Tuning impurity states in bilayer graphene.

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We study the impurity states in bilayer graphene in the unitary limit using Green’s function method. Unlike in single layer graphene, the presence of impurities at two non-equivalent sites in bilayer graphene produce different impurity states which is understood as the change in the band structure due to interlayer hopping of electrons. The impurity states can also be tuned by changing the band structure of bilayer graphene through external electric field bias.

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I. INTRODUCTION

In recent years, the fabrication of few layers of graphene systems1,2,3 has attracted a lot of attention to study the electronic properties of these systems. The electrons in single graphene show some unconventional electronic properties such as the half integer quantum Hall effect, and Klein paradox. The electrons in bilayer systems also show some interesting properties as seen in quantum Hall effect. Many properties of single and bilayer graphenes also differ because of the different crystal structure. In this communication we present a systematic study of impurity effects in bilayer graphene and contrast it with those of the single layer counterpart.

The fundamental difference between single and bilayer graphenes originates from their crystal structure. Single layer graphene is an atomically thin two-dimensional hexagonal packing of sp2 bonded carbon atoms. It is the building block of (multi-layer) graphene. One unit cell of single layer graphene has two non-equivalent lattice sites (A, B). As a result, the electron wave function is pseudo-spin. The tight binding calculation shows that the electrons in single layer graphene disperse linearly, i.e., \( E_k = \pm v_F k \), where \( v_F = \frac{\hbar}{m} \) is the Fermi velocity, \( t = 3.0 \text{eV} \) is the nearest neighbor hopping energy in the plane, and \( \hbar \) is the lattice constant, and hence are called the massless Dirac fermions. The bilayer graphene, as shown schematically in Fig. 1, can be thought of as a stacking of two identical single layer graphenes in the third dimension. In one of the common ways of layer stacking, known as Bernal stacking, only one of the non-equivalent lattice sites (site-A) stay on top of each other, another site (B) lies in the middle of the hexagon of the other layer.\(^\text{4}\) The electron can hop between the layers along the bonding of these two A-sties with a hopping energy \( t_{\perp} \), which is about ten times smaller than the hopping energy along the plane. This interlayer hopping hybridizes the \( p_z \) orbital of the carbon atom at site-A resulting in different dispersion relation of the electrons, \( E_k = \pm \sqrt{\frac{v_F^2}{4} + t_{\perp}^2 k^2} \).\(^\text{5,6,7,8}\) Two of the branches of the electronic band touch each other at the Fermi energy, whereas the other two branches become gapped with energy gap equal to \( t_{\perp} \). The dispersion relation of the electrons corresponding to the gapless branches can be expressed in parabolic form at low momenta. The electron energy in this case have parabolic dispersion at low momenta. In addition to this difference of the band structure between single and bilayer graphenes, the bilayer system gives a freedom of tailoring the band structure by applying an external electric field bias \( (V) \) on the two layers. The dispersion relation in the presence of the external field bias becomes,\(^\text{8,9}\)

\[
E_k = \pm \sqrt{\frac{V^2}{4} + \frac{t_{\perp}^2}{2} k^2} \pm \sqrt{\frac{t_{\perp}^2}{4} + (V^2 + t_{\perp}^2) v_F^2 k^2},
\]

which shows that the two valence (conduction) bands shift below (above) the Fermi energy by \( V/2 \).

To understand the electronic property of these systems, it is important to study the revealing impurity effects. The impurity states in single layer graphene has been studied by Wehling et al.\(^\text{10,11}\) and by Bena.\(^\text{12}\) It has been shown that if an impurity is introduced on a lattice site, a virtually bound impurity resonance state can be induced, which can be seen as an enhancement of the local density of states (LDOS) at the neighboring site. This effect is symmetric with respect to the sublattice the impurity is on, i.e., an impurity at site B shows exactly the

FIG. 1: (Color online) Lattice structure of bilayer graphene under consideration for a tight binding calculation. The green (dashed) line forms the top layer and the red (dotted) line forms the bottom layer.
same effect as it is at site A. In bilayer graphene, due to the bonding between the sites A of the two layers, the site A and B in each layer are no longer equivalent. The interlayer hopping distinctly differentiates the two sites. So we expect to see different impurity states with respect to the location of the impurity. In addition, it is natural to expect that the external bias which changes the band structure also modifies the properties of the impurity states. This motivates us to study the impurity states in bilayer graphene as a function of both purity states. This motivates us to study the impurity states in bilayer graphene as a function of both °t⊥ and V. The impurity effect in single layer graphene is contained in Sec. IV.

