Intra-valley Spin-triplet $p+ip$ Superconducting Pairing in Lightly Doped Graphene

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We analyze various possible superconducting pairing states and their relative stabilities in lightly doped graphene. We show that, when inter-sublattice electron-electron attractive interaction dominates and Fermi level is close to Dirac points, the system will favor intra-valley spin-triplet $p+ip$ pairing state. Based on the novel pairing state, we further propose a scheme for doing topological quantum computation in graphene by engineering local strain fields and external magnetic fields.

PACS numbers: 74.20.-z, 73.22.Pr, 03.67.Lx

Graphene has attracted great experimental and theoretical interests since its successful fabrication.\textsuperscript{1,2} The unique electronic structure of graphene, characterized by massless relativistic particle-like dispersion near two inequivalent corner points of Brillouin zone, gives rise to exotic physical properties.\textsuperscript{3} One of interesting questions would be: how electrons could be paired in such a system? There had been many theoretical studies that explore the possibility of the superconductivity in single/multilayer graphenes.\textsuperscript{4–9} First principles calculation has suggested that superconductivity could be induced by doping alkaline adatoms.\textsuperscript{10} Recently, superconductivity has been realized in potassium-doped few-layer graphene.\textsuperscript{11}

In this Brief Report, we investigate possibility of obtaining intra-valley spin-triplet $p+ip$ superconducting state (see below) in lightly doped graphene. Unlike the spin-singlet $p+ip$ pairing state,\textsuperscript{4} the intra-valley spin-triplet $p+ip$ state may support topological excitations of Majorana fermions, and could be useful for implementing topological quantum computation. We carry out a systematic investigation on the possible superconductivity pairing states and their relative stabilities in lightly doped graphene, taking account of multiple degree of freedoms of orbit, spin and valley. We find that, when effective $e-e$ attractive interaction between the nearest neighboring sites (inter-sublattice) dominates and Fermi level is close to the Dirac points, the intra-valley spin-triplet $p+ip$ pairing state will be favored. Based upon the novel pairing state, we propose a scheme for doing quantum computation in graphene by engineering local strain fields and external magnetic fields.

We start our investigation from a simplified lattice model introduced in Ref.\textsuperscript{1} which assumes that effective

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure1.png}
\caption{Two scenarios of pairings: (a) intervalley pairing, (b) intravalley pairing. $Q_0 = (0, 4\pi/(3\sqrt{3}a))$.}
\end{figure}

\begin{equation}
H_{\text{int}} = \frac{g_0}{2} \sum_{i,s} [a_{i,s}^{\dagger} a_{i,s} a_{i-s} a_{i-s} + b_{i,s}^{\dagger} b_{i,s} b_{i-s} b_{i-s}] + g_1 \sum_{i < j, s < s'} [a_{i,s}^{\dagger} a_{i,s} b_{j,s'}^{\dagger} b_{j,s'}],
\end{equation}

where $g_0$ and $g_1$ denote the strength of onsite interaction and interaction between the nearest neighboring sites ($NN$), respectively. $a_{i,s}^{\dagger}$ ($b_{i,s}^{\dagger}$) and $a_{i,s}$ ($b_{i,s}$) are the creation and annihilation operators on the unit cell $i$ with the spin index $s = \uparrow, \downarrow$, and in the sublattice $A(B)$. $(i,j)$ denotes all pairs of NN sites.

We rewrite Eq.\textsuperscript{1} in the basis of non-interacting eigenstates: $\eta_l(k) = (1/\sqrt{2}) [1, -\exp(-i\varphi) ]^T$, where $l = 1 (-1)$ for conduction (valance) band, $\exp[i\varphi] = \gamma_k/|\gamma_k|$, $\gamma_k \equiv \sum_{\delta} e^{i\delta \cdot k}$ for $\delta_1 = a (3, \sqrt{3})/2$, $\delta_2 = a (3, -\sqrt{3})/2$, $\delta_3 = 0$, and $a$ is the C-C bond length. We obtain:

\begin{equation}
H_{\text{int}} = \frac{1}{2N} \sum_{k_1, k_2, \ldots, k_N} V^{s's'}(k_1) \delta_{k_1+k_2-k_3-k_4-K} \times c_{\bar{s}}^{\dagger}(k_1)c_{s,s'}(k_2)c_{s,s'}(k_3)c_{\bar{s}}(k_4),
\end{equation}

where $c_{\bar{s}}(k)$ and $c_{s}(k)$ are creation and annihilation operators of conduction (valance) band with wavevector $k$ and spin $s$, respectively. $N$ is the total number of unit
cells in the system, \( K \) is a reciprocal unit vector, and
the sumation of \( k_i \) is over the Brillouin zone. We assume
that inter-band contribution can be ignored, and the band index \( l \) is dropped for brevity. The interaction matrix elements have the form:

\[
V_{s's'}(k_i) = \frac{g_0}{4} \left[ 1 + e^{i\varphi_{k_i} + i\varphi_{k_{-i}} - i\varphi_{k_i} - i\varphi_{k_{-i}}} \right] \delta_{s',s} + \frac{g_1}{4} \left[ \gamma_{k_{-i} - k_i} e^{i\varphi_{k_{-i}} - i\varphi_{k_i}} + \gamma_{k_{i} - k_{-i}} e^{i\varphi_{k_i} - i\varphi_{k_{-i}}} \right].
\]  

(3)

We focus on the case of lightly doped graphene with \( k_F a \ll 1 \), where \( k_F \) is the Fermi momentum of the two Fermi pockets around the corners of the Brillouin zone at \( \pm Q_0 \), as shown in Fig. 1. We introduce valley index \( \lambda = \pm \) to denote which valley the electron is in, and the corresponding valley electron annihilation operator is defined as \( c_{\lambda \lambda_s} \equiv c_s(\Lambda Q_0 + k) \), where \( k \) is electron momentum relative to the center of the corresponding valley.

It is easy to see that there could exist two forms of superconducting pairings in graphene, i.e., inter-valley and intra-valley pairings, as shown in Fig. 1. In all the previous studies, only the inter-valley pairing, i.e., two electrons in a pair have the opposite momentums and reside at the different valleys (Fig. 1(a)), is considered. On the other hand, the intra-valley pairing, i.e., two electrons in a pair reside in the same valley, and the two valleys in the vicinity of \( \pm Q_0 \) act like two independent sub-systems (Fig. 1(b)), is also possible. To consider both possibilities, we enumerate all possible combinations of \( k_i \) in the proximity of \( Q_0 \) or \( -Q_0 \) in Eq. (3), and collect all the terms relevant to the superconducting pairings, i.e., those terms satisfying either \( k_1 + k_2 = k_3 + k_4 = 0 \) (for the inter-valley pairing) or \( k_1 + k_2 = k_3 + k_4 = \pm 2Q_0 \) (for the intra-valley pairing). The effective electron-electron interaction can then be written as,

\[
H^{\text{int}}_r \approx \frac{1}{2N} \sum_{kk'\lambda=\pm,ss'} \left[ V_{s's'}^{\text{intra}}(k,k') c_{k'\lambda s}^\dagger c_{-k'\lambda s}^\dagger c_{-k\lambda s} c_{k\lambda s} + V_{s's'}^{\text{inter}}(k,k') c_{k'\lambda s}^\dagger c_{-k'\lambda s}^\dagger c_{-k\lambda s} c_{k\lambda s} \right],
\]  

(4)

and to the first order of \(|k|a, |k'|a\), the matrix elements can be approximated as:

\[
V_{s's'}^{\text{intra}}(k,k') \approx \frac{g_0}{2} \cos(\theta_k - \theta_{k'}) e^{i\lambda(\theta_k - \theta_{k'})} \delta_{s,-s'},
\]  

(5)

\[
V_{s's'}^{\text{inter}}(k,k') \approx \frac{g_0}{2} \delta_{s,-s'} + \frac{g_1}{2} \cos(\theta_k - \theta_{k'}) c_{k\lambda s} c_{-k\lambda s} c_{k\lambda s} c_{-k\lambda s},
\]  

