Energy-gap Opening and Quenching in Graphene under Periodic External Potentials

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Abstract

In this letter, we investigated the effects of periodic external potentials on properties of charge carriers in graphene using both the first-principles method based on density functional theory (DFT) and a theoretical approach based on a generalized effective spinor Hamiltonian. DFT calculations were done in a modified Kohn-Sham procedure that includes effects of the periodic external potential. Unexpected energy band gap opening and quenching were predicted for the graphene superlattice with two symmetrical sublattices and those with two unsymmetrical sublattices, respectively. Theoretical analysis based on the spinor Hamiltonian showed that the correlations between pseudospins of Dirac fermions in graphene and the applied external potential, and the potential-induced intervalley scattering, play important roles in energy-gap opening and quenching.

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Graphene has attracted great interests due to its peculiar electronic properties \cite{1,7}. Recently there has been a surge in research pertaining to properties of charge carriers in graphene under periodic external potentials. Based on the commonly used two-component effective Spinor Hamiltonian \cite{8}, periodic external potentials were found to have significant effects on behaviors of low-energy quasi-particles in graphene (i.e. the massless Dirac fermions), leading to exciting new phenomena such as anisotropic group velocities of Dirac fermions \cite{8}, emerging zero-energy states \cite{9}, new massless charge carriers \cite{10}, unusual Landau levels and quantum Hall effects \cite{11}, and the supercollimation of electron beam in graphene superlattice \cite{12}, all of which suggested a promising direction for future design of graphene-based electronic devices without the need for cutting or etching.

The linear energy dispersion of charge carriers in graphene near the Dirac points enables us to describe the behaviors of low-energy quasi-particles in the vicinity of each Dirac point using a simple two-component effective spinor Hamiltonian \cite{13,14},

\[
\mathcal{H}_0(\mathbf{k}) = \hbar v_0 \begin{pmatrix} 0 & \hat{k}_x - i\hat{k}_y \\ \hat{k}_x + i\hat{k}_y & 0 \end{pmatrix},
\]

(1)

where \(v_0\) is the Fermi velocity. The eigenstates of this spinor Hamiltonian have a degree of freedom of pseudospin, \(s \in \{\uparrow, \downarrow\}\), originating from two sublattices A and B in graphene, and can be expressed as \(|s, \mathbf{k} + \mathbf{K}\rangle\), where \(\mathbf{K}\) is the reference Dirac point. When the graphene is subject to a periodic external potential, the aforementioned commonly used effective Hamiltonian \cite{8–12} is

\[
\mathcal{H}(\mathbf{k}) = \mathcal{H}_0(\mathbf{k}) + U(\mathbf{r})\mathcal{I},
\]

(2)

where \(U(\mathbf{r})\) is the external potential, and \(\mathcal{I}\) is a \(2 \times 2\) unit matrix. This effective Hamiltonian has been widely used in various types of graphene-based superlattice structures \cite{8–12,15}. This Hamiltonian neglects the charge redistribution in graphene induced by the external potential, the interaction between the external potential and two different pseudospin channels, and the intervalley scattering between different Dirac points, all of which are assumed to be unimportant when the potential size and periodicity are big (\(~ 10 \text{ nm}\)). As the current technology makes it possible to fabricate electric gates of intermediate size in a few nanometers \cite{16}, it is therefore important to investigate all these neglected effects on properties of charge carriers in graphene superlattice, and to test their convergence for potential periodicity close to 10 nm.
In current work, two different shapes of periodic external potentials, circle and triangle (as shown in Fig. 1), were considered. Each of these applied external potentials has a 2-dimensional (2-d) \((N \times N)\) triangular periodicity. For each potential shape, we considered two possible center positions: on top or on hollow. In Fig. 1, we show two examples, a circular potential centered on top (Fig. 1a) and a triangular potential centered on hollow (Fig. 1c), each of which has a \((4 \times 4)\) superlattice periodicity. The potential size is denoted as \(R\), and the superlattice periodicity \(L\) equals to \(N \times a_0\), where \(a_0\) is the lattice constant of pristine graphene. In one supercell, the external potential is assumed to have the form \(V_{\text{ext}}(x, y) = V_0/(e^{d/\Delta} + 1)\), where \(d\) is the nearest distance between the considered point in graphene plane \((x, y)\) and the pre-defined potential edges (\(d\) is negative if the considered point is inside the potential). Throughout the paper, the smearing distance \(\Delta\) is taken to be 0.1 Å. When crossing the edges of the potential from inside to outside, \(V_{\text{ext}}\) continuously and rapidly changes from \(V_0\) to zero. Along the direction normal to the graphene plane, the external potential is assumed invariant. It is worthy noting here that for above-mentioned circular and triangular potentials, the widely used effective Hamiltonian described in Eq. 2 gives zero energy band gaps regardless of center positions, the potential size \(R\), and the periodicity \(L\).

