I. INTRODUCTION

The graphene-based superconductors have attracted great interest in the past few years. Experimentally, superconductivity was proposed to be induced to the monolayer graphene growing on the superconducting Rhenium film [1]. Evidence of superconductivity was also observed on a Ca-intercalated bilayer graphene [2, 3], and Li-decorated monolayer graphene [4]. Recently, superconductivity was reported to be induced to the monolayer graphene by placing it on an electron-doped cuprate superconductor [2]. Quite interestingly, signatures of the $p$-wave pairing symmetry were observed through the scanning tunnelling spectroscopy investigation. Very recently, it was reported that superconductivity is realized in the twisted bilayer graphene [5], which is the first purely carbon-based two-dimensional superconductor.

On the theoretical side, the graphene was predicted to go into the superconducting state through doping or the proximity effect [6, 7]. However, the favored pairing symmetry is still unclear. Different pairing symmetries have been proposed by different groups. In particular, a $p + ip$-wave symmetry was proposed based on an extended Hubbard model [11, 12]. A $d + id$ pairing symmetry was proposed based on the renormalization group method [13, 14] or the random phase approximation [10]. It was also proposed that the triplet $f$-wave pairing might occur under some particular conditions [14, 15]. And an exotic $s$-wave pairing was proposed to be the favored pairing symmetry in the bilayer graphene [17]. Therefore, so far there is no agreement about the preferred pairing symmetry in graphene-based superconductors. Actually, theoretically the favored pairing symmetry may depend strongly on the parameters, the starting model, the pairing mechanism and the approximation considered. Since identifying the pairing symmetry is crucial to clarify microscopic details of the superconductivity, it is quite important to provide more detailed experimental information to resolve the pairing symmetry.

The impurity effect has been one powerful tool to explore the pairing symmetry of unconventional superconductors [19]. One prominent feature is the impurity induced mid-gap resonance state in the superconducting state of cuprate superconductors [19]. This feature was used to identify the $d$-wave pairing symmetry [19, 20]. In iron-based superconductors, the existence of the impurity induced in-gap states was proposed to be a signature of the sign-reversal of the $s_{\pm}$-wave pairing gap [21, 22]. So far the theoretical studies about the impurity effect in graphene-based superconductors are still rare. It is rather insightful to look into the single impurity effect of the possible superconducting state in the graphene lattice.

In the present work, motivated by the above considerations, we study theoretically the impurity effect of a superconductor in the graphene lattice. Four different pairing symmetries, i.e., the $p + ip$-wave pairing, the $d + id$-wave pairing, the extended $s$-wave pairing, and the $f$-wave pairing, are considered. For the cases of the extended $s$-wave pairing and the $f$-wave pairing symmetries, no in-gap states are obtained. For the $d + id$ pairing symmetry, the results depend on the chemical potentials. As the chemical potential is small, there exist sharp resonance peaks lying symmetric with the Fermi energy. As the chemical potential increases, the resonance peaks shift to the gap edge and disappear for large chemical potentials. For the $p + ip$ pairing symmetry, sharp in-gap peaks also exist for small chemical potentials. As the chemical potential increases, the peaks are suppressed significantly while considerably strong in-gap peaks still
exist for rather large chemical potentials. Our results indicate that the impurity effect may be useful to probe the pairing symmetry of the graphene-based superconductor.

The rest of the paper is organized as follows. In Sec. II, we introduce the model and derive the formalism. In Sec. III, we report numerical calculations and discuss the obtained results. Finally, we present a brief summary in Sec. IV.

II. MODEL AND HAMILTONIAN

For the honeycomb lattice which describes the monolayer graphene, each unit cell contains two inequivalent lattice sites. The whole system includes two sublattices $A$ and $B$. We start from a BCS-type Hamiltonian, including the nearest-neighbor hopping term, the chemical potential term, and the superconducting pairing term. Then the Hamiltonian is written as,

$$H = \sum_k \psi_k^\dagger M_k \psi_k,$$

where

$$\psi_k^\dagger = (A_{k\uparrow}^\dagger, B_{k\uparrow}^\dagger, A_{-k\downarrow}, B_{-k\downarrow}).$$

$A_{k\uparrow}$ and $B_{k\uparrow}$ are creation operators of a spin up electron on the sublattices $A$ and $B$, respectively.

