Numerical studies of confined states in rotated bilayers of graphene

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Rotated graphene multilayers form a new class of graphene related systems with electronic properties that drastically depend on the rotation angles. It has been shown that bilayers behave like two isolated graphene planes for large rotation angles. For smaller angles, states in the Dirac cones belonging to the two layers interact resulting in the appearance of two van Hove singularities. States become localized as the rotation angle decreases and the two van Hove singularities merge into one peak at the Dirac energy. Here we go further and consider bilayers with very small rotation angles. In this case, well defined regions of AA stacking exist in the bilayer supercell and we show that states are confined in these regions for energies in the $[-\gamma_t, +\gamma_t]$ range with $\gamma_t$ the interplane mean interaction. As a consequence, the local densities of states show discrete peaks for energies different from the Dirac energy.

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I. INTRODUCTION

Graphene exceptional electronic properties are predicted for an isolated layer of C atoms arranged on a pristine honeycomb lattice.2 Stacking several layers on top of each other, may affect the original electronic structure. Indeed AB or Bernal stacking (such as what is found in graphite) destroys both the linear dispersion and the chirality properties even in a bilayer.3–5 Many experimental realisations of graphene lead to the formation of multilayers (on SiC6–8 but also on metal surfaces such as Ni9–11 and in exfoliated flakes12) where interactions between successive layers play a crucial role. While on the Si face of SiC, multilayers have an AB stacking and do not show graphene properties on the C-face, multilayers have been shown to present graphene like properties even when they involve a large number of C planes. ARPES12–14 STM15 transport16 and optical transitions17 indeed show properties characteristic of a linear graphene like dispersion. These multilayers are rotated with respect to each other and the rotations show up as moiré patterns on STM images.14,20,21 This apparent controversy - thick multilayers exhibiting graphene properties - was partially solved recently when different theoretical approaches14,22–31 showed that rotated multilayers are decoupled, at least for large rotation angles. Going further, theory predicts the existence of three domains that in fact correspond to two regimes: for large rotation angles, $\theta > 15^\circ$, the layers are decoupled and behave as a collection of isolated graphene layers. For intermediate angles, $2^\circ < \theta < 15^\circ$, the dispersion remains linear but the velocity is renormalised. For these large and intermediate angles, Dirac cones persist and the interaction between rotated layers is a perturbation. What happens at the smallest values of $\theta$ is more puzzling. As already shown by different theoretical groups, for the lowest $\theta$, flat bands appear and result in electronic localization.

From the experimental point of view, while some experiments with graphene on SiC show none of the effects predicted by theory (no renormalisation nor van Hove singularities)15 others16 do find them. Furthermore, Landau Level (LL) Scanning Tunneling Spectroscopy (STS) gave results in close agreement with theory and the three domains were observed for CVD graphene grown on Ni.15

Here we go further and show that in the very small angle regime, confinement occurs and states become confined in the AA (all atoms on top of each other) region. Furthermore, confinement effects lead to the formation of sharp peaks in the local density of states in an energy window that is fixed by the interplane mean interaction. Thus, this apparently simple system -a graphene bilayer- presents a complex behavior ranging from ballistic to confined electrons when the rotation angle is changed.

Tackling very small rotation angles - smaller than 1° - means handling very large cells that involve a huge number of atoms - more than 60 000 -. This cannot be done from ab initio calculations and we developed a tight binding scheme31 using only $p_z$ orbitals to do so. Rotated multilayers are described in part II, the method used is outlined in the third part and described in more details in the Appendix A. Part IV gives the variation of the van Hove singularity position with the rotation angle and parts V and VI describes the electronic structure of graphene rotated bilayers in the case of very small rotations angles.

II. ROTATIONALY STACKED COMMENSURATE BILAYERS

In the following we consider two graphene layers rotated in the plane by an angle $\theta$. We start from an AA bilayer and choose the rotation origin O at an atomic site. Since we want to perform ab initio and Tight Binding cal-
calculations, we need a periodic system. A commensurate structure can be defined if the rotation changes a lattice vector \( \overrightarrow{OB} \) \((m, n)\) to \( \overrightarrow{OB'} (n, m)\) with \(n, m\) the coordinates with respect to the basis vectors \( \vec{a}_1 (\sqrt{3}/2, -1/2) \) and \( \vec{a}_2 (\sqrt{3}/2, 1/2) \). The rotation angle is then defined as follows:

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

and the commensurate cell vectors correspond to :

\[
\vec{t} = \overrightarrow{OB'} = n\vec{a}_1 + m\vec{a}_2, \quad \vec{t}' = -m\vec{a}_1 + (n + m)\vec{a}_2.
\]

The commensurate unit cell contains \( N = 4(n^2 + nm + m^2) \) atoms. As we have already shown, the rotation angle is a good parameter to describe the system but the number of atoms is not since cells of equivalent size can be found for different angles. Indeed, large cells can be obtained for \( \theta \sim 0 \) - large \( n \) and \( m \) and small \( |m - n| \) - but also for large angles \( \theta \sim 30^\circ \) - then \( |m - n| \) is large.

A good way to name the rotated layers is to give the \((n, m)\) couple defined above, which is what we use in the present paper. \( \theta = 60^\circ \) is the perfect AB stacking. \( \theta \) close to \( 60^\circ \) is obtained for \( n = 1 \) \((m = 1)\) and large \( m \) \((n)\), it is equivalent in our calculations to \( \theta \sim 0^\circ \).

### III. METHODS

Our approach combines ab initio and tight binding calculations. First principle approach can tackle cells with up to \( \sim 1000 \) atoms. The tight-binding (TB) scheme allows electronic structure calculations by diagonalisation in reciprocal space for crystal structures containing up to \( 59\,644 \) atoms in a unit cell - corresponding to \( \theta = 0.469^\circ \) and the \((70, 71)\) bilayer -. By the using recursion technique in real space, very large structures up to several millions - \( 3\,006\,004 \) for the \((500, 501)\) with \( \theta = 0.067^\circ \) - of atoms are studied. The tight binding scheme is described in Ref. \[31\] and in the Appendix; it is restricted to \( p_z \) orbitals. It was developed from ab initio calculations and it gives a good description of the rotated bilayers, for small angles as well as large ones but also for trilayers, graphene and graphite. The TB parameters were fitted to reproduce the velocity of monolayer graphene and the interlayer mean interaction \( \gamma_1 = 0.34 \) eV (see Appendix). Flat layers were used. We performed an ab initio calculation for the \((6, 7)\) bilayer allowing all the atoms to relax and found only minor changes: the layer corrugation is small and the effect on the band structure is very small. Velocities are calculated from the slope of the dispersions at the Dirac point along \( \Gamma K \).

### IV. VAN HOVE SINGULARITIES

The rotated bilayer has already been the subject of many theoretical developments either analytical or numerical.\[14,22–31\] The main results are only briefly recalled in the following since we want to focus on the very small rotation case and the confinement effect that results. These theoretical predictions are in very good agreement with Scanning Tunneling Spectroscopy experiments on CVD graphene grown on nickel.\[15\] Properties are symmetric with respect to \( \theta \sim 30^\circ \). In our calculations, the behavior is the same for angles decreasing to \( 0^\circ \) or increasing to \( 60^\circ \).

For large angles, \( \theta > 15^\circ \), the rotated bilayer behaves like two isolated graphene layers. For intermediate angles, \( 2^\circ < \theta < 15^\circ \), the dispersion remains linear but the velocity is strongly renormalised. In this regime, one important feature is the appearance of van Hove singularities on both sides of the Dirac energy. In the following, we consider that layer 2 is rotated by an angle \( \theta \) with respect to layer 1. Layer 2 Brillouin zone is then rotated by the same \( \theta \) with respect to layer 1 Brillouin zone. The closest Dirac cones belonging to layer 1 and 2 intersect at a point \( P \) which is at mid-distance between the \( K_1 \) and \( K_2 \) points of the \( 1 \times 1 \) Brillouin zones (see Fig. \[iv\]). \( P \) is backfolded to point \( M \) of the supercell Brillouin zone. Interaction of the states with similar energies opens two gaps at the saddle point \( M \) (Fig. \[iv\]). Flat bands have a drastic effect on the electronic structure of a two-dimensional system and appear as van Hove singularities on each side of the Dirac energy (Fig. \[iv\]). In fact, each gap creates two van Hove singularities. Singularities closest to the Dirac point appear as peaks \( E_+ \) and \( E_- \) in Fig. \[iv\], they are followed by a dip and a sharp
to smaller angles and confirmed the localisation of the states in the AA regions of the moiré pattern.