For small systems \((L < 3\text{nm})\), first-principles calculations based on DFT are possible. In order to take into account the effects of external potential, we modified the Vienna \(ab\) \(initio\) simulation package \[17, 18\] to read in aforementioned external potential \(V_{\text{ext}}\) and add the potential to the system’s Kohn-Sham Hamiltonian. In Fig. 1b and Fig. 1d, we showed the external-potential-induced charge redistribution from DFT calculations in two graphene superlattice structures as shown in Fig. 1a and Fig. 1c, respectively. We will see later in this paper that the potential-induced charge redistribution has significant effects on properties of charge carriers in graphene. Details of DFT calculations can be found in reference \[19\].

First, we calculated electronic properties of various small graphene superlattice structures with a fixed \((4 \times 4)\) periodicity for both circular and triangular external potentials using aforementioned DFT method. In all these calculations, the potential strength \(V_0\) is fixed to 1.0 eV. The energy band gaps from DFT as functions of potential size \(R\) for different superlattice structures are shown in Fig. 2. Except for the circular potential centered on hollow position (CH in the figure) which has a zero energy gap regardless of the potential size, all superlattice structures present non-negligible energy gaps for most values of potential.
size, and show complicated behaviors of energy gap when the potential size varies, which
can not be understood by the aforementioned widely used effective Hamiltonian.

We then generalized the widely used spinor Hamiltonian to take into account previously-
neglected effects such as the charge redistribution, the pseudospin-potential correlation, and
the potential-induced intervalley scattering. Based on the generalized spinor Hamiltonian,
we showed that both the PseudoSpin-potential correlation (PS) and the Intervalley Scattering (IS) have great effects on behaviors of Dirac fermions, resulting in unexpected opening
or quenching of energy band gap in the graphene superlattice.

In order to take into account the external-potential induced intervalley scattering, we
consider the following $4 \times 4$ spinor Hamiltonian for pristine graphene [14], which is ess en-
tially the combination of two independent single-valley Hamiltonian (see Eq. 1) for two
inequivalent Dirac points, $K$ and $K'$,

$$
H_0(k) = \hbar v_0 \begin{pmatrix}
0 & -\omega (\hat{k}_x - i\hat{k}_y) & 0 & 0 \\
-\omega^*(\hat{k}_x + i\hat{k}_y) & 0 & 0 & 0 \\
0 & 0 & 0 & \hat{k}_x + i\hat{k}_y \\
0 & 0 & \hat{k}_x - i\hat{k}_y & 0
\end{pmatrix},
$$

where $\omega = e^{-2\pi i/3}$. Then, the potential-induced scattering between different pseudospin
channels and different Dirac points can be evaluated as,

$$
U_{s',s;K',K} = \langle s', K' | U(r) | s, K \rangle,
$$

where

$$
s \in \{\uparrow, \downarrow\}, \; K \in \{K, K'\}.
$$

Under the framework of the single-orbital ($2p_z$ of carbon) tight-binding approach [7], the potential-induced scattering can be worked out after some simple algebra,

$$
U_{s',s;K',K} = \delta_{s',s} \sum_{R_s} e^{-i(K' - K) \cdot R_s} \bar{\rho}_{2p_z}(r - R_s) \cdot U(r).
$$

In above equation, the summation is over the sublattice A ($R_\uparrow$) or B ($R_\downarrow$) of graphene.
$\bar{\rho}_{2p_z}(r)$ is the charge density of carbon $2p_z$ orbital averaged along $z$ direction (perpendicular to graphene), which is approximated by a 2-dimensional Gaussian function $\frac{1}{2\pi\sigma^2} e^{-|r|^2/2\sigma^2}$ with $\sigma = 0.25$ Å in this work. $\delta_{s',s}$ is present because of the neglection of pseudospin flip. Combining
we obtain the effective Hamiltonian for graphene under external potential with the pseudospin-potential correlation and the intervalley scattering,

$$\mathcal{H}_{PS-IS}(\mathbf{k}) = \mathcal{H}_0(\mathbf{k}) + c_{scf}\mathcal{U},$$

where the constant $c_{scf}$ is introduced to account for effects of self-consistent field such as potential-induced charge redistribution which is not included in the derivation of the scattering matrix. This parameter can be determined by fitting DFT results for small systems. If the fitted $c_{scf}$ is close to one, the effects of self-consistent field are not important. Otherwise, it cannot be neglected.

