudbø, Phys. Rev. Lett. **100**, 187004 (2008).
[13] A. G. Moghaddam and M. Zareyan, Phys. Rev. B **78**, 115413 (2008); Y. Asano, T. Yoshida, Y. Tanaka, and A. A. Golubov, *ibid.* **78**, 014514 (2008).
[14] F. S. Bergeret *et al.*, Rev. Mod. Phys. **77**, 1321 (2005); A. I. Buzdin, *ibid.* **77**, 935 (2005).
[15] V. L. Berezinskii, JETP Lett. **20**, 287 (1974).
[16] A. Balatsky and E. Abrahams, Phys. Rev. B **45**, 13125 (1992); A. V. Balatsky and J. Bonca, *ibid.* **48**, 7445 (1993).
[17] A. M. Black-Schaffer and S. Doniach, Phys. Rev. B **78**, 024504 (2008); **79**, 064502 (2009).
[18] J. Linder, A. M. Black-Schaffer, T. Yokoyama, S. Doniach, and A. Sudbø, Phys. Rev. B **80**, 094522 (2009).
[19] K. Halterman, P. H. Barsic, and O. T. Valls, Phys. Rev. Lett. **99**, 127002 (2007); K. Halterman, O. T. Valls, and P. H. Barsic, Phys. Rev. B **77**, 174511 (2008).
[20] T. Yokoyama, Y. Tanaka, and A. A. Golubov, Phys. Rev. B **75**, 134510 (2007).