V. CONFINEMENT IN AA REGIONS

It is interesting to look at the band structures of bilayers with small angles—small enough to have van Hove singularities at the limit of the linear variation (Fig. 4). The (19,20) bilayer is at the edge of the linear regime: the band structure still shows a linear dispersion and van Hove singularities. For the (31,32) bilayer, bands are flat and velocity is equal to zero but in the case of the (45,46) bilayer, the peak at $E_D$ is split in two and the velocity at the Dirac point increases again and is equal to $\pm20\%$ of the graphene velocity. This is coherent with the increase of velocity between magic angles found by Bistritzer and MacDonald (section VI).

It is important to notice that near the Dirac point one observes the existence of two bands that disperse linearly. These bands have a twofold degeneracy (Dirac cones from the two layers). The 4 bands contributes to the central peak of the total density of states. The weight of the eigenstates close to the Dirac energy is strong in the AA zone as shown by diagonalization.

The analysis of the density of states, shows that a specific regime occurs for very small angles, typically $\theta \leq 1^\circ$. The total DOS (Fig. 5b) contains sharp peaks at energies different from the Dirac energy. Figs. 5b and 5c show the local DOS at the center of an AA stacked zone for decreasing $\theta$, and Fig. 5d the local DOS at the center of an AB stacked zone.

For so small rotation angles, the moiré pattern presents well defined regions of AA and AB stacking. In the center of these regions, the local DOS follows the AA or AB DOS (dotted lines in Figs. 5b, c and d), except for energies close to the Dirac energy. Indeed according to Fig. 5 peaks appear in an energy window defined by the mean interplane interaction $\gamma$. DOS in intermediate regions (not shown) are very similar to DOS in AB regions and do not show large peak.

These results are consistent with confinement effect that can explain the discrete character of the spectrum in the $\left[-\gamma, +\gamma\right]$ range. Indeed, in large moiré patterns, AA regions seem isolated by AB and intermediate regions. From Fig. 5d, we can say that confinement in AB regions is much less efficient than in AA regions. In a nanostructure, confinement results in peak in the DOS whose position depends on the size of the nanostructure. Here the size of the AA region is inversely proportional to the rotation angle $\theta$. In Fig. 6 we plot the energy of the first peak away from the Dirac energy as a function of $\theta$. As expected this energy decreases when the size of the AA region increases, which is when the angle $\theta$ decreases.

In the energy range $\left[-\gamma, +\gamma\right]$, the symmetry of the wavefunction is different in an AA or AB bilayer (Fig. 4). Interestingly, the DOS at the center of the AA regions increase linearly with the mean interplane interaction $\gamma$. DOS in intermediate regions (not shown) are very similar to DOS in AB regions and do not show large peak.

As shown in our previous article this sharp peak corresponds to states strongly localised in AA stacking regions of the moiré. Recently Lopes Dos Santos et al. extended their treatment based on the continuum model
the different symmetry of the wavefunctions, matching is difficult which could explain that the AA stacked region is isolated. We note also that in this energy range the coupling between electrons and holes which have opposite velocities could favor localization. On the contrary out of the energy range $[-\gamma_t, +\gamma_t]$, the mixing between the hole states of one plane and the electron states of the other plane is weak. Indeed the coupling occurs between electron states of one plane and hole states of the other plane that have the same wave vector but have a difference in energy that is much larger than $\gamma_t$. Therefore outside of the energy range $[-\gamma_t, +\gamma_t]$ the mixing of states of the two planes occurs separately between the electron states of the two planes and between the hole states of the two planes. We suggest that this absence of mixing between electrons and holes which have opposite velocities suppresses the localization.

FIG. 5: (color on line) TB DOS in bilayers: (a) Total DOS. Local DOS: (b) (c) on atom at the center of an AA zone, (d) on atom at the center of an AB zone (At. A: with an atom directly on top or below and at. B: without an atom on top or below). (n,m) bilayers: values (100,101) $\theta = 0.33^\circ$, (200,201) $\theta = 0.16^\circ$ and (300,301) $\theta = 0.11^\circ$. (400,401) $\theta = 0.08^\circ$.