(6)

\[
V_{s's'}^{\text{inter}}(k,k') \approx \frac{g_0}{2} \delta_{s,-s'} + \frac{g_1}{2} \cos(\theta_k - \theta_{k'}) c_{k\lambda s} c_{-k\lambda s} c_{k\lambda s} c_{-k\lambda s},
\]  

(7)

where we have made use of approximations: \( \gamma_k \approx 3, \gamma_{\pm Q_0 + k} \approx \gamma_{\pm 2Q_0 + k} \approx 0 \), \( \exp(i\varphi_{\pm Q_0 + k}) \approx -\exp(\mp i\theta_k) \), to the first order of \( ka \), and \( \theta_k \) is the azimuth of \( k \).

We can then determine all possible pairing states and their relative stabilities. First, we consider the case \( g_0 < 0 \) and \( g_1 > 0 \). For the inter-valley pairing, we define the superconducting gap \( \Delta_1 = -(|g_0|/2N) \sum_k (c_{-k\lambda s} c_{k+\uparrow}) \), and \( \Delta_2 = -(|g_0|/2N) \sum_k (c_{-k\lambda s} c_{k-\uparrow}) \). It is easy to show that self-consistent gap equations read: \( \Delta_1 = \Delta_2 = (|g_0|/2) \sum_k \Delta \tanh(\beta E_k/2)/(2E_k) \), where \( E_k = \sqrt{(\epsilon_k - \mu)^2 + \Delta^2} \), and \( \Delta_1 = \Delta_2, \epsilon_k = \pm |k| \) is the free electron dispersion of graphene, \( \mu \) is the chemical potential of the system. The equations yield usual s-wave pairing with superconducting gap \( \Delta = \Delta_0 = 2\hbar\omega_0 \exp(-1/|g_0|N_0) \) at the zero temperature, where \( \hbar\omega_0 \) is the cut-off energy of the attractive interaction (e.g., Debye energy in the case of phonon-mediated interaction) and \( N_0 \) is the density of state per unit cell per valley at the Fermi level. We note that the pairing correlation function has even parity when exchanging the valley indices, and odd parity when exchanging the spin indexes, respectively, corresponding to a spin-singlet pairing state \((|+\rangle + |-\rangle)(|\uparrow\rangle - |\downarrow\rangle)\) or \((|+\rangle - |-\rangle)(|\uparrow\rangle + |\downarrow\rangle)\).

For the intra-valley pairing, the relevant interaction component is \( U_{kk'} = -(|g_0|/2) \cos(\theta_k - \theta_{k'}) \exp[i\lambda(\theta_k - \theta_{k'})] \) in Eq. (3). We define the superconducting gap as \( \Delta^\lambda(k) = (1/N) \sum_k U_{kk'} (c_{k\lambda s} c_{k'\lambda s}) \), and \( \lambda = \pm \). The self-consistent gap equation reads: \( \Delta^\lambda(k) = -(1/N) \sum_k U_{kk'} \Delta^\lambda(k') \tanh(\beta E_k/2)/(2E_k) \) and \( E_{kk'} = \sqrt{(\epsilon_k - \mu)^2 + |\Delta^\lambda(k)|^2} \). The equation has an s-wave solution \( \Delta^\lambda(k) = \Delta_0 \) and a \( d + i d \) solution \( \Delta^\lambda(k) = \Delta_0 \exp(2i\lambda\theta_k) \), where \( \Delta_0 = 2\hbar\omega_0 \exp(-4/3|g_1|N_0) \).