The outline of the paper is as follows: In Sec. II, we present a Green’s function method to study the impurity effects. For the clean system, the results from the Green’s function method is benchmarked with the exact diagonalization. In Sec. III, we present a systematic set of results and discussions. Concluding remarks are given in Sec. IV.

II. THEORETICAL METHOD

In this section we describe the theoretical method used to calculated the LDOS in the bilayer graphene using Green’s function. We need to find the form of the Hamiltonian to define the free particle Green’s function. The Green’s function in the presence of the impurity potential is obtained by using the Dyson’s equation. We derive a tight binding Hamiltonian using the lattice structure of the bilayer graphene as shown in Fig. 1. The basis vectors are chosen to be, a1 = (3a/2, −√3a/2), and a2 = (3a/2, √3a/2). The correspond basis vectors of the reciprocal space is given by b1 = (√3/2a, 2a/√3), and b2 = (√3/2a, 2a/√3). Sites A1 and A2 are connected along the z-direction, the electrons have t⊥ hopping energy in this direction. We have assumed that the layer which has lattice sites A1, B1 is biased with V/2 and the layer which has lattice sites A2, B2 with −V/2 so that the potential difference between the two layers is V. For the convenience of discussion, these two layers are called the top and bottom layers, respectively.

The tight binding equations for this lattice structures in the clean case can be written as,

\[
\frac{V}{2} \phi_{A_1} - t[2 \exp(-\frac{ik_x a}{2}) \cos(\frac{k_y a \sqrt{3}}{2}) + \exp(i k_x a)] \phi_{B_1} - t_\perp \phi_{A_2} = E \phi_{A_1},
\]

\[
- t[2 \exp(\frac{ik_x a}{2}) \cos(\frac{k_y a \sqrt{3}}{2}) + \exp(-i k_x a)] \phi_{A_1} + \frac{V}{2} \phi_{B_1} = E \phi_{B_1},
\]

\[
- t_\perp \phi_{A_1} + \frac{V}{2} \phi_{A_2} - t[2 \exp(\frac{ik_x a}{2}) \cos(\frac{k_y a \sqrt{3}}{2}) + \exp(-i k_x a)] \phi_{B_2} = E \phi_{A_2},
\]

\[
- t \frac{V}{2} \exp(-\frac{ik_x a}{2}) \cos(\frac{k_y a \sqrt{3}}{2}) + \exp(i k_x a)] \phi_{A_2} + (\frac{V}{2}) \phi_{B_2} = E \phi_{B_2}.
\]

These equations can be written in a matrix form,

\[
\hat{H}_k \begin{pmatrix} \phi_{A_1} \\ \phi_{B_1} \\ \phi_{A_2} \\ \phi_{B_2} \end{pmatrix} = \varepsilon_n \begin{pmatrix} \phi_{A_1} \\ \phi_{B_1} \\ \phi_{A_2} \\ \phi_{B_2} \end{pmatrix}.
\]

Here,

\[
\hat{H}_k = \begin{pmatrix} V/2 & \bar{t} & -t_\perp & 0 \\ \bar{t}^* & V/2 & 0 & 0 \\ -t_\perp & 0 & -V/2 & \bar{t}^* \\ 0 & 0 & \bar{t} & -V/2 \end{pmatrix},
\]

with \(\bar{t} = -t[2 \exp(-\frac{ik_x a}{2}) \cos(\frac{k_y a \sqrt{3}}{2}) + \exp(i k_x a)]\) and \(\bar{t}^*\) is the complex conjugate of \(t\).

The Green’s function corresponding to this Hamilton-
nian can be expressed as,
\[ \hat{G}^{(0)}(\mathbf{k},\omega) = [\omega \hat{T} - \hat{H}]^{-1}, \] (5)
where \( \hat{T} \) represents the unit matrix. As long as all introduced impurities (up to 4) are located within a single cell, we can express the local Green’s function exactly through the T-matrix method, which leads to
\[ \hat{G}_{ij}(\omega) = \hat{G}^{(0)}_{ij}(\omega) + \hat{G}^{(0)}_{ik}(\omega)\hat{T}(\omega)\hat{G}^{(0)}_{kj}(\omega). \] (6)
Here the T-matrix \( \hat{T}(\omega) = \hat{U}(1 - \hat{G}^{(0)}(\omega)\hat{U})^{-1} \), the local Green’s function \( \hat{G}_{ij}(\omega) = \frac{1}{N} \sum_{\mathbf{k}} \hat{G}^{(0)}_{ij}(\mathbf{k},\omega) \) where the summation is over the first Brillouin zone, and \( \hat{U} \) is the matrix representation of the impurity potential.