VI. MAGIC ANGLES

As discussed previously, at very small angles, the velocity of rotated bilayers is no longer monotonic but shows minima and maxima (Fig. 8). Minima correspond to a flat band with zero velocity at the Dirac energy. Bistritzer and MacDonald in Ref. 29 found that the velocity is equal to zero for special magic angles $\theta_n$. The
values in degrees are $\theta_1 = 1.05$, $\theta_2 = 0.5$, $\theta_3 = 0.35$, $\theta_4 = 0.24$, $\theta_5 = 0.2$. We note that this series is simply given by $\theta_n = 1.05/n$. In the present calculations we recover by a full tight-binding calculation the first two angles $n = 1$ and $n = 2$ (see Fig.8) which are given by $\theta_n = 1.13/n$ in good accordance with the more simplified model\textsuperscript{36} of Ref.\textsuperscript{29}.

Below we propose a simple heuristic argument which relates these magic angles to quantization conditions. At these magic angles the bands become flat which means that the states of the different AA zones are decoupled and thus confined in the AA zones. In the following, we use a hard wall model to describe the confinement effect. The confinement condition is typically:

$$kd + 2\Phi = 2n\pi,$$

where $k$ is the wavevector counted from the K point of the Dirac wave in the AA zone, $d$ is the typical size of the AA zone and $\Phi$ is the phase accumulated at the reflexion at the boundary of the AA zone. We assume that this phase can be integrated in an efficient size of the AA zone so that the quantization condition finally gives:

$$xkD = 2n\pi,$$

where $D$ is the period of the moiré and $x$ is a numerical coefficient of the order of 1 such that $xD/2$ is the effective size of the AA zone. This expression can be cast in terms of the parameters of the present study. Indeed the period $D$ of the moiré expressed in nanometers and the angle $\theta$ of the rotation expressed in degrees are related by $D(\text{nm}) = \frac{22}{\theta(\text{deg})}$ for small angles. In addition, we have the relation $h\nu_F k = \gamma t$ between the parameter $\gamma t$ and the wavevector $k$ at the Dirac energy in the AA zone. Then the quantization relation leads to:

$$\frac{3.4x\gamma t(\text{eV})}{n} \sim \theta(\text{deg}).$$

For the present value of the parameter $\gamma t = 0.34$ eV and with a reasonable value of the parameter $x \sim 0.95$ this relation leads exactly to the magic angles $\theta(\text{deg}) = 1.13/n$ found here. This value is close to the series $1.05/n$ found in Ref.\textsuperscript{29}.

Why the simple hardwall argument discussed here can describe the magic angles series is not obvious. Indeed Bistritzer and MacDonald\textsuperscript{29} used an interplane interaction hamiltonian with a sinusoidal variation in space. For free electrons a sinusoidal interaction potential would probably not lead to the localization with hard wall conditions. Yet as discussed above, the localization in the energy range $[-\gamma t, +\gamma t]$ that is found in this work suggest that the spinor character of the electronic wavefunction in graphene leads to more complex localization phenomena.
VII. CONCLUSION

Thanks to the tight binding scheme that we developed, we studied the electronic structure of rotated bilayers in the case of very small rotation angles, which is beyond what was recently proposed. We showed that states are confined in regions of well defined AA stacking and as a consequence that the LDOS shows discrete peaks not only at the Dirac energy but in the $[-\gamma_t, +\gamma_t]$ range with $\gamma_t$ the mean interlayer hopping integral. Very large moiré patterns (corresponding to angles close to $1^\circ$) have already been observed experimentally. This system could then offer the possibility to study the physics of a regular array of weakly interacting dots. To conclude we note that the rotated bilayers of graphene present analogies with quasicrystals and approximant crystals that have also large unit cells and tend to confine electrons (Ref. 37 and references within). In the context of quasicrystals this localization by large unit cells leads to unique transport properties.

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Appendix A: Tight Binding scheme for bilayers

In this appendix we present in details the tight binding (TB) scheme that we have used in our previous work and in the present results. It reproduces the \textit{ab initio} calculations of the electronic states for energies within $\pm 2$ eV of $E_D$ whatever the rotation angle is (Fig. 9 and Ref. 31). Here $E_D$ is set to zero.