$M_k$ is the $4 \times 4$ matrix in the momentum space:

$$M_k = \begin{pmatrix} -\mu & \gamma_k & 0 & -\Delta_k \\ \gamma_k^* & -\mu & \xi \Delta_{-k} & 0 \\ 0 & \xi \Delta_{-k}^* & -\mu & -\gamma_k \\ -\Delta_k & 0 & -\gamma_k^* & \mu \end{pmatrix}.$$  (3)

Here $\xi = 1$ and $-1$ are for the spin triplet pairing and the spin singlet pairing, respectively. $\gamma_k$ describes the nearest-neighbor electron hopping, with

$$\gamma_k = -t \sum_{j=1,2,3} e^{i k \cdot e_j},$$  (4)

with $e_1 = (1, 0)$, $e_2 = \frac{1}{2}(-1, \sqrt{3})$, and $e_3 = \frac{1}{2}(-1, -\sqrt{3})$. $\Delta_k$ represents the superconducting pairing. For the electron pairing of the nearest-neighbor sites, it is expressed as,

$$\Delta_k = \sum_{j=1,2,3} \Delta_j e^{i k \cdot e_j}.$$  (5)

For the extended s-wave pairing symmetry and the f-wave pairing symmetry, we have $\Delta_j = \Delta_j(1, 1, 1)$, and for the $p+i p$-wave pairing symmetry and the $d+i d$-wave pairing symmetry, we have $\Delta_j = \Delta_j(1, e^{i \frac{\pi}{3}}, e^{i \frac{2\pi}{3}})$.

We consider a single impurity being placed on the sublattice $A$ in the unit cell $(0, 0)$. The impurity Hamiltonian is written as,

$$H_{imp} = V_s (A_{(0,0)\uparrow}^\dagger A_{(0,0)\downarrow} + A_{(0,0)\downarrow}^\dagger A_{(0,0)\uparrow}).$$  (6)

Then we can define the $T$ matrix as,

$$\hat{T}(\omega) \equiv \hat{U}_0 \left( \hat{I} - \hat{U}_0 \hat{G}_0(\omega) \hat{V}_0 \right).$$  (7)

Here $\hat{I}$ is the $4 \times 4$ identity matrix. $\hat{G}_0(k, \omega)$ is the bare Green’s function in the momentum space, with $\hat{G}_0(k, \omega)_{ij} = \sum_{n=1}^{N} \frac{u_{n,i}(k) u_{n,j}^*(k)}{E_n(k) + \omega}$. $u_{n,i}(k)$ and $E_n(k)$ are obtained by diagonalizing the $4 \times 4$ Hamiltonian matrix [Eq. (3)]. The non-zero elements of the matrix $\hat{U}_0$ include $U_{01} = V_s$ and $U_{04} = -V_s$, respectively.

The local density of states (LDOS) is then expressed as,

$$\rho(r, \omega) = \frac{1}{\pi} \text{ImTr} \hat{G}(r, \omega),$$  (8)

with

$$\hat{G}(r, \omega) \equiv \hat{G}_0(0, \omega) + \hat{G}_0(r, \omega) \hat{T}(\omega) \hat{G}_0(-r, \omega).$$  (9)

The bare Green’s functions $\hat{G}_0(r, \omega)$ in the real space can be obtained by performing a Fourier transformation to the bare Green’s function in the momentum space [$\hat{G}_0(k, \omega)$].

In the results presented below, we use $1 \text{eV}$ as the energy unit. The nearest hopping constant $t$ is chosen as $2.7$. The gap magnitude is usually very small in real materials. In the present work, as usually done, we consider a much larger inputting gap to make the detailed in-gap features clear. Our main results do not change qualitatively with different gap magnitudes.

