Localization of Dirac Electrons in Rotated Graphene Bilayers

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ABSTRACT For Dirac electrons the Klein paradox implies that the confinement is difficult to achieve with an electrostatic potential although it can be of great importance for graphene-based devices. Here, ab initio and tight-binding approaches are combined and show that the wave function of Dirac electrons can be localized in rotated graphene bilayers due to the Moiré pattern. This localization of wave function is maximum in the limit of the small rotation angle between the two layers.

KEYWORDS Graphene, graphite, Moiré pattern, electron localization, ab initio, tight binding

Graphene is a two-dimensional carbon material that takes the form of a planar lattice of sp² bonded atoms. Its honeycomb lattice consists in two sublattices which gives a specific property to the wave function, the so-called chirality. The linear dispersion relation close to the charge neutrality point implies that, in this energy range, the electrons obey an effective massless Dirac equation.1–3 The properties of electrons in graphene, deriving from the Dirac equation, are fundamentally different from those deriving from the Schrödinger equation. In particular the quantum Hall effect is quantized with integer plus half values4,5 and can even be observed at room temperature.6 Another example of the unique behavior of Dirac electrons is the so-called Klein paradox which is intimately related to the chirality of their wave function. The Klein paradox is the fact that, in a one-dimensional configuration, a potential barrier is perfectly transparent for electrons. As a consequence it is difficult to localize Dirac electrons with an electrostatic potential, although it can be of great interest to realize this confinement, in particular for the production of elementary devices.7,8

Therefore it is necessary to improve our knowledge of the behavior of Dirac electrons in various types of potentials. For disordered potentials specific behavior related to the chirality of Dirac electrons, such as weak antilocalization effects, have been predicted theoretically9 and observed in epitaxial graphene.10–13 Recent STM measurements, performed on epitaxial graphene, have also confirmed the absence of backscattering related to the Klein paradox.14 For periodic systems several studies have been published concerning either a simple graphene sheet in an applied periodic potential or periodic bilayers.15,16 The bilayer system17–21 has shown an unexpected and rich behavior. The well-known Bernal AB stacking leads to massive quasi-particles with quadratic dispersion close to the Dirac point. Yet it has been recognized recently in the scientific community (see for instance the recent review in ref 22) that another important case is that of rotated graphene bilayers, which are observed for example in epitaxial graphene on the C-terminated face of SiC.17

In a rotated bilayer the superposition of the two honeycomb lattices generates a Moiré pattern with a longer period. The two Dirac electron gases are then coupled by a periodic interaction, with a large supercell, which can restore a Dirac-like linear dispersion. Graphene-like Dirac cones were recently observed by angle-resolved photoemission spectroscopy (ARPES) on a sample that consists in 11 C layers on the C face of SiC.23 However fundamental issues are controversial. In particular Lopez dos Santos et al.19 conclude, from a tight-binding perturbative treatment of the interplane coupling, that the velocity can be renormalized and tend to decrease in a rotated bilayer with respect to its value in pure graphene. On the contrary Shallcross et al.20 conclude from ab initio calculations and from some general arguments that the velocity is unchanged in rotated graphene bilayers.

In this Letter we combine ab initio and tight-binding (TB) approaches. In agreement with ref 19, we conclude that there is a renormalization of the velocity for bilayers as compared to pure graphene. Our main result is that the velocity tends to zero in the limit of small twist angles which means that this type of coupling is able to confine the two Dirac electron gases. We also show that the electronic wave function tends to localize in regions of the bilayer which are locally similar to the AA arrangement. This new localization regime should be observable since angles close to a degree, for which we predict strong localization effects, are found in some rotated multilayers. Indeed recent ARPES results show the existence of many possible rotation angles —large and small.23 Furthermore, large Moiré patterns —and then
small rotation angles—have been observed on STM image of graphite multilayers on top of SiC C-face24 and also on graphene.25

Moiré Patterns and Geometry of Rotated Bilayer. Moiré patterns can be obtained in two cases: when two lattices with slightly different parameters are superimposed or when two identical lattices are rotated by an angle $\theta$.26 The rotation situation corresponds to the later case. A commensurate cell is defined when $\theta$ is equal to $\frac{n}{m}$ for any integer $n$ and $m$. The rotation angle is then defined as

$$\cos \theta = \frac{n^2 + 4nm + m^2}{2(n^2 + nm + m^2)}$$

and the commensurate cell vectors correspond to

$$\vec{t} = \vec{V} = n\vec{a}_1 + m\vec{a}_2; \quad \vec{t}' = -m\vec{a}_1 + (n + m)\vec{a}_2$$

The commensurate unit cell contains $N = 4(n^2 + nm + m^2)$ atoms. It is important to notice that $\theta \sim 0$ results in a large cell if $n$ and $m$ are large and small if $|m - n|$. Large commensurate cells can be also obtained for large angles $\theta \sim 50^\circ$, where $|m - n|$ is large.26 $\theta = 60^\circ$ is the perfect AB stacking, and $\theta$ close to $60^\circ$ is obtained for $n = 1$ ($m = 1$) and large $m$ ($n$).