For a periodic external potential which has a two dimensional $(N \times N)$ periodicity with respect to the primitive cell of graphene, the intervalley scattering terms in Eq. 4 (those for $K' \neq K$) are only significant when $N$ is multiples of 3 due to the phase $e^{-i(K'-K)\mathbf{R}_s}$. Therefore, for $N$ is not multiples of 3, the effective Hamiltonian $\mathcal{H}_{PS-IS}$ reduces to

$$\mathcal{H}_{PS}(\mathbf{k}) = \hbar v_0 \begin{pmatrix} 0 & \hat{k}_x - i\hat{k}_y \\ \hat{k}_x + i\hat{k}_y & 0 \end{pmatrix} + c_{scf} \begin{pmatrix} U_\uparrow(\mathbf{r}) & 0 \\ 0 & U_\downarrow(\mathbf{r}) \end{pmatrix},$$

where $U_{s\in\{\uparrow,\downarrow\}}(\mathbf{r}) = \sum_{\mathbf{R}_s} \rho_{2p_z}(\mathbf{r} - \mathbf{R}_s) \cdot \mathcal{U}(\mathbf{r})$. In the rest of the paper, effective Hamiltonians $\mathcal{H}_{PS-IS}$ and $\mathcal{H}_{PS}$ are represented by EH-PS-IS and EH-PS respectively. These two Hamiltonians are suitable for potentials of arbitrary sizes. They can be diagonalized in the same way as diagonalizing the commonly used Hamiltonian (Eq. 2) by expanding the Hamiltonian in plane-wave basis.

For small superlattice structures with $(4 \times 4)$ periodicity, we applied the effective Hamiltonian with the pseudospin-potential correlation (EH-PS) as described in Eq. 6 and found good agreement with DFT results for all systems when setting the parameter $c_{scf}$ to 1.6 as shown in Fig. 2. The zero energy gap for the CH potential can be easily understood by the fact that in this case, the external potential interacts with two different pseudospin channels in the exactly same way, resulting in the identical $U_\uparrow$ and $U_\downarrow$ in $\mathcal{H}_{PS}$. Therefore in this case, the EH-PS is essentially the same as the conventionally used effective Hamiltonian as described in Eq. 2 which gives zero energy gap for all cases. For other potentials (CT, TT and TH in the figure), the symmetry between the up and down pseudospins is broken, leading to different $U_\uparrow$ and $U_\downarrow$ in $\mathcal{H}_{PS}$, and the energy-gap opening. The value of $c_{scf}$, 1.6, clearly shows the importance of the effects of the self-consistent field. Actually, if neglecting
these effects by setting $c_{scf} = 1$, the energy gaps are generally underestimated by EH-PS by about 50%.

We then change the potential periodicity $L$ from 1 nm to 8 nm to examine the $L$-dependence of the energy band gap. In these calculations, $V_0$ is set to 1 eV as before, and the potential size is taken to be $R = \frac{3}{4a_0}L$ for triangular potentials, and $R = \frac{1}{4}L$ for circular potentials. DFT calculations were performed for $L < 3$ nm. Results are presented in Fig. 3. For triangular potentials, regardless of center positions, the intervalley scattering has negligible effects. For small systems, the EH-PS gives good results compared to DFT, and for cases that the periodicity $N$ is multiples of 3, where EH-PS-IS is applicable, two Hamiltonians, EH-PS and EH-PS-IS, agree with each other quite well, indicating the fact that the intervalley scattering for triangular potentials are not important regardless of the system size. For circular potentials, the intervalley scattering show great effects on energy gaps, and interestingly, these effects are completely different when the center positions of potentials are different. For the case of circular potential centered on top (CT), the EH-PS tends to open significant energy gaps. When the intervalley scattering is not turned on ($N$ is not the multiples of 3), EH-PS gives good results compared to DFT for small systems. While, when $N$ is multiples of 3, the inclusion of the intervalley scattering (EH-PS-IS) greatly decreases or quenches the energy gap opened by EH-PS. For small systems, $N = 6, 9, 12$, the quenching of the energy gap due to the intervalley scattering is confirmed by DFT calculations. For the case of circular potential on hollow (CH), EH-PS predicts zero energy gap regardless of the potential size and periodicity due to the reserved symmetry between up and down pseudospins as mentioned before. While, in this case, the presence of the intervalley scattering ($N$ is multiples of 3) opens significant energy gaps as shown in the figure. The gap-opening by the intervalley scattering was verified by DFT calculations for small systems when $N = 6, 9, 12$. The energy-gap opening and quenching, as well as the convergence of the energy-gap for large potential periodicity we presented here clearly suggest that in order to correctly understand the behaviors of quasi-particles in graphene under periodic external potential, the pseudospin-potential correlation (PS) and the intervalley scattering (IS) have to be properly included in the effective Hamiltonian.