III. RESULTS AND DISCUSSION

The normal state energy bands [obtained by setting $\Delta_k = 0$ in Eq.(3)] along the high symmetric lines in the Brillouin zone are plotted in Fig. 1(a). As is seen, the top of the valence band and the bottom of the conduction band touch at the Dirac point. There are two saddle points at the energies about $\pm 2.8$, which yield the van
Hove singularities in the density of states. As the chemical potential is zero, the Fermi level is located at the Dirac points. The Fermi surface shrinks to points thus usually the superconductivity cannot occur. We add a chemical potential term (for doped graphene materials) into the system to pull the Fermi level away from the Dirac points. The Fermi surfaces of the system for different chemical potentials are shown in Fig. 1(b). As the chemical potential is small, there are six disconnected Fermi pockets. The pockets become large when the chemical potential increases. When the Fermi level is doped to near the saddle point, the Fermi pockets connect and the Fermi surface becomes a large pocket centered around the Brillouin zone center.

We now study the impurity effect for the \( p + ip \)-wave pairing symmetry. The LDOS spectra at the nearest-neighbor site of the impurity for the \( p + ip \)-wave pairing symmetry is presented in Fig. 2. Without the impurity \((V_s = 0)\), the LDOS spectra are \( V \)-shaped, indicating that the system has nodal points in the superconducting state. The most prominent feature revealed here is the existence of the in-gap resonance peaks. For the case of \( \Delta_s = 0.4 \), as presented in Fig. 2(a), two strong in-gap resonance peaks show up for a rather strong impurity strength. The in-gap peaks locate symmetric with respect to the Fermi energy, due to the particle-hole symmetry of the superconducting Hamiltonian. Note that the intensities of the superconducting coherence peaks are only about 0.05, much smaller than the impurity induced in-gap peaks. When the chemical potential increases, as is seen in Figs. 2(b-d), the intensity of the in-gap peaks decreases. For the cases of \( \mu = 0.8 \) and \( \mu = 1.8 \), the intensities of the in-gap peaks for a strong impurity \((V_s = 100)\) are still stronger than that of the coherence peaks. As the chemical potential increases to \( \mu = 2.8 \), at which the Fermi level is at the saddle point, it seems that the in-gap peaks still exist, while they are suppressed significantly and their strengths are weaker than those of coherence peaks.

Let us discuss the impurity states for the \( d + id \)-wave pairing symmetry. The corresponding LDOS spectra are presented in Fig. 3. Here \( U \)-shaped spectra are obtained for the case of \( V_s = 0 \), indicating that the system is nodeless. Moreover, here the effective gap magnitudes obtained from the positions of the superconducting coherence peaks are larger compared to those of \( p + ip \)-wave pairing symmetry even if the same inputting magnitude \( \Delta_s \) we considered. The possible in-gap states for the \( d + id \)-wave pairing are revealed in Fig. 3. For the case of \( \mu = 0.4 \), as is seen in Fig. 3(a), very strong in-gap peaks exist as the impurity strength is strong. Similar to the cases of the \( p + ip \)-wave pairing symmetry, the intensities of the in-gap peaks decreases significantly as the chemical potential increases. For the case of \( \mu = 2.8 \), as is presented in Fig. 3(d), the in-gap resonance disappears. Only some rather small in-gap peaks exist, qualitatively consistent with previous numerical calculations [23]. Obviously such small in-gap features are not resonance state, and their intensities are much smaller than that of the superconducting coherence peaks, thus it is difficult to be detected experimentally.

We turn to study the impurity effect for the extended \( s \)-wave pairing symmetry and the \( f \)-wave pairing symmetry, respectively. For both the \( s \)-wave pairing and the \( f \)-wave pairing, the effective gap magnitude becomes rather small, especially for tiny Fermi pockets when the chemical potential is small. Thus we would like to consider a larger input gap magnitude \( \Delta_s \) to obtain a large enough effective energy gap. In the following presented results, \( \Delta_s = 0.7 \) is used for the cases of \( \mu = 0.4 \) and 0.8, and \( \Delta_s = 0.4 \) for the cases of \( \mu = 1.8 \) and \( \mu = 2.8 \).

The numerical results for the impurity effect in the extended \( s \)-wave pairing are displayed in Fig. 4. Here the LDOS spectra behave \( U \)-shaped thus the system is fully gapped. As the chemical potential is small, the superconducting coherence peaks are enhanced greatly due to the impurity scattering. While when the chemical potential increases to 1.8 and 2.8, as is seen, the coherence
peaks are significantly suppressed. Note that, here for all of the parameters we considered, no in-gap resonance peaks exist, which is significantly different from the cases of the $p + ip$-wave and $d + id$-wave pairing symmetries. For the case of $\mu = 2.8$, there also exist some small peaks inside the gap, while the intensity is rather weak and is difficult to be detected. The numerical results for the cases of the $f$-wave pairing symmetry are presented in Fig. 5. Generally the numerical results are qualitatively the same with those of extended $s$-wave pairing, except that for the case of $f$-wave pairing, the system is nodal.