The local density of states at different sites is given
\[ \text{DOS} = \sum_{\mathbf{k},\epsilon} \delta(\epsilon - \epsilon_{\mathbf{k}}) \]
where \( \epsilon_{\mathbf{k}} \) represents the four eigenvalues. Note that the linearization of Eq. (7) near the corner of the Brillouin zone reduces to Eq. (1).

The corresponding eigenvectors are given by a general equation,
\[ \begin{pmatrix} \phi_{A1,\epsilon_n} \\
\phi_{B1,\epsilon_n} \\
\phi_{A2,\epsilon_n} \\
\phi_{B2,\epsilon_n} \end{pmatrix} = \begin{pmatrix} \sqrt{\left| \frac{\omega^2}{4} + \frac{\omega^2}{2} + \tilde{\mu}^* \right|} \left( \frac{\tilde{\mu}^2 - \left( \frac{\omega}{2} + \epsilon_n \right)^2}{\tilde{\mu}^2} \right) \\
\left( \frac{\omega}{2} + \epsilon_n \right) \left( \frac{\tilde{\mu}^2 - \left( \frac{\omega}{2} + \epsilon_n \right)^2}{\tilde{\mu}^2} \right) \\
\tilde{\mu}^2 - \epsilon_n^2 \\
\frac{\gamma}{\epsilon_n} \end{pmatrix} \] (8)
where substituting four different values of \( \epsilon_n \) gives the four sets of eigenvectors. We normalize thus obtained 4 \times 4 matrix of the eigenvectors and calculate the density of states on four nonequivalent sites using the standard equation,
\[ N_{\alpha\beta}(E) = \frac{1}{N\pi} \sum_{\mathbf{k},\epsilon_n} |\phi_{\alpha\beta,\epsilon_n}(\mathbf{k})|^2 \frac{\gamma}{(E - \epsilon_n)^2 + \gamma^2}, \] (9)
where \( \alpha = A, B, \beta = 1, 2, \phi_{\alpha\beta,\epsilon_n}(\mathbf{k}) \) is the normalized eigen-vectors. We used this DOS to check the result obtained by Green’s functions method in the absence of impurity.

FIG. 2: (Color online) The density of states as a function of energy is shown. a) For \( t_\perp = 0 \) the DOS at all sites is equal, and vanishes linearly at the Fermi energy. b) For \( t_\perp = 0 \) and \( V \neq 0 \), the DOS curve for sites of the top (bottom) layer shifts above (below) the Fermi energy by \( V/2 \) creating finite DOS at the Fermi level. c) For \( t_\perp \neq 0 \) DOS at \( A \) sites of both layers is equal and for \( -t_\perp < E < t_\perp \) decreases compared to the single layer case. d) DOS at sites \( B \) of both layers is equal and for \( -t_\perp < E < t_\perp \) increases compared to the single layer case.

III. RESULTS AND DISCUSSIONS

A. Clean limit

Before getting in to the discussion of the impurity states, we first discuss the effects of \( V \) and \( t_\perp \) on the DOS in the absence of the impurity. For \( V = 0 \) and \( t_\perp = 0 \), the DOS at every sites is equal and it vanishes linearly in \( E \) close to the Fermi energy as shown in Fig. 2(a). For \( t_\perp = 0 \) but \( V \neq 0 \) the DOS in two layers is different. The overall variation of the DOS is still preserved but the DOS curve of upper (lower) layer shifts towards positive (negative) energy region by \( V/2 \). So, the minima in the DOS for upper (lower) layer lies at \( E = |V|/2 \). This results in a finite density of states at the Fermi energy. The shift in the position of the DOS minima will have nontrivial influence on impurity states as discussed below.