Second, we consider the case \( g_0 > 0 \) and \( g_1 < 0 \). For the inter-valley pairing, the relevant interaction component is \( U_{kk'} = -3(g_1/2) \cos(\theta_k - \theta_{k'}) \) in Eq. (3). We define the superconducting gap as \( \Delta^s(k) = -(1/N) \sum_k U_{kk'} (c_{k\lambda s} c_{-k\lambda s} c_{k'\lambda s}) \). The self-consistent gap equation reads \( \Delta^s(k) = -(1/N) \sum_k U_{kk'} \Delta^s(k') \tanh(\beta E_k/2)/(2E_k) \) and \( E_{kk'} = \sqrt{(\epsilon_k - \mu)^2 + |\Delta^s(k')|^2} \). The equation yields two stable zero temperature solutions in p-wave channel: \( \Delta^s(k) = \Delta_0 \exp(\pm i\theta_k) \) and \( \Delta_0 = 2\hbar\omega_0 \exp(-4/3|g_1|N_0) \). The pairing can be either spin singlet or triplet, with the corresponding valley states \((|\pm\rangle - |-\rangle)(|\uparrow\rangle + |\downarrow\rangle)\) or \((|\pm\rangle + |-\rangle)(|\uparrow\rangle - |\downarrow\rangle)\), respectively. 24

For the intra-valley pairing, the relevant interaction component is \( U_{kk'} = -(3g_1/2) \exp[i\lambda(\theta_k - \theta_{k'})] \) in Eq. (3). We define the superconducting gap as \( \Delta^s(k) = (1/N) \sum_k U_{kk'} (c_{k\lambda s} c_{-k\lambda s} c_{k'\lambda s}) \). The self-consistent gap equation reads \( \Delta^s(k) = -(1/N) \sum_k U_{kk'} \Delta^s(k') \tanh(\beta E_k/2)/(2E_k) \) and \( E_{kk'} = \sqrt{(\epsilon_k - \mu)^2 + |\Delta^s(k')|^2} \). The equation yields the spin triplet \( p + ip \) pairing state at zero-temperature: \( \Delta^s_p = \Delta_0 \exp(i\lambda\theta_k) \) and \( \Delta_0 = 2\hbar\omega_0 \exp(-2/3|g_1|N_0) \).
The above considerations assume that the Fermi level is close enough to the Dirac points, such that the quasi-particle dispersion has perfect rotation symmetry within each valley. However, real graphene systems only have three-fold rotation symmetry. The asymmetry, i.e., \( \epsilon_{Q+k} \neq \epsilon_{Q-k} \), becomes more pronounced when Fermi level is removed from the Dirac points, leading to pair breaking that destabilizes the intra-valley pairing. On the other hand, the inter-valley pairing is not affected because the symmetry between \( \epsilon_k \) and \( \epsilon_{-k} \) is guaranteed by time-reversal symmetry. To see symmetry effect to the intravalley pairings, we expand the tight-binding dispersion to the second order, and for the asymmetry effect to the intravalley pairings, we expand the general form of the interaction. We introduce a general model yielding extra possibility of forming inter-sublattice attractive interaction as the effective pairing strength as well as the effective pairing strength \( V_0 \) are shown. The amplitude of the zero temperature superconducting gap is related to \( V_0 \) by \( \Delta_0 = 2\hbar \omega_0 \exp(-1/N_0 V_0) \).

The discussion can be further extended to the more general form of the interaction. We introduce \( g_{ij}^{ab} \) as e-e interaction between two electrons residing in the unit cell i sublattice \( \alpha \) and the unit cell j sublattice \( \beta \) with \( \alpha, \beta \in \{A, B\} \). The Fourier transformations are \( \tilde{g}_0(q) = (1/N) \sum_{ij} g_{ij}^{ab} \exp[-i \mathbf{q} \cdot (\mathbf{R}_i - \mathbf{R}_j)] \) and \( \tilde{g}_1(q) = (1/N) \sum_{ij} g_{ij,ap} \exp[-i \mathbf{q} \cdot (\mathbf{R}_i - \mathbf{R}_j)] \), corresponding to intra-sublattice and inter-sublattice interactions, respectively. In the limit of \( k_F a \ll 1 \), only Fourier components at \( q = 0 \) and \( q = \pm Q_0 \) are relevant. Moreover, we can show that \( \tilde{g}_1(\pm 2Q_0) \) always vanishes because of Cs rotational symmetry. The interaction matrix elements in Eq. (4) are then modified to:

\[
V_{\text{intra}}^{\lambda,ss'}(k, k') \approx \frac{\tilde{g}_0(0)}{2} \cos(\theta_k - \theta_{k'}) e^{i\lambda(\theta_k - \theta_{k'})},
\]

\[
V_{\text{inter}}^{\lambda,ss'}(k, k') \approx \frac{\tilde{g}_0(0)}{2} + \frac{\tilde{g}_1(0)}{2} \cos(\theta_k - \theta_{k'}) ,
\]

\[
V_{\text{inter}}^{s,s'}(k, k') \approx \frac{\tilde{g}_0(2Q_0)}{2} .
\]  

Table I: The possible superconducting pairing states. The momentum dependence of gap function \( \Delta(k) \), the parity in exchanging the valley (‘valley’*) and spin (‘spin’) index, as well as the effective pairing strength \( V_0 \) are shown. The amplitude of the zero temperature superconducting gap is related to \( V_0 \) by \( \Delta_0 = 2\hbar \omega_0 \exp(-1/N_0 V_0) \).

| \( \Delta(k) \) | Intervalley | Intravaly (\( \mu < 2\sqrt{\hbar v/a} \)) |
|---|---|---|
| spin | \( \pm \) | \( \pm \) | \( + \) | \( + \) |
| \( V_0 \) | \( \frac{\tilde{g}_0(0)}{2} + \frac{\tilde{g}_1(0) + i\tilde{g}_0(2Q_0)}{2} \) | \( \frac{\tilde{g}_0(0)}{2} \) | \( \frac{\tilde{g}_0(0)}{2} \) | \( \frac{\tilde{g}_0(0)}{2} \) | \( \frac{\tilde{g}_0(0)}{2} \) |

The intra-valley triplet \( p + ip \) superconducting phase in lightly doped graphene, once realized, could be used to implement graphene-based topological quantum computation. This could be achieved if one could generate half quantum vortices (HQV) in the superconducting phase. Each vortex core will confine a Majorana fermion. The quantum state of a macroscopic system with a number of such vortices could be transformed by adiabatically moving them, with robustness topologically protected by their spatial separations.

For graphene, there exists a very useful and unique tool for implementing the novel quantum computing scheme, i.e., pseudo-magnetic fields generated by strains or topological defects. Using a strain field or topological defect, it is possible to create a spatially localized pseudo-magnetic flux, which is not easily achievable using a real magnetic field. One can use the pseudo-magnetic fluxes as nuclei for creating HQVs. For instance, one can

\[
\Delta(k) \quad \tilde{g}_0(0) \quad \tilde{g}_1(0) + i\tilde{g}_0(2Q_0) \quad \tilde{g}_0(0) \quad \frac{\tilde{g}_0(0)}{2} \frac{\tilde{g}_0(0)}{2} \frac{\tilde{g}_0(0)}{2} \frac{\tilde{g}_0(0)}{2} \]

\[
\Delta_0 = 2\hbar \omega_0 \exp(-1/N_0 V_0). \]

Table I: The possible superconducting pairing states. The momentum dependence of gap function \( \Delta(k) \), the parity in exchanging the valley ('valley') and spin ('spin') index, as well as the effective pairing strength \( V_0 \) are shown. The amplitude of the zero temperature superconducting gap is related to \( V_0 \) by \( \Delta_0 = 2\hbar \omega_0 \exp(-1/N_0 V_0) \).
Figure 2: Phase diagram of lightly doped graphene. For given $\tilde{g}_1(0)$ and $\tilde{g}_2(0)$, the pairing states also depend on the parameters $\tilde{g}_0(2Q_0)$ and $\mu$, and the corresponding conditions are shown for each phase.