The impurity induced resonance peaks can be explained numerically through the denominator of the $T$-matrix, namely, its imaginary part at the low energy is usually rather small due to the existence of the superconducting gap. Then a resonance occurs when its real part approaches to zero. We have checked numerically (not presented here) that our main results can also be explained based on the above analysis. On the other hand, we here provide another sound physical picture which can account for the in-gap states of the $p + ip$-wave and $d + id$-wave pairing symmetries, through analyzing the superconducting order parameter near the Fermi surface. The superconducting gap magnitudes and their phases [from Eq.(5)] are plotted in Fig. 6. As is seen in Figs. 6(a) and 6(b), for the $p + ip$-wave and $d + id$-wave pairing symmetries, the maximum superconducting gap is just near the normal state Fermi surface pockets, indicated by pockets $1 - 6$. The phases of the superconducting gap

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**FIG. 4:** (Color online) The LDOS spectra at the nearest-neighbour site of the impurity for the extended $s$-wave pairing symmetry.

**FIG. 5:** (Color online) The LDOS spectra at the nearest-neighbour site of the impurity for the $f$-wave pairing symmetry.

**FIG. 6:** (Color online) The intensity plots of superconducting gap magnitude. The arrows indicate their phases. The solid lines are the replots of the normal state Fermi surfaces shown in Fig. 1(b).
almost keep the same in one pocket and the phases are reversed for the pockets 1/2 and 3 (or pockets 5/6 and 4). Such sign reversal behavior is similar to the cases of the iron-based superconductors. Therefore, here the physical origin of the in-gap states is the same with the case in the iron-based superconductor [21, 22], which is suggested to be caused by the Andreev reflection due to the opposite phases of the order parameters [23]. As the chemical potential increases, the Fermi surface becomes rather large and the disordered phases are induced, as a result, the in-gap resonance states are suppressed. For the case of the $s$-wave and $f$-wave pairing states, as seen in Fig. 6(c), the maximum gap is always far away from the Fermi surface, as a result, the effective superconducting gap magnitudes are much smaller. And the phases of the gap are in disorder thus no in-gap resonance peaks exist.

Finally, it would be very useful to discuss whether different pairing states can be resolved from the LDOS near a single impurity. At low doping densities, there exist strong in-gap resonance peaks induced by a strong impurity for the $p + ip$ and $d + id$ pairing symmetries, while there is no in-gap states for the extended $s$-wave and $f$-wave pairing symmetries. On the other hand, for the $s$-wave pairing and $d + id$-wave pairing the system is fully gapped which may be resolved from the LDOS spectra. These features can be used to distinguish these four pairing symmetries. For the case of heavily doped sample where the Fermi level is close to the van Hove singularities, the $p + ip$-wave pairing symmetry is different from other three ones, i.e., there exist considerably strong in-gap peaks for the case of $p + ip$-wave pairing. However, there is no significant differences for other three pairing symmetries. Especially the system is fully gapped for both $d + id$-wave pairing and the extended $s$-wave pairing. Therefore, we conclude that, at low doping densities, a single impurity with strong scattering potential can easily distinguish different pairing symmetries in graphene-based superconductors. For heavily doped sample, the impurity effect provides some useful information and the $p + ip$-wave pairing symmetry can be resolved.

**IV. SUMMARY**

In summary, we study theoretically the single impurity effect of graphene-based superconductors. Four different pairing symmetries, i.e., the $p + ip$-wave pairing, the $d + id$-wave pairing, the extended $s$-wave pairing and the $f$-wave pairing, are considered. When the chemical potential is small, the strong in-gap resonance states are revealed for the cases of the $p + ip$-wave pairing and $d + id$-wave pairing. As the chemical potential increases, the resonance states are suppressed. For the $f$-wave and the extended $s$-wave pairing symmetries, no in-gap resonance states are obtained for all of the parameters we considered. All of the features can be explained through analyzing the superconducting order parameter phase along the Fermi pockets. We conclude that the impurity effect may provide useful information to resolve different pairing symmetries in graphene-based superconductors.