The difference in the DOS of single and bilayer graphene can be studied by using finite value of \( t_\perp \). In Fig. 2(c-d) we show the DOS at four sites for various values of \( t_\perp \) but fixed \( V = 0 \). The DOS at \( A_1, A_2 \) is equal and similarly DOS at \( B_1, B_2 \) is equal but those at \( A \) sites and \( B \) sites are not equal in the energy range \(-t_\perp < E < t_\perp \). In this energy range, the DOS at \( A \) sites is smaller than that at \( B \) sites. In particular, at the Fermi energy, the DOS at \( B \) sites is finite but that at \( A \) sites is zero. These effects can be understood in terms of the difference in the band structure caused by finite \( t_\perp \). The band structure corresponding to sites \( A_1 \),
and $A_2$ describe the anti-bonding states characterized by band gaps of $\pm t_{\perp}$, which results in the decreased density of states compared to that of the single layer graphene where corresponding bands are gapless. On the other hand, the band structure corresponding to the sites $B_1$ and $B_2$ is gapless at the Fermi energy and has more flat band compared to the single layer case resulting in finite density of states at the Fermi level. An interesting point is that the DOS at $B$ sites is also linear even though the dispersion relation of the electron corresponding to $B$ sites can be approximated by parabolic dispersion at low momenta.

Here, we also discuss the combined effect of bias and interlayer hoping on the DOS. In Fig. 3(a-d) we have shown the DOS at four sites for fixed $t_{\perp} = 0.1$ and different $V$. In Fig. 3(e-f) we have also shown the DOS at $A_1$ and $B_1$ for fixed $V = 0.5$ and different $t_{\perp}$. Some new features are seen in these figures. The DOS at all sites gets modified compared to the unbiased case (compare with Fig. 2(c) and (d)). There is a shift of DOS minimum to $E = \pm V/2$ compared to $V = 0$ case. There is also a gap opening up around the Fermi energy which increases with the increase in $t_{\perp}$. These unique features of band structure will lead to non-trivial impurity states.

### B. Impurity states

We now discuss a single impurity in the absence of the external bias. First we put an impurity at $A_1$ and study the DOS for various values of $t_{\perp}$. The result of the actual calculation is shown in Fig. 4 The impurity has the following effects: The DOS at the impurity site, $A_1$, decreases sharply. The DOS at site $B_1$ increases sharply which is the signature of a virtually bound impurity resonance state. The position of the resonance peak shifts slightly below the Fermi energy with the increase in $t_{\perp}$. This shift of the resonance peak is expected because the $t_{\perp}$ also affects the pole of the Greens function as determined by the band structure. The width of the resonance peak decreases with $t_{\perp}$. This is expected because increase in $t_{\perp}$ depresses the band DOS on site $A_1$, which suppresses the scattering rate from the generated impurity state. It corresponds to an increase of lifetime, signifying a sharp resonance.

The effect on the DOS at $A_2$ due to the impurity at $A_1$ is very small. The overall behavior of the DOS curve does not change as shown in Fig. 4(c). We see a finite DOS at $A_2$ at the Fermi energy which is nothing but the finite size effect, which is not seen in Fig. 2(c) because of the extended scale used to show the DOS. When we
corresponding to the site effect can be understood in terms of the band structure at dip-hump structure. Compared to the similar effect seen in the case when the impurity is at site $A_1$, there is no much change in the overall behavior of the DOS at site $A_2$ compared to the clean case, which is different from the result of the single impurity at $A_1$ case. The DOS at $A_1$ increases sharply which signifies the virtual bound state due to the impurity resonance. We notice that the height of the resonance peak at site $A_1$ decreases with the increase in $t_{\perp}$. Simultaneously, the resonance becomes more broader. This effect is just opposite to the effect seen in the case when the impurity is at site $A_1$. This effect can be understood in terms of the band structure corresponding to the site $B$. The increase in $t_{\perp}$ enhances the band DOS on site $B_1$, which increases the scattering rate from the generated impurity state. It corresponds to a decrease of lifetime, signifying a broader resonance. There is no much change in the overall behavior of the DOS at site $A_2$ compared to the no impurity case, Fig. 2(c). At site $B_2$ we see some new features, namely the dip-hump structure. Compared to the similar effect seen at $B_2$ due to impurity at site $A_1$, the structure of DOS in the present case is weaker. It is because the effect gets communicated to site $B_2$ through $A_1$ and $A_2$ which will be weaker than the previous case where the effect was communicated through only one bonding length.