Table 2: Phase diagram of lightly doped graphene.

| Condition | Pairing State |
|-----------|---------------|
| $\tilde{g}_0(2Q_0) > 0$ | Spin singlet s-wave |
| $\tilde{g}_0(2Q_0) < 0$ | Spin triplet s-wave |
| $\mu > 2\sqrt{\frac{\tilde{g}_2(0)}{\tilde{g}_0(0)}}$ | Intervally $p+ip$ |
| $\mu < 2\sqrt{\frac{\tilde{g}_2(0)}{\tilde{g}_0(0)}}$ | Intervally $p-ip$ |

The system has its electronic structure significantly modified, and cannot be expected to support the novel $p+iq$ phase we predict, it does give the hope that one may find other dopants that serve the purpose.

In summary, we systematically investigate the superconducting phases for lightly doped graphene. We find that an intra-valley spin triplet $p+ip$ superconducting phase could be achieved in the certain parameter regime. We further show that the novel superconducting phase could be used to implement topological quantum computation in graphene by utilizing pseudo-magnetic fluxes created by strain field or topological defects. These possibilities make graphene a promising candidate for implementing topological quantum computation.

This work is supported by MOST 973 program No. 2009CB929101.

[1] Novoselov K S, Geim A K, Morozov S V, Jiang D, Katsnelson M I, Grigorieva I V, Dubono S V and Firsov A A 2005 Nature 438 197
[2] Zhang Y B, Tan Y W, Stormer H L and Kim P 2005 Nature 438 201
[3] Castro Neto A H, Guinea F, Peres N M R, Novoselov K S and Geim A K 2009 Rev. Mod. Phys 81 109
[4] Uchoa B and Castro Neto A H 2007 Phys. Rev. Lett. 98 146801
[5] Black-Schaffer A M and Doniach S 2007 Phys.Rev. B 75 134512
[6] Honerkamp C 2008 Phys. Rev. Lett 100 146404
[7] Hosseini M V and Zareyan M 2012 Phys. Rev. Lett 108 147001
[8] Nandkishore R, Levitov L S and Chubukov A V 2012 Nature Phys 8 158
[9] Roy B and Herbut I F 2010 Phys. Rev. B 82 035429
[10] Profeta G, Calandra M and Mauri F 2012 Nature Phys 8 131
[11] Xue M, Chen G, Yang H, Zhu Y, Wang D, He J and Cao T B 2012 J. Am. Chem. Soc 134 6536
[12] Shi J R and Niu Q 2006 arXiv: 0610531[cond-mat]
[13] Mao L, Shi J R, Niu Q and Zhang C W 2011 Phys. Rev. Lett 106 157003
[14] Larkin A J and Ovchinnikov Y N 1965 Sov. Phys. JETP 20 762
[15] Fulde P, and Ferrell R A 1964 Phys. Rev. 135 A550
[16] Jang, J, Ferguson D G, Vakaryuk V, Budakian R, Chung S B, Goldbart P M, and Maeno Y 2005 Nature 438 197
[17] Ivanov D A 2001 Phys. Rev. Lett 86 268
[18] Guinea F, Katsnelson M I and Geim A K 2009 Nature Phys 6, 30
[19] Vozmediano M A H, Katsnelson M I and Guinea F 2010 Phys. Rep 496, 109
[20] Levy N, Burke S A, Meaker K L, Panlasigui M, Zettl A, Guinea F, Neto A H C and Crommie M F 2010 Science 329, 544
[21] Chung S B, Bluhm H and Kim E A 2007 Phys. Rev. Lett 99. 197002
[22] Wu X S, Li X, Song Z, Berger C and de Heer W A 2007 Phys. Rev. Lett 98. 136801
The other solutions have the form $\Delta^\lambda(k) = \sqrt{2}\Delta_0 \cos(\theta_k + \phi) \exp(i\lambda\theta_k)$, and $\Delta_0 \approx 1.72\hbar\omega_0 \exp(-4/|g_0|N_0)$. The corresponding states have the higher energy. The degeneracy between the spin singlet and triplet states will be lifted in the order of $(k_F a)^2$, in favor of the singlet state.

To minimize elastic energy, it is usually necessary to create pseudo-magnetic fluxes in pairs of opposite directions. In this case, each pair of the fluxes will create a pair of Majorana fermions residing in the different valleys, spatially separated.