Only $p_z$ orbitals are taken into account since we are interested in what happens at the Fermi level. Since the planes are rotated, neighbours are not on top of each other (as it is the case in the Bernal AB stacking). Interlayer interactions are then not restricted to $pp\sigma$ terms but some $pp\pi$ terms have also to be introduced. The Hamiltonian has the form :

$$H = \sum_i \epsilon_i |i\rangle\langle i| + \sum_{i,j} t_{ij} |i\rangle\langle j|,$$

where $|i\rangle$ is the $p_z$ orbital located at $\vec{r}_i$, and $(i,j)$ is the sum on index $i$ and $j$ with $i \neq j$. The coupling matrix
element, \( t_{ij} \), between two \( p_z \) orbitals located at \( \vec{r}_i \) and \( \vec{r}_j \) is given by:

\[
t_{ij} = n^2 V_{p\sigma}(r_{ij}) + (1 - n^2) V_{p\pi}(r_{ij}),
\]

where \( n \) is the direction cosine of \( \vec{r}_{ij} = \vec{r}_j - \vec{r}_i \) along \((Oz)\) axis and \( r_{ij} \) the distance \( r_{ij} \) between the orbitals,

\[
n = \frac{z_{ij}}{r_{ij}} \quad \text{and} \quad r_{ij} = |r_{ij}|.
\]

\( z_{ij} \) is the coordinate of \( \vec{r}_{ij} \) along \((Oz)\). It is either equal to zero or to a constant because the two graphene layers have been kept flat in our model.\(^{41}\) We use the same following dependence on distance of the Slater and Koster parameters:

\[
V_{p\pi}(r_{ij}) = -\gamma_0 e^{\sigma c (1 - \frac{r_{ij}}{a_0})} F_c(r_{ij}),
\]

\[
V_{p\sigma}(r_{ij}) = \gamma_1 e^{\sigma c (1 - \frac{r_{ij}}{a_0})} F_c(r_{ij}).
\]

FIG. 11: Coupling term \( t \) between two \( p_z \) orbitals versus the distance \( r \): (full line) in two layers (inter-layer coupling); (dashed line) in the same layer (intra-layer coupling). Here, the smooth cut-off function \( F_c \) is not taken into account (ie large \( r_c \) value in \((A4)\)).

where \( a \) is the nearest neighbor distance within a layer, \( a = 1.418 \text{Å} \), and \( a_1 \) is the interlayer distance, \( a_1 = 3.349 \text{Å} \). First neighbors interaction in a plane is taken equal to the commonly used value, \( \gamma_0 = 2.7 \text{eV} \). Second neighbors interaction \( \gamma' \) in a plane is set to \( 0.1 \times \gamma_0 \) which fixes the value of the ratio \( \frac{\gamma_0}{a_1} \) in equation \((A1)\). The inter-layer coupling between two \( p_z \) orbitals in \( \pi \) configuration is \( \gamma_1 \). \( \gamma_1 \) is fixed to obtain a good fit with ab-initio calculation around Dirac energy in AA stacking and AB bernal stacking and then to get \( \gamma_1 = 0.34 \text{eV} \) (figures 7, 9 and 10) which results in \( \gamma_1 = 0.48 \text{eV} \). We chose the same coefficient of the exponential decay for \( V_{p\pi} \) and \( V_{p\sigma} \).

\[
\frac{q_c}{a_1} = \frac{q_c}{a_0} = \frac{\ln (\gamma_0/\gamma_1)}{a - a_0} = 2.218 \text{Å}^{-1},
\]

with \( a_0 = 2.456 \text{Å} \) the distance between second neighbors in a plane. Intra-layer and inter-layer coupling terms \( (r_{ij}) \) calculated with these parameters are shown on figure 11. In \((A4)\) and \((A5)\), a smooth cut-off function is introduced:\(^{42}\)

\[
F_c(r) = \left(1 + e^{r/r_c} \right)^{-1},
\]

with \( r_c \) the cut-off distance and \( l_c = 0.5 \text{a.u.} = 0.265 \text{Å} \). For \( r < r_c \), \( F_c(r) \approx 1 \); and for \( r > r_c \), \( F_c(r) \approx 0 \). All results presented in this article are calculated with \( r_c = 2.5 a_0 = 6.14 \text{Å} \). We have checked that the results are independent of \( r_c \) for \( r_c > 4.9 \text{Å} \).

All \( p_z \) orbitals have the same on-site energy \( \epsilon_i \) (equation \((A1)\)). \( \epsilon_i \) is set to \(-0.78 \text{eV} \) so that the energy \( E_D \) of the Dirac point is equal to zero in mono-layer graphene. \( \epsilon_i \) is not zero because the intra-layer coupling between atoms beyond first neighbors breaks the electron/hole symmetry and then shifts \( E_D \).

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