For small angles, if the rotation axis, perpendicular to the planes, passes through atomic positions in both layers, atoms in the four corners of the supercell are directly superimposed (Figure 1). This corresponds to the so-called AA stacking. For cells $(n, m)$ such that $m = n + 1$, zone with Bernal AB stacking are located at $1/3$ and $2/3$ of the long diagonal (Figure 1).

Quite generally the structures that we study are fully characterized by the two index $(n, m)$ of the rotation and also by the value of the translation vector between the two layers. However for sufficiently small values of the rotation angle $\theta$, the Moiré pattern depends essentially on the rotation angle and the translation of one layer only results in a rigid shift of the overall Moiré structure. Therefore we expect and indeed observe from our results that the rotation angle $\theta$ is the main parameter that dictates the electronic structure.

Also in the small angle limit, all dimensions of the Moiré pattern scale like $1/\theta$ and in particular the size of locally AA or AB stacked regions and the distance between theses zones are proportional to $1/\theta$. Let us emphasize that the limit of small angle is discontinuous: when the rotation angle decreases the dimensions of the Moiré structure scale like $1/\theta$ and therefore the structure does not tend to that for exactly zero angle. This singular, discontinuous, geometric evolution is associated to singular electronic properties as we show in this work.

Ab Initio and Tight-Binding Calculations of Electronic Structure. Our approach combines ab initio calculations that can be used for unit cells containing up to 600 atoms and tight-binding (TB) calculations that can be used for unit cells containing up to 15000 atoms or even more. Ab initio calculations are performed with the code VASP27 and the generalized gradient approximation (GGA-PW 91).28 The C ultrasoft pseudopotential29 has been extensively tested previously.17,30 The plane wave basis cutoff is equal to 21 eV. The empty space width is equal to 21 Å, the interlayer distance is fixed to its experimental value ($\approx$3.35 Å) and no atoms are allowed to relax for direct comparison with TB calculations. For multilayers, van der Waals forces should be important, but a precise treatment of the electron correlations is unknown for such large systems. We acknowledge this fact, yet following previous work on multilayers,17−20,30 we expect that a sound physical representation of electronic band structure is given by TB and ab initio calculations. This is for example the basis of the famous band model of graphite (Slonczewski–Weiss–McClure 3D band structure) which is used to interpret many electronic and optical properties of graphite and multilayer graphene (ref 31 and references therein).

In the tight-binding scheme only $p_z$ orbitals are taken into account since we are interested in electronic states close to the Fermi level. Since the planes are rotated, neighbors are not on top of each other (as is the case in the Bernal AB stacking). Interlayer interactions are then not restricted to $pp\pi$ terms but some $pp\sigma$ terms have also to be introduced. For both terms, a parameter and a characteristic length have been fitted on AA, AB, (1,3), and (1,4) cells32 to reproduce the ab initio dispersion curves according to

$$V_{pp\pi} = -\gamma_o \exp\left[q_n\left(1 - \frac{d}{a}\right)\right]$$

FIGURE 1. Commensurate bilayer cell $(n, m) = (6, 7)$ for a rotation of $\theta = 5.08^\circ$. Full (dashed) line circle AB (AA) region.
\[ v_{pp0} = \gamma_1 \exp\left( q_{a\ell} \left( 1 - \frac{d}{a_1} \right) \right) \]  \[ \frac{q_{a\ell}}{a_1} = \frac{q_\pi}{a} \]  (4)

\[ d \] is the distance between two orbitals, \( a \) is the nearest neighbor distance within a layer, \( a = 1.42 \text{ Å} \), and \( a_1 \) is the interlayer distance, \( a_1 = 3.35 \text{ Å} \). The first neighbor interaction in a plane is taken equal to \( \gamma = 2.7 \text{ eV} \) and second neighbor interaction in a plane equal to 0.1\( \gamma \) which fixes a value of the ratio \( q_\pi \) in eqs 3 and 4. \( \gamma_1 = 0.48 \text{ eV} \) is the interlayer coupling between two orbitals in AA stacking. All \( p_\pi \) orbitals have the same on-site energy in both planes. We have chosen this on-site energy such that the energy of the Dirac point equals 0.

**Localization by Moiré Patterns.** We have performed band structure calculations on a large number of structures. For structures that could be studied by both ab initio and TB methods, the agreement is always excellent.\(^\text{32}\) In all \((n, m)\) bilayers, except the Bernal AB stacking, band dispersions \( E(k) \) around Dirac points \( K \) are linear with \( k \) for energy \( E > 0.5 \text{ meV} \). Note that the small energy range, \( E < 0.5 \text{ meV} \), is not experimentally relevant in most circumstances. For example Figure 2 presents the band structure calculated with VASP and with the TB method for \((n, m) = (6, 7)\) and therefore \( \theta = 5.08^\circ \) and \( N = 508 \). From calculated band dispersions along \( \Gamma - K \), we compute the velocity \( V \)

\[ V = \frac{1}{\hbar} \frac{\partial E}{\partial k} \]

of Dirac states around the \( K \) point. VASP and TB agree very well and show a decrease of the velocity by about 15\% in the \((6, 7)\) bilayer with respect to monolayer graphene velocity. We have checked that the velocity remains isotropic in the linear region up to a few percent. We note also that for angles within a few degrees of 0° or 60° the bands become flat and the energy range in which the bands are linear decreases (Figure 3).