The predicted energy-gap opening and quenching in graphene superlattice are further illustrated in schematic diagrams shown in Fig. 4. In Fig. 4a, we demonstrate the gap opening due to the breaking of the symmetry between two pseudospin channels caused
by the pseudospin-potential correlation in EH-PS. In Fig. 4b, an example of the energy-gap quenching due to the intervalley scattering is shown. First, the pseudospin-potential correlation breaks the symmetry between up and down pseudospins for both Dirac points $K$ and $K'$, and then the intervalley scattering breaks the symmetry between $K$ and $K'$ for the same pseudospin, resulting in two degenerate states in the middle, one for spin up and one for spin down. This is exactly what happens in graphene under CT potential when the potential periodicity $N$ is multiple of 3. In Fig. 4c, we show the mechanism of the gap opening due to the intervalley scattering for the case of CH potential. In this case, the symmetry between two pseudospin channels are reserved in EH-PS (i.e. in Eq. 6, $U_{\uparrow}$ is identical to $U_{\downarrow}$), and the intervalley scattering breaks the symmetry between two Dirac points, leading to the gap opening.

In summary, in this paper, we investigated properties of Dirac Fermions in graphene under periodic external potential via both the first-principles method and a theoretical approach based on a generalized effective spinor Hamiltonian. The generalized effective spinor Hamiltonian takes into account the pseudospin-potential correlation and the intervalley scattering, and is suitable for systems with arbitrary potential size and periodicity. The intervalley scattering is found to be significant only when the potential periodicity $N$ is multiples of 3. Unexpected energy-gap opening and quenching in graphene superlattice due to the interplay between the pseudospin-potential correlation and the intervalley scattering are predicted. For small systems, results from the generalized effective Hamiltonian agree very well with DFT calculations, and for large systems, the proposed Hamiltonian gives qualitatively different results from the commonly used Hamiltonian in previous studies. The generalization of the effective Hamiltonian to other graphene superlattice structures with complicated boundary conditions such as antidot lattice and graphene nanoribbon-based superlattice will be done in our future work.

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Figure 1: Graphene superlattices and charge redistribution.  

a, 2D (4×4) graphene superlattice with a circular muffin-tin type of potential on the top position. 

b, The DFT charge redistribution, $\rho^V(r) - \rho^0(r)$, due to the potential in a. The red (blue) isosurface corresponds to a charge density difference of $4 \times 10^{-3}$ e/Å$^3$ ($-4 \times 10^{-3}$ e/Å$^3$). 

c, Same as a but for a triangular potential and the hollow position. 

d, Similar quantity as in b for the potential in c.
Figure 2: Variation of band gaps as a function of $R$. Band gaps were calculated using DFT and effective Hamiltonian with pseudospin-potential correlation (EH-PS) with $V_0 = 1$ eV and $L = 4a_0$. The first character of legends refer to potential shapes, with C and T standing for circle and triangle, respectively, and the second character, H or T, specifies the hollow or top position for the potential center.
Figure 3: Variation of band gaps as a function of $L (= Na_0)$. Band gaps were obtained from DFT, effective Hamiltonian with pseudospin-potential correlation (EH-PS) and effective Hamiltonian with pseudospin-potential correlation and inter-valley scattering (EH-PS-IS). The denotation for different potentials is the same as that in Fig 2. Other parameters are $V_0 = 1$ eV, $R = \frac{3}{4a_0}L$ for triangular potentials and $R = \frac{1}{4}L$ for circular potentials.
Figure 4: Schematic diagrams of band-gap opening and quenching in graphene superlattice. 

a. Due to the pseudospin-potential correlation, the symmetry between up and down pseudospin channels is broken, and a gap is open.

b. The pseudospin-potential correlation breaks pseudospin symmetry at both Dirac points, $K$ and $K'$, and the intervalley scattering mixes different states with the same spin at two Dirac points, leading to two degenerate states in the middle and the quenching of the energy-gap.

c. For the case that the symmetry between two pseudospin channels is reserved in the pseudospin-potential correlation (CH potential), the mixing of two states with the same pseudospin at $K$ and $K'$ due to the intervalley scattering results in an energy gap.