Now we proceed to discuss the effect of bias on the impurity states in bilayer graphene. When there are two impurities at sites $A_1$ and $A_2$, the impurity resonance occurs at site $B_1$ and $B_2$. The DOS at $B_1$ and $B_2$ are identical. The height of the resonance peak increases with the increase in $t_{\perp}$ and the resonance becomes sharper and sharper. When there are two impurities at sites $B_1$ and $B_2$, the impurity resonance occurs at site $A_1$ and $A_2$. The DOS at $A_1$ and $A_2$ are identical. The height of the resonance peak decreases with the increase in $t_{\perp}$ and the peak width becomes broader.
at $E_g = \frac{V}{2} \left[ \frac{t_\perp}{t_\perp + V} \right]^2$. This is equal to the energy gap of the second dip in the dispersion relation of the bilayer graphene in the presence of the external bias. The edge of the band gap seen in Fig. 3 is also at $E = E_g$. Similar behavior is seen at site $B_1$. The enhancement of the DOS seen in Fig. 3(c) for $V = 0.5$ increases with $t_\perp$. The position of the peak also moves away from the Fermi energy by $E_g$. At site $B_2$ new features are seen. The height of the small satellite peak increases with $t_\perp$. The position of the peak also shifts symmetrically above and below the Fermi level by $E_g$. With the increase in $t_\perp$ a clear sign of the gap opening is seen around the Fermi energy.

When there is a single impurity at site $B_1$ (see Fig. 8), we see different features than when there is an impurity at $A_1$. At $V = 0$ there is a single impurity resonance close to the Fermi energy. When there is an external bias, the resonance peak at site $A_1$ splits in two peaks. One of the peaks lies at $E = V/2$ above the Fermi energy. Other remains close to the Fermi energy. With the increase in $V$, the intensity of the peak at $V/2$ increases and that close to the Fermi energy decreases. At site $A_2$ and $B_2$ we see impurity assisted enhanced DOS close to the Fermi energy.

To better understand the result presented in Fig. 8 we perform another calculation for LDOS at fixed $V = 0.5$ and different $t_\perp$. The result is shown in Fig. 9(a) In the Fig. 9(a) we can see that the weight of LDOS at $E = V/2$ decreases with $t_\perp$. This loss of weight is transferred close to the Fermi energy. This phenomenon can be understood in terms of the change in LDOS (at fixed $V = 0.5$ in the absence of the impurity) due to the change in $t_\perp$, (see Fig. 9(e), and 9(f)), where we see that finite $t_\perp$ opens up a gap around the Fermi energy and the gap becomes more and more well defined for increased $t_\perp$. This gap leads to a new resonance state around the Fermi energy in the presence of the impurity. The shift of the weight of the LDOS close to the Fermi energy at site $A_2$ and $B_2$, can also be understood using the same logic. We can also see in Fig. 9(f) that the LDOS at site $B_1$ at $E = V/2$ increases with the increase in $t_\perp$ which explains the broadening effect seen in Fig. 9(a) near $E = V/2$.

When we have two impurities at $A_1$ and $A_2$ we see impurity resonances at $B_1$ and $B_2$. The position of the impurity resonance is again determined by $V/2$. Interestingly, the impurity resonance at site $B_1$ lies above the Fermi energy whereas that at site $B_2$ is below the Fermi energy. The DOS at $B_1$ can be obtained by mirror reflection of the DOS at $B_2$ about the axis of $E = 0$.

When we put two impurities at $B_1$ and $B_2$ impurity resonance arises at $A_1$ and $A_2$. The position of the impurity resonance is again determined by $V/2$. The impurity resonance at site $A_1$ lies above the Fermi energy whereas that at site $A_2$ is below the Fermi energy. The DOS at
$A_1$ can be obtained by mirror reflection of the DOS at $A_2$ about the axis of $E = 0$.

IV. CONCLUDING REMARKS

Before concluding, we would like to make two comments. To our knowledge two studies have been done which resembles to our work. Wang et. al.\textsuperscript{12} have studied the effects of voids in the absence of external bias. In particular they investigated the quantum interference pattern in a specific energy and no impurity induced resonance states were discussed. Similarly, the disorder problem in biased bilayer graphene was studied by Nilsson and Castro Neto.\textsuperscript{9} In our work we have addressed the issue about the sensitivity of the impurity induced resonance states to the underlying electronic band structure in a bilayer graphene, through the application of pressure or/electric bias, which were not touched in these literatures.

In conclusion we study the possibility of tuning impurity states in a bilayer graphene. We systematically study the signature of the impurity resonance states by looking at the local density of states at four inequivalent sites of the bilayer graphene. This work should be the most detailed study of the impurity states in bilayer graphene. We have shown that in bilayer graphene the impurity states can be tuned using an external bias and changing the interlayer hopping energy. Our predictions about the evolution of the impurity states in bilayer graphene can be tested by the scanning tunnelling microscopy.

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