As stated above the geometry of the Moiré depends essentially on the angle \( \theta \), in the limit of small \( \theta \). This reflects in the band dispersion which depends essentially on the rotation angle \( \theta \) between the two layers for all cases studied here and in particular in the small angle limit.

We performed a systematic study of the renormalization of the velocity close to the Dirac point, compared to its value in a monolayer graphene, for rotation angles \( \theta \) varying between 0° and 60° (Figure 4). The renormalization of the velocity varies symmetrically around \( \theta = 30° \). Indeed, the two limit cases \( \theta = 0° \) (AA stacking) and \( \theta = 60° \) (AB stacking) are different, but Moiré patterns when \( \theta \rightarrow 0° \) and when \( \theta \rightarrow 60° \) are similar because a simple translation by a vector transforms an AA zone to an AB zone.

Focusing on angles smaller than 30°, we define three regimes as a function of the rotation angle \( \theta \) (Figure 4). For large \( \theta (15° \leq \theta \leq 50°) \) the Fermi velocity is very close to that of graphene. For intermediate values of \( \theta (5° \leq \theta \leq 15°) \) the perturbative theory of Lopez dos Santos et al.\(^\text{19}\) predicts correctly the velocity renormalization. But for the small rotation angles \( \theta < 5° \) a new regime occurs where bands are very flat (Figure 3) and the velocity tends to zero. This remarkable localization regime cannot be described by the perturbative theory of Lopez dos Santos et al.\(^\text{19}\).

This new localization mechanism by the potential of the Moiré with very small angle leads to a strong peak in the local dispersion along \( \theta \).
The delocalized eigenstate $i$ and compute the participation ratio of each eigenstate $\langle i\rangle$. To analyze quantitatively this localization, we whereas for a larger angle no strong localization occurs density of states (local DOS) on atoms in the AA zone (Figure 5b) whereas for a larger angle no strong localization occurs (Figure 5a). To analyze quantitatively this localization, we compute the participation ratio of each eigenstate $|\psi\rangle$ defined by $p(\psi) = (N\sum_i|\langle i|\psi\rangle|^4)^{-1}$. $\langle i\rangle$ is the $p_z$ orbital on atom $i$ and $N$ is the number of atoms in a unit cell. For completely delocalized eigenstate $p = 1$, whereas state localized on 1 atom have a small $p$ value: $p = 1/N$. The $p$ value for states at K point with Dirac energy $E = 0$ is 0.80, 0.66, 0.44, 0.14, and 0.12 for (6, 7), (12, 13), (19, 20), (30, 31), and (33, 34) bilayers, respectively. For very small $\theta$ angles these states are strongly localized. Their spatial repartition shows that they are localized on the AA zones of the Moiré. This is illustrated in Figure 5b showing 80% of the weight of an eigenstate with energy very close to 0 in the (30, 31) bilayer cell ($\theta = 1.08^\circ$).

The localization regime that we predict here derives from a peculiar complex crystallographic structure in the large unit cell due to a large Moiré pattern (small rotation angle). In the literature, it is known that complex structures can localize electron states, like it is the case in approximants of quasi-crystals (ref 34 and references within). It would be interesting to check whether these localized states in rotated graphene bilayers can be observed from STS experiments. Indeed, rotated multilayer graphene with small $\theta$ is observed for $\theta \approx 1^\circ$ or even less. In these systems, the strong peak in local DOS in AA zone at Dirac energy should increase significantly the contrast between AA zone and AB zone in Moiré pattern. This new localization should also reduce considerably the mobility of the electrons and thus modify transport properties. A study of quantum transport by these states would be of great interest.

Finally, these Moiré patterns induce strong changes in the local density of states that depend on the local stacking. It should then induce strong differences in the chemical reactivity of the different superstructure regions. Rotated graphene layers could then provide new templates for the selective adsorption of atoms or clusters. This is already the case for graphene on transition metal surfaces where the lattice parameter discrepancy gives rise to a Moiré pattern that is used to self-organize arrays of metallic or magnetic clusters.

Conclusions. In summary, by combining ab initio and tight-binding calculations, we have demonstrated that the dispersion relation stays linear in rotated graphene bilayers close to the Dirac point. Yet the velocity of electrons is renormalized. This renormalization depends essentially on a single parameter which is the rotation angle $\theta$. For large $\theta$ (15° $\leq \theta \leq 30^\circ$), the Fermi velocity is very close to that of graphene. For intermediate values of $\theta$ (3° $\leq \theta \leq 15^\circ$), the perturbative theory of Lopez dos Santos et al.\textsuperscript{19} predicts correctly the velocity renormalization. But for the small rotation angles ($\theta < 3^\circ$), a new regime occurs where the velocity tends to zero. In this regime electrons with energy close to the Dirac point are localized in AA stacked regions. We believe that this localization regime should be observable since angles as small as a fraction of a degree occur in some rotated multilayers.

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