*Note added:* As we almost complete our paper, we find one very recent paper discussing the impurity effect of the graphene-based superconductors [24]. Their results are basically consistent with ours.

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[1] C. Tonnoir, A. Kimouche, J. Coraux, L. Magaud, B. Desol, B. Gilles, and C. Chapellier, Phys. Rev. Lett. 111, 246805 (2013).
[2] Satoru Ichinokura, Katsuaki Sugawara, Akari Takayama, Takashi Takahashi, and Shuji Hasegawa, Acs Nano 10, 2761 (2016).
[3] Satoru Ichinokura, Katsuaki Sugawara, Akari Takayama, Takashi Takahashi, and Shuji Hasegawa, Sci. Rep. 6, 23254 (2016).
[4] B. M. Ludbrook, G. Levy, P. Nigge, M. Zonno, M. Schneider, D. J. Dvorak, C. N. Veenastra, S. Zhdanovich, D. Wong, P. Dosanjh, C. Strafter, A. Stohr, S. Forti, C. R. Ast, U. Starke, A. Damascelli, Proc. Natl. Acad. Sci. U.S.A., 112, 11795 (2015).
[5] A. Di Bernardo, O. Millo, M. Barbone, H. Alpern, Y. Kalcheim, U. Sassi, A. K. Ott, D. De Fazio, D. Yoon, M. Amado, A.C. Ferrari, J. Linder, and J. W. A. Robinson, Nat. Commun. 8, 14024 (2017).
[6] Yuan Cao, Valla Fatemi, Shiang Fang, Kenji Watanabe, Takashi Taniguchi, Efthimos Kaxiras, and Pablo Jarillo-Herrero, Nature doi:10.1038/nature26154 (2018).
[7] Bruno Uchoa and A. H. Castro Neto, Phys. Rev. Lett. 98, 146801 (2007).
[8] N. B. Kopnin and E. B. Sonin, Phys. Rev. Lett. 100, 246808 (2008).
[9] Jacob Linder, Annica M. Black-Schaffer, Takehito Yokoyama, Sebastian Doniach, and Asle Sudbo, Phys. Rev. B 80, 094522 (2009).
[10] Annica M. Black-Schaffer and Sebastian Doniach, Phys. Rev. B 81, 014517 (2010).
[11] T. Ma, F. Yang, H. Yao, and H. Q. Lin, Phys. Rev. B 90, 245114 (2014).
[12] J. P. L. Faye, P. Sahebsara, and D. Senechal, Phys. Rev. B 92, 085121 (2015).
[13] Rahul Nandkishore, L. S. Levitov and A. V. Chubukov, Nat. Phys. 8, 158 (2012).
[14] Maximilian L. Kiesel, Christian Platt, Werner Hanke, Dmitry A. Abanin, and Ronny Thomale, Phys. Rev. B 86, R020507 (2012).
[15] Rahul Nandkishore, Ronny Thomale, and Andrey V. Chubukov, Phys. Rev. B 89, 144501 (2014).
[16] Long-Yun Xiao, Shun-Li Yu, Wei Wang, Zi-Jian Yao, and Jian-Xin Li, Europhys. Lett. 115, 27008 (2016).
[17] M. V. Hosseini and M. Zareyan, Phys. Rev. Lett. 108,
147001 (2012).

[18] J. L. Lado and J. Fernandez-Rossier, 2D Mater. 3, 025001 (2016).

[19] A. V. Balatsky, I. Vekhter, and Jian-Xin Zhu, Rev. Mod. Phys. 78, 373 (2006).

[20] Chia-Ren Hu, Phys. Rev. Lett. 72, 1526 (1994).

[21] D. G. Zhang, Phys. Rev. Lett. 103, 186402 (2009).

[22] W. F. Tsai, Y. Y. Zhang, C. Fang, and J. P. Hu, Phys. Rev B 80, 064513 (2009).

[23] Tomas Lothman and Annica M. Black-Schaffer, Phys. Rev. B 90, 224504 (2014).

[24] Oladunjoye A. Awoga and Annica M. Black-Schaffer, arXiv: 